

ABSTRACTS

June 10-14, 2012, Montecatini Terme, Tuscany, Italy

4th International Conference

smart materials structures systems

adaptive, active and multifunctional
smart materials systems

shape memory alloys

electroactive polymers

smart and interactive textiles

next generation micro/nano systems

smart & adaptive optics

intelligent structures

mechatronics & robotics

mining smartness from nature

bioinspiration biomimetics

bioreplication

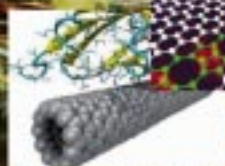
wearable/wireless & implantable

body sensor networks

for healthcare

biomedical applications

of "smart" technologies



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2012

“PALAZZO DEI CONGRESSI”

Via Amendola, 2



Symposium A

Adaptive, Active &
Multifunctional Smart
Materials Systems

Symposium C

Electroactive Polymers:
Advances in Materials &
Devices

Symposium D

Smart & Interactive
Textiles

Symposium E

Next Generation
Micro/Nano
Systems

Symposium F

Smart & Adaptive
Optics

Symposium G

Emboding Intelligence in
Structures & Integrated
Systems

“VITTORIA CONGRESSI”

Via Baccelli, 2



Symposium B

State-of-the-art
Research & Application of
SMAs Technologies

Symposium H

Mining Smartness
from Nature

Symposium I

Progress in Wearable/Wireless and
Implantable Body Sensor Networks
for Healthcare Applications

Symposium J

Biomedical Applications of
“Smart” Technologies

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4th International Conference "SMART MATERIALS, STRUCTURES AND SYSTEMS"

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SPECIAL SESSION A-10 - Emerging Non-volatile Memory Devices

Programme Chair: Shashi PAUL, UK

FOCUSED SESSION A-11 - Multiferroics

Programme Chair: Gopalan SRINIVASAN, USA *Members:* Agnes BARTHELEMY, France Mark BLAMIRE, UK Gustau CATALAN, Spain Ying-Hao CHU, Taiwan Chun-Gang DUAN, China Arunava GUPTA, USA Milko ILIEV, USA Hyun M. JANG, Korea Masashi KAWASAKI, Japan Michel KENZELMANN, Switzerland Tsuyoshi KIMURA, Japan Hermann KOHLSTEDT, Germany Jeremy LEVY, USA Alois LOIDL, Germany B.S. MURTY, India Naoto NAGAOSA, Japan Thomas T.M. PALSTRA, Holland Jordi PASCUAL, Spain Vladimir PETROV, Russia Silvia PICOZZI, Italy Shashank PRIYA, USA Vladimir Ya. SHUR, Russia Evgeny Y. TSYMBAL, USA Thomas TYBELL, Norway Dwight VIEHLAND, USA John WANG, Singapore

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SPECIAL SESSION A-14 - Multifunctional Smart Materials for Energy Harvesting

Programme Chairs: Yoon-Bong HAHN, Korea & S.R.P. SILVA, UK

FOCUSED SESSION A-15 - Actively Moving Polymers

Programme Chair: Andreas LENDLEIN, Germany *Members:* Christopher BOWMANN, USA Filip E. DU PREZ, Belgium Urs DUEBIG, Switzerland Yakai FENG, P.R.China Shunichi HAYASHI, Japan Jozsef KARGER-KOCSIS, Hungary Duncan J. MAITLAND, USA Patrick MATHER, USA Abhay PANDIT, Ireland Hans-Joachim RADUSCH, Germany U. Gianfranco SPIZZIRRI, Italy Christoph WEDER, Switzerland Timothy J. WHITE, USA Tao XIE, USA Ryo YOSHIDA, Japan

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SYMPOSIUM C - Electroactive Polymers: Advances in Materials and Devices

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SPECIAL SESSION G-6 - Advances and Challenges in the SHM of Civil and Aerospace Structures

Programme Chair: Piervincenzo RIZZO, *USA*

SYMPOSIUM H - Mining Smartness from Nature

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 Mehmet SARIKAYA, *USA* Mitsuhiro SHIONOYA, *Japan* Friedrich C. SIMMEL, *Germany* Uwe B. SLEYTR, *Austria* Lloyd SMITH, *USA* Christina D. SMOLKE, *USA* Shigeru SUNADA, *Japan* Andrew J. TURBERFIELD, *UK* Reidun TWAROCK, *UK*
 Julian VINCENT, *UK* Joseph WANG, *USA* Daniel WEIHS, *Israel* Marc WEISSBURG, *USA* Itamar WILLNER, *Israel* Hao YAN, *USA* Byoung-Tak ZHANG, *Korea* Di ZHANG, *P.R.China*

SPECIAL SESSION H-7 - Biomimetic Flow Control in Aquatic and Aerial Systems and its Application to Bioinspired Autonomous Vehicles

Programme Chair: Luca SCHENATO, *Italy*

SYMPOSIUM I - Progress in Wearable/Wireless and Implantable Body Sensor Networks for Healthcare Applications

Co-Chairs: Dermot DIAMOND, *Ireland (Programme Chair)* Toshiyo TAMURA, *Japan* Vijay V. VARADAN, *USA* Guang-Zhong YANG, *UK* *Members:* Roger ARMITAGE, *UK* M.T. ARREDONDO W., *Spain* I. BALASINGHAM, *Norway* Dinesh BHATIA, *USA*
 Paolo BONATO, *USA* Dongyi CHEN, *P.R.China* Hui CHEN, *USA* Lorenzo CHIARI, *Italy* Wan-Young CHUNG, *Korea* Giovanni DE MICHELI, *Switzerland* Danilo DE ROSSI, *Italy* Eryk DUTKIEWICZ, *Australia* Thomas FALCK, *The Netherlands*
 Joerg HABETHA, *The Netherlands* Robert ISTEPANIAN, *UK* Emil JOVANOVIĆ, *USA* John LACH, *USA* Insup LEE, *USA* S. LEONHARDT, *Germany* Paul LUKOWICZ, *Germany* M. MARSCHOLLEK, *Germany* Eric McADAMS, *France* Mehran MEHREGANY, *USA*
 KwangSuk PARK, *Korea* Niilo SARANUMMI, *Finland* Majid SARRAFAZADEH, *USA* Mohamad SAWAN, *Canada* Wee SER, *Singapore* William C. TANG, *USA* Chris VAN HOOFF, *Belgium* A. VASILAKOS, *Greece* Peter VELTINK, *The Netherlands* Lei WANG, *China*

SYMPOSIUM J - Biomedical Applications of "Smart" Technologies

Co-Chairs: François A. AUGER, *Canada* Kazunori KATAOKA, *Japan* Robert N. MULLER, *Belgium* Thomas J. WEBSTER, *USA* *Programme Chair:* E. Pasquale SCILINGO, *Italy* *Members:* Silvio AIME, *Italy* Toshihiro AKAIKE, *Japan* Cameron ALEXANDER, *UK*
 Anthony J. ATALA, *USA* Yoshinobu BABA, *Japan* Rolando BARBUCCI, *Italy* Yilin CAO, *P.R.China* Patrick COUVREUR, *France* Tejal DESAI, *USA*
 Sandra DOWNES, *UK* Jennifer H. ELISSEFF, *USA* Antoine FERREIRA, *France* Aaron FLEISCHMAN, *USA* Robert A. FREITAS Jr., *USA* Yasuhisa FUJIBAYASHI, *Japan* Rogerio GASPARI, *Portugal* Juri GELOVANI, *USA*
 Norbert GRETZ, *Germany* J. Zach HILT, *USA* Jari HYTTINEN, *Finland* Koji IKUTA, *Japan* Esmail JABBARI, *USA* Ming JIANG, *China* David S. JONES, *UK*
 Bengt KASEMO, *Sweden* Ick Chan KWON, *Korea* Vinod LABHASSETWAR, *USA* Robert LANGER, *USA* Feng-Huei LIN, *Taiwan* Nigel LOVELL, *Australia* Atsushi MARUYAMA, *Japan* Takeo MATSUMOTO, *Japan* Klaas NICOLAY, *Holland*
 Konstantina S. NIKITA, *Greece* Vasilis NTZIACHRISTOS, *Germany* Kinam PARK, *USA* Josep A. PLANELL, *Spain* Buddy D. RATNER, *USA* Michael L. REED, *USA* Michael S. SACKS, *USA* David SAMPSON, *Australia* Francesco STELLACCI, *Italy*
 Samuel I. STUPP, *USA* Maryam TABRIZIAN, *Canada* Vladimir P. TORCHILIN, *USA* Valery TUCHIN, *Russia* Pankaj VADGAMA, *UK* Janos VOROS, *Switzerland* Anthony WEISS, *Australia* Carsten WERNER, *Germany* Jackie YING, *Singapore*
 Nobuhiko YUI, *Japan* Christiane ZIEGLER, *Germany*

Code Number of contributions by Presenting Author (in alphabetical order)

The Code Number X-Y:W00 includes: X Symposium; Y Session; W Type of presentation (PL, KL, IL, L, P)*; 00 Paper number

*** PL Plenary KL Key-Note IL Invited Lecture L Contributed Lecture P Poster presentation**

NOTE: Due to the restructuring of some symposia, the session number included in the Code may differ from the one selected by the Presenting Author in the Abstract Submission Form.

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Acet Mehmet	B-1:IL07	Bochenek Dariusz	A-1:P09	Chen Tze-Lung	A:HP108
Aghalovyan Lenser A.	G-1:L10	Boese Holger	A-4:IL02	Chen Yu-Chie	J-5:P17
Agreda Carola	J-2:P05	Bogachev Vladimir	F:P08	Chen Yu-Liang	H:P12
Ahn Yu Jin	D:P03	Boland John J.	E-4:L06	Cheng Hui-Ming	A-13.4:IL02
Akiyoshi Kazunari	J-5:IL02	Bonora Stefano	F:P05	Cheng Zhongyang	C-2:IL07
Akyurtlu Alkim	A-12.2:L11	Booth Martin	F-7:IL03	Chernenko Volodymyr	B-5:IL01
Albertini Franca	B-1:L08	Bortolozzo Umberto	F-4:L07	Chin Bryan A.	H-3:L08
Alderson Andrew	A-3:IL02	Bosowski Patrycja	D-3:L15	Chirita Mihai	H-2.1:IL10
Alexe Marin	A-11.4:IL03	Bouazaoui Mohamed	F-2:IL08	Cho Hiroki	B:P12
Allen Martin	I:P01	Bowman Christopher	A-15.2:L05	Choi Haecheon	H-7:IL09
Allerdissen Merle	E-7:L08	Brailovski Vladimir	B-3:IL09	Choi Sang	F-6:IL03
Alvarez-Puebla Ramon	F-5:IL03	Briand Danick	E-8:IL03	Chorkendorff Ib	A-14.1:IL14
Alves Junior Severino	A-7:P39	Brock Elizabeth	A-12.1:L03	Chutipakdeevong Jesada	J-4:L09
Amato Massimiliano	E:P01	Broer Dirk J.	A-15.3:IL04	Cicogna Francesca	A-15.3:L06
An Yuanlin	H:P02	Buchelnikov Vasilij	B-2:L11	Clark Natalie	F-4:IL01
Anand Theerthan R.	A-11.4:L04	Bucko Miroslaw M.	A-11:P56	Clemens Frank	D-1:L04
Anderson Iain	C-3:IL06	Buonsanti Raffaella	A-6.2:L02	Coda Alberto	B-3:L12
Andrés Pedro	F-1:IL06	Burgert Ingo	H-1:IL07	Collet Manuel	A-3:L03
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Arndt Karl-Friedrich	A-2:L03	Caetano Bruno	J:HP24	Coricciati Angela	G-3:L16
Asanuma Hiroyuki	H-4:IL02	Cakir Oznur	B-2:L18	Cotica Luiz Fernando	A-11:P59
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Averitt Richard	A-12.1:IL01	Caldino Ulises	F-2:IL07	Crego-Calama Mercedes	I-1:IL06
Bae Jungmin	A-6:P29	Calva Yanez Julio Cesar	A-14.1:L05	Curto Vincenzo Fabio	I-1:L08
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Baier Horst J.	G-3:IL09	Candini Andrea	A-13.3:IL10	Dahiya Ravinder	E-1:IL04
Balachandran Bala	H-7:IL01	Carlos Luis	A-6.1:IL11	Dai Zhendong	H-4:IL05
Balk Maria	A-15.1:L08	Carpi Federico	C-3:IL05	Dammacco Giada	D-3:IL06
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Bartali Ruben	E-7:L09	Carta Fabio	A-15.7:L05	Dapino Marcelo	A-1.1:IL16
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Bechtold Christoph	B-5:L06	Castagnetti Davide	G-2:L07	De Baets Johan	D-3:IL07
Beeby Stephen	I-2:IL06	Castelvetto Valter	A-8:L07	de Kok Margreet	D-2:L09
Behl Marc	A-15.1:IL04	Cavalcanti Rodrigues Vaz E.	A-6.1:L21	De Los Cobos Olivia	A-1.2:L03
Bein Thilo	G-2:IL01	Cesari Eduard	B-2:L12	De Riccardis Maria Federica	C:P09
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Belyaev Sergey	B-2:L15	Chanthaanont Pojjawan	A:HP103	Del Grosso Andrea E.	G-3:IL11
Ben Zineb Tarak	B-3:IL08	Chareyre Laetitia	A-6.2:L06	Desbrieres Jacques	H-3:IL09
Benjeddou Ayech	G-3:IL12	Chavez Tom P.	A-1:P09b	Detert Heiner	A-5:P19
Berry Simon	A-12.1:L08	Chen Bin	A-14.3:L02	Dharmadasa I.M.	A-14.1:L04
Beruete Miguel	A-12.1:IL07	Chen Chia-Chun	A-13.4:L03	Di Credico Barbara	A:HP88
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Bezerra Vasconcelos Iane	A-7:P39b	Chen Fang-Chung	A-14.1:IL02	Diamond Dermot	E-2:IL04
Bhushan Bharat	H:KL	Chen Fei	A-12.4:L03	DiAntonio Chris	A-1.1:L09
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Dyer Patrick	D-1:L16	Gorb Stanislav	H-1:IL01	Jafari Roozbeh	I-4:IL09
Eichhorn Stephen	H-1:IL06	Gottwald Martin	H:P10	Jamal Mustapha	J-2:L07
Ekabutr Pongpol	J-4:P11	Goulbourne Nakhiah	A-15.1:L09	Jana Sadhan	A-15.6:IL01
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Enokibori Yu	D-3:L23	Granqvist Claes G.	A-5.2:IL03	Jeong Ki-Hun	H-3:IL04
Ensslin Klaus	A-13.3:IL07	Graz Ingrid	C-1:IL04	Jiang Anquan	A-10:IL02
Entel Peter	B-2:IL09	Griffin Anselm C.	A-3:IL01	Jiang Lei	A-8:IL03
Esashi Masayoshi	E-5:IL03	Guan Xinchun	G-1:IL01	Jiang Xiaoning	A-1.1:IL11
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Eufinger Karin	D-3:L04	Guzdek Piotr	A-11:P55	Jonas Alain	C-2:IL06
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Fähler Sebastian	B-5:IL05	Han Jae-Hung	G-4:IL01	Kainuma Ryosuke	B-1:IL06
Fainman Yeshaiahu	F-1:IL07	Han Seungwoo	E:P04	Kamonsawas Jirarat	A:HP89
Falcaro Paolo	A-7:IL01	Haraguchi Kazutoshi	A-2:IL06	Kaner Richard	A-13.1:IL06
Fang Nicholas X.	A-12.2:IL09	Hari Parameswar	A-14.1:L03	Kang Chong-Yun	A-14.2:L11
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Faucher Marc	E-1:IL02	Hassan Maguid	G-3:L18	Kauranen Martti	A-12.3:IL05
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Fiori Gianluca	A-13.3:L04	Herzog Matthias	A-6.1:L13	Khlebtsov Nikolai	J-2:IL04
Fleischer Maximilian	E-2:IL01	Hess Henry	H-4:IL01	Khoo lam Choon	F-2:IL06
Florea Larisa	A-15.3:L03	Heuberger Manfred	D-2:IL06	Kikuchi Naoki	A-8:P45
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Fujita Koji	A-5.1:IL01	Hosoda Naoe	H-4:IL11	Kim Moonkeun	A:HP106
Fukuda Takashi	B-2:IL07	Hsieh You-Lo	H-2.1:IL07b	Kim Sang-Woo	A-14.2:IL02
Furukawa Shuhei	A-7:IL07	Hu Biru	H-6:IL03	Kim Seong Hun	D-3:L08
Galantini Fabia	C-1:L15	Hu Jinlian	D-1:IL10	Kim Sung Dong	A:HP102
Galea Stephen	G:HP06	Hu Xinhua	A-12.5:IL03	Kim Wan Doo	H:P11
Gallo Katia	F-3:IL02	Huang W.M.	B-1:L12	Kim Yeon-wook	B:HP18
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Garrido Jose A.	A-13.3:IL03	Hurren Christopher	J-6:L04	King Glen C.	F-1:L12
Gasior Pawel	G:P02	Iannacci Jacopo	E-5:IL02	Kinkeldei Thomas	D-2:L05
Ge Yanling	B-2:IL08	Ieropoulos Ioannis Andrea	H-4:IL10	Kinloch Ian	A-13.5:IL01
Gebhardt Sylvia	A-1.1:IL12	Ihara Tadashi	C-3:IL02	Kiremidjian Anne S.	G-5:IL02
Gelling Victoria	C-1:L06	Iima Makoto	H-7:IL02	Kiryukhina Kateryna	A-1:P02
Genzer Jan	A-8:IL05	Ikedo Tomiki	A-15.3:IL01	Kishi Yoichi	B-5:IL03
Gerardot Brian D.	F-1:IL05	Ikenaga Noriaki	B:P13	Kishimura Akihiro	J-5:L11
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Klajn Rafal	A-1.2:IL02	Lisi Fabio	J-3:L09	Moriyama Satoshi	A-13.3:IL06
Klimiec Ewa	C:P10	Liu Dongqing	A-8:P40	Mossé Aurélie	D-3:IL01
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Knor Grzegorz	G-3:L13	Liu Shiyang	A-12.3:IL04	Munisso Maria Chiara	J-5:L07
Koh Cheongyang	A-12.6:IL02	Liu Yanju	A-15.7:L08	Murakami Yasukazu	B-2:IL04
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Kohri Hitoshi	A-14.2:L04	Liu Yunqi	A-13.1:IL03	Muro Hideo	E-1:IL03
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Kolb Andrea	D-3:L05	Llorens Domenjo Elena	J-4:P15	Nah Changwoon	C-1:L05
Koledov Victor	B-1:IL05	Lopez Malo Daniel	A-7:L10	Nakajima Hiromasa	I:P04
Kono Kenji	J-5:IL05	Lorenzo Daniela	A-15.6:L05	Nakashima Motomu	H-7:IL11
Konstas Kristina	A-7:L04	Lotz Peter	C-3:IL03	Nam Tae-hyun	B:HP16
Kornev Kostya	D-3:IL11	Lounis Brahim	J-3:IL01	Namavar Fereydoon	J-4:L05
Kovac Mirko	H-7:L08	Low Sze Hsien	C-1:L12	Nardinocchi Paola	C-2:L13
Krasnikovs Andrejs	G-6:L05	Lucas Kerstin	D-3:L14	Neudeck Andreas	D-1:IL11
Krebber Katerina	D-3:IL27	Luo Ningsu	G-5:IL03	Neumaier Daniel	A-13.3:IL02
Krijnen Gijs	H-3:IL03	Luprano Jean	J-6:IL01	Ng Jun Jye	J-4:P14
Krucinska Izabella	D-1:IL07	Lustfeld Hans	A-1.2:L04	Nguyen Cong Tam	E:P07
Kudryashov Alexis	F-4:IL02	Lutolf Matthias	J-1:IL06	Nguyen Ha Xuan	E-4:L05
Kuipers L. (Kobus)	A-12.4:IL09	Luzzati Silvia	A-14.1:IL11	Ni Yi-Qing	G-5:IL07
Kuksenok Olga	A-2:IL02	Ma Yungui	A-12.4:IL05	Nickel Janice	A-10:L12
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Kuroiwa Yoshihiro	A-1.1:IL04	Marcelli Romolo	A-12.1:L04	Nithitanakul Manit	A-6:P34
Kussow Adil-Geraï	A-12.6:L07	Marie Camille	J:HP23	Oates William	A-1.1:IL02
Labhasetwar Vinod	J-5:IL04	Marrani Alessio	C:P02	Occhipinti Tommaso	F-4:IL06
Ladegaard Skov Anne	C-1:L16	Martel Sylvain	H-1:IL05	Ohkoshi Shin-ichi	A-5.1:IL03
Lagoudas Dimitris C.	G-1:IL07	Martins Pedro	A:HP105	Ohya Yuichi	J-1:IL04
Lakany Heba	I-5:IL03	Maruyama Atsushi	J-1:IL05	Okuzaki Hidenori	C-4:IL02
Landa Michal	B-2:IL06	Maslovski Stanislav	A-12.6:IL05	Omori Momoru	A-6.1:L09
Lanza di Scalea Francesco	G-6:IL01	Masuda Yoshitake	A-6.1:IL05	Omori Toshihiro	B-1:L13
Lapine Mikhail	A-12.6:IL03	Mather Patrick	A-15.6:IL02	Op de Beeck Maaïke	I-1:IL05
Laschi Cecilia	H-4:IL06	Mathur Sanjay	A-6.1:IL19	Orsini Andrea	E:HP10
Lau Gih-Keong	E-3:L03	Matsusaki Michiya	J-4:IL02	Osada Minoru	A-1.1:L10
Leckie Joy	H:P05	Matzeu Giusy	A-2:L05	Otero Toribio F.	C-1:IL08
Lee Chin-Hyung	G:HP05	McCall Martin	A-12.4:IL02	Ottaviano Luca	A-13.1:L08
Lee Haeshin	G-4:IL02	McConney Michael	A-5.2:IL06	Ouisse Morvan	A-15.1:L07
Lee Hee Young	A-11.2:L05	McGrath Kathryn	H-2.1:L12	Padilla Willie	A-12.2:IL01
Lee Jin	H:P03	Medina Francisco	A-12.1:IL02	Pagel Kenny	B-6:L07
Lee Jonghwi	J-1:L07	Melchert Christian	A-15.2:L04	Pagounis Emmanouel	B-3:L14
Lee Keon Jae	A-14.2:IL08	Melnik Roderick	B-3:L19	Paidar Vaclav	B-2:L21
Lee Kwan Hyi	J-3:P08	Mendes Marcio	A-6:P24	Pakeyangkoon Pornsri	A-6.2:L12
Lee Sang Bong	A-13:P70	Michielsen Stephen	D-3:IL17	Pandey Dhananjai	A-11.2:IL02
Lee Seunghun	A-1.1:L22	Mih Thomas Attia	A-10:P48	Pandini Stefano	A-15:P83
Lee Woo-Jung	A-6:P32	Milliron Delia	A-5.2:IL01	Papadimitriou Costas	G-1:IL03
Lee Youngkyu	C-3:L09	Mingallon Maria	D-3:IL16	Papagno Marco	A-13.2:IL10
Lei Ying	G-4:IL04	Mingazzini Claudio	A:HP110	Pappalardo Fulvio	C:P07
Lendlein Andreas	A-15.6:IL03	Miranda Leila Figueiredo de	J-5:P20	Paradee Nophawan	J-5:P21
Leng Jinsong	C:KL	Mitcheson Paul	I-4:IL01	Paradiso Rita	D-3:IL22
Leonhardt Steffen	I-1:IL01	Mitsuno Hidefumi	H-3:IL02	Parakhonskiy Bogdan	J-5:L03
Li Hui	G-3:IL07	Miyata Kanjiro	J-5:P18	Park Ji-Hun	A-1:P10
Li Jensen	A-12.5:IL01	Miyata Takashi	A-2:IL01	Park Kwang Suk	I-1:IL03
Li Jing-Feng	E-6:IL02	Miyazaki Shuichi	B-1:IL01	Park Seunghee	G-6:L04
Li Rongjin	A:HP107	Mokwa Wilfried	I-3:IL03	Park Yeonjoon	F-5:IL02
Li Ya-Li	D-3:IL02	Mora Parra Nicolas	A-12.1:L05	Parkova Inese	D-3:L10
Liao Wei-Hsin	G-5:IL05	Morganti Elisa	E-7:L05	Parry Maria	A-6.1:L08
Lin K.C.	G-5:L08	Morishima Keisuke	H-4:IL08	Paschew Georgi	F-3:L04

Passos Aline	A:HP95	Rossi Enrico	A-13.2:IL06	Skuz Jonathn	F-1:LO8
Paukstelis Paul	H-2.1:IL05	Rousseau Ingrid	A-15.7:IL02	Smela Elisabeth	C-2:IL01
Paul Shashi	A-10:IL05	Rovira Concepci	A-2:L11	Smith Kathryn	J-6:L03
Pavlova-Verevkina Olga	A-1:P12	Rozhkova Elena	J-1:IL03	Smolyaninov Igor	A-12.6:IL06
Pazos Perez Nicolas	F-1:L11	Rudchenko Sergei	H:HP16	Smolyaninova Vera	A-12.4:L04
Pellegrini Vittorio	A-13.4:IL01	Ruggeri Giacomo	A-5.2:L08	Smyth Andrew	G-2:IL04
Penders Julien	I-4:IL03	Ruhmann Ralf	A-5.2:IL07	Sodano Henry A.	A-6.1:L14
Perelman Lev T.	J-3:IL08	Sachdev Hermann	A-13.1:IL07	Sohn Hoon	G-6:IL06
Perera Rathna	D-2:IL07	Safranski David	A-15.5:L04	Song Sung-Hyuk	H-4:L12
Perez-Landazabal J.I.	B:P06	Sajin Gheorghe Ioan	A-12:P63	Soong Tsu T.	G-3:IL01
Permpool Tharaporn	A:HP90	Sakai Hiroki	J-1:P02	Soria Silvia	F-6:IL02
Persico Paola	D-1:IL12	Salaoru Iulia	A-10:P46	Sorrentino Luigi	H-2.1:L11
Petcharoen Karat	J-1:P04	Salas Daniel	B-2:L20	Souza Susana	F-2:L05
Petraru Adrian	A-11.5:L03	Salazar-Alvarez German	A-6.1:IL12	Spaggiari Andrea	B-3:L15
Petrillo Caterina	F-5:IL01	Sambri Alessia	A-14.2:IL06	Spontak Richard J.	A-15.1:IL02
Petroni Simona	A-1.1:L06	Sampath Vedamanickam	B-6:L09	Srinivasan Gopalan	A-11.4:IL02
Picozzi Silvia	A-11.1:IL01	Sampson David D.	F-7:IL06	Stamm Manfred	A-2:IL15
Pimenta Marcos	A-13.2:IL09	San Juan Jose	B-5:IL02	Starikov Fedor	F-4:IL05
Pittaccio Simone	B-6:IL03	Sanchez Clement	A-6.1:IL01	Staszewski Wieslaw Jerzy	G-6:IL07
Plokhikh Alexander	A-11.1:L09	Sandhage Kenneth	H-2.1:IL01	Stefanini Cesare	H-4:IL03
Plonska Malgorzata	F:P03	Santa-Cruz Petrus	A-2:P14	Stojanovic Milan	H-5:IL01
Polini Marco	A-13.2:IL04	Santos Ana	D-3:L09	Stylios George	D-1:L08
Pond Robert	B-2:L23	Sapouna Kyriaki	G-1:L12	Sugiyama Masakazu	E-4:IL02
Pons Jaume	B-1:IL03	Sarrafzadeh Majid	I-5:IL02	Sun Kyung Ho	A:HP101
Popov Alexander	A-12.3:L06	Sarro Pasqualina	E-9:IL01	Sunada Shigeru	H-7:IL06
Preumont Andre	G-1:IL04	Sato Kazuo	E-1:IL01	Suzuki Hiroaki	E-2:IL03
Prikhna Tatiana	A-1.1:L23	Sawan Mohamad	I-3:IL02	Suzuki Katsuaki	F:P02
Priya Shashank	A-11.1:IL07	Saxena Avadh	B-2:IL01	Swartzlander Grover	F-2:IL03
Pucker Georg	F-1:IL03	Schäfer Immanuel	H-6:L04	Szkutnik Pierre David	A-14.1:L09
Qiu Cheng-Wei	A-12.6:L08	Scheibel Thomas	H-2.1:IL04	Szleifer Igal	H-5:IL02
Quandt Eckard	A-11.2:L04	Schlaak Helmut F.	C-1:IL03	Tabrizian Maryam	J-1:IL01
Radusch Hans-Joachim	A-15.1:L03	Schlettwein Derck	D-1:IL02	Taguchi Yasujiro	A-11.2:IL01
Rai Pratyush	I-5:L04	Schlierf Andrea	A:HP112	Tailhades Philippe	A-12.6:L04
Rambausek Lina	D-2:L10	Schlüter Kathrin	B-6:L08	Takabayashi Susumu	A-13.3:L13
Ramirez Cristina	A-13.5:L03	Schmid Ulrich	A-1:P08	Takahashi Masahide	A-8:IL04
Ramstad Tor	I-4:IL02	Schmidt Oliver G.	E-8:IL04	Takano Naoki	A-14.2:L10
Rance Helen	A-12.1:L12	Schmitz Helmut	H-3:L06	Takeuchi Ichiro	B-6:IL02
Randriamahazaka Hyacinthe	C-2:L12	Schneider Kai	H-7:IL03	Tamura Akito	J-4:P13
Ratera Imma	A-7:L03	Schneider Michael	A-1.1:L05	Tamura Rui	F-2:IL01
Raty Jean-Yves	A-10:IL16	Seeman Nadrian C.	PL-3	Tamura Toshiyo	I-5:IL05
Razov Alexander	B-6:L06	Seidel Robin	H-1:IL09	Tan Loon-Seng	A-15.3:L05
Razzaq Muhammad Yasar	A-15.6:L07	Selhuber-Unkel Christine	J-2:L06	Tanaka Katsuhisa	A-1.1:IL17
Reboul Julien	A-6.2:L04	Sen Indrani	B-2:L19	Tanaka Takuo	F-1:IL09
Reimhult Erik	H-2.2:IL03	Seneor Pierre	A-13.3:IL11	Tande Shrirang	G-6:L09
Reinicke Stefan	A-2:L09	Seo Yongsok	A-4:L07	Tanzi Maria Cristina	J-6:IL02
Rendina Ivo	E-3:IL02	Serrano-Guisan Santiago	A-10:IL09	Taskaev Sergey	B:P01
Resnina Natalia	B-3:L18	Shah Tahir	A-14.2:L12	Tateo Flaviano	G-2:L09
Restaino Sergio	F-4:IL03	Shahinpoor Mohsen	C-1:IL13	Tatkiewicz Witold Ireneusz	J-4:L04
Ribeiro Clarisse	J:HP25	Shea Herbert	C-3:IL01	Taya Minoru	G-2:IL06
Richter Andreas	E-7:L04	Shimomura Masatsugu	H-2.2:IL04	Taylor Antoinette	F-1:IL10
Righi Lara	B-2:IL03	Shoureshi Rahmat	I-4:L06	Teramoto Takeshi	B:P07
Rizzi Francesco	H-7:L16	Shtein Max	G-1:IL06	Teresi Luciano	A-2:L04
Rizzo Piervincenzo	G-6:IL02	Shyamkumar Prashanth	I-2:L03	Terzo Mario	A-4:L06
Robertson Sara	D-1:IL13	Silva S.Ravi P.	A-14.1:IL01	Thierry Benjamin	J-2:IL02
Rocha Joao	A-1.2:IL05	Simmel Friedrich	H-5:IL03	Thubsuang Uthen	A-6.2:L03
Rodellar Jose	G-2:IL03	Simon Erik	D-3:L03	Tietze Marcus	C:P13
Rodrigues Ribeiro Roberto	J-1:P01	Sirivat Anuvat	C:P04	Tinnefeld Philip	H-6:IL02
Rodriguez Rafael	D:HP08	Sirivisoot Sirinrath	J-3:IL04	Toeters Marina	D:HP09
Rodriguez-Ulibarri Pablo	A-12.1:L11	Sirleto Luigi	F-2:IL02	Tokeshi Manabu	J-3:IL03
Romano Giovanni Paolo	H-7:L12	Sittner Petr	B-3:IL05	Tokoro Hiroko	A-5:P21
Romano-Rodriguez Albert	E-2:L07	Skryabin Dmitry	A-12.3:IL03	Tondu Bertrand	H-3:L11
Roorda Austin	F-7:IL01	Skulski Ryszard	A:HP92	Tonouchi Masayoshi	A-11.3:IL01

Torchilin Vladimir P.	J-5:L13	Voirin Guy	D-3:IL26	Xu Xiao	B-2:L24
Torra Vicenç	B-6:IL01	Voit Walter	A-15.7:L07	Xu Zhuo	C:P06
Toyoda Noriaki	F-1:IL04	Volkova Viktorjia	G-6:L11	Yakacki Christopher	A-15.1:L06
Treossi Emanuele	A:HP111	von Krshiwoblozki Malte	I-2:IL02	Yamamoto Takaei	B-3:L13
Tsamis Christos	E:HP13	Vones Katharina	A:HP94	Yamaoka Tetsuji	J-3:IL02
Tsoukalas Dimitris	A-10:IL11	Vorobiev Andrei	A-11.5:L02	Yang Guang-Zhong	I-5:IL01
Tsuchiya Koichi	B-3:IL03	Wagenaar Robert Cornelis	I-1:IL02	Yang KiYeul	A-14:P74
Tsymbal Evgeny	A-11.4:IL01	Wagg David	G-3:IL10	Yates Matthew	J:HP26
Tuchin Valery	J-5:L12	Waitz Thomas	B-1:IL02	Ying Jackie Y.	J-5:IL10
Tuissi Ausonio	B-3:IL02	Wallmersperger Thomas	C-2:IL02	Yoo Jung Whan	A-8:L06
Tungkavet Thawatchai	C:HP12	Wandowski Tomasz	G-6:L13	Yoo Mi Kyong	D:P07
Uhl Tadeusz	G-6:L10	Wang Kon-Well	G-4:IL07	Yoon Hargsoon	F-6:IL01
Uragami Tadashi	A-6.2:L05	Wang Leeyih	A:HP97	Yoshimura Masahiro	A-8:IL01
Urata Chihiro	A-6.1:L03	Wang Meng-Jiy	H:P08	You Inseong	G:P03
Urayama Kenji	A-15.2:IL02	Wang Wei-Hua	A-13.2:IL02	Yu HongYu	A-10:IL08
Uzun Muhammet	D-3:L24	Wang Wenxin	A-15.5:IL03	Yu Liyun	C:P01
Valev Ventsislav	A-12.2:L07	Wang Yinmin (Morris)	E-2:IL02	Yu Pu	A-11.1:IL08
van Breemen Albert	A-10:L04	Wang Zhong Lin	A-14.2:IL07	Yui Nobuhiko	J-1:IL02
van den Berg Albert	E-7:IL02	Wang Zhong Lin	E-6:IL01	Zambelli Tomaso	J-2:IL01
van der Boom Milko	A-7:IL06	Watanabe Kazuo	B:P05	Zanoni Michele	C-1:L10
Van der Schueren Lien	D-1:L14	Webster Thomas J.	J-4:IL01	Zanotti Claudio	B:P02
van Leeuwen Johan L.	H-7:IL14	Weder Christoph	A-15.6:IL06	Zentel Rudolf	A-15.2:IL01
Van Os Koen	D-3:IL21	Weiss François	A-1.1:IL01	Zhang Haixia	E-6:IL05
van Spengen W. Merlijn	E-5:IL01	Weiss Robert	A-15.1:IL01	Zhang Jun	H-7:IL05
Vandecandelaere Nicolas	J-4:L03	Weissburg Marc	H-4:IL09	Zhang Qiming	C-1:IL02
Vandeparre Hugues	C-1:L11	Wessely Pia Juliane	A-13.3:L09	Zhao Yong	A-15.7:L06
Varadan Vijay	I-3:IL01	White Timothy	A-15.3:IL02	Zhou Lei	A-12.2:IL02
Varenberg Michael	H-6:IL01	Wilkinson James	E-7:IL01	Zhou Qi	H-2.1:IL02
Vaz de Araujo Ana Claudia	A-6:P28	Windisch Markus	A-2:L08	Zhou Shaobing	A-15.5:IL02
Veciana Jaume	A-10:IL01	Wischke Christian	A-15.7:IL04	Zhou Yaopeng	F-7:IL04
Vestroni Fabrizio	G-3:L21	Wodecka-Dus Beata	A-1:P04	Ziennicka-Sylwester Marta	A:HP98
Vichi Flavio	F-2:L11	Wood David	E-3:IL01	Ziolkowski Andrzej	B-3:IL01
Vidal Frédéric	C-2:IL10	Wu Jih-Jen	A-10:P49	Ziólkowski Bartosz	A-15.4:L03
Violin Kalan	A-6:P36	Wu Po-Ching	F-2:L10	Zrinyi Miklos	A-15.4:IL02
Viscuso Stefano	B:P15	Wurtz Gregory	A-12.2:IL04	Zugasti Ekhi	G-6:L12
Vogel Eric	H-4:L04	Xia Chao	A-13.1:L10	Zukalova Marketa	A-14:P76

ABSTRACTS

4th International Conference

SMART MATERIALS, STRUCTURES AND SYSTEMS

OPENING SESSION

Plenary Lectures

PL-1 Report on the 2011 off the Pacific Coast Tohoku Earthquake: Its Impact and Control/Monitoring Performances

A. NISHITANI, Waseda University, Tokyo, Japan

The 2011 off the Pacific coast Tohoku earthquake and its following tsunami severely damaged Japan. Those damages were not only physical-wise but also mental-wise to Japan. We, Japanese, have still suffered from the effects of the severely damaged nuclear power plants in Fukushima-ken. The speaker talks about how some monitoring systems worked during the earthquake, in particular how effectively and efficiently a railroad company's monitoring system performed. In addition, the performances of high-rise buildings with several types of control schemes installed (including base-isolation schemes), and nuclear power plants in the seismic event are presented. It seems the earthquake may significantly change the view of Japanese about the safety for civil/building structures. Such impact will be also mentioned.

PL-2 MEMS Sensors and Actuators: From Actual Market Explosion to New Frontiers

B. MURARI, ST Microelectronics, Agrate Brianza, Italy

On this speech will be analyzed the reasons of the MEMS Sensors and Actuators success with an overview of different products in existing applications. New challenges for Silicon Solutions to answer emerging needs are analyzed and proposed.

PL-3 DNA: Not Merely the Secret of Life

N.C. SEEMAN, Department of Chemistry, New York University, New York, NY, USA

We build branched DNA species that can be joined using sticky ends to produce N-connected objects and lattices. We have used ligation to construct DNA stick-polyhedra and topological targets, such as Borromean rings. Branched junctions with up to 12 arms have been produced. Nanorobotics is a key area of application. We have made robust 2-state and 3-state sequence-dependent devices that change state by varied hybridization topology. We have constructed a molecular assembly line by combining a DNA origami layer with three 2-state devices, so there are eight different states represented by their arrangements. A central goal of DNA nanotechnology is the self-assembly of periodic matter. Recently, we have self-assembled a 3D crystalline array and have solved its crystal structure to 4 Å resolution, using unbiased crystallographic methods. Many other crystals have been designed following the same principles of sticky-ended cohesion. We can use crystals with two molecules in the crystallographic repeat to control the color of the crystals. Thus, structural DNA nanotechnology has fulfilled its initial goal of controlling the structure of matter in three dimensions. A new era in nanoscale control awaits us.

(This research has been supported by the NIGMS, ONR, ARO and NSF)

Adaptive, Active and Multifunctional Smart Materials Systems

Oral Presentations

Session A-1

Smart Inorganic Materials Systems

A-1.1 Electroceramics

A-1.1:IL01 Multifunctional Thin Films and Heterostructures by MOCVD and Combined Chemical Routes

F. WEISS, A. BARTASYTE, C. JIMENEZ, J.L. DESCHANVRES, E. SARIGIANNIDOU, M. AUDIER, S. PIGNARD, J. KREISEL, V. CONSONNI, G. REY, E. PUYOO, G. GIUSTI, D. BELLET, LMGP - Grenoble INP - CNRS - Minatec, Grenoble, France

In relation with the continuous reduction in size of electronic systems and smart devices, multifunctional nanostructures face today very challenging questions in materials science: ultimate size reduction, integration of heterogeneous functions, system characterisation or process control at an atomic scale. We present here different studies devoted to solid state oxide systems, containing functional oxides for active devices, read-write and storage memories, optoelectronics or photovoltaics. Indeed, with the size reduction of the systems, very original physical phenomena can occur. They are particularly enhanced in multi-layers or superlattices, nanowires or dots, where strain, surfaces and interfaces play a crucial role and can tune the physical properties. We approach these phenomena by using MOCVD and combined chemical synthesis routes and present specific considerations on the growth conditions to design complex 3D, 2D and 1D smart structures. Selected case studies will finally be presented, illustrating the powerful development of different oxide nanostructures based on superconducting oxides (YBaCu3O7.), dielectric or ferroelectric oxides (Pb(Zr1-xTi)xO3, BaTiO3/SrTiO3.), manganites and nickelates, as well as smart films or nanowires for photonic or photovoltaic devices

A-1.1:IL02 Unusual Higher Order Coupling in Piezoelectric and Ferroelectric Materials

W.S. OATES, Department of Mechanical Engineering Florida A&M/ Florida State University, Tallahassee, FL, USA

Piezoelectricity is often described to be proportional to the polarization of a solid; however, Martin (Phys. Rev. B, v.5(4), 1974) has illustrated that piezoelectricity is uniquely derived from bulk properties using polarization and the next higher order quadrupole. This coupling is analyzed using nonlinear continuum mechanics and field theory by describing the internal state using both polarization and the electric quadrupole. The results show that anisotropic piezoelectricity can be predicted from a free energy function that only includes elastic energy of the solid combined with a Landau-deGennes free energy that describes the ferroelectric behavior without introducing explicit piezoelectric or electrostrictive coefficients. Rotational invariance is used to obtain coupling for finite deformation problems. Limits to infinitesimal strain show unusual predictions of piezoelectricity that match data given in the literature based on time-resolved x-ray strain data of lead zirconate titanate ceramics. Additional coupling effects between the quadrupole, strain gradients, and flexoelectricity are also discussed.

A-1.1:IL04 Charge Density Studies of Piezoelectric Ceramics: Characteristic Chemical Bonding and Thermal Motion

Y. KUROIWA, Department of Physical Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima, Hiroshima, Japan

Pb-containing perovskite solid solutions, such as PbZr1-xTixO3 (PZT), show outstanding piezoelectric performance. In these ceramics, ferroelectricity related to the large lattice distortion enhanced by the Pb-O covalent bonding is suggested to be a clue to the excellent piezoelectricity. Meanwhile, every PZT does not show high piezoelectric performance. PZT near the morphotropic phase boundary (MPB) composition (x ≈ 0.5) possesses the prominent piezoelectric properties, which means that a conflict between the fluctuation leading to ferroelectric and antiferroelectric lattice distortions also plays an important role for the excellent piezoelectricity. In the present paper, high-energy synchrotron-radiation powder-diffraction experiments are performed to provide the structural information essential for better understanding of the piezoelectric properties. We succeed in visualizing the Pb-O covalent bonding and the anisotropic valence-electron density distributions on the Pb ion in PbTiO3 which cause the electric polarization in the Pb ion. A change in the thermal motion of the Pb ion in PZT in the paraelectric phase is detected at the MPB composition as a function of x. Similar changes in the thermal motion are observed in Pb-free piezoelectric solid solutions such as (Na,K)NbO3.

A-1.1:IL05 Impact of Sputter Deposition Parameters on the Leakage Current Behaviour of Aluminum Nitride Thin Films

M. SCHNEIDER, T. STRUNZ, A. BITTNER, U. SCHMID, Vienna University of Technology, Institute of Sensor and Actuator Systems, Vienna, Austria

In MEMS (micro electromechanical system) devices, piezoelectric aluminum nitride (AlN) thin films are commonly used as functional material for sensing and actuating purposes. Furthermore, AlN features excellent dielectric properties as well as a high chemical and thermal stability. In this work, we investigate the leakage current behavior (IV characteristic and charging curve) of AlN thin films sputter deposited at varying plasma powers (i.e. 300 W - 800 W) and deposition pressures (i.e. 4 μbar - 8 μbar) up to an electric field of 0.1 MV/cm. First results show a Poole-Frenkel behavior for all samples with an increase in leakage current by orders of magnitude as the degree of c-axis orientation decreases. In addition, the charging curves agree well with the empirical Curie-Van Schwedler Law ($I(t) = I + C \cdot t^{-n}$) and an exponential increase of the parameter C with temperature is observed. Basically, these results are expected and show a strong positive correlation between the parameters I and C representing the static and the transient current fraction, respectively. In the final paper, we will also discuss in detail the influence of temperature on the parameter n.

A-1.1:IL06 Study of Piezoelectric Actuation in Flexible AlN Cantilevers

S. PETRONI, M. AMATO, Center for Biomolecular Nanotechnologies @UNILE, Istituto Italiano di Tecnologia, Arnesano (LE), Italy; G. MARUCCIO, F. GUIDO, M. DEVITTORIO, Dip. Ingegneria dell'Innovazione di Università del Salento, Lecce, Italy; M.T. TODARO, A. CAMPÀ, A. PASSASEO, National Nanotechnology Laboratory of CNR-INFM, Lecce, Italy

In the recent years the development of soft actuators for robotic and medical applications is attracting great interest. The interest from medical science is motivated by the growing demand of smart devices: sensors and actuators able to perform analysis and diagnosis exploring human body by means of minimal invasive surgeries (MIS), so avoiding pains and long convalescence time to the patients. The strategy of employing

smart structures characterized by flexibility and electro-mechanical transduction is the most attracting for this application. In this work we study flexible cantilever structures based on Aluminum Nitride (AlN) integrated on kapton to realize smart micro-actuators. The integration is achieved by the sputtering deposition of a layer sequence Molybdenum(Mo)/ AlN/Mo, characterized by high crystal quality, on kapton. After the fabrication process the resulting suspended cantilevers are bent downward because of the residual stress. The application of an electrical stimulus by means of top and bottom Mo electrodes generates a cantilever deflection, measured by Atomic Force Microscopy converting the voltage signal of the detector into mechanical displacement. The displacement is measured on cantilevers with different geometries.

A-1.1:L09 Dielectric and Ferroelectric Analysis of Nanoparticle/ Nanocrystalline Barium Titanate and PLZT for use in Smart Inorganic Materials Systems

C.B. DIANTONIO, T. MONSON, M.R. WINTER, T.P. CHAVEZ, P. YANG, Sandia National Laboratories, Albuquerque, NM, USA

Attractive for numerous technological applications, ferroelectric oxides constitute an important class of multifunctional compounds. Intense experimental efforts have been made recently in synthesizing, processing and understanding ferroelectric nanostructures. An objective being to optimize and implement the active functions of these materials into 'smart' devices that elicit the appropriately designed response. This work will present the systematic characterization and optimization of barium titanate and lead lanthanum zirconate titanate nanoparticle based ceramics and how these materials are being examined to meet needs for present and future applications. The nanoparticles have been synthesized using several solution and pH-based synthesis processing routes and employed to fabricate polycrystalline ceramic and nanocomposite based components. The dielectric and ferroelectric properties of these various components have been gauged by impedance analysis and electromechanical response and will be discussed.

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A-1.1:L10 Controlled Assembly of Two-dimensional Oxide Nanosheets for Tailored Dielectric Materials

M. OSADA, T. SASAKI, International Center for Materials Nano-architectonics, National Institute for Materials Science, Tsukuba, Japan, & CREST, Japan Science and Technology Agency (JST), Japan

We report on a rational approach to produce high performance nanodielectrics using molecularly thin perovskite nanosheets as a building block¹. Perovskite nanosheets (Ca₂-xSr_xNb₃O₁₀) were prepared by delaminating Dion-Jacobson-type layered perovskites (KCa₂-xSr_xNb₃O₁₀) into their molecular single sheets. We approached the fabrication of multilayered nanocapacitors by a layer-by-layer assembly using the Langmuir-Blodgett process. These perovskite nanofilms exhibit high dielectric constant (200-240), the largest value seen so far in perovskite films with the thickness down to 5 nm. Such high-k properties are fairly temperature-independent with low leakage current density (<10⁻⁷ A cm⁻²). We also utilized these high-k nanosheets as a building block in the bottom-up assembly, and successfully developed various nanodevices such as high-k capacitors, all nanosheet FET, nano-ferroelectrics.

1. M. Osada et al, *Adv.Mater. ASAP* (2011). DOI: 10.1002/adma.201001722, *ACS Nano* 4, 5225 (2010); *ACS Nano* 4, 6673 (2010).

A-1.1:IL11 Flexoelectric Materials, Structures and Sensing Applications

XIAONING JIANG, North Carolina State University, Raleigh, NC, USA

Flexoelectricity refers to the electromechanical coupling that polarization can be generated by strain gradient. Flexoelectricity exists in many organic and inorganic materials including liquid crystals, ferroelectrics, etc., and many applications utilizing flexoelectricity have been reported. In this paper, a review will be given to flexoelectric materials, structures and the existing applications. Analysis on dramatic enhancement of effective piezoelectric properties through flexoelectric effect and scale

effect will be next presented. Design, fabrication and characterization of flexoelectric sensing structures will be discussed at the end. It is believed that flexoelectricity will play a significant role in miniaturization of sensors for a broad range of applications.

A-1.1:IL12 Integrated Piezoelectrics for Adaptive Microsystems - Teamwork of Substrate and Piezo

S. GEBHARDT, Fraunhofer Institute for Ceramic Technologies and Systems, Dresden, Germany

The trend towards highly miniaturized and complex microsystems demands for new solutions of integrated sensor and actuator functions. Microelectronic substrates like Silicon, alumina and LTCC (Low Temperature Cofired Ceramics) allow for 3D packaging (electrical connection, channels, cavities and membranes), high robustness and reliability as well as integration and application of electronic components whereas piezoceramic materials offer sensor and actuator operations. To combine the advantages of both integrated solutions are of great interest. The functionality of the smart systems not only depends on design and construction but also on material interactions. A thorough choice of substrate and piezoceramic material as well as the understanding and prevention of chemical reactions are necessary to build effective systems. The presentation will give an overview covering design aspects, technology and applications of integrated piezoceramic thick films and plates in multilayer material systems. Detailed information on application for active optics, adaptive structures, force sensors and ultrasonic transducers will be shown.

A-1.1:IL13 Dielectric Anisotropy as an Additional Tunability of Ferroelectric Based Composites

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An extensive literature is devoted to the permittivity and dielectric losses of ferroelectric based composites. The distribution of dielectric inclusions in a ferroelectric matrix affects the electric field distribution. A drawback to experimentally fit with the proposed models lies in the interdiffusion between the two phases, which can be overcome using Spark Plasma Sintering. The sharpness of the interfaces between the different components allows a reliable description of their physical properties. The orientation of the oblate dielectric inclusions versus the external field is a determining parameter. We show here an original way to control the effective permittivity and its anisotropy through the increase of the 3D microstructure anisotropy, which can be adjusted by the uniaxial pressure applied during SPS. Pyroelectric and piezoelectric coefficients were also shown to be anisotropic. To understand this anisotropy, we have used a 3D microstructural imaging based on X-Ray tomography and quantitative 3D image processing leading to particles agglomeration, size distribution and morphology. 3D reconstruction allows to map out the geometry of the inclusions and their interfaces with the matrix, which are required for a reliable matching between experiment and models.

A-1.1:IL16 Modeling of 3D Magnetostrictive Systems with Application to Galfenol and Terfenol-D Actuators

M. DAPINO, The Ohio State University, Department of Mechanical and Aerospace Engineering, Columbus, OH, USA; S. CHAKRABARTI, Cummins Inc., Columbus, IN, USA

We present a model for 3D, dynamic magnetostrictive systems. Maxwell's equations for electromagnetics and Navier's equations for mechanical systems are formulated in weak form and coupled using a generalized constitutive law. The overall system is approximated hierarchically; first, piecewise linearization is used to describe quasistatic responses and perform magnetic bias calculations. A linear dynamic solution with piezomagnetic coefficients computed at the bias point describes the system dynamics for moderate inputs. Dynamic responses at large input fields and stresses are described through an implicit dynamic solution method based on the trapezoidal rule. The model simultaneously describes the effect of magnetostructural dynamics, flux leakage, eddy currents, and transducer geometry. The model is applicable to arbitrary magnetostrictive materials as long as a differentiable 3D constitutive law for the material is available. The model is implemented into a finite element (FE) solver and applied to two case studies, a Galfenol unimorph actuator and a magnetohydraulic Terfenol-D actuator for active engine

mounts. Model results are compared with experiments, and parametric analyses are conducted which provide guidelines for optimization of actuator design.

A-1.1:IL17 **Magnetic and Dielectric Properties of EuTiO₃ Thin Film under Strain**

K. TANAKA, Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan

Bulk EuTiO₃ is known to show magnetodielectric effect. In addition, theoretical study suggests that application of stress or formation of strain leads to a drastic change in magnetic and dielectric properties of EuTiO₃. In the present study, effects of strain induced by a substrate, on which EuTiO₃ thin film is deposited, on the magnetic and dielectric properties have been examined. By using a pulsed laser deposition method, the EuTiO₃ thin film was grown on different kinds of substrates, i.e., LaAlO₃, SrTiO₃, and DyScO₃; the lattice constant of these compounds is smaller than, just the same as, and larger than that of EuTiO₃, respectively. Magnetic and dielectric properties were measured for the resultant thin films. Temperature dependence of magnetization indicates that all the thin films exhibit ferromagnetic behavior at low temperatures. The magnetization at 2 K under a magnetic field of 100 Oe is the largest for EuTiO₃ on DyScO₃ and the smallest for EuTiO₃ on LaAlO₃. The experimental result is coincident with first-principles calculation which predicts that ferromagnetic spin configuration becomes more stable as the lattice volume of EuTiO₃ is increased.

A-1.1:IL18 **First-principles Study of New Multiferroic Perovskite Oxides**

O. DIEGUEZ, J. INIGUEZ, ICMA-B-CSIC Campus de la UAB, Bellaterra, Spain

In this talk I will briefly introduce the subject of researching the properties of novel materials by numerically solving the quantum mechanical equations that govern the behavior of their electrons. I will then show applications of this kind of studies to the field of multiferroic materials, which show coexistence of both ferroelectric and (anti)ferromagnetic ordering. This property lends itself to potential applications in technological devices such as computer memories. In particular, I will present our recent results for two kinds of materials: (i) we have found new supertetragonal phases for the prototype multiferroic bismuth ferrite [Dieguez et al, *Phys Rev B* 83, 094105 (2011)], and (ii) we propose to use a solid solution of bismuth ferrite and bismuth cobaltite to create a material where it is possible to switch between two very different phases in a way that involves strong piezoelectric, electric, and magnetoelectric effects [Dieguez and Iniguez, *Phys Rev Lett* 107, 057601 (2011)]. If time permits, I will also show new results in our quest to find new multiferroics with improved properties.

A-1.1:IL22 **Rewritable Magnetic Patterning and its Application Based on Hydrogen Mediated Ferromagnetism**

SEUNGHUN LEE, WON-KYUNG KIM, JI-HUN PARK, YONG CHAN CHO, H. KOINUMA, SE-YOUNG JEONG, Department of Cogno-mechatronics Engineering, Pusan National University, South Korea

Manipulating the shape, size and inversion of magnetic domain indispensable to development of the information technology and the understanding of the physical interaction between magnetic domains has been attractive research for future spin logic devices. We have reported theoretical and experimental results for ferromagnetism of Co doped ZnO(ZnCoO) based on hydrogen mediation, and Co-H-Co complex. Its magnetization was controlled according to hydrogen content and was reversible to convert between paramagnetism and ferromagnetism by hydrogen ejection and injection process. In this study, we present magnetic patterning and its applicability based on hydrogen mediated ferromagnetism. To fabricate the mask for selective hydrogen injection to ZnCoO thin film, conventional lithography technique was used and plasma treatment and hot isostatic pressing were carried out for hydrogen injection through patterned photoresist layer. In magnetic force microscope image, clear magnetic contrast was observed according to applied magnetic field. It suggests the new paradigm for manipulation and tailoring of the magnetic domain structure through a selective hydrogenation process and it will be applied to rewritable spin device based on reversible ferromagnetism.

A-1.1:IL23 **Structure and Properties of High-pressure-manufactured MgB₂-based Superconductors for Smart Applications**

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Reversible transition from superconducting to non-superconducting state inducing by external magnetic field variation makes it possible to attribute superconducting materials to smart materials as well (MgB₂-based ones, in particular). Estimated critical current densities, AC losses and AC and DC voltage-current characteristics of high-temperature high-pressure manufactured (2 GPa quasi-hydrostatically pressed or 30 MPa hot pressed, or 50 MPa spark plasma sintered and synthesized) ring-shaped MgB₂-based superconductors allowed us to demonstrate the availability of the smart MgB₂-based materials for effective application in inductive transformer-type fault current limiters. Correlations between structural features (studied by X-ray using Rietveld refinement, high resolution SEM equipped with X-ray microanalyzer and Auger-spectrometer), superconducting and mechanical characteristics of MgB₂-based materials synthesized (from Mg and B powdered mixture) or sintered (from MgB₂ powders) without and with additions of titanium, carbon or silicon carbide under different pressure-temperature conditions will be under the consideration. Influences of higher magnesium borides and oxygen segregation in MgB₂-based materials on pinning forces, critical current densities, upper critical fields and fields of irreversibility have been demonstrated. Correlations between pressure, temperature, type of addition and amount, distribution of oxygen and higher borides have been revealed.

A-1.2 **Biologically, Chemically and Environmentally Responsive Inorganic Materials**

A-1.2:IL02 **Light-switchable Nanoparticles**

R. KLAJN, S. DAS, Department of Organic Chemistry, Weizmann Institute of Science, Rehovot, Israel

Recent years have witnessed an explosion of interest in dynamic materials - that is, materials capable of changing their structure and properties upon exposure to external stimuli. Of these stimuli, light is particularly interesting for numerous reasons. Herein we present a new photoresponsive system based on metallic nanoparticles functionalized with a molecular photoswitch - a moiety capable of existing in various isomeric configurations depending on the wavelength of light it is exposed to. First, we investigated whether and how the immobilization of the photoswitch on the surface of nanoparticles affected its photochemical properties. Second, we found that various configurations of the photoswitch provided the nanoparticles with contrasting solubilities - as a result, the isomerization process induced aggregation of nanoparticles originally dispersed in a good solvent, or dissolution in a non-solvent. This finding which led to the development of new light-induced self-assembly systems. Finally, we discuss the advantages of the new system over the previously reported ones based on azobenzene.

A-1.2:IL03 **Towards Molecular Recognition by Smart Multifunctional Mesoporous Silica Microdot Arrays through the Combination of Ink-jet Printing, EISA and Click Chemistry**

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The ink-jet printing (IJP) and Evaporation Induced Self-Assembly (EISA) processes are combined in order to achieve with a high flexibility patterned mesoporous silica microdot arrays while the click chemistry mechanism allows to selectively post-functionalize microdots. Indeed, the addition of the 3-azidopropyltriethoxysilane (AzPTES) precursor into the ejected silica sol formulation enables to obtain azide functionalized

silica mesoporous microdots arrays: the azide functional groups brought by AzPTES are co-localized with the surfactant micelles during the EISA. After the surfactant removal, these azides become accessible and a 1,3-dipolar Huisgen copper-catalyzed cycloaddition with alkynes, known as "click reaction", is performed. This configuration offers the opportunity to specifically post-functionalize each microdot via multiple click reactions with selected alkynes capable of performing molecular recognition of interest. Furthermore, by tailoring the pore size and structural organization of the mesoporous silica microdots through different parameters, such as sol formulation, sol aging time and ink-jet printing deposition settings, the sensitivity of these smartly designed multi-chemically responsive inorganic devices can be improved.

A-1.2:LO4 **Metallic Electrolyte Composites in the Framework of the Brick-layer Model**

H. LUSTFELD, PGI-1 Forschungszentrum Juelich, Juelich, Germany; C. PITHAN, PGI-7 Forschungszentrum Juelich, Juelich, Germany; M. REISSEL, Fachhochschule Aachen, Abteilung Juelich, Juelich, Germany

It is well known that the already large dielectric constants of some electrolytes like BaTiO₃ can be enhanced further by adding metallic (e.g. Ni, Cu or Ag) nano particles. The enhancement can be quite large, a factor of more than 1000 is possible. The consequences for the properties will be discussed here applying a brick-layer model (BLM) for calculating dc-resistivities of thin layers and a modified one (PBLM) that includes 3d percolation for calculating dielectric properties of these materials. The PBLM results in an at least qualitative description and to an understanding of the physical phenomena: This model gives an explanation for the steep increase of the dielectric constants below the percolation threshold and why this increase should be connected to a dramatic decrease of the breakdown voltage as well as the ability of storing electrical energy. We conclude that metallic electrolyte composites like BaTiO₃ composites may be useful for getting high capacitances but are not at all appropriate for energy storage¹.

1. Paper to be published in *J. Eur. Ceram. Soc.*

A-1.2:LO5 **Smart Luminescent Microporous Materials**

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Lanthanide-bearing luminescent materials find numerous applications in lighting, photonics optical communications, and biomedical devices. The grand challenges in the field of materials engineering of photoluminescent (PL) centres include the design of efficient, stable, cheap, environmentally-friendly and multifunctional phosphors. I shall review our approach to meet these challenges, which is based on both microporous Ln³⁺ silicates and Ln³⁺ organic frameworks (MOFs). Highlights of our work include: (i) an intriguing PL chiral silicate, and a silicate possessing both isolate Eu³⁺ and Eu³⁺-Eu³⁺ dimers, and a rather long 5D₀ lifetime (12 ms at 10 K)¹; (ii) MOFs with quantum yields and efficiencies among the highest reported, which allowed the development of an ethanol sensor², and a miniaturized, self-calibrating, Ln-MOF pH sensor operative at physiological pH. The combination of Ln³⁺-light emission and meso porosity (ca. 20 nm) has also been accomplished with lanthanide oxide nanotubes. In particular, we report an approach towards the use of the light-emission features of Ln ions in real-time imaging applications³.

1. *J. Am. Chem. Soc.*, 2009, 131: 8620; 2. *Angew. Chem. Int. Ed.*, 2008, 47: 1080; 3. *Macedo et al, Nanotechnol.*, 2008, 19: 295702

A-1.2:LO6 **Nanostructured Vanadium Oxide Films Made by Liquid Phase Deposition: Morphology, Structure and Optical Property Control**

M. ES-SOUNI, R. MINCH, Institute of Materials & Surface Technology, University of Applied Sciences Kiel, Kiel, Germany

Vanadium oxides are the subject of intense research for many decades due to their technologically important properties like thermochromism and catalysis. Especially VO₂ and V₂O₅ that undergo a well studied semiconductor to a metal transition at 68 and 257 °C, respectively, were largely investigated. Structure-property correlations in these oxides, including the effects of different parameters like grain size, annealing temperature, film thickness and morphology on the physical properties were described and discussed in a number of papers. It is agreed upon that synthesis methods parameters and underlying substrate are crucial for controlling morphology and physical properties of the films. The

most widely used techniques of vanadium oxide film and nanoparticles preparations are summarised elsewhere. In this paper we first review some of the interesting results obtained elsewhere, and present our own new results on nanostructured vanadium oxide films obtained using liquid-phase deposition. We present and discuss the effects of the following parameters on film morphology, structure and optical properties: 1) the precursor solution composition, 2) the drying treatment of spin-coated layers before final annealing, 3) gel film ageing before final annealing.

Session A-2

Stimuli Responsive Polymers and Gels

A-2:LO1 **Biologically Stimuli-responsive Hydrogels that Recognize Target Biomolecules**

T. MIYATA, Department of Chemistry and Materials Engineering, Kansai University, Suita, Osaka, Japan

Biologically stimuli-responsive hydrogels that undergo changes in volume in response to a specific biomolecule, so-called biomolecule-responsive hydrogels, are useful tools for fabricating molecular diagnostic systems and self-regulated DDS. We proposed a novel strategy to prepare biomolecule-responsive hydrogels; our strategy uses biomolecular complexes as reversible crosslinks that dissociate and associate in the presence and absence of a target biomolecule, respectively. On the basis of this strategy, we prepared various biomolecule-responsive hydrogels that exhibit swelling/shrinking behavior in response to a target biomolecule. Biomolecule-crosslinked hydrogels that can swell in response to a target biomolecule have been designed by using saccharide-lectin complexes, antigen-antibody complexes and DNA duplexes as reversible crosslinks in the hydrogel networks. Biomolecule-imprinted hydrogels that can shrink in the presence of a target biomolecule have been strategically prepared by molecular imprinting using various biomolecules as ligands for the target biomolecule. The responsive behavior of the biomolecule-crosslinked and biomolecule-imprinted hydrogels is based on dissociation and association of biomolecular complexes as reversible crosslinks. In addition, a method for preparing biologically stimuli-responsive gel particles that undergo changes in size in response to a target biomolecule is also reported.

A-2:LO2 **Toward Autonomic Response: Self-oscillating Gels**

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Polymer gels undergoing the Belousov-Zhabotinsky reaction are unique materials because the polymer network can undergo autonomous oscillations in the absence of external stimuli. These self-oscillating gels provide an ideal medium for probing the interplay between chemical energy and mechanical action. Here we focus on two distinctive examples of the autonomous response of these gels to the external environment. In the first example, we consider gels with gradients in their crosslink density. Free in solution, these samples undergo a self-propelled motion in the direction of lower crosslink density. Moreover, if the same samples are attached with one end to a flat surface, variations in the concentration of the reagents in the external solution effectively control the motion of the free end. In the second example, we focus on artificial cilia made of self-oscillating gels and show that this system can communicate to undergo a biomimetic, collective response to small-scale chemical changes. We also show that the cilia oscillations can be controlled remotely and non-invasively by light. The findings from these studies provide guidelines for creating autonomously moving objects and biomimetic self-oscillating cilia which can be used in robotic or microfluidic applications.

A-2:LO3 **Monitoring the Swelling/Deswelling of Stimuli-responsive Hydrogels with Magneto-resistive Methods**

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Magneto-resistive sensors have been proposed as detection components in biological devices (biosensors, biochips). They directly provide an

electrical signal that can be evaluated with standard electronics. The change of a magnetic field can be followed by giant magneto-resistive (GMR) elements or sensors based on the Hall-effect. The application of a smart hydrogel (decorated with magnetic particles) as a sensor layer in combination with a Hall-effect sensor is demonstrated on monitoring the swelling/deswelling process. The distance between magnetic particles and the Hall sensor depends on the degree of swelling. The Hall voltage is determined by the degree of swelling and thus by the properties of the liquid environment. The design of a magneto-resistive device based on a GMR platform is reported. GMR and a gel are coupled in different geometries (planar, rolled-up, reaction vessel). The used smart polymers are filled with different magnetic particles. The functionality of the designs is demonstrated on different tasks: Following the swelling/deswelling curve, monitoring the change of an analyte concentration, and counting of gel containers in a flow stream. The main properties of a GMR-based sensor are discussed, even in comparison with the Hall-based principle.

A-2:L04 Non-homogeneous and Anisotropic Swelling of Polymer Gels

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As it is well known, the modeling of the swelling-induced mechanical behaviour of polymer gels involves the analysis of two concurrent evolutive processes determined by the solvent transport and by the elastic response of the polymer network¹. The swelling-induced deformation patterns depends strongly on the boundary conditions. Appropriate constraints may induce distinguished stress states and deformation patterns; likewise, localized exposure to the solvent². Our aim is the theoretical modeling and numerical simulation of specific experiments characterized by non-homogeneous and anisotropic swelling due to a localized exposure to the solvent together with mechanical constraints which keep the polymer gel free to bend and twist. Specific surface absorbing models are analysed to investigate the influence of the difference between the bulk and the surface diffusivities of a polymer gel.

1. M. Doi. *Gel Dynamics*. J. Phys. Soc. Japan 78(5), 052001, 2009.
2. D.P. Holmes, M. Roch , T. Sinha and H.A. Stone. *Bending and twisting of soft materials by non-homogenous swelling*. *Soft Matter* 7, 5188-5193, 2011.

A-2:L05 Recent Progress in Flexible Screen-printed Ion-selective Sensors for Environmental and Wearable Applications

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New understanding and the introduction of novel materials in Ion Selective Electrodes (ISEs) has boosted their use as low cost analytical platform. Their compatibility with thick film technology is intriguing because they can also be screen printed on flexible substrates suitable for wearable applications. Their coupling with screen printed reference electrodes has a potential as cheap, disposable, wireless sensing platform applied to environmental and physiological monitoring. Here we report on the use of conducting polymers (CPs) and ionogels, as new types of solid contact for the ISEs applied to the monitoring of lead in water and of chloride and sodium in sweat samples in real time experiments. The accuracy of the methods is validated with standard analytical methods. The key factor in the use of the ionogels is tuning their hydrophobicity while the preparation of the ISE solid contact from the CPs is more straightforward. A comparison of the experimental results thus obtained will be presented at the light of the materials employed.

A-2:IL06 Nanocomposite Hydrogels (NC gels) with Excellent Optical, Mechanical and Stimuli-responsive Properties

K. HARAGUCHI, Kawamura Institute of Chemical Research, Sakura, Chiba, Japan

Poly(N-isopropylacrylamide) (PNIPA) hydrogels have been extensively studied, from both scientific and industrial application points of view, as typical stimuli-responsive hydrogels. However, PNIPA hydrogels used so far had some serious disadvantages, such as weak and brittle mechanical properties, structural inhomogeneities, low degree of swelling, and slow de-swelling rate, because of their chemically crosslinked network structure. Here, we present a new type of PNIPA hydrogel which solves all these problems simultaneously. The novel hydrogel is a

nanocomposite hydrogel (NC gel) with a unique organic (polymer)/inorganic (clay) network structure. NC gels are prepared by in-situ free radical polymerization using exfoliated clay, instead of an organic crosslinker. NC gels exhibit high transparency, high degrees of swelling, high de-swelling rate, and superb mechanical properties with extraordinarily large deformations. Also, these optical, mechanical and swelling/de-swelling properties can be controlled over a wide range by altering the gel composition. Furthermore, NC gels exhibit a number of new characteristics related to the properties of their gel-air and gel-water interfaces, coil-to-globule transition, optical anisotropy, interactions with cells, and control of morphology.

A-2:L08 Hydrogel Sensors for Process Monitoring

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For the direct measurement of chemical concentrations of substances in process liquids, sensors need to be fast and reliable. We investigated the usability of hydrogels as sensitive coating materials for piezo-electric thickness shear mode resonators. Hydrogels are cross-linked polymer networks that show well-defined shifts of their degree of swelling upon changes of environmental parameters such as ionic concentrations, concentrations of organic solvents or temperature. These changes of gel properties are then transferred into an electrical signal. The novel sensor solution exhibits response times of only few seconds and matches the reliability of innovative process measuring technology. A method for its application specific adaption is presented. It is based on optimizing the interrelation of the sensor structure, the manufacturing technology for the hydrogel layer, and the processing of the measured data. The performance of the method is illustrated with the example of a PVA/PAA-hydrogel coated sensor which monitors the concentration of a cleaner used in surface technology. The developed measurement device for this application was approved with a measurement error of less than 5%.

A-2:L09 Multi-responsive Hydrogels for Sensing Applications from Thiolactone Functionalized Polymers

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Within the here presented work we made use of a novel synthetic protocol to create multi-responsive, degradable hydrogels for sensing applications in an easy, widely applicable way. This protocol includes the recently established method of in situ thiol release from a thiolactone moiety by nucleophilic attack of a primary amine. By choosing a suitable functional amine, thiolactone containing polymer precursors were equipped with a sensing moiety and subsequent (reversible) formation of disulfide bridges from the released thiol groups led to gelation. In order to demonstrate the modular nature and therefore the versatility of the applied thiolactone protocol two different sensing purposes were targeted, namely glucose and heavy metal ion sensing. For that purpose, the ring opening amine was equipped with a boronic acid and a morpholine moiety, respectively. It is emphasized, that the presented synthetic protocol generally has a high potential for the synthesis of complex, multi-responsive materials since it is not only modular, but also starts from cheap commercial sources and works in a one-pot fashion without external trigger such as heat. Besides, no side products are formed and the resulting gels are easily degradable under reductive conditions

A-2:L11 Development of Ultra Sensitive Strain Sensors Based on All-organic Flexible Thin-films

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Over the last thirty years tetrathiafulvalene (TTF) and its derivatives have been successfully used as building blocks for charge transfer salts giving rise to a multitude of organic conductors and superconductors. These conductors are obtained as single crystals and, therefore, their applications are limited. However, micro and nanocrystals of conducting TTF salts embedded in a polymeric matrix (BL films) offer great potential for applications in electronic devices. These materials are very promising since they combine the unique physical properties of molecular

conductors with the processability and flexibility of polymeric films. In addition "all organic" circuits can be drawn by local thermal treatment of these composite materials. BL films are also extremely sensitive to strain changes (gauge factors between 18 and 9) and exhibit fast and completely reversible responses¹. Such BL films have a sensitivity one order of magnitude larger than the most commonly used metal-based electromechanical sensors. In addition, a few proof-of-concept experiments with simple prototypes will be also reported demonstrating that these flexible, low-weight, and transparent composites are very attractive as a new generation of durable and low-cost all-organic strain sensors being highly promising for a wide range of applications. It will also be presented the integration into a polyester textile of one of this kind of materials. The resulting textiles, in addition to be conducting, exhibit the excellent strain sensing properties of BL films maintaining at the same time their flexibility².

1. E. Laukhina et al, *Adv. Mater.*, 22 (2010) 977 and .. Patents PCT/ES/2006/02087 and US2009/2/515009.

2. L. Ferreras et al, *J. Mater. Chem.* 21 (2011) 637-640.

A-2:IL15 Stimuli-responsive Polymer Brushes for Sensing Applications and Protein Adsorption

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Polymer chains can be covalently attached to solid surfaces and mixed polymer brush layers are versatile surface coatings which reveal stimuli-responsive behaviour with different stimuli like pH, temperature or salt concentration. The degree of swelling can be detected by optical means utilising fluorescence interference effects or plasmon resonance excitation¹⁻³. Also chemical sensing becomes possible if surface enhanced Raman scattering from nanoparticles in polymer brushes is used⁴. Polymer brushes with nanoparticles thus offer different possibilities for sensing at nanoscale. They are effectively used to control adsorption of biomolecules, where adsorption and desorption of proteins can be tuned by pH^{5, 6}.

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Session A-3

Auxetic Materials

A-3:IL01 Toward Auxetic Shape Memory Liquid Crystalline Elastomers

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As part of an ongoing program aimed at creating molecular-level organic auxetic materials, we have synthesized and examined a series of SmC main-chain liquid crystalline elastomers. The key structural feature is the presence of a laterally-attached rod that, upon tensioning the polymer main chain, would rotate into a position approximately perpendicular to the stretching direction leading to lateral expansion. This site-connectivity driven rod reorientation mechanism is examined in a series of experiments: x-ray diffraction, stress/strain measurement, and strain retention/thermal recovery (shape memory) measurement. Uniaxial stretching of these polydomain films at room temperature produces a monodomain structure that can, upon removal of load, retain a significant level of strain. Although these films show ordinary elastic response at temperatures near the isotropization (clearing) temperature, at room temperature - far below the clearing temperature - the mechanical response is anelastic. A rationale for the shape memory behavior is proposed that involves moving of crosslink points in the smectic lamellar arrangement during the stretching event and trapping of these crosslinks

in different positions at low temperatures. This trapping is driven by the chemical segregation of the crosslink points from the mesogenic unit which can be thermally overcome at elevated temperatures allowing full elastic recovery.

A-3:IL02 The Use of Auxetic Materials in Smart, Gradient and Multifunctional Systems

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Auxetics are attracting attention due to the novel property of expanding widthwise when stretched axially, and also because other properties can reach extreme values when Poisson's ratio assumes negative values characteristic of auxetic behaviour. Auxetic materials may form an important component of a system displaying 'smart' behaviour in some way. An example is the concept of a smart bandage which releases an active pharmaceutical ingredient from the fibre micropores due to opening of the micropores in response to swelling of the wound to which the bandage is applied. Controlled release of guest material in the bandage and other devices exploiting the stress-induced storage-release mechanism may be further optimised if gradient structure can be designed into the auxetic component. Similarly, the design of hierarchical auxetic behaviour into a system can lead to multifunctional response. For example, in the bandage application auxetic response at the fabric structure level might lead to enhanced breathability function in addition to the controlled release function from the fibre structure level. In this presentation progress towards the development of auxetic materials and structures having gradient properties for smart or multifunctional applications will be reported.

A-3:L03 Auxetic Foam Pads: Experiments and Parameters Identification

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Auxetic materials are known to exhibit smart and efficient mechanical properties such as high energy absorption and fracture resistance been able to be used for a variety of applications (personal protection clothing, packing material, robust shock absorbing material, sponge mops and filtration). The particular hinge-like structures of auxetic materials typically induce macroscopic negative Poisson's ratio. The material used in this work has been obtained from conventional foam that becomes auxetic after a specific forming process. Numerical and experimental approaches are conducted using conventional and auxetic samples made from the same base material, together with classical melamine foam for comparison purpose. Several acoustic properties are investigated. Finally, in order to identify some parameters values including the Poisson's ratio, a procedure allowing identification from simple measurements has been tested: a preliminary sensitivity study is performed, and the optimization step is then conducted in order to efficiently identify the parameters from experimental measurements. The particular case of the Poisson's ratio is considered in details. Aspects related to visibility of the parameter, anisotropy of the material and confidence of the identification are discussed.

Session A-4

Electrorheological and Magnetorheological Fluids

A-4:IL02 Novel Adaptive Damping Systems Based on Magneto-rheological Fluids

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In present magnetorheological (MR) dampers, the magnetic field for the control of the MR fluid is generated by the coil current of an electromagnet. This operation causes drawbacks in terms of poor fail-safe behaviour and low energy efficiency. In a novel approach, a MR damper was developed whose magnetic circuit contains permanent

magnets in addition to the electromagnet. The permanent magnets generate a strong magnetic field in the MR gap of the damper without any supply of electric energy. With the additional electromagnet, the magnetic field strength in the MR fluid can be strongly decreased or increased, which gives an improved fail-safe behaviour compared to MR dampers with an electromagnet solely. In another type of new MR dampers, the magnetic circuit is equipped with a switchable hard magnet consisting of AlNiCo as well as with an additional coil. Upon variation of the coil current, the magnetization in the AlNiCo magnet can be changed with only short pulses of the current. Electric power is only required for the change of magnetization, which makes the MR damper very energy-efficient. The design of such novel MR damping systems is introduced in the lecture. Moreover, the damping characteristics of the systems filled with special MR fluid compositions are described.

A-4:L06 **A Model Reference Adaptive Control of a Magneto-rheological Fluid Brake**

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The paper describes an experimental/theoretical activity that involves a magnetorheological fluid brake (MRFB). A device model is derived taking into account the viscous and the magnetic contribution to the braking torque. The viscous contribution is based on a purely algebraic relationship while the magnetic one is characterized by a nonlinear dynamic model. By means of parameters identification procedure, the influence of temperature and speed on model parameters is evaluated. The analyzed parameter variability suggests the employment of a model reference adaptive control finalized to regulate the braking torque. This feedback control method is able to minimize the tracking error in presence of a plant characterized by a known dynamics and uncertain parameters. According to this approach, the MRFB torque measurement only is necessary as feedback signal. Numerical simulations have been carried out and the obtained results confirm the goodness of the proposed approach.

A-4:L07 **Modeling and Analysis of the Electrorheological Fluids (Suspension Flow) with Aligned-Structure Reformation**

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A model capable of describing the suspension (electrorheological (ER) fluids) flow behavior under different electric field strengths through the full range of shear rates is proposed. Structural reformation in unyielded regions is included where part of the material is in undeformed state while the aligned structures reform by shear. The model's predictions were compared with experimental data of some ER fluids (snowman-like anisotropic microparticles as well as the ER fluid of dodecyl benzene-sulfonic acid-doped polyaniline) and the CCJ model. This simple model's predictions of suspension flow behavior with aligned structure reformation agreed well experimental data both quantitatively and qualitatively. Master curve of the apparent viscosity could be obtained by proper scaling of both axes, which shows that combination of the flow curve analysis by proposed model and dimensional analysis allows quantitatively and qualitatively precise prescription of the ER fluid's rheological behavior by relatively few experimental measurements.

field of optoelectronics, primarily owing to the unique property known as localized surface plasmon resonance in metallic nanostructures. In studies on spontaneous emissions, both of fluorescence enhancement and quenching are observed for fluorophores in the vicinity of metallic nanostructures. The enhancement factor largely depends on the distance between fluorophores and metal, because the radiative and non-radiative transitions of fluorophores vary much with their spatial separation. In contrast to continuous efforts to spontaneous emissions, much less has been known in stimulated emissions, although the incorporation of metallic nanostructures into gain media may lead to a breakthrough of laser devices. In this paper, we report on how lasing resonance varies with the distance between fluorophores and metallic nanoparticles. The system under consideration is composed of dye solutions suspended with metallic-dielectric core-shell nanoparticles, known as a random lasing medium that utilizes multiple scattering to elongate the residual time of photons so as to realize light amplification. We demonstrate the capability to control the stimulated emissions utilizing local field enhancement by surface plasmons.

A-5.1:IL02 **Luminescent Organic Nanofibers**

J. KJELSTRUP-HANSEN, L. TAVARES, P.B.W. JENSEN, H.-G. RUBAHN, NanoSYD, Mads Clausen Institute, University of Southern Denmark, Soenderborg, Denmark

For optoelectronic applications, organic semiconductors have several advantages over their inorganic counterparts such as tunability via synthetic chemistry and low temperature processing. Self-assembled, molecular crystalline nanostructures are of particular interest as they could form ultra-small light-emitters. For example, hexaphenylene molecules can form organic nanofibers upon epitaxial surface growth. The nanofibers emit polarized blue light when excited with UV light and can function as waveguides and random lasers. However, well-ordered nanofibers must be grown on mica substrates, which are not further processable. Here, we show a method to transfer such mica-grown nanofibers onto transistor platforms to facilitate a nanofiber-based light-emitting transistor. Device configurations with either top or bottom contacts have been explored. The electrical characteristics of top contact devices are dominated by the nanofiber bulk as opposed to bottom contact devices, which exhibit injection limited behavior. Finally, we demonstrate blue electroluminescence from the fibers using a sinusoidal gate voltage. This constitutes an important step in the sequence towards a nanoscale light-emitter with a desired color, which could be realized through synthesis of suitable molecules.

A-5.1:IL03 **Photoresponsive Inorganic Materials**

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The development of functional magnetic materials is an important issue in the field of material science. Up to date, we have developed unique functional materials using cyano-bridged assembly¹⁻³. In this paper, we report a light-induced spin-crossover ferromagnetism in Fe₂[Nb(CN)₈](4-pyridinealldoxime)₈·2H₂O⁴. In addition, as metal oxide nanomaterial, we report epsilon iron oxide (epsilon-Fe₂O₃), exhibits gigantic coercive field (20 kOe) and high frequency millimeter wave absorption (182 GHz)^{5,6} and a photo-reversible metal-semiconductor phase transition in lambda-titanium oxide (λ-Ti₃O₅)⁷.

1. S. Ohkoshi et al, *Nature Materials*, 3, 857 (2004); 2. S. Ohkoshi et al, *Angew. Chem. Int. Ed.*, 46, 3238 (2007); 3. S. Ohkoshi et al, *J. Am. Chem. Soc.*, 132, 6620 (2010); 4. S. Ohkoshi et al, *Nature Chemistry*, 3, 564 (2011); 5. S. Ohkoshi et al, *Angew. Chem. Int. Ed.*, 46, 8392 (2007); 6. A. Namai et al, *J. Am. Chem. Soc.*, 131, 1170 (2009); 7. S. Ohkoshi et al, *Nature Chemistry*, 2, 539 (2010).

Session A-5

Luminescent and Chromogenic Materials Systems

A-5.1 **Luminescent Materials**

A-5.1:IL01 **Plasmonically Controlled Lasing Oscillation with Metallic-dielectric Core-shell Nanoparticles**

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The research on plasmonics has led to extensive applications in the

A-5.1:IL04 **Preparation of Optoelectronics Glass Using Mesoporous SiO₂/PVA**

S. FUJINO, K. NAGANO, H. IKEDA, T. KAJIWARA, Kyushu University, Fukuoka, Japan

We developed a glass preparation process by use of inorganic-organic nanocomposite. To obtain monolithic transparent silica glass by sintering SiO₂ nanoparticles, we prepare an SiO₂/PVA mesoporous material. We demonstrated fabrication of submicron patterns on silica glass by room-temperature imprinting method. Micropatterns on the nanocomposite are fabricated by imprinting a mold at room temperature at 5 MPa in air atmosphere. The nanocomposite has a strong network made of hydrogen bonding interactions between the silanol groups of

SiO₂ nanoparticles and the hydroxyl groups of PVA. This strong network structure prevents destruction of the nanocomposite due to compressive stress during imprinting. After sintering the nanocomposite at 1100°C, micropatterned silica glass is obtained. The process described, herein, provides an attractive, low-temperature alternative to fabricate micropatterns on silica glass. Nano metals such as Cu, Au, Pt can be printed on the surface or inside of nano composite and can form circuit pattern by co-sintering. Thus circuit on glass can be formed. The novel transparent glass we prepared would be conducive to its use in optical sensor, light guide, optical lens, microchip.

A-5.2 Chromogenic Material Systems

A-5.2:IL01 Electrochromism of Nanocrystal-based Metal Oxide Films

G. GARCIA, A. LLORDES, R. BUONSANTI, R.J. MENDELSBERG, E.L. RUNNERSTROM, **D.J. MILLIRON**, Lawrence Berkeley National Laboratory and University of California, Berkeley, CA, USA

Fundamentally new opportunities for the electrochemical manipulation of optical properties emerge when the active electrochromic material is deliberately structured on the nanometer length scale. For instance, we have demonstrated that the surface plasmon absorption of indium tin oxide (ITO) nanocrystal films can be tuned across the near infrared (NIR) spectral range by reversible electrochemical doping. We use a modified Drude model to analyze transmission spectra demonstrating that electrochemical modulation of the electron concentration is responsible for their unprecedented NIR electrochromic response. Optimizing the film parameters, we achieve 35% modulation of solar NIR while retaining >90% visible transmittance. Embedding such colloidal nanocrystals in a transition metal oxide matrix, we have fabricated metal oxide nanocomposite films that bring a new dimension to optical modulation. Here, we combine our plasmonic electrochromic concept with conventional electrochromics to modulate both NIR and visible light transmission. These properties are of keen interest for a new breed of energy-saving, dynamic window coatings that can separately manage solar heating and daylight.

A-5.2:IL03 Chromogenic Windows

C.G. GRANQVIST, Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, Uppsala, Sweden

The weakest part of a building's energy system is normally its windows and glass facades, which let in too much energy so that cooling is needed or let out too much energy so that heating is needed. The windows and glass facades are required to create indoors-outdoors contact and for day-lighting, so the issue cannot be solved by making the windows small. This talk outlines the international endeavors to create windows that can adjust over the day and season, so that they admit an appropriate amount of visible light and solar energy in order to maximize the energy efficiency jointly with providing good indoor comfort. Two technologies will be introduced--electrochromics and thermochromics--which make it possible to vary the throughput of light and energy by use of a low electrical voltage or as a response to a change in temperature, respectively. Device designs, materials, and progress towards low-cost manufacturing are discussed, and perspectives are given on the energy efficiency that can be accomplished.

A-5.2:IL06 Dynamic Coloration Enabled by Polymer/Cholesteric Liquid Crystal Composites

M.E. McCONNEY, M. DUNING, L. NATARAJAN, V.P. TONDIGLIA, T.J. WHITE, T.J. BUNNING, Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, OH, USA

We explore thin films of polymer/liquid crystal mixtures which exhibit dynamic coloration properties. Cholesteric liquid crystals (CLCs) are well-known to have circularly polarized reflection, which makes them highly promising in a myriad of photonic-based applications. One drawback of this material system is the helical nature that defines CLCs inherently limits their reflection to 50% of unpolarized light. Another drawback of CLCs is their propensity to switch on and off, rather than analog change their color. By using the ability of liquid crystals to impart a degree of order onto the molecular structure of polymers, we demonstrate examples of systems where these two drawbacks are overcome. Spatially heterogeneous polymer is formed through

anisotropic photopolymerization of LC monomers in a chiral LC fluid which is only attached from one surface of a single cell and only spans a fraction of the cell thickness. Thus from one cell, reflection of both polarization states of light is obtained. We demonstrate a unique swelling-deswelling phase transition involving the ordered liquid crystal solvent and structured polymer to demonstrate tunability of the color over 100's of nanometers.

A-5.2:IL07 Thermotropic Materials for Adaptive Solar Control

R. RUHMANN, A. SEEBOTH, O. MUEHLING, D. LOETZSCH, Fraunhofer Institute for Applied Polymer Research, Berlin, Germany

Thermotropic materials offer an immense potential in adaptive solar control. They combine specific optical properties like absorbance and reflection, and high stability against solar radiation and heat with technology compatible processing capacities. Therefore, they represent perfect energy efficient materials. In detail, polymer blends, polymer-based hydrogels, casting resins, and thermoplastic films with a reversible temperature-dependent switching behavior have been investigated. The presentation gives a comparative evaluation of the different concepts with a view to their application in adaptive solar control. Own current results exploit the well-known phase change materials and describe its use for adaptive solar control with extruded films or highly stable casting resins with thermotropic properties. Therewith, the status has changed from diffuse sunblind systems to intrinsic solar energy reflecting materials and a first smart window system based on phase change materials has now commercialized¹. In summary: It is amazing that the solar energy itself is used as a promoter against solar heat.

1. A. Seeboth, R. Ruhmann, O. Muehling, *Materials* 2010, 3, 5143-5168. *Thermotropic and Thermochemical Polymer Based Materials for Adaptive Solar Control*.

A-5.2:IL08 Modeling, Preparation and Characterization of New Fluorophores for Smart Polymer Composite Films

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Polymer composite films containing dyes of different nature and structure, characterized by optical responsiveness to external stimuli, are studied because they are very promising for the development of smart and intelligent polymer devices for sensing and safety applications¹. In this context, a computational work was carried out for the screening of UV-Vis absorption and emission spectra of a series of fluorophores containing functionalized thiophene rings with push-pull groups. The theoretical most promising structures, based on new 1,4-bis-(thienylethynyl)benzene derivatives, were synthesized by a two-step sequence involving a Cassar-Heck coupling reaction followed by a Sila-Sonogashira reaction and their main optical features were characterized in solution by UV-Vis and emission spectroscopies.

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Session A-6

Multifunctional Materials, Composites and Active Hybrid Materials Systems

A-6.1 Multifunctional Materials, Hybrids and Nanocomposites

A-6.1:IL01 Bottom up Strategies to Nanostructured and Hierarchically Structured Functional Solids

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Hybrid inorganic-organic materials can be broadly defined as synthetic materials with organic and inorganic components which are intimately mixed. They can be either homogeneous systems or heterogeneous asystems where at least one of the components' domains has a dimension ranging from a few Å to several nanometers. Hybrid phases can also be used to nanostructure or texture new inorganic nanomaterials. Research on hybrids has experienced an explosive growth since the 1980s, with the expansion of soft inorganic chemistry processes. The mild synthetic conditions provided by the sol-gel process and the versatility of the colloidal state allow for the mixing of the organic and inorganic components at the nanometer scale in virtually any ratio. These features, and the advancement of organometallic chemistry and polymer and sol-gel processing, make possible a high degree of control over both composition and structure of these materials, which present tunable structure-property relationships. This, in turn, makes it possible to tailor properties in very broad ranges, and to design specific systems for applications. This lecture will describe some recent advances on the Chemistry and processing of Nanostructured and Hierarchically structured Functional Inorganic and hybrid Solids.

A-6.1:L03 Sol-gel Derived Multifunctional Layered Hybrid Films for Anti-corrosive Coating

C. URATA, D.F. CHENG, A. HOZUMI, National Institute of Advanced Industrial Science and Technology (AIST), Nagoya, Japan

Many efforts have been made to protect metals from corrosion in a wide variety of engineering fields. In this study, we report a novel strategy to prevent corrosion of metals based on the use of layered siloxane-organic hybrids (LSHs). Our LSHs, composed of alternating alkyl chain and siloxane layers with nanometer-scale interval distance between the layers, are derived from cohydrolysis and condensation of an alkylsilane and an alkoxy silane. Such hybrid materials offer several attractive advantages. First the resulting coatings are highly transparent and curable at room temperature. Second the surface of the coatings shows excellent dynamic hydrophobicity due to the low surface energy and flexibility of the alkyl chains. Third, the layered nanostructures are capable of carrying functional molecules such as corrosion inhibitors (CI) between the layers, and are expected to show self-healing properties when the samples are subjected to harsh environments. For example, our copper samples coated with CI-loaded LSH films showed not only excellent hydrophobicity but also corrosion resistance against salt spray test more than 2000 h. Thanks to the relative contributions of hydrophobicity and self-healing properties, long-term corrosion resistant coatings have been successfully prepared.

A-6.1:IL05 Smart Morphology Control of Metal Oxide Nano/Micro-crystals in Aqueous Solution

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Morphology control of metal oxide nano-structures was realized in aqueous solutions to form various nanostructures. They were applied to dye-sensitized molecular sensors. [TiO₂ structure] Anatase TiO₂ particles with high surface area of 270 m²/g were prepared at 50°C. The particles were assemblies of nano TiO₂ crystals covered with nanorelief surface structures. The crystals grew anisotropically along the c-axis to form acicular crystals. TiO₂ films consisting of anisotropic acicular crystals were also prepared. The films showed high c-axis orientation. [SnO₂ structure] Tin oxide particles having BET surface area of 85 m²/g were synthesized in aqueous solutions. They consisted of nanosheet crystals. The sheets were about 50-100 nm in size and 5-10 nm thickness. [ZnO] ZnO rod arrays were fabricated on FTO substrates for dye-sensitized molecular sensors. They were formed on the substrates without seed layers and high temperature annealing. ZnO was crystallized in aqueous solutions to form hexagonal cylindrical rods on the substrates directly. The rods elongated along the c-axis and stood perpendicular to the substrates. The rod arrays showed only a 0002 X-ray diffraction peak, indicating a high c-axis orientation. Signal-to-noise ratio (S/N) reached 53.

A-6.1:IL06 Polymer Nanocomposites for Functional Applications

F. FAUPEL, V. ZAPOROJCHENKO, T. STRUNSKUS, Christian-Albrechts University at Kiel, Institute for Materials Science - Multi-component Materials, Kiel, Germany; M. ELBAHRI, Christian-Albrechts University at Kiel, Institute for Materials Science - Nanochemistry and Nanoengineering, Kiel, Germany and Institute of Polymer Research, Helmholtz-Zentrum Geesthacht, Geesthacht, Germany

Nanocomposites combine favorable features of the constituents on the nanoscale to obtain new functionalities. The present talk is concerned with the preparation of polymer-based nanocomposites consisting of metal nanoparticles in a polymer matrix and the resulting functional properties¹. Emphasis is placed on vapor phase deposition² which inter alia allows the incorporation of alloy clusters with well defined composition and tailored filling factor profiles. Examples presented include optical composites with tuned particle surface plasmon resonances for plasmonic applications³, magnetic high frequency materials with cut-off frequencies well above 1 GHz⁴, sensors that are based on the dramatic change in the electronic properties near the percolation threshold, and antibacterial coatings which benefit from the large effective surface of nanoparticles and the increased chemical potential which both strongly enhance ion release¹. Moreover, photoswitchable composites containing chromophores and nanoparticles will be addressed.

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A-6.1:L08 New Silver Chloride - Silver Hybrid Polymers with Nylon and Polyurethane Showing Enhanced Antimicrobial and Photocatalytic Properties

M. PARRY, J.H. JOHNSTON, School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand

Silver chloride attracts attention for its electronic, antimicrobial and catalytic properties. We report the synthesis of silver chloride nanoparticles directly onto porous nylon and polyurethane polymer substrates to form new silver chloride-silver polymer hybrid materials. The nanosize is controlled by the polymer porosity and synthesis conditions. The AgCl-polymers are initially white but on exposure to light they change progressively to purple, due to the photo-reduction of some Ag⁺ in the AgCl nanoparticle lattice to Ag⁰, forming domains of spherical silver nanoparticles a few nm in size. Spherical silver nanoparticles are normally yellow. The purple colour is due to a red shift of the surface plasmon resonance absorption through a change in the dielectric constant from water to AgCl and a core-shell effect. Antimicrobial measurements show the AgCl-Ag composite nanoparticles exhibit enhanced antimicrobial effectiveness towards E. coli in visible light compared to that in the dark, and the precursor Ag and AgCl components. The photocatalytic properties of the composite nanoparticles in degrading organic compounds are also more effective than those of Ag and AgCl. These new hybrid AgCl-Ag polymers are therefore more effective in antimicrobial and photocatalytic applications.

A-6.1:L09 Fabrication of Carbon Nanotube-alumina Composite and Coating with Graphite Film

M. OMORI, G. YAMAMOTO, K. SHIRASU, T. HASHIDA, Graduate School of Mechanical Engineering, Tohoku University, Sendai, Japan

We tried two new attempts to fabricate carbon nanotube-alumina composites, using aluminum hydroxide instead of alumina powder and selecting dispersive multi-walled carbon nanotubes (MWNTs). MWNTs were classified into two groups of thick and thin ones. Thick MWNTs consist of a large number of graphene and diameter more than 30 nm. Thin MWNTs of a small number of graphene are less than 30 nm in diameter. Thick MWNTs are dispersive because of low agglomeration. Thin MWNTs tend to be greatly agglomerated but the size of the agglomerated varies from product to product. We selected a thin MWNT of which the agglomerated size is less than 10 microns. The composites were prepared from 0.3 to 5 mass% of thick MWNTs and the dispersive thin MWNT and aluminum hydroxide by spark plasma sintering (SPS). The strength of all the composites was over 400 MPa. To promote applications of the composite, it was coated with graphite film by rubbing graphite powder on its surface and changed into a low friction material. The graphite film was bonded to the MWNTs exposed on the surface of the composite by van der Waals force. The composite can be applied to self-lubricating bearing and acetabular cup of total hip joint replacement.

A-6.1:IL11 Organic-inorganic Hybrid Materials for Green Photonics

L.D. CARLOS, Department of Physics and CICECO, University of Aveiro, Aveiro, Portugal

The realization of cost effective, eco-friendly and sustainable photonic components based on sol-gel derived organic-inorganic hybrid (OIH)

matrices has received increasing attention in the past years. The talk presents examples of OIHs that can be used in green photonics (namely as non-contact luminescent micro/nanothermometers, luminescent solar concentrators, LSCs, and integrated optics, IO, substrates in the new generation of optical networks). The molecular thermometers reported, based on OIHs embedded trivalent lanthanide ions, are self-referencing, allowing absolute measurements in the 10-350 K temperature range. The combination of the molecular thermometer with a nanometric magnetic/luminescent host matrix provides the device multifunctionality at the nanoscale. LSCs with optical conversion efficiency up to 4% are fabricated based on thin layers of Eu³⁺-containing hybrid materials. For IO substrates, emphasis will be given to approaches for materials processing and refractive index control that permits the design of passive applications in access/indoor optical architectures, particularly, planar and channel waveguides, couplers, filters and Y power splitters.

A-6.1:L12 **Light-weight, Transparent, and Hard Multifunctional Materials Based on Nanocellulose-inorganic Nanoparticle Hybrids**

G. SALAZAR-ALVAREZ, Department of Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden, & Wallenberg Wood Science Center, Royal Institute of Technology, Stockholm, Sweden

In the quest for light, biodegradable, and functional materials biopolymer-inorganic hybrids are emerging as one of the strongest alternatives. Early work on the fabrication of organic-inorganic nanocomposites focused on the functionalisation and subsequent dispersion of various nanoparticles in a polymer matrix. Our approach is based on the use of the most abundant biopolymer on Earth in its mesoscopic version, nanocellulose, as both nucleating agent and scaffold for different nanoparticles systems. This talk will present our work on the fabrication of multifunctional materials based on three types of nanocellulose: bacterial nanocellulose (BNC), nanofibrillated cellulose (NFC), and nanocrystalline cellulose (NCC); and three different classes of functional nanoparticles: CoFe₂O₄ (magnetic material),¹ TiO₂ (UV absorber), and amorphous calcium carbonate (ACC, biomineral).² The hybrids have rather low apparent densities, are mechanically hard, and possess also additional magnetic, optical, or structural properties. The influence of the different approaches used for the fabrication of the hybrids on their properties will be discussed.

1. G. Salazar-Alvarez et al, *Nat. Nanotechnol.* 2010, 5, 584-588.
2. D. Gebauer et al, *Nanoscale* 2011, 3, 3563-3566.

A-6.1:L13 **Superhydrophilic and Superhydrophobic Patterned Surfaces**

M.B. HERZOG, J.H. JOHNSTON, School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand

The alternating superhydrophobic and superhydrophilic patterning on the back of the *Stenocara* beetle allows this desert insect the unique ability to collect water by condensing water vapour from the atmosphere on its back. Inspired by this ability, modern nanotechnology and layer-by-layer assembly were used to synthesize both superhydrophobic and superhydrophilic patterned surfaces on various substrates such as polymer sheets and patterned woolen textiles. Through the use of functionalised silica or other nanoparticles, either produced in the laboratory or as a commercially available colloidal suspension of such spherical nanoparticles, the necessary hierarchical surface structure in the micro- and nano-range was created. Surface analyses, contact angle measurements and advancing and receding angles will be presented. A combination of both superhydrophobic and superhydrophilic surfaces allows the creation of such patterning which in turn provides a new generation of materials with a wide range of consumer applications such as water harvesting, stain resistant self-cleaning and water-repellent breathable surfaces.

A-6.1:L14 **High Dielectric Nanocomposite Interleaves for Multifunctional Structural Composites**

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Future air and ground vehicles will continue to rely upon capacitive energy storage for a variety of sensing and functional tasks. Unfortunately, the present generation of capacitors is too large and too

heavy to enable these functions in the next generation of vehicles. Much work has focused on improving the energy density of capacitors by engineering higher dielectric ceramics and employing nanocomposites to reduce the component mass. A different approach is to reduce the need for on board capacitors by using the structure of vehicle to augment the existing energy storage system. In order for a multifunctional composite system to save overall system mass, the tradeoffs in the structural material properties must be minimized so that additional structure need not be added. The polymer rich interlaminar region is often where fatigue cracks initiate and can limit lifetime and overall strength of the material. This work will present a multifunctional composite material by employing a high energy density nanocomposite interleave that will enable energy storage as well as inhibiting interlaminar crack growth. The results will show a composite that offers capacitive energy storage in addition to preserving the interlaminar shear properties of the composite.

A-6.1:L15 **Nanogold and Nanosilver Hybrid Materials with Paper Fibres for Anti-microbial Applications**

T.W. NILSSON, J.H. JOHNSTON, School of Chemical and Physical Sciences, MacDiarmid Institute for Advanced Materials and Nanotechnology, Victoria University of Wellington, Wellington, New Zealand

A novel approach for the formation of nanogold and nanosilver composites with lignin-containing cellulose fibres with antimicrobial properties will be presented, where the lignin component of unbleached paper fibres forms and stabilises nanogold and nanosilver. The methodology does not require external reducing agents or chemical alteration of the cellulose fibres, and is applicable to unbleached kraft fibres and mechanical pulp only. The phenol and possibly the aromatic methoxy groups prevalent in lignin are considered to reduce Au³⁺ to Au⁰ and Ag⁺ to Ag⁰, and bind the nanogold and nanosilver to the fibre surface. SEM and UV-visible spectroscopy confirm the formation of nanogold and nanosilver on the fibres. Infrared spectroscopy shows the changes between blank fibres and composite fibres are consistent with this role of phenol and methoxy groups. The antimicrobial activity of the composites is observed at low levels of nanogold, and very low levels of nanosilver. The antimicrobial properties of nanogold and nanosilver are synergistically combined with the flexibility of paper fibres and provide the opportunity to produce paper products suitable for antimicrobial packaging, medical dressings and air filters.

A-6.1:L19 **Chemically Grown Nanoparticles, Nanowires and Nanocomposites: Processing, Applications and Devices**

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Chemical nano-sciences enabling controllable manipulation of matter at molecular length scale have become fundamental generators for innovations in materials processing. The successful synthesis, modification and assembly of nanobuilding units such as nanocrystals, -wires and -tubes of different materials have demonstrated the importance of chemical influence in materials synthesis, and have generated great expectations for the future. Inorganic nanostructures inherit promises for substantial improvements in materials engineering mainly due to improved physical and mechanical properties resulting from the reduction of microstructural features by two to three orders of magnitude, when compared to current engineering materials. This talk will present how chemically grown nanoparticles, nanowires and nanocomposites of different metal oxides open up new vistas of material properties, which can be transformed into advanced material technologies. The examples will include application of superparamagnetic iron oxide nanoparticles for drug delivery applications, molecule-based synthesis of nanowires and development of single-nanowire based devices.

A-6.1:L21 **Functionalization of Carbon Nanotubes for Use of Active Nanostructured Substrates in Integrated Devices**

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Smart system integration for applications of lab-on-a-chip devices in clinical diagnostics may include molecular devices, increasing sensitivity for early diagnosis. Carbon nanotubes (CNT) can be employed in these devices, for molecular assays, if functionalized to allow connection with more complex molecules such DNA and luminescent markers. In the present work, to functionalize multi-walled carbon nanotubes (MWCNT)

for recognition of DNA, a non-acid alternative route is proposed, mainly to be compatible with active substrates produced in our group. MWCNT are first functionalized with nitrobenzene by cycloaddition reaction with 1-azido-4-nitrobenzene activated by UV. The nitro group is reduced by a reaction catalyzed by zinc, compatible with the active vitreous substrates produced in our lab, with silver nanoparticles grown over it by a bottom-up process (starting from silver ions). The metallic silver nanoparticles act as a catalyst to the vertical growth of carbon nanotubes, and its bond with the glassy substrate is not affected by the present functionalization route. The material was characterized by TGA, FTIR, UV-visible and Raman.

A-6.1:L22 Interconnects Fundamental Properties and Magnetically Stimulated Nanoprocesses on Fe-Pt Substrates

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The cluster approach based on the multiple scattering theory formalism, realistic analytical and coherent potentials, as well as effective medium approximation (EMA-CPA), can be used effectively for modeling of nano-sized systems. Much attention is paid nowadays to applications of carbon nanotubes (CNTs) and graphene nanoribbons (GNRs) of various morphology which possess unique physical properties in nanoelectronics, e.g., contacts of CNTs or GNRs with other conducting elements of a nanocircuit which can be promising candidates for interconnects in high-speed electronics. *Interconnects' resistance*. The main problems to be solved for resistance of C-Me junctions with metal particles appear due to the influence of chirality effects inside interconnects of single-wall (SW) and multi-wall (MW) CNTs, single-layer (SL) and multi-layer (ML) GNRs with the fitting metals (Me = Ni, Cu, Ag, Pd, Pt, Au) for the pre-defined carbon system geometry. Using the models of 'liquid metal' and 'effective bonds' developed in the framework of EMA-CPA approach and Landauer theory, it is possible to predict resistivity properties for the considered interconnects. We have also developed the model of the inter-wall interaction inside the MW CNTs and inter-shell interaction along ML GNRs, which demonstrates possible 'main current' losses. *Interconnects' capacitances*. Simulation of electromagnetic properties of interconnects essentially depends on the calculations of interconnect impedances. Evaluations of capacitances of the considered interconnects have been carried out. Frequency properties analysis has shown particular changes for THz range which is principal for electromagnetic waves propagation. *Interconnects' magnetism*. There is a relation between the use of magnetic catalysts and the CVD growth of CNTs determining the most commonly used materials for the CNT growth - Fe, Co and Ni. The nanoparticles of the latter catalysts are magnetically isotropic. It is possible to use magnetically anisotropic nanoparticles such as those in the alloys with a different substitutional disorder (e.g., Fe_{1-x}Pt_x), to manage the CVD process with the formation of the predefined CNT chiralities. This also means that we can control the number of effective bonds inside interconnects. Special attention is paid to the unique property of interconnects such as the presence of *dangling atomic bonds* that make interconnects chemically, electrically and magnetically sensitive. Magnetic susceptibility of interconnects essentially depends on the number of dangling atomic ('non-effective') bonds inside the interconnects' space, which makes them promising as perspective media for nanosensor devices. This property allows for considering interconnects as perspective sensor nanomaterials.

A-6.2 Functional Porous Materials

A-6.2:L02 Long-range Ordered Hierarchical Mesoporous Films for Energy Saving Applications by Rational Selection of the Templating Agent

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Energy conversion/storage devices employing mesoporous metal oxide (MO) films are well known to exhibit enhanced performance through engineered mesoscale porosity. An attractive alternative to the classical evaporation-induced-self-assembly would employ pre-synthesized colloidal metal oxide (MO) nanocrystals, instead of MO precursors. This would allow a superior control over the crystallinity and composition of the films by uncoupling the crystallization step from the assembly and

thermal processing required to remove the surfactant. Herein, we demonstrate how a careful manipulation of the chemical affinity between the nanocrystal surface and the templating agent is the key to obtain long-range ordered hierarchical mesoporous films. We designed a block copolymer that readily forms ordered assemblies in an opportunely chosen solvent mixture and interacts with the nanocrystal surface through tailored interactions. The generality of the method was shown by assembling MO nanocrystals of various size, shape and composition widely sought for use in next generation energy conversion/storage devices (i.e. ITO and CeO₂ pseudospherical nanocrystals, TiO₂ nanorods).

A-6.2:L03 Polybenzoxazine-based Porous Carbon: Pore Structure Design and its Application

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Polybenzoxazine (PBZ) has received great attention and been commercialized recently because of its advantages that overcome those problems of traditional phenolic resins. Due to a substantial increase in the needs for porous materials in industrial applications and daily life, nanoporous PBZ has been successfully synthesized at room temperature via sol-gel process before solvent removal. The resulting porous carbon can then be obtained through pyrolysis. The effects of various synthesis routes have been investigated. PBZ-based porous carbon could maintain mesopore structure without the need of supercritical CO₂ drying during drying process. Nanoporous carbon derived from monofunctional amine exhibited microporous structure whereas the one derived from diamine showed mesoporous property with mesopore diameter of 8 nm. In addition, surfactant-assisted nanoporous carbon also exhibited the mesoporous property with the mesopore diameter of 25.38 nm. The resulting nanoporous carbon was then used as a hard template for the syntheses of MFI zeolite. The as-synthesized MFI with mesoporous properties showed well-defined crystalline phase with the intensities less than that of traditional MFI, indicating the presence of small crystals.

A-6.2:L04 Preparation of Microporous Carbon Fibers Through Carbon-ization of Al-based Porous Coordination Polymer with Furfuryl Alcohol

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Carbon materials are one of the most studied materials because of their applications in a large variety of fields such as adsorbents, catalyst supports and electrode materials. Among the different methods of preparation, nanocasting is an effective and successful way to prepare porous carbon materials. Porous inorganic templates such as zeolites, colloidal crystals and mesoporous silica materials are used with various carbon source/precursors. Here we show that a novel class of microporous materials, porous coordination polymers (PCPs) containing metal ions and bridging organic ligands can also be used as templates due to their very high surface area and large pore volume. This study focuses on the use of Al-based PCP [Al(OH)(1,4-NDC).2H₂O]. The crystal structure of this material exhibits a three-dimensional framework composed of infinite chains of corner-sharing octahedral Al(OH)2O₄ with 1,4-naphthanedicarboxylate ligands forming two types of channels with squared-shape cross-section. This PCP accommodates many hydroxyl groups bridging two Al ions which can act as brønsted acid to accelerate the polymerization of the furfuryl acid used as carbon source. The textural characteristics of the obtained materials as a function of the loading amount of FA were carefully investigated.

A-6.2:L05 **Combination of Porous Polymer Membrane and Novel Membrane Separation Technique for High Energy Conversion Efficiency**

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Porous poly(dimethylsiloxane) (PDMS) membranes were prepared by freeze drying aqueous emulsions of organopolysiloxane for the concentration of aqueous solutions of dilute ethanol which are produced from the fermentation of biomass. This paper introduces the preparation of porous PDMS membranes and the development of a new membrane separation technique for the concentration of bioethanol. Porous PDMS membranes were applied to a temperature-difference controlled evaporation (TDEV) method developed as a new membrane separation technique that can be controlled temperatures of the feed solution and the membrane surroundings. When the temperature of the feed solution was kept constant but the temperature of membrane surroundings was lowered, the ethanol/water selectivity increased remarkably and the permeation rate decreased. The ethanol/water selectivity of a porous PDMS membrane in TDEV operation was almost equal to that of a dense PDMS membrane in TDEV, however, the permeation rate of the porous membrane was higher by three orders of magnitude. The relationship between the permeation and separation characteristics in concentrating of bioethanol through porous PDMS membranes by TDEV and the permeation and separation mechanisms for aqueous ethanol solutions through porous PDMS membranes in TDEV are discussed.

A-6.2:L06 **Development of New Non Oxide Hybrid and Ceramic Membranes for Hydrogen Separation**

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The development of an efficient hydrogen production method is a tremendous parameter for future energy systems. Preparation of a hydrogen permselective membranes for high temperature application (beyond 250°C) is one of the key techniques for efficient hydrogen production. Silica-based membranes are serious candidates but their low resistance to water vapor is seriously prejudicial to their competitiveness. We will make and investigate the potential of non oxide membranes in the system "Si-M-C-N" with M: a transition metal or metalloid. We will study complex quaternary phases, which due to the incorporation of a metal should overcome the permeance and selectivity performances already obtained on the ternary phases "Si-C-N" at I.E.M.. This project is divided into two major tasks, the first is based on the synthesis of single molecular precursors that will contains all desired elements (single-source) to realize inorganics materials. Secondly, to achieve these membranes, several deposition techniques will be used: first P.E.C.V.D. (Plasma Enhanced Chemical Vapor Deposition), secondly liquid coating (dip, spin, electrospray) approaches will be developed.

A-6.2:IL07 **Optically and Electrically Responsive Periodic Mesoporous Organosilicas**

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Periodic mesoporous organosilicas (PMOs) are attracting increasing attention due to their highly functional framework structures. Various organic bridging groups (R) ranging from aliphatic and aromatic hydrocarbons to heterocyclics and metal complexes can be densely and covalently embedded within the framework of mesoporous materials by surfactant-templated polycondensation of well-designed organosilane precursors $R[Si(OR)_3]_n$ ($n = 2$). Expansion of the variation of organic bridges has broadened potential applications of PMOs to not only catalysts and adsorbents but also optical and electronic devices. Here, I present our latest results on the synthesis of optically and electrically responsive PMOs exhibiting unique framework functionalities such as light-harvesting, electron-donating, and charge transporting properties. These results strongly suggest that PMOs have great potential for optical and electrical applications, especially for artificial photosynthesis, color-tunable visible-light emissive PMO, and a new class of photovoltaic devices.

A-6.2:L08 **Dynamic Cavity Response in Adaptive Porous Materials**

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Porous materials are crucial for a variety of applications such as energy¹⁻⁴, sensing⁵⁻⁶ and water purification⁷. Advanced porous and ultra-

porous materials actively respond to environmental changes (eg. temperature, pressure, humidity and gas environments). One emerging technique to investigate porosity in adaptive materials is Positron Annihilation Lifetime Spectroscopy (PALS) which can accurately measure pore sizes and distributions. In the proposed work, we discuss novel results related to the dynamic pore response of Zeolites, Metal Organic Frameworks and Mesoporous materials under different environments. The ability to finely control the pore size and observe the changes under various conditions is critical for the advancement of porous materials.

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A-6.2:L10 **Synergic Photocatalyst of Mesoporous Silica for Environmental Purification**

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Mesoporous silica can be applied to highly-efficient adsorbent and catalyst support to eliminate harmful chemical species because of its large surface area. Various metal oxides can be incorporated into the amorphous silica network to control the adsorption behavior and add a catalytic function. When titania is composited with silica, two functions are expected. One is the enhancement of adsorption ability owing to the formation of acidic points. Another is the photocatalytic activity owing to the separative deposition of titania nanoparticles. The mesoporous silica-titania has been synthesized by a sol-gel process using metal alkoxides and organic template. It was found that titania was incorporated into the silica network at small content, whereas separately deposited at large content. The adsorption ability and the photocatalytic activity were evaluated for methylene blue and acetaldehyde. The mesoporous silica-titania exhibited strong adsorption and photocatalytic activities. The function of the "Synergic Catalyst" will be discussed in detail.

A-6.2:L11 **Magnetoactive Superhydrophobic Foams for Oil-water Separation**

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We present a novel composite material, based on polyurethane foams functionalized with colloidal superparamagnetic iron oxide nanoparticles and sub-micrometer polytetrafluoroethylene (PTFE) particles, which can efficiently separate oil from water. The hydrophobic and oleophobic untreated foam surfaces are rendered water-repellent and oil-absorbing by a solvent-free electrostatic transfer method of PTFE particles. The combined functionalization of the PTFE-treated foam surfaces with colloidal iron oxide nanoparticles significantly increases the speed of oil absorption. Microscopic, wettability and thermogravimetric analysis reveal that both the surface morphology and the chemistry of the functionalized foams greatly affect the oil absorption dynamics. In particular nanoparticle capping molecules are found to play a major role in the absorption mechanism. In addition to the water-repellent and oil-absorbing properties, the treated foams exhibit also magnetic responsivity. Thus, since they float on water due to their light weight, they can be moved around oil polluted waters using a magnet. As a result, they can absorb the floating oil from the polluted regions, purifying the water underneath. This low cost process can easily be scaled up to clean large-area oil spills in water.

A-6.2:L12 **Highly Porous Polymeric Foam of Maleimide-Terminated Poly(arylene ether sulfone) Oligomers via High Internal Phase Emulsions**

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PolyHIPEs are highly porous polymeric form, prepared through emulsion

templating by polymerizing the continuous phase of high internal phase emulsions (HIPEs). A maleimide-terminated aryl ether sulfone oligomer (MAPES) was copolymerized with divinylbenzene (DVB) in the continuous phase, using a mixed surfactants system (sorbitan monooleate (Span80), cetyltrimethylammonium bromide (CTAB), dodecylbenzenesulfonic acid sodium salt (DDBSS)), and peroxide initiator, to improve CO₂ adsorption and the mechanical properties of obtained materials. PolyHIPEs were prepared by two different ratios of mixed surfactants; (SPAN80, DDBSS, and CTAB; 6.3, 0.4, and 0.3 wt%, which was denoted as 7s) and (SPAN80, DDBSS, and CTAB; 11.3, 0.4, and 0.3 wt%, which was denoted as 12s). 0, 2.5, 5, 10, 20, and 30 wt% of maleimide-terminated aryl ether sulfone oligomer were copolymerized with DVB. All polyHIPE nanocomposites foam were characterized for phase morphology, thermal behavior, surface area, mechanical properties and adsorption of CO₂ by using SEM, TG-DTA, N₂ adsorption-desorption, LLOYD universal testing machine and CO₂ adsorption unit, respectively. The obtained PolyHIPEs showed an open cell and a secondary pore structure with surface areas of approximately 400m²/g. CO₂ adsorption tests were characterized by pilot gasification unit and the obtained materials showed higher adsorption than neat poly(DVB) without MAPES. Compressive modulus test of the materials showed a higher modulus than for poly(DVB) PolyHIPEs.

Session A-7

Smart Molecular and Supramolecular Systems, Metallorganic Frameworks and Coordination Polymers

A-7:IL01 Combining Metal Organic Frameworks with Functional Micro- and Nano-particles

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Ultra-porous materials with highly accessible surface areas are very promising systems in catalysis, drug delivery, proton conductors and water/gas purification. Metal-Organic Frameworks (MOFs) are a novel class of porous materials. The nanoporosity is characterized by a narrow distribution with interconnected cavities which allow for fabrication of molecular selective sieves or matrices for controlled molecular diffusion: both are very important for gas separation, selective catalysis, sensing, and drug delivery. The aim of this work is to show that by combining inorganic micro- and nano-particles, several technological hurdles can be tackled. Indeed it has been possible to master MOF growth in precise locations, to increase the MOF production rate, and to position functional nanoparticles into the MOF crystals. This discovery opens a fascinating route to prepare a new class of smart nanocomposite materials based on MOFs for advanced devices or to speed up the production rate using an inexpensive technology.

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A-7:IL02 Hydrazone-based Rotary Switches

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We have recently developed hydrazone-based rotary switches that can be chemically stimulated to undergo reversible E/Z modulations.¹ Hydrazones, similar to imines, isomerize by either rotation around the C=N double bond or inversion (lateral shift) at that nitrogen. In these H-bonded switches, however, a novel mechanism comes into play; hydrazone-azo tautomerization followed by rotation around a C-N single bond.² When quinoline is used as the stator a multistep switching cycle can be accomplished.^{1b} More importantly, Zn²⁺ can now be used to activate the switch via a novel switching mechanism, which is based on coordination coupled proton transfer.³ This presentation will deal with our recent advances with the switching of these modular hydrazone-based systems.

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A-7:L03 Bistability in Neutral Radical Dyads: Towards Multifunctional Molecular Switching Materials

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A model for bistability driven by electrostatic intermolecular interactions in molecular crystals of polar chromophores was proposed and demonstrated in crystals of the valence tautomer Fc-PTM (ferrocene linked to a neutral polychlorotriphenylmethyl radical).¹⁻² T-dependent Mössbauer spectroscopy of the Fc-PTM dyad demonstrated that at r.t. both states coexist in similar proportions.³ Such bistability was explained through a bottom-up two-state model.⁴ The PTM radical has also been linked to a tetrathiafulvalene: TTF-PTM dyad where the intramolecular electron transfer induce a spontaneous self-assembly of the TTFs. In this system, the interplay between magnetic and conducting properties will be crucial for developing molecule-based spintronic devices. The cooperative intermolecular interactions of this system promoted bistability already in solution.

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A-7:L04 Adaptive Porous materials for Gas Storage Application

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There is a dependence on the combustion of fossil fuels to power our transportation demands. The replacement of petrol and diesel fuelled engines with alternative gases such as hydrogen and natural gas are feasibly and attractive substitutes, due to their natural abundance and minimal emissions when utilised. However, there are limitations to using these low emission gases and research is being undertaken to find suitable methods to store these gases safely in automotive vehicles. One such method being investigated is the use of metal organic frameworks (MOFs) and porous aromatic frameworks (PAFs).^{*} The porous materials can be adapted and tuned to give a higher surface area for absorbance and be preferential towards a single gas type. This can be achieved by tailoring the organic linker and/or providing addition open metal ion sites for contact. The presentation will report the synthesis of alternative porous materials with open metal sites, techniques to identify these materials and their ability to store various gases.

^{*}T. Ben, et al, *Energ. Environ. Sci.*, 2011, 3991-3999

A-7:L05 Light-activated Healing of Metallosupramolecular Polymers

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Optically-healable metallosupramolecular materials consisting of poly(ethylene-co-butylene) polymers end-capped with pyridine-type ligands (BKB) and metal salts (Zn²⁺) were developed (Zn²⁺-BKB). Upon exposure of deliberately damaged polymers films to appropriate stimuli (e.g., light, heat), certain supramolecular motifs can easily disengage, causing a controlled local decrease of the polymer's molecular weight concomitant with an increase of the crack-healing rate. Using light as a stimulus for dissociation of the supramolecular motifs is that heat can be applied locally, i.e. at the defect site only, which allows one to heal a damaged object under load. Metallosupramolecular polymer films were also reinforced with cellulose nanowhiskers, that can form a percolating network and improve the mechanical properties of a material. The combination of Zn²⁺-BKB polymers and cellulose nanowhiskers gave rise to materials with an

increased mechanical strength. These materials healed in a similar fashion to Zn²⁺-BKB films and the original mechanical properties of the healed materials were recovered. An overview on the parameters that govern the mechanical properties and healing ability of metallosupramolecular polymers will be presented.

A-7:IL06 Self-propagating Molecular Assemblies

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Exponential growth and/or self-propagating processes with molecular systems, where surface-bound assemblies actively participate rather than being static platforms with reactive end-groups for the incoming molecular layers, are rare. Utilizing our assembly strategy, we designed a molecular-based material that is an active participant in its continuing self-propagated assembly. This unique process involves inclusion of excess palladium into a network consisting of polypyridyl complexes linked via palladium. Our materials exhibit electrochromic properties which are comparable to industrially important conducting polymers. The electrochromic properties of these films can be used for (i) detecting various analytes in solution and in the air, (ii) interlayers for efficient inverted bulk-heterojunction solar cells, (iii) electron-transfer studies, and (iv) molecular (Boolean) Logic and Computing (MBLC). Our concept toward MBLC with functionalized surfaces is applicable to electrochemical and chemical inputs coupled with optical readout. Using this approach, we demonstrated various logic architectures with redox-active functionalized surfaces. Electrochemically operated sequential logic systems (e.g., flip-flops), multi-valued logic, and multi-state memory have been designed.

A-7:IL07 Sequential Functionalization of Porous Coordination Polymers

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Porous coordination polymers (PCPs), assembled by metal ions and organic bridging ligands, are an intriguing class of crystalline porous materials, as it is possible to design their framework topologies and pore sizes and the functionality of the pore surfaces. On the other hand, functionalization of PCP other surfaces (crystal surfaces) is a great challenge, but it is a promising methodology not only for modification of the porous properties but also for the addition of a new function to the PCP without changing the characteristic features of the PCP crystal itself, resulting in the fabrication of multifunctional PCPs. One way to decorate the crystal surfaces of a PCP is to hybridize the core PCP crystal with a different shell crystal by epitaxial growth at the single-crystal level, thus creating core-shell PCP heteroepitaxial crystals. Such a lattice match promises pore connections at the interface between crystals. We demonstrated the synthesis of hybridized PCP single crystals by taking the advantage of coordination equilibrium at the crystal interfaces and determined the structural relationship between the shell and the core by using surface X-ray diffraction analysis. Furthermore, we demonstrated the integration of size selectivity with high storage based on this concept.

A-7:LO8 Size and Morphology Controlled Formation of Porous Coordination Polymers

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Porous Coordination Polymers (PCPs) are an intriguing class of hybrid materials intensively investigated for their potential applications in gas sorption, molecular separation and catalysis. While most of the property studies are based on materials obtained largely as microcrystalline powders, a growing interest in the particles size and shape control has recently emerged. Controlling the crystal size and morphology is indeed a key feature not only for a better understanding PCPs growth mechanism but also to facilitate their application in various emerging fields such as porous membranes, thin film devices and sensors or even drug delivery. Recently we have proposed a novel "coordination modulation method" for the fabrication of PCP nanocrystals, by influencing the coordination equilibrium at the crystal surface during the growth process. This method, further combined with microwave-assisted heating provides PCPs with finely controllable size and morphology, ranging from few tenths of nanometers up to several micrometers. As a demonstration of the advantage of nanosized PCPs, nanocrystals were immobilized on gold electrodes and could be further integrated in a highly sensitive solvent vapor sensing device.

A-7:L10 Comparative Study of Automated Adsorption of Commercial Dyes Using Metal-organic Frameworks (MOFs)

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Questions related with the quality of river waters have been arisen due to their use as source for human supply, irrigation for agriculture and leisure activities. One of the factors influencing the quality of the water is the color. A very low concentration of dye can color a large amount of water making it undesirable; in addition some dyes are toxic and/or carcinogenic. The removal of dyes from the industrial dumpings has importance due to the negative impact on the quality of the waters and on environmental health. This work is dealing with the use of Metal Organic Frameworks (MOFs); namely, MIL-53(Al) and [Zn(BDC)(H₂O)₂]_n as adsorbent materials for different dyes used in the Brazilian textile industry. The choice of employing MOFs is mostly due to the capability of tuning their pore size and shape, and because of its known applications as adsorbent material in different fields. The aim of this work is to monitor the process of adsorption by means of an automated system employing the technique known as multicommutation to handle the different solutions and UV/Vis detection. The results obtained with MOFs will be compared with C18 solid phase extraction cartridges and activated carbon adsorption on the same conditions. The influence of temperature and flow rate will be studied.

Session A-8

Adaptive/Responsive Surfaces and Multifunctional Smart Coatings

A-8:IL01 Growing Integration Layer [GIL] Strategy: Direct Fabrication of Compositionally, Structurally and Functionally Graded Ceramic Films and/or Coatings from Mother Materials in Solution

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In the fabrication of graded [Compositionally, Structurally and Functionally] ceramic materials and/or ceramic/metal coating and joining, the most difficult problem is how to overcome weak interfacial bonding and poor adhesion of ceramic layers by their cracking and /or peeling arising from their intrinsic brittleness. On the basis of accumulated results and discussion, we have proposed a novel concept and technology of the formation "Growing Integration Layer" [GIL] between ceramics and metallic materials to improve the adhesion performance. Those GIL(s) can be prepared via integration of ceramic film formation from a component of the metallic materials by chemical and /or electrochemical reactions in a solution at low temperature of RT-200 °C. They have particular features: 1) Widely diffused interface(s), 2) Continuously graded layers grown from the bulk(substrate), 3) Low temperature process, etc. They are quite different from Layer-by-Layer [LBL] strategy, where every layer is deposited from the Top. BaTiO₃ or SrTiO₃/TiO_x GIL films on Ti plates formed by hydrothermal-electrochemical method showed good adhesion. CaTiO₃/Al₂O₃/Ti₂Al GIL films on TiAl exhibited excellent adhesion and anti-oxidation performances: they could be sustained for 10 times cyclic oxidation test at 900 °C in air for 5 hrs.¹ The GIL strategy is effective for many metallic alloys and bulk metallic glassed because they generally contain active component(s). On a Ti-base Bulk Metallic Glass, we could succeed to prepare bioactive titanate nano-mesh layer by hydrothermal-electrochemical techniques at 90-120 °C². Similarly, bioactive oxide layers could be prepared on different Bulk Metallic Glasses. Carbon film formation on SiC³ can be regarded as one of GIL methods. The GIL methods are typical "Soft Process" and "Green Process" using aqueous solutions, and applicable for various functional and structural ceramics layers.

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A-8:IL03 Bio-inspired, Smart, Multiscale Interfacial Materials
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Learning from nature, we revealed that a super-hydrophobic surface needs the cooperation of micro- and nanostructures. Considering the arrangement of the micro- and nanostructures, the surface structures of the water-strider's legs were studied in detail. Accordingly, a series of super-hydrophobic surfaces have been fabricated. Under certain circumstances, a surface wettability can switch between superhydrophilicity and superhydrophobicity. Most recently, we developed a superoleophobic and controllable adhesive water/solid interface which opens up a new strategy to control self-cleaning properties in water. To expand the "switching" concept of the smart 2D surface, we also did a lot of interesting work in 1D system. For example, we discovered the water collection ability of capture silk of the cribellate spider *Uloborus walckenaerius* and then prepared artificial spider silk which will have great applications in water collection. In addition, we developed the novel biomimetic ion channel systems with a variety of intelligent properties, which were controlled by our designed biomolecules or smart polymers responding to the single external stimulus, provided an artificial counterpart of switchable protein-made nanochannels. These intelligent nanochannels could be used in energy-conversion system, such as photoelectric conversion system inspired by rhodopsin from retina or bR, and concentration-gradient-driven nanofluidic power source that mimic the function of the electric eels.

A-8:IL04 Stimuli-responsive Periodic Micro Structures on Oxide-polymer Hybrid Films

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Titania-polymer hybrid films with hierarchical microstructures were fabricated under non-equilibrium state by combining mesophase formation and photo induced wrinkling of the surface organic polymer layer. The wrinkles in micrometer scale were formed by mismatch of elastic constant between the surface organic layer formed by UV polymerization of acrylamide and titania gel layer under the surface skin. The wrinkled surface, which shows a periodicity on micrometer scale, was responsive to the surrounding atmosphere. The spontaneous deformation of the surface wrinkles is due to the swelling of gel layer by absorbing water molecules in hydrophilic mesophase of titania gel. Hierarchical structured hybrid titania film opens great potentiality to realize smart devices such as lab-on-a-chip, optical sensor for environmental monitoring and biological materials.

A-8:IL05 Responsive Materials Based on Silicone Elastomer Networks

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Silicone elastomer networks (SENs) represent a promising new class of materials that enable fabrication of soft material surfaces with tunable characteristics. The functionality of SENs will be demonstrated through 1) the formation of responsive soft surfaces with ultrafast (seconds) response time and 2) fabrication of flexible photochromic films with tunable color. Responsive soft surfaces will be demonstrated that are made by chemical modification of parent SEN based on poly(vinylmethylsiloxane) (PVMS) networks via thiol-ene chemistry. Attaching hydrophilic thiol moieties will endow the networks with environmental responsiveness. We will present various avenues towards tailoring the response time by varying the chemistry of thiol molecules. Photochromic films with tunable color are fabricated by impregnating PVMS networks with spyropiran. We will demonstrate that the color response of the networks after UV irradiation depends on the chemical composition of the PVMS matrix (modified via thiol-ene chemistry) and addition of external salts.

A-8:L06 Hydrophilic and UV-shielding Protective Films Containing TiO₂@SiO₂ Hybrid Nanoparticles

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Recently, the protection films of advertisement pictures have been greatly concerned due to decolorization by sun light including UV light, distortion by water drop, and organic dust on the film surface. To solve these problems, dual functions with increase of hydrophilicity and decrease

of photo-catalytic activity using TiO₂@SiO₂ hybrid nanoparticles are applied to the filler of the protective films. In this study, we report the hydrophilic and UV-shielding films containing TiO₂@SiO₂ hybrid nanoparticles to decrease decomposition of organic substrates. The properties of TiO₂@SiO₂ hybrid nanoparticles were evaluated by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), Ultraviolet-visible spectroscopy (UV-vis), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). The hydrophilicity of films was assessed by water contact angle measurement. Moreover, the band gap energy of TiO₂@SiO₂ hybrid nanoparticles was estimated by using valence band XPS and reflection electron energy loss spectroscopy (REELS).

A-8:L07 Wearable Sensors Based on a pH-responsive Hybrid Layer from Water Borne Carbon Nanotubes, pH-sensitive Polymers and Film-forming Latex

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Wearable pH sensors were fabricated by depositing a thin electroactive coating from water borne (WB) colloidal hybrid dispersions onto electroplated gold electrodes prepared on a flexible polyimide film. The active component of the acrylic polymer coating was a nearly percolating or percolating dispersion of surface-modified multi-walled carbon nanotubes (MWNTs) combined with a pH-responsive homo- or block copolymer. The pH-sensitive polymer amplified the changes in resistivity of the MWNT-loaded (typically around 0.5 wt %) coatings by enhancing local perturbations originating from the variable swelling which occurs in aqueous solutions at different pH. The hybrid WB systems were prepared either by blending the three components or by blending the MWNTs and the film-forming latex particles, previously modified by covalently attaching a functional polymer. Sensor linearity, reproducibility and stability, as well as correlation among sensor response, composition and topological distribution of the various components within the stimuli-sensitive coatings are discussed.

A-8:L08 Design and Development of Self-stratifying Polymers and Coatings

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Certain coating applications including those used in automotive, electronics, medical devices, industrial maintenance and aerospace require a combination of primer/topcoat or basecoat/clearcoat layers. These multilayered systems require a complex application and curing procedures. Multiple formulation, application and processing steps not only contributes to complexity of the composite system it also results in unnecessary waste generation, differential properties such as adhesion and thermal expansion coefficient. It would be desirable to reduce the number of layers to a minimum while providing the same or better overall performance that current systems provide. In this paper we report the design and development of thermosetting polyurethane coatings that self-stratify to two distinct phases upon application and cure. Prototype pigmented systems were applied and cured and were characterized by FTIR, SEM/EDX and were evaluated using standard coating test methods. Microtome and adhesion studies verified that the stratified layers were presumably linked through a urethane linkage. This finding may be taken as an evidence of multi-phase, preferential reactivity, mass transport, and surface tension gradient hypothesis as the basis of the above self-stratification phenomenon.

Poster Presentations

A-1:P02 Silver Oxalate Thermal Decomposition Mechanism

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Silver oxalate is a reactive powder that decomposes with an exothermic reaction during heating. This decomposition produces gaseous CO₂ and a network of porous silver. Silver has an excellent thermal conductivity and is perfectly compatible with common electronics surface materials such as gold. This makes it an excellent thermal interface material for use in high power satellite electronics where the thermal flow is a critical issue. Silver oxalate decomposition proceeds below 300 °C, i.e. this route produces silver at much lower temperatures than its bulk melting point (around 962 °C). In our study thermal cycles up to 300 °C have been used. A Differential Scanning Calorimetry study showed the kinetic effect of the heating rate and the dependence of the reaction on particle morphology. Unexpectedly, several distinct and successive thermal effects were reproducibly observed on the DSC records. The origin of these steps has been investigated by rapidly cooling down the material to stop the reaction at various stages during the decomposition. Scanning Electron Microscopy on the partially transformed material clearly show crystallographic effect, namely that the reaction proceeds differently on the surface of the particle, depending on the local crystallographic orientations.

A-1:P04 Dielectric Properties of Ba_{1-x}La_xTi_{1-x}/4O₃ Ceramics with different La³⁺ Content

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In the present research n-doped BaTiO₃ compositions, with lanthanum contents $x=0; 0.1, 0.2, 0.3$ and 0.4% mol. were prepared by the free sintering method, at $T=1350$ °C. The grain size distribution and morphology of the powders was studied as well as the X-ray diffraction analysis was performed to confirm formation of the desired crystalline structure. Influence of La³⁺ doping on dielectric properties of Ba_{1-x}La_xTi_{1-x}/4O₃ ceramics was studied in the temperature range $T=20-220$ °C, and frequency $\nu=10\text{Hz}-10\text{MHz}$. The measurements in a large range of temperatures were considered for describing their interrelation between semiconductor and ferroelectric properties. Impedance spectroscopy was utilized to analyze the properties of the intergranular and interfacial regions as well as their interrelations, by the Quad-tech 1920-type precision LCR meter. In addition, their temperature and frequency dependences and the dc and ac phenomena in order to separate the individual contributions of electrode effects were employed. The bulk effects and the interfaces in the frequency domain from the total cell impedance as well parameters of the phase transition were determined. At the end the equivalent circuit method was applied to fit the experimental data.

A-1:P05 Electrical Properties of CaCu₃Ti₄O₁₂ Films Prepared by RF Magnetron Sputtering

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The discovery of the colossal dielectric constant (CDC) in the CaCu₃Ti₄O₁₂ (CCTO) generates a great scientific interest in this perovskite type of material. The CCTO, with no dopants, displays also strong current-tension nonlinear behavior with possibility to be used as varistor. The CCTO electrical behavior has been intensively discussed in the literature and has been attributed to intrinsic and extrinsic defects. However, there is no agreement in the literature about the mechanisms which allow explaining the origin of these properties. The main objective of this work was to deposit compact thin films on Si/SiO₂/Ti/Pt substrates by RF sputtering technique using CCTO targets prepared by mixed oxide method. Post annealing in nitrogen and oxygen atmosphere of nano-sized CCTO films were evaluated by X-ray Photoelectron Spectroscopy (XPS) and X-ray Diffraction (XRD). Films morphology was

characterized by Field Emission Scanning Microscopy (FE-SEM) and show homogeneous microstructure. The dependence of annealing atmosphere on the AC and DC transport measurements was analyzed. Results and electrical properties of the films suggest the existence of polaronic defects due changes in the chemical composition.

A-1:P08 The Impact of Titanium Film Properties on the c-axis Orientation of Sputter-deposited AlN Thin Films

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Sputter-deposited aluminium nitride (AlN) thin films are an interesting material due to a CMOS compatible fabrication process and good piezoelectric properties. Besides the influence of sputter conditions on the microstructure of AlN thin films the surface-related properties of the substrate or the underlying metallization are of utmost importance. In this study, the influence of 350 nm thin titanium films sputter-deposited on SiO₂/Si substrates at varying pressure levels $p_{\text{b,Ti}}$ in the range of 2×10^{-3} to 14×10^{-3} mbar on the c-axis orientation of 600 nm AlN thin films is investigated. Both the plasma power for Ti deposition ($P_{\text{p,Ti}}=100$ W) and the parameters for AlN synthesis ($P_{\text{p}}=1000$ W, $p_{\text{b,AlN}}=4 \times 10^{-3}$ mbar in 100% N₂ atmosphere) are fixed. The surface roughness of the Ti bottom layer is the dominating factor resulting either in a high c-axis orientation (i.e. at low $p_{\text{b,Ti}}$ values) or in an amorphous AlN microstructure (i.e. at high $p_{\text{b,Ti}}$ values). Under low pressure conditions, a smooth and dense Ti surface is achieved due to a higher kinetic energy associated with the adatoms. When reducing the root mean square roughness by a factor of 1.8 by decreasing the Ti film thickness to 60 nm, the intensity associated with the AlN (002) peak is increased by a factor of 1.6.

A-1:P09 Multilayer Ceramic Capacitors Based on the PMN-PT-PFN Solid Solution

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We present the technology and properties of multilayer ceramic capacitors (MLCC) based on the PMN-PT-PFN solid solution. PMN-PT-PFN is the abbreviation of $(1-y)[(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3]-y\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$. In our work $x=0.25$, $y=0.1$. PMN is known as a classic relaxor. The addition of PbTiO₃ (PT) into PMN gives the $(1-x)\text{PMN}-x\text{PT}$ solid solution with T_{m} depending on x , and less diffused phase transition. $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PFN) belongs to so called biferroics, in which antiferromagnetic and ferroelectric/relaxor properties are observed in some temperature regions. Addition of PFN into PMN-PT decreases the temperature of final annealing what is important in MLCC. The powder of $0.9(0.75\text{PMN}-0.25\text{PT})-0.1\text{PFN}$ has been obtained in three steps. In first steps we obtained MgNb₂O₆ and FeNbO₄. In final step the $0.9(0.75\text{PMN}-0.25\text{PT})-0.1\text{PFN}$ was obtained. Thick film pastes for obtaining MLCC were prepared by mixing of PMN-PT-PFN powder with organic vehicle and firing in furnace in the temperature range up to 1050 °C. Platinum paste has been used as electrodes. The thickness of one layer was about 45 micrometer (including electrodes). For obtained ceramics and MLCC, XRD investigations were performed as well as investigations of microstructure, EDS and main dielectric properties.

A-1:P09b Synthesis and Electrical Analysis of Nano-crystalline Barium Titanate and PLZT Nanocomposites

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Ceramic based nanocomposites have recently demonstrated the ability to provide enhanced permittivity, increased dielectric breakdown strength, and reduced electromechanical strain making them potential materials systems for high energy density applications. A systematic characterization and optimization of barium titanate and PLZT based nanoparticle composites employing a glass or polymer matrix to yield a high energy density component will be presented. This work shows the

systematic characterization and optimization of barium titanate and lead lanthanum zirconate titanate nanoparticle based ceramics. The nanoparticles have been synthesized using solution and pH-based synthesis processing routes and employed to fabricate polycrystalline ceramic and nanocomposite based components. The dielectric/ferroelectric properties of these various components have been gauged by impedance analysis and electromechanical response.

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A-1:P10 **A Study on the Correlation Between Carrier and Ferromagnetism Based on Hydrogen Mediation**

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Diluted magnetic semiconductor (DMS) has been recently one of the important research fields in spintronics. ZnO based DMS materials such as Co doped ZnO (ZnCoO) have been regarded as one of strong candidates for room temperature DMS. We have reported theoretical and experimental results about ferromagnetic individual spin unit, Co-H-Co complex by hydrogen mediation in ZnCoO, but it is still not clearly evidenced what mediates its interaction with Co-H-Co magnetic units for macroscopic ferromagnetism. In this work, we investigate the correlation between carrier and ferromagnetism of ZnCoO. Through additional doping of Al impurity, carrier concentration increased by about 104 times, but ZnCoO still kept paramagnetic property. However, ferromagnetism was induced in both samples with/without Al doping after hydrogen injection process. The difference of ferromagnetic hysteresis loop was insignificant despite difference by 100 times in carrier concentration by Al doping. We investigated the magnetization of the ZnCoO in term of carrier concentration and studied the correlation between its mobility and ferromagnetism for use as high efficient spin injection layer.

A-1:P12 **Influence of the Medium Composition on Aggregation of Titania Nanocrystals**

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TiO₂ hydrosols are used as precursors for preparation of various nanomaterials. The structure of nanomaterials can be modified through the morphology of nanosized TiO₂ aggregates in the hydrosols. This work is devoted to the study of slow aggregation of monodisperse TiO₂ nanocrystals in acidic hydrosols. The long-term behavior of monodisperse TiO₂ hydrosols with various pH and electrolyte concentration was studied by static and dynamic light scattering as well by small angle X-Ray scattering. It was established that the most stable sols exist in narrow intervals of pH depending on nanoparticles structure, temperature and impurities. The additions of electrolytes with concentrations below the thresholds of fast coagulation induce slow growth of nanoparticles which is reflected in the change of turbidity spectra and sometimes sedimentation. The rate of the process generally accelerates strongly with electrolyte concentration. The obtained results reveal that the electrolyte induced particles growth was mainly due to aggregation of primary TiO₂ nanocrystals but not to the Ostwald ripening. The structure and stability of aggregates depended on the pH and ionic strength of the medium.

A-2:P14 **Polyvinyl Butyral from Laminated-glass Waste for Encapsulating Photonic Molecular Nanodevices**

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Polyvinyl butyral (PVB) resins are widely employed as core polymer in most laminated glasses. In the present work, we have prepared and characterized PVB films obtained from discarded laminated automotive windshield glasses, aiming to explore the properties of the PVB to cover and preserve photonic molecular nanodevices patented in our group¹, contributing, at the same time, to remove these wastes from the environment. Spectroscopic characterization and thermochemical characterization of the PVB was performed by IR, UV-vis absorption spectroscopy and TGA analysis. The PVB film obtained from the recycled by-product is very transparent for visible radiation and, in addition, they

act as a perfect filter for UV A and B, in the same way that the commercial polymer. A hybrid system was obtained by a double thermal evaporation, performed in a BOC Edwards Auto 306 evaporator activating a carousel to move from an active photonic Eu(III) complex to the PVB encapsulating polymer without break of vacuum. We presented a single film device, but sandwich-based nanodevices like OLEDs were also tested as potential molecular devices to be protected.

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A-2:P15 **Calix[4]arenes Appended with Thioamide and Hydroxamic Acid Moieties: Powerful Tools for Heavy Metals Recognition**

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The need of monitoring, controlling and removal of heavy metal cations such as Pb²⁺ or Cd²⁺, which have toxic effects on all living organisms inspires chemists to synthesise more and more selective compounds. Modified calix[4]arenes are the object of great interest for many years due to their remarkable binding ability. Two classes of p-tert-butylcalix[4]arene derivatives: thioamides and hydroxamic acids are presented and tested as selective extractants or ionophores for heavy metal cations. Hydroxamic acids of calix[4]arene extract selectively Pb²⁺ in the presence of Cd²⁺ in solution and Cu²⁺ in the presence of Ni²⁺ and Zn²⁺ which are often found together. Those results are very important in the context of the removal and separation of heavy metal cations. Selectivity of thioamide derivatives was assessed using those ligands as sensor materials in ion-selective membrane electrodes and tested towards Pb²⁺ - selectivity. The influence of the nature of the thioamide function (secondary or tertiary) on their ionophoric properties was also tested. Electrodes based on tertiary thioamides are promising analytical tools for monitoring Pb²⁺ concentration in natural and drinking waters.

A-5:P19 **Tristriazaolotriazines with pi-conjugated Segments: Solvatochromic Fluorophors and Discotic Liquid Crystals**

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Planar polycyclic hydrocarbons with high symmetry are important materials in organic electronics and as mesogenes for discotic liquid crystals. C/N exchange allows a tuning of electrical and optical characteristics, therefore aza-analogous aromatic polycycles gained considerable attention in these fields. Recently, Gallardo and we discovered the ability of the tristriazaolotriazine (TTT) to be a new core for discotic liquid crystals. A convergent synthesis, following the Huisgen procedure connects three aryl-tetrazoles to cyanuric chloride. A 3-fold ring transformation generates the TTT. We report the synthesis, optical and thermal properties of TTTs with a 3-fold alkoxy- or dialkylaminophenyl substitution and higher conjugated analogues. These planar fluorophores can form broad mesophases, typically with a hexagonal columnar structure. Whereas the TTT core acts as an acceptor, lateral alkoxy and amino groups are donors on the C3-symmetrical p-system. Pronounced solvatochromism and a high pH-sensitivity of optical properties are reported.

A-5:P21 **Light-induced Phase Collapse in a Rubidium Manganese Hexacyanoferrate**

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Research associated with the photo-induced phase transition phenomena is an attractive topic in the field of solid state material. A rubidium manganese hexacyanoferrate, is an attractive material since it shows various functionalities, e.g., photomagnetic effects, ferroelectric-ferromagnetism, and so on¹⁻⁵. In this paper, we report a new type of photoinduced phase transition, light-induced phase collapse (LIPC), using rubidium manganese hexacyanoferrate Rb_{0.43}MnII[FeIII(CN)₆]0.81·3H₂O, which does not exhibit a phase transition upon changing the temperature. When the material is irradiated with blue light at 100-200 K, the MnII-FeIII phase collapses and the

valence isomer MnIII-FeII phase appears. The MnII-FeIII phase is perfectly recovered as the temperature increased. Theoretical analysis suggests that the initial MnII-FeIII phase is a thermodynamically metastable phase, while the photogenerated MnIII-FeII phase is the true thermodynamically stable phase.

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A-6:P24 **Production and Characterization of Ti-27Nb-13Zr Alloys by Powder Metallurgy**

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Titanium alloy are widely used in biomedical applications due to their excellent properties such as high strength, good corrosion resistance and excellent biocompatibility. Researches are being developed with elements such as Nb and Zr that reach all criterions for excellent biocompatibility and provide titanium alloys with low Young's modulus. The aim of this paper was to produce and characterize Ti-27Nb-13Zr alloy by powder metallurgy process. The mixtures were performed by high energy milling and sintering in high vacuum furnace with temperature of 1300 °C / 3 h. The microstructures of samples were analyzed by SEM and XRD, while the mechanical behavior was evaluated by elastic modulus and Vickers hardness test. The diffraction results of treatment at 1300 °C indicate that the alloys are composed of α and β phases. Images gotten by SEM indicate the formation of bimodal structures. Vickers hardness measurements taken for the samples sintered at 1300 °C / 3 h (2 hours of milling) indicate average values around 400 HV. Vickers hardness measurements are also determined for the other treatment conditions.

A-6:P26 **Influence of Hydrochloric Acid Concentrations on the Formation of AgCl-doped Iron Oxide-Silica Coreshell Structures**

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It was found that silver chloride (AgCl) particles with cubical morphology exist together with silver (Ag) nanoparticles during the chemical reduction of silver ions onto the surface of iron oxide-silica coreshell powder in ethanol-containing polyvinylpyrrolidone (PVP) at room temperature, due to the contamination of the powder during the synthesis. To confirm the formation of the particles, immobilizing of AgCl particles onto the surface of the iron oxide-silica coreshell powders has been studied by using the same reduction process, with injection of small amount of hydrochloric acid at room temperature. The concentration of acid was varied from 0.012 M to 12.0 M of concentrations. Results showed that acid concentration greatly influenced the formation of AgCl particles where the uniform with cubic morphology was obtained with lower concentration of acid used. Based on scanning electron microscope (SEM) study, the size of AgCl particles also varied with the acid concentrations and amount of the precursor used. The uniform size with cubic morphology of AgCl-doped iron oxide-silica coreshell process might have a good potential to become a mobile plasmonic photocatalyst when was put under light irradiation to induce the Ag formation on the surface of AgCl structures.

A-6:P28 **Multifunctional Carbon-magnetite Nanocomposite Using Polyaniline as a Precursor**

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Due to their high surface area and morphological diversity, activated carbons find applications as filters, catalyst supports and adsorbing media. Combining these properties with additional functionality will expand current applications and give rise to new ones. We prepared novel porous carbonaceous materials by pyrolyzing polyaniline (PAni) in the presence of Fe₃O₄ nanoparticles. Pyrolysis was carried out at several temperatures, yielding fine dark powders that were attracted by a magnet. SEM showed that the base morphology was globular agglomerates, with an increase in the occurrence of short fibrillar structures

with the synthesis temperature. Accordingly, the BET surface area of the material reached up to 400 m²/g, while still containing a fraction of iron oxide. Porosimetry and microscopy results suggest that the final porosity develops around 800 °C for that precursor mixture. The observed fibrillar morphology is possibly due to the use of PAni as the carbon source, and it is likely that some nitrogen remains in the material. In summary, a new magnetic composite material was obtained, which has a reasonable porosity, and shows interesting morphological features.

A-6:P29 **The Oxidation Mechanism of Si1-xGex Nanowires**

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The Silicon-Germanium system is known for its complete miscibility which, in turn, enables compositional modulation through the entire range, which can have an influence on physical properties, such as electron and hole mobility, band gap, and lattice parameters. Conventional strained-SiGe films are thought to be an attractive material for attaining superior properties when used in ultrafast electronic devices and optoelectronic devices. In addition, in recent, as devices are becoming increasingly miniscule, conventional 2-D planar-SiGe are being replaced by 1-D SiGe nanostructures such as nanobelts, nanorods, and nanowires (NWs) due to their possible applications in new kinds of nanoscale devices. Accordingly, this increased interest in SiGeNWs has led to further interest in understanding the process of thermal oxidation on cylindrical SiGeNWs. Si1-xGex NWs were prepared by a Vapor-Liquid-Solid (VLS) procedure using Au as the catalyst at a fixed growth temperature of 400 °C. They were investigated the thermal oxidation at a temperature from 300 °C to 600 °C. We systematically analyzed the oxidation mechanism of the Si1-xGexNWs as a function of oxidation time by using scanning electron microscope (SEM) and transmission electron microscope (TEM).

A-6:P31 **Characterization of Novel Materials, Biogenous Iron Oxide, Produced by Iron-Oxidizing Bacteria**

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A variety of iron oxides are produced by iron-oxidizing bacteria living in natural aquatic environment¹. *Leptothrix ochracea* produces an extracellular iron oxide having unique tubular shape of ~1 µm in diameter. In addition to this kind of morphological uniqueness, its compositional and structural features are very intriguing. We have regarded this microbial ceramics as a novel functional material, which we call "L-BIOX" (BIOX: biogenous iron oxide). Here we will exhibit the compositional and structural characteristics which are vitally important for future material scientific developments. The present L-BIOX microtubules were obtained from an enrichment culture tank using groundwater as the Fe source. The outer surface of the tubular wall is made of fibrillar particles, about 20 nm wide and 50-100 nm long, while the inner surface is made of globular particles of 20-120 nm in diameter. The EDX spectroscopy showed that not only Fe and O but also Si and P are contained considerably, at an atomic ratio of Fe: Si: P = 73: 22: 5. The XRD pattern is similar to that of 2-line ferrihydrite but, unlike ferrihydrite, L-BIOX is completely amorphous; the Fourier-transformed HAADF-STEM image showed a halo pattern without any spot, expelling a possibility of nano-scaled structural ordering.

A-6:P32 **Incorporation of Carbon into Silicon Nanowires Grown with Au Catalyst**

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C-containing group-IV semiconductor alloys are of intense technological

and scientific interest due to the potential such as bandgap and strain-state engineering of layers used in microelectronic and optoelectronic devices. Conventionally complete incorporation of C atoms into substitutional sites in Si1-yCy has only been achieved at C concentration only up to ~2 at.%. This could be explained by the lattice mismatch between C and Si (~52 %) and very low equilibrium solid solubility of C in Si (10^{-4} at.% C at 1400 °C). On the other hand, semiconductor nanowires are considered to be an interesting topic in new electronic and optoelectronic nanodevices due to their structure with high surface-to-volume ratio, and physical properties. In this study, to observe the possibility of C incorporation into 1-dimensional nanostructure SiNWs were synthesized by Vapor-Liquid-Solid procedure using Au as a catalyst, injecting CH₃SiH₃ gas as a C precursor in conjunction with SiH₄ gas during wire growth. The morphological characteristics and crystalline structures of C-incorporated SiNWs were investigated by FE-SEM and FEI TEM. To verify the concentration C atoms and chemical states in the wire X-ray photoelectron spectroscopy (XPS) is employed.

A-6:P34 **Surface Modification of High Internal Phase Emulsion Foam as a Scaffold for Tissue Engineering Application via Atmospheric Pressure Plasma Treatment**

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Atmospheric pressure plasma treatment was used to improve hydrophilic properties and scaffold/cell interaction of poly(S/EGDMA)polyHIPE highly porous foam, prepared from poly(styrene/ethylene glycol dimethacrylate) using a high internal phase emulsion technique. With our synthesis procedure and surface treatment, this bioactive material, featuring a highly porous structure and good mechanical strength, can be applied as a scaffold for tissue engineering applications. The treatment time and external plasma parameters were investigated in regards to the polyHIPE foam surface's appropriate for fibroblast implantation. The changes in surface properties were characterized by SEM, FT-IR, and contact angle measurement, showing that the exposure to air-plasma induced polyHIPE foam with hydrophilic surfaces, as observed by a decrease in contact angle degree. Moreover, the characteristic peaks of various functional groups were found in the FT-IR spectrum of poly(S/EGDMA)polyHIPE foam modified with plasma surface treatment. Enhancement of the interaction between the polyHIPE foam and the L929 fibroblast-like cells would imply the hydrophilic improvement of the polyHIPE foam surface due to the polar-like property of the biofluid cell medium.

A-6:P35 **Development of Porous Carbon Derived from Polybenzoxazine and its Application as an Electrode for Supercapacitors**

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Novel porous carbon was prepared by using polybenzoxazine, a new type of phenolic resins, through a sol-gel process before carbonization in an inert atmosphere at 800 °C. The BET surface area of the resulting porous carbon was approximately 360 m²/g. The activation of this porous carbon was also investigated in order to compare the physical and electrochemical properties. The BET surface area of the activated porous carbon was increased more than twice in comparison with that of the unactivated porous carbon. The electrochemical behaviors were studied by cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy. The results showed that the polybenzoxazine-based porous carbon exhibited good electrochemical performance. The best electrochemical behaviors with the specific capacitance of 109 F/g were obtained from the electrode prepared from porous carbon which underwent heat treatment at 300 °C in air.

A-6:P36 **Lectin histochemistry Evaluation of Bone after Implantation with Macroporous Titanium Samples**

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Titanium and its alloys are widely used as biomaterials and interacts well with bone tissue. In order, to evaluate more than just morphological osseointegration by histological slides our work aimed to approach a molecular evaluation of bone implant interaction using lectin histochemistry (LHC), which bond to and mark carbohydrates presents in membrane glycoproteins with lectins. The implanted samples were commercially pure titanium (cpTi) and Ti-13Nb-13Zr alloy both with and without pores obtained by powder metallurgy, the pores were achieved by adding natural polymers to the hydrogenated metallic powder, after near net shape, the samples were thermal treated (350 °C/1h) and sintered. The samples were characterized for porosity (content 40%), and then were implanted in animal models bone and LHC were performed in histological slides using the lectins PNA, sWGA and RCA1. All samples osseointegrated well with the bone, no fibrous capsule was present between the bone-implant interface, besides this osseointegration feature the implants allowed bone ingrowth inside the pores towards the center of implant. With the molecular approach of osseointegration, adjustments in the processing and structure of macroporous titanium based implants can be performed to achieve friendly structure.

A-7:P38 **Synthesis, Characterization and Spectroscopic Properties of Calix[4]arenes Derivatives of Lanthanides ions under Solvothermal and Hydrothermal Conditions**

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In recent decades the chemistry of calixarenes has been investigated in order to study the separation technology, catalysts, biomimetic, sensors and others. Reactions of calixarenes with various ions Ln(III) have been published, but the supramolecular chemistry of these compounds has been little explored. Calixarenes are highly preorganized compounds, showing a controllable conformational behavior, which could be beneficial for the construction of metal coordination polymers. In recent newspaper was published that some conformational changes of the calix[4]arene core could be controlled by regulating reaction temperature under solvothermal conditions, which may lead to the generation of various coordination polymers with different poly-dimensional topological structures. In the present work we report the reactions of p-tert-butylcalix[4]arene tetracarboxylic acid with Eu³⁺ and Tb³⁺ (hydrothermal) and Tm³⁺ (solvothermal). The compounds were characterized by infrared and luminescence spectroscopy, elemental analysis, X-ray single crystal and scanning electron microscopy.

A-7:P39 **Understanding the Doxorubicin Interaction with Zeolite Imidazolate Frameworks (ZIF-8): A Theoretical and Experimental Investigation**

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Metal Organic Frameworks (MOFs), extensive class of crystalline and porous materials, have been continuously outlined as platform for drug delivery which offer the possibility of continuous release of the drug in the plasma environment within the therapeutic range increasing the activity of the drug. This fact minimizes potential side effects by improving the welfare of the patient during treatment. We wish to report a detailed experimental and theoretical study of the interaction between the Zeolite Imidazolate Frameworks (ZIF-8) and the doxorubicin drug. The adsorbed amount of doxorubicin into the porous solids was 99%. This result was estimated by elemental analysis, UV-Vis spectroscopy, thermogravimetric analysis, Fourier transform infrared, scanning electron microscopy, X-ray diffraction and photoluminescence spectroscopy. The viability of inclusion through comparison of size pores and dimensions of the drugs was investigated and the inclusion simulation was analyzed theoretically by AM1, PM3 and PM6 semiempirical methods. We observed that the AM1 method reproduce reasonably the crystallographic unit cell. However, the considerable increase of the unit cell volume, about 15%, suggests that this method causes stretching of chemical bonds in this structure. This increase is less pronounced, about 10%, when the unit cell is calculated using the PM3 structure. If we analyze all cell parameters the PM6 structure is the most accurate.

A-7:P39b Zeolitic Imidazolate Framework (ZIF-8) for Anticancer Drug Delivery: Fluorescence Study

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Metal-organic frameworks (MOF) or coordination polymers are crystalline solids assembled by the connection of metal ions or clusters through tunable organic linkers whose structures are held together either by strong metal-ligand bonding or by weaker bonding forces (e.g. hydrogen-bonding and p-p interactions). Its modular nature coupled to an infinity of different types of bridging ligands allows for a multitude of frameworks with desirable topologies, architectures, and properties inherent to the building blocks, such as geometric rigidity, chemical functionality, or chirality. The versatility of MOFs led to its broad application in gas separation and/or storage, sensors, non-linear optics, catalyses, forensic chemistry and drug carriers. Doxorubicin (Dox) is a cytostatic drug of first choice in many malignancies with a high efficacy rate and unwanted side-effects. In this report, we describe the incorporation of the anticancer drug doxorubicin into the ZIF-8 with high-load and progressive release, and characterize the antitumoral potential and cytotoxicity of the doxorubicin-ZIF-8 conjugate towards the HL-60 cell line. In order to address host-guest interactions from a microscopic perspective.

A-8:P40 Infrared Thermochromic Properties of VO₂ Thin Films Prepared through Aqueous Sol-gel Process

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Vanadium dioxide (VO₂) is one representative thermochromic material, and it can change its optical properties reversibly at about 68 °C, especially in the IR region, depending on environmental temperature. A relatively simple aqueous sol-gel method followed by vacuum annealing was proposed to prepare IR thermochromic VO₂ thin films. The thermochromic phase transition and the IR thermochromic property of 400nm and 900nm VO₂ thin films in the 7.5-14 μm region were discussed. The derived VO₂ thin film samples were characterized by Raman, XRD, XPS, AFM and SEM. The resistance and infrared emissivity under different temperature were measured, and the thermal images of films were obtained using infrared imager. The results show that the VO₂ thin film annealed at 550 °C for 10 hours through aqueous sol-gel process is pure and uniform. The resistance of 900nm VO₂ film can change by 4 orders of magnitude and the emissivity can change by 0.6 during the phase transition, suggesting outstanding IR thermochromic property. The derived VO₂ thin film can control its infrared radiation intensity and lower its apparent temperature actively when the real temperature increases, which is very promising in the fields of energy saving, thermal control and camouflage.

A-8:P42 Development of Superhydrophobic Surface Morphology
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A surface on which water contact angle is greater than 150°, and sliding angle less than 10°, is called a superhydrophobic surface. To exhibit superhydrophobic feature, a surface should have nano/micron scale roughness on an inherently hydrophobic material. This extreme water-repellency feature attracted much attention for many applications in industry and in daily-life. In this study, we use a nano/micron powder system that can form needle/plate shapes after calcination. Surface roughness on ceramic was aimed to be obtained. Morphology evolution of powders was examined by scanning electron microscopy, and the effect of surface roughness on superhydrophobic behaviour was investigated.

A-8:P45 Study on the Fabrication of Visible Light Response Type N-doped TiO₂ Photocatalyst by SPS

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Photocatalyst has attracted a wide attention in these years as a promising material for environmental use. However, it is recognized that TiO₂, the most popularly used photocatalyst, has a disadvantage that it only reacts with ultraviolet light. In this study, nitrogen-doped TiO₂ was selected as strategy for promoting the absorption of visible light, and SPS (spark plasma sintering) method was tried to fabricate a dense

specimen without using of binder materials. Preparation methods of specimen are as follows; yellow-colored N-doped TiO₂ powders were synthesized from a mixed aqueous solution containing TiCl₃ (50ml) and an NH₃ (70ml). The precipitate was air dried for 1 week. Then dried in a drying oven the day (50 °C). And heat-treated at 400 °C (1h). N-doped TiO₂ powder and non-doped TiO₂ powder were sintered by SPS in the temperature range of 400 or 700 °C. N-doped TiO₂ fabricated by SPS showed a favorable crystal structure of anatase, and successful existence of doped nitrogen was confirmed by XPS analysis. UV-vis results showed that N-doped TiO₂ response to visible light, which indicates an increasing possibility of this type of photocatalyst. Further study to extend the range of adsorption wavelength is being carried out.

SPECIAL SESSION A-10

Emerging Non-volatile Memory Devices

Oral Presentations

A-10:IL01 Towards Charge Storage Memory Devices Based on Electroactive Organic Molecules

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The increasing interest in miniaturizing electronic devices to achieve denser memories will eventually entail the utilization of molecules as active components. In particular, self-assembled monolayers attached to substrates appear as suitable candidates in Molecular Electronics for the development of switchable and memory devices based on electroactive molecules grafted on surfaces. Polychlorinated triphenylmethyl (PTM) radicals and tetrathiafulvalenes TTF derivatives are persistent electroactive organic compounds that can be easily reduced/oxidized to the corresponding anionic/cationic species which also show a high stability in solution. All such species exhibit different optical and magnetic properties and can be reversibly interconverted in solution by electrochemical techniques. We will report efforts addressed to functionalize transparent and conducting ITO and Gold surfaces with appropriately functionalized PTM radicals and TTF derivatives. Such hybrid organic/inorganic surfaces behave as chemical and electrochemical redox switches with bistable optical (absorption and fluorescence), magnetic, and wetting responses exhibiting an exceptionally high long-term stability and excellent reversibility and reproducibility. Moreover, such hybrid surfaces can be patterned as well as electrochemically locally addressed enabling to write-store-read information reversibly on the patterned clusters of electroactive molecules.

A-10:IL02 Nanosecond Timescale Characterization of FeRAMs with Fast-speed Charge Injection

A.Q. JIANG, State Key Lab of ASIC & System, Department of Microelectronics, Fudan University, Shanghai, China

Binary information in capacitive ferroelectric random access memories is destructively readable through polarization charge difference between switching and non-switching events of the cells. Nondestructive readout is possible from high- and low-conductance bipolar switching of a ferroelectric diode with a large on/off current ratio. Fundamental

understanding of both memories needs short-time characterization of imprint and depolarization under writing/reading pulses. With our improved characterization technique, we can transfer domain switching currents under pulses into P-V hysteresis loops from which both remanent polarization and coercive voltage can be derived with time as short as 35 ns. The imprinted coercive voltage is evidenced to decay with time in a semi-log behavior due to the fast-speed charge injection across interfacial layers. After separation of film leakage current from domain switching current, we measured P-V hysteresis loops in a leaky BiFeO₃ semiconducting film. Finally, we can control domain switching speed by inputting a resistor with variable resistance in the circuit. From field dependence of domain switching speeds at different temperatures, we derived an ultimate domain switching time of 0.47 ps in Pb(Zr_{0.4}Ti_{0.6})O₃ thin films.

A-10:L04 Organic and Oxide Ferroelectric Transistor and Diode Arrays for Non-volatile Memories

A. VAN BREEMEN, F. GONZALEZ-RODRIGUEZ, B. VAN DER PUTTEN, G. GELINCK, Holst Centre/TNO, Eindhoven, The Netherlands; A. MARRANI, M. BASSI, Solvay Specialty Polymers s.p.a., Bollate (MI), Italy

Flexible and organic electronics has emerged as a promising technology for low-cost, large-area micro-electronic applications. Most of these applications require memory, preferable non-volatile memory - semiconductor memory that does not lose its data when the power is turned off - that can be programmed, erased and read electrically. Ferroelectric polymers based on copolymers of vinylidene fluoride and trifluoroethylene (P(VDF-TrFE), Solvay Specialty Polymers), possess a large remnant polarization. The use of this ferroelectric polarization field allows for extremely large modulation of the charge carrier density and electronic properties of semiconducting materials. In this presentation we will show the potential of the ferroelectric effect to control and manipulate in a reversible fashion charge transport in diodes and thin-film transistors, and its relevance in non-volatile memory applications. Key device parameters for memory application like switching time, cycle endurance, and data retention will be discussed. Careful optimization of processing conditions has allowed us to integrate ferroelectric polymers with organic and oxide semiconductors towards fabrication of flexible non-volatile memory arrays.

A-10:IL05 Working Model for Electronic Polymer Memory Devices

S. PAUL, Emerging Technologies Research Centre, De Montfort University, Leicester, UK

The growth in the usage of organic materials in the fabrication of electronic devices owes to the ease of fabrication of organic electronic devices as well as the applicability of inexpensive substrates in such configurations. Polymer Memory Devices is a recent addition to the organic or plastic electronic field. Polymer memory devices are fabricated by depositing a blend (an admixture of organic polymer, small organic molecules and nanoparticles) between two metal electrodes. These devices show two electrical conductance states ("1" and "0") when voltage is applied, thus rendering the structures suitable for data retention. These two states can be viewed as the realisation of non-volatile memory. The progress in the polymer memory devices over the last one decade will be presented, and invoke the conundrums that scholars of this field are currently faced with, such as questions about the electrical charging mechanism and stability of devices, proposed theories explaining the experimental data, contradictions in the published work by different groups. The proposed answers to the puzzles, wherever applicable, will be presented. On the basis of various measurements by different techniques, a working model for polymer memory devices will also be presented.

A-10:IL08 Self-rectifying Unipolar HfO_x Based RRAM

HONGYU YU, South University of Science and Technology of China; X.A. TRAN, Nanyang Technological University, Singapore

In this talk, we report the effect of highly-doped n⁺/p⁺ Si as bottom electrode on unipolar RRAM with Ni-electrode/HfO_x structure. With heavily doped p⁺-Si as bottom electrode, RRAM devices illustrate coexistence of bipolar and unipolar resistive switching. Meanwhile, substituting by heavily doped n⁺-Si, the switching behavior changes to self-rectifying unipolar device. The asymmetry and rectifying reproducible behavior in Ni/HfO_x/n⁺ Si device results from the Schottky barrier of defect state level in SiO_x/HfO_x junction and n⁺ Si substrate, but this is not seen for the p⁺-Si electrode case. With rectifying characteristics

and high forward current density observed in Ni/HfO_x/n⁺ Si device, the sneak current path in conventional cross-bar architecture was effectively eliminated. We believe that the proposed structure is a promising candidate for future cross-bar type RRAM applications.

A-10:IL09 Ultrafast MRAM Data Storage

S. SERRANO-GUISAN, N. LIEBING, H.W. SCHUMACHER, Physikalisch-Technische Bundesanstalt, Braunschweig, Germany

Spin transfer torque (STT) is an alternative mechanism to induce magnetization reversal in magnetic nanostructures. The main advantage of this technique in comparison to field-induced magnetization reversal is its scalability allowing the development of ultra fast high-density magnetic random access memory (MRAM) devices with low power consumption. However, STT magnetization reversal by ultra short current pulses can leave the magnetization in an excited state after reversal. Such excitations result in a precessional motion of the magnetization after the decay of the current pulse (the so-called magnetization ringing) which can take several nanoseconds. Therefore, for ultrafast and reliable non volatile STT memories it is essential to ensure the suppression of magnetization ringing after the decay of the current pulse. Here we present time and frequency resolved magneto transport measurements in MgO based magnetic tunnelling junction (MTJ) nanopillars. Time-resolved measurements allow us to determine optimum conditions for coherent control of the free layer magnetization dynamics and for reliable ultrafast ballistic STT magnetization reversal by a single precessional turn¹. By comparison to STT ferromagnetic resonance experiments different magnetization dynamic regimes are identified. This study will allow determination of optimum parameter range for reliable ultra fast and low power consumption STT magnetization reversal for future STT-MRAM devices.

1. S. Serrano-Guisan et al, PRL 101, 087201 (2008)

A-10:IL11 Inorganic Nanoparticles for either Charge Storage or Memristance Modulation

D. TSOUKALAS^{1,2}, E. VERRELLI¹, ¹National Technical University of Athens, Zographou, Greece, ²Institute of Microelectronics, NCSR Demokritos, Agia Paraskevi, Greece

We present electronic memory applications of nanoparticles prepared by a room temperature vacuum technique based on sputtering and atom condensation. We have first investigated nanoparticles as charge storage elements embedded in an insulating matrix of silicon oxide, used as tunneling layer and a hafnium oxide used as the control insulating film. We investigate platinum nanoparticles of different size and density distributions as measured by Transmission Electron Microscopy in order to conclude for the most promising distribution in terms of memory window, retention and endurance characteristics of the proposed nanoparticle flash type memory. Using the same method of nanoparticle fabrication we grow Titanium oxide nanoparticles to form a resistive memory device using the nanoparticle layer in between two metal electrodes. We present electrical results of this memristive device showing an ON/OFF resistance ratio that depends on nanoparticle film porosity that we are able to tune through process parameter variation. Electrical results are supported by structural analysis of the TiO film using Field Emission Scanning Electron Microscopy and X-Ray Diffraction measurements.

A-10:L12 Memristive Memory: a Fundamental Shift

J. NICKEL, J. JOSHUA YANG, M. PICKETT, M. ZHANG, J.P. STRACHAN, G. RIBEIRO, R.S. WILLIAMS, HP Laboratories, Palo Alto, CA, USA

Memristors, the fourth fundamental circuit element, were predicted in the early 1970's. Memristors have recently been reduced to practice and are promising for applications from digital memory to analogue or digital computation. Memristor devices operate significantly different than other known systems: the doping profile (typically charged vacancies) is dynamic, controllable, and repeatable. This presents advantages and challenges not seen in other memory technologies. For instance, the dynamical nature provides highly non linear behavior of some memristive systems, negating the need for access devices. This will allow true cross-point memory architectures resulting in random access to individual bits, 3D stacking of memory, and the ability to integrate NVM on core processor chips. This talk will define the memristor and discuss its physical operation. I will touch on a few of the possible applications this fundamental circuit element enables. For memory

applications, data on devices showing thermodynamic stability, high endurance ($> 10^4$ cycles), fast switching and low power operation will be presented. Memristors are compatible with, and have been fabricated in, CMOS compatible Back End of Line processes. Results from 300 mm fabricated wafers will be presented.

A-10:IL13 Phase Change Memory Technology

R. BEZ, Micron, Agrate Brianza (MB), Italy

At the beginning of last decade, in early 2000, few disruptive technologies had been proposed to replace the standard Non-Volatile Memory technology in the semiconductor industry and to enlarge the memory application. As a fact any new technology takes long time to be accepted; after the concept demonstration and the technology validation it must enter into the production phase, demonstrating to be solid for manufacturing and strongly reliable for the product specification. Another key aspect of a new technology is the medium-long term scalability with the perspective to realize a memory cell and array that can be miniaturized following the leading edge roadmap. PCM technology is demonstrating the capability to enter the broad memory market and to be a mainstream memory thanks to a new set of features interesting for novel applications, combining components of NVM and DRAM and being at the same time a sustaining and a disruptive technology. Moreover there are intense efforts on the PCM technology development. On one side the industry is focused on the increase of the memory density through the scalability and the 3-dimensional integration. On the other side the chalcogenide material research is devoted to facilitate the scaling path and to enlarge and open new application field. In this paper we will show the status of the Phase Change Memory (PCM) in the semiconductor industry and the perspectives of the most important research lines for the near future.

A-10:IL15 Recent Progress and Applications of PRAM

HONGSIK JEONG, Memory Division of Samsung Electronics, Yongin-city, Korea

PRAM is a promising next generation memory due to its advantages of scalability, reliability and compatibility with Si technology. First product of PRAM has been introduced by Samsung electronics for cellular phone. This is the first step of PRAM business, which has to be considered a big business. Therefore, we have to develop technologies for PRAM, considering applications. In this presentation, the technologies and applications for PRAM will be discussed emphasizing the big chance for PRAM business. Especially, recent progress of technologies beyond 20nm node in leading edge will be presented. In conclusion, I will suggest novel cell structures, materials and device technologies for PRAM.

A-10:IL16 Phase Transformations in PCMs

F. HIPPERT, LMGP (CNRS, Grenoble-INP), Minattec, Grenoble, France; **G. GHEZZI**, **S. MAITREJEAN**, CEA LETI, Minattec campus, Grenoble, France; **J.Y. RATY**, Physics Department, University of Liege, Sart-Tilman, Belgium

Phase change materials (PCMs), such as GeTe and Ge₂Sb₂Te₅, are excellent candidates for use in non volatile memories thanks to rapid phase transformation (10th of ns) between amorphous and crystalline states and to large variation of resistivity between the two structures. In memory cells, switching from the crystalline (low resistivity) to the amorphous (high resistivity) phase is obtained by applying a short and high current pulse that locally melts the material. A longer and lower pulse is used for crystallization. Memories based on PCMs offer high scalability, fast programming and good cyclability. To allow operation at relatively high temperatures, it is crucial to improve the stability of the amorphous phase. Carbon doping has been shown to increase significantly the crystallization temperature. Understanding the change of electronic properties and the mechanisms of the phase transformation requires to compare the local order in the amorphous and crystalline phases. Recent results on the structure of carbon doped GeTe will be presented. By combining X-ray total scattering experiments and ab initio molecular dynamics we show that carbon induces a strong structuration of the amorphous phase through long carbon chains and tetrahedral and triangular units centered on carbon.

Poster Presentations

A-10:P46 Memory Effect of a Different Materials as Charge Storage Elements for Memory Applications

I. SALAORU, **S. PAUL**, Emerging Technologies Research Centre, De Montfort University, Leicester, UK

In recent years, the interest in the application of organic materials in electronic devices (light emitting diodes, field effect transistors, solar cells), has shown a rapid increase. Polymer memory devices (PDMs) is a very recent addition to the organic electronics. The polymer memory devices can be fabricated by depositing a blend (an admixture of organic polymer, small organic molecules and metal or semiconductor nanoparticles) between two metal electrodes¹⁻³. We demonstrate the memory effect in the device with simple structure based on blend of polymer with different materials like ionic compound (NaCl), ferroelectrical nano-particles (BaTiO₃) and small organic molecules. In 2007⁴ Paul has proposed a model to explain memory effect a switching between two distinctive conductivity states when voltage is applied based on electrical dipole formation in the polymer matrix. Here, we investigate if our memory devices based on different types of materials are fitted with the proposed model.

1. S. Paul, A. Kanwal, M. Chhowalla, *Nanotechnology*, 17, (2006), 145.
2. D. Prime and S. Paul, *Mater.Res.Soc.Symp.Proc.*, 0997-I03-01, (2007).
3. I. Salaoru, S. Paul, *Mater.Res.Soc.Symp.Proc.*, 1114-G12-09, (2009).
4. Shashi Paul, *IEEE Transactions on Nanotechnology*, 6, (2007), 191.

A-10:P47 Multilevel Resistance Switching in TaOx-based RRAM Device

YING-CHIUAN CHEN, **YU-LUNG CHUNG**, **BO-TAO CHEN**, **JEN-SUE CHEN**, Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan

In this study, a Ta/TaOx/Pt MIM structure is investigated as a resistance random access memory (RRAM) device. The device exhibits both bipolar and unipolar resistive switching characteristics. With bipolar operation mode, multilevel resistance states can be obtained by controlling the high resistance state by varying the sweeping-stop-voltage (Vreset-stop) during the reset process; nevertheless, the multilevel states are not achievable with unipolar operation mode. To understand the multilevel resistance switching mechanism, the electrical conduction in the Ta/TaOx/Pt device is investigated using impedance spectroscopy. Based on the impedance measurement, the degree of conduction of the Ta/TaOx/Pt device depends on the competition between field-driven oxygen vacancy migration and local Joule-heating effect, which leads to the multilevel resistance states for RRAM application.

A-10:P48 Charge Retention in Low Temperature Poly-Si Rewritable Memory on Glass

T.A. MIH, **S. PAUL**, Emerging Technologies Research Centre, De Montfort University, Leicester, UK

We have developed a low temperature method of growing silicon structures for applications in flash memory. Memory behaviour on glass substrates has been observed with these silicon structures as storage medium grown at less than 400 °C. We report on the influence of various factors of this novel technique on the retention and reliability of the rewritable memory fabricated on glass. This will be investigated through various electrical measurements on metal-insulator-semiconductor (MIS) and metal-insulator-metal (MIM) devices containing these films, as well as other physical characterization techniques. The new growth method is highly promising for use in vertically stacked 3-dimensional memory.

A-10:P49 Modulation of Bipolar Resistive Switching for Fuel-assisted NiOx Film via Tailoring of its Interface with Al Electrode

KUN-KENG CHIANG¹, **JEN-SUE CHEN**², **JIH-JEN WU**¹, ¹Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan; ²Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan

In this work, the resistive switching behaviors of the devices composed of the glycine-assisted NiOx films on ITO substrates with Al top electrodes (Al/NiOx/ITO) were investigated. The glycine-assisted nickel oxide films were deposited on ITO substrates by spin coating using an aqueous

solution of nickel acetate hydrate, hydrogen peroxide and glycine (fuel), followed by high-temperature calcination. Transmission electron microscopy and X-ray photoelectron spectroscopy (XPS) analyses indicate that the glycine-assisted NiOx film consists of nanocrystalline NiO embedded in a porous and amorphous Ni/Ni₂O₃ matrix. Unlike unipolar switching in the reported NiO RRAMs, the Al/NiOx/ITO devices demonstrate the bipolar resistive switching behaviors. In addition, the resistive switching behaviors of the device are strongly influenced by the thickness of the Al electrode. XPS analyses suggest that it is attributed to the composition of the active layer modulated by the interfacial reactions with the Al top electrode. We propose that the conducting channels in the Al/NiOx/ITO device are composed of the interconnected Ni atoms and the adjunct oxygen vacancies. The resistive switching mechanism of the Al/NiOx/ITO device will be proposed and discussed in this presentation.

FOCUSED SESSION A-11

Multiferroics

Oral Presentations

Session A-11.1

Theory, Modeling, Processing

A-11.1:IL01 **Electronic Ferroelectricity: Modeling and Understanding** **S. PICOZZI**, CNR, Istituto CNR-SPIN L'Aquila, Italy

Electronic magnetic ferroelectrics, i.e. complex insulating magnets in which ferroelectricity is driven by non-centrosymmetric spin- or charge- or orbital-arrangements, have recently attracted great interests. By means of density functional studies, possibly complemented by symmetry analysis and/or model Hamiltonian approaches, we will focus on the presence and efficiency of different microscopic mechanisms for multiferroicity (i.e. coexistence of long-range dipolar and magnetic orders) and magnetoelectricity (i.e. control of magnetism via electric fields and of ferroelectricity via magnetic fields), based on the interplay between electronic and structural degrees of freedom. In closer detail, we will present examples based on transition metal oxides as well as on organic-inorganic hybrids, such as metal-organic frameworks.

A-11.1:IL03 **From Magneto-Elasto-Electric Device to Ultra-low Noise Magnetic Sensor**

CH. DOLABDJIAN¹, X. ZHUANG¹, S. SAEZ¹, M. LAM CHOK SING¹, C. CORDIER¹, C. DOLABDJIAN¹, J.F. LI², D. VIEHLAND², ¹Groupe de Recherche en Informatique, Image, Automatique et Instrumentation de Caen (GREYC), CNRS UMR 6072-ENSICAEN and the University of Caen, Caen Cedex, France; ²Department of Materials Science and Engineering, Virginia Tech, Blacksburg, VA, USA

Laminate composite Magneto(elasto)Electric (ME) devices can be used as very sensitive magnetic field sensors. Usually, a laminated ME sensor is made with two elastically coupled proof bodies, a magnetostrictive layer and a piezoelectric layer. They convert the sensed magnetic field as elastic strain or stress and the elastic strain or stress as an electric signal, respectively. Usually, the intrinsic magnetic sensor sensitivity to a small magnetic field variation could be evaluated by an equivalent magnetic noise spectral density in T/sqrt(Hz), the sensor resolution. In that way, we will present the best development of ME sensor, give their equivalent magnetic noise spectral density measurement and compare their performance to our theoretical model. This model based on constitutive equation of magneto-electro-elastic material and main ME

device noise sources, is compared well to our experimental results. From our best developments, we achieve a noise spectral density close and down to pT/sqrt(Hz) at 1 Hz and at high frequencies, respectively. Some techniques of magnetic field modulation will be outlined. They allow to extend the sensor performances in term of noise and sensitivity down to DC signal measurement.

A-11.1:IL04 **First-principles Design of Multiferroics with Novel Functional Properties**

J. INIGUEZ, ICMA-B-CSIC, Bellaterra, Barcelona, Spain

In the past decade a lot of experimental and theoretical work has focused on room-temperature multiferroic bismuth ferrite (BiFeO₃ or BFO). Yet, BFO continues to surprise us, and novel results are being obtained on a regular basis in both bulk and thin-film forms of this material. Interestingly, many of the new results seem related with BFO's ability to present atomic arrangements of very diverse nature (e.g., the so-called super-tetragonal phases in thin films or the structures observed at the skin of bulk samples). In this talk I will present recent first-principles results that corroborate what we may call BFO's polymorphism. Indeed, we found that BFO presents many local energy minima that are almost as stable as the ground state of the compound. I will discuss the origin of such a multiple-minima character and its implications as regards current experimental and theoretical work on BFO. I will also argue that the existence of many robustly (meta)stable phases can be used to our advantage: If we were able to switch between such minima by means of external electric fields, large functional responses of various kinds would be obtained. I will illustrate such "phase-change responses" with first-principles results for BiFeO₃-BiCoO₃ multiferroic solid solutions.

A-11.1:IL07 **Textured Ferroelectrics and Magnetoelectrics**

S. PRIYA, YONGKE YAN, Center for Energy Harvesting Materials and Systems (CEHMS), Virginia Tech, Blacksburg, VA, USA

Ferroelectric single crystals such as Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) and Pb(Zn_{1/3}Nb_{2/3})O₃-PbTiO₃ (PZN-PT) with compositions near the morphotropic phase boundary exhibit high piezoelectric coefficients (d₃₃ > 2000 pC/N), large strains (> 1%), and high electromechanical coupling factors (k₃₃ > 92%). These excellent piezoelectric property arise largely from the "engineered" domain states that facilitate the polarization rotation under external electric field drive. However, the application of PMN-PT and PZN-PT single crystals has been limited to niche applications such as medical transducers and sonars where cost is not an issue. High production cost is often related to use of platinum crucibles and small size of useful sample due to compositional heterogeneity across the ingot. Ceramic processing is low-cost technique, but superior properties of single crystals are not observed in polycrystalline ceramics because they are averaged out as each grain possesses different crystallographic orientation. In order to exploit the anisotropic properties of single crystals, <001> textured ceramics with similar compositions are expected to be a cost-effective way to achieve enhanced properties comparable to that of single crystal. We present here our progress in developing textured ceramics.

A-11.1:IL08 **Manipulating Charge and Spin Interactions Across multiferroic BiFeO₃ and Ferromagnetic La_{0.7}Sr_{0.3}MnO₃ Interfaces**

PU YU, RIKEN-Advanced Science Institute, Saitama, Japan

In this talk, I will present our recent studies of the reconstruction/interplay between the charge and spin degrees of freedom in an all-oxide model heterostructure system consisting of the ferromagnet (FM) La_{0.7}Sr_{0.3}MnO₃ (LSMO) and the multiferroic (ferroelectric (FE) and antiferromagnetic (AFM)) BiFeO₃ (BFO). Firstly, I will demonstrate that the interfacial valence mismatch (charge reconstruction) between BFO and LSMO layers can be employed to influence the electrostatic potential step across interfaces and control the ferroelectric state of BFO layer. On the other hand, a novel ferromagnetic state has also been revealed in the AFM BFO sublattice at the interface due to the spin reconstruction, and is responsible for the existence of exchange bias coupling across the interface. Finally, we demonstrate that the interplay between charge and spin degrees of freedom across the interface can lead to a fascinating realm, called magnetoelectric coupling. The measurement clearly shows a reversible switch/control between two distinct exchange bias states by isothermally switching the FE polarization of BFO. This is an important step towards controlling magnetization with electric fields, and may enable a new class of electrically controllable spintronic devices.

A-11.1:L09 **Ex-situ Solid-phase Epitaxy of MOCVD-deposited LuFe₂O₄ Thin Films**

A. PLOKHICH, A. AKBASHEV, A. KAUL, MSU, Moscow, Russian Federation

The compounds from the MeFe₂O₄ (Me = rare earth element) family are among the most promising multiferroic materials. The properties of these substances in bulk state, for example LuFe₂O₄, have been described in many articles, however, there are no data about the synthesis of MeFe₂O₄ thin films, although it is in the thin film form that these materials will most likely find application. The goal of our work was to synthesize LuFe₂O₄ epitaxial thin films in a two-stage process. At the first stage we deposited Lu-Fe-O thin films by MOCVD on substrates of several types: (111) ZrO₂(Y₂O₃), (111) MgO, (111), MgAl₂O₄, and (0001) Al₂O₃. At the second stage, the films were annealed ex-situ in an atmosphere with low concentration of oxygen. According to XRD data, the films with optimized Lu : Fe = 1 : 2 composition contained two phases: hexagonal ferrite LuFeO₃ and iron oxide Fe₂O₃. After the second stage, partial reduction of iron from Fe(II) to Fe(III) and formation of the LuFe₂O₄ phase was observed. After the anneals, LuFe₂O₄, FeO and Lu₂O₃ phases were observed in the XRD patterns. We studied the kinetics of phase formation during the ex-situ anneals. Notable is the phenomenon, which we call ex-situ solid-phase epitaxy: the LuFe₂O₄ phase grows epitaxially on the (111) YSZ substrate.

Session A-11.2

Magnetoelectric Characterization

A-11.2:IL01 **New Multiferroic Manganite and Ferrite with Strong Magnetoelectric Coupling**

Y. TAGUCHI, H. SAKAI, D. OKUYAMA, D. HASHIZUME, Y. TOKURA, RIKEN, Wako, Japan; J. FUJIOKA, F. KAGAWA, Univ. of Tokyo, Tokyo, Japan; T. FUKUDA, JAEA/SPring-8, Hyogo, Japan; H. NAKAO, Y. MURAKAMI, CMRC-PF, IMSS, KEK, Tsukuba, Japan; T. ARIMA, Univ. of Tokyo, Kashiwa, Japan; A.Q.R. BARON, RIKEN SPring-8 Center, Hyogo, Japan

We discuss two multiferroic materials showing strong magnetoelectric coupling: One is perovskite-type manganite (Sr,Ba)MnO₃ and the other is rare-earth ortho-ferrite RFeO₃. In the manganite, magnetic Mn⁴⁺ ions with S=3/2 are found to exhibit off-centering, independently from the magnetic ordering. In this sense, this material is quite different from the known multiferroic materials, such as BiFeO₃ with off-center non-magnetic Bi ions and TbMnO₃ in which ferroelectricity is driven by magnetic ordering. The ferroelectric transition in (Sr,Ba)MnO₃ is governed by a soft phonon mode, and its dynamics is revealed in detail by far-infrared reflectivity and momentum-resolved inelastic x-ray scattering measurements. Strong coupling between spin and polarization is also found in the temperature-dependent crystal structure. In the rare-earth ferrite, polarization is induced by the symmetric exchange striction working between the rare-earth moment and iron spin. We succeed in reversing the weak-ferromagnetic moment associated with the antiferromagnetically ordered iron spins only with the electric field.

This work was in part supported by JSPS through "Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program)".

A-11.2:IL02 **Magnetoelectric Coupling and Isostructural Phase Transitions in the Solid Solutions of the Multiferroic BiFeO₃ with BaTiO₃ and PbTiO₃**

D. PANDEY, School of Materials Science and Technology, Institute of Technology, Banaras Hindu University, Varanasi, India

In this talk I shall present results of our work on the study of magnetoelectric coupling due to an isostructural phase transition (IPT) in two solid solution systems (1-x)BiFeO₃-xBaTiO₃ (BF-xBT) and (1-x)BiFeO₃-xPbTiO₃ (BF-xPT) on the basis of the analysis of the x-ray and neutron powder diffraction data as a function of temperature. The IPT is accompanied with a change in the atomic positions leading to excess polarization below T_n which scales linearly/quadratically with magnetization in the BF-xBT/ BF-xPT systems. Our work provides the

first unambiguous and atomic level evidence for linear/quadratic magnetoelectric coupling in the two solid solutions of BiFeO₃. In addition, we have recently discovered an IPT between two ferroelectric phases with P4mm space group in the BF-xPT system and established the complete phase diagram showing the existence of a critical point at T ~ 677 K for x=0.63.

This work is based on the PhD thesis work of Mr Shuvrajyoti Bhattacharjee and Mr Anar Singh.

1. A. Singh, V. Pandey, R.K. Kotnala and D. Pandey, *Phys. Rev. Lett.* 101, 247602 (2008); 2. A. Singh, A. Senyshyn, H. Fuess and D. Pandey, *Phys. Rev. B* 83, 054406 (2011); 3. S. Bhattacharjee, K. Taji, C. Moriyoshi, Y. Kuroiwa and D. Pandey, *Phys Rev B* 84,104116 (2011)

A-11.2:IL03 **Isothermal Electric Control of Exchange Bias near Room Temperature**

C. BINEK¹, XI HE¹, YI WANG¹, N. WU¹, A. WYSOCKI¹, T. KOMESU¹, U. LANKE², A.N. CARUSO³, E. VESCOVO⁴, K.D. BELASHCHENKO¹, P.A. DOWBEN¹, ¹Department of Physics & Astronomy and Nebraska Center for Materials and Nanoscience, University of Nebraska, Lincoln, NE, USA; ²Canadian Light Source Inc., University of Saskatchewan, Saskatoon, Saskatchewan, Canada; ³Department of Physics, University of Missouri, Kansas City, KS, USA; ⁴Brookhaven National Laboratory, National Synchrotron Light Source, Upton, NY, USA

Voltage-controlled spintronics promises continued progress in information technology. Controlling magnetism at thin-film interfaces by electrical means is a key challenge to better spintronics. I report on the antiferromagnetic (AF) magnetoelectric (ME) Cr₂O₃ (chromia) for voltage-controlled magnetism. Specifically, robust isothermal electric control of exchange bias (EB) is achieved at room temperature in Cr₂O₃(0001)/CoPd. Our findings serve as macroscopic evidence for equilibrium boundary magnetization (BM) in ME antiferromagnets. BM is a generic property at interfaces of ME single domain antiferromagnets. In chromia, an AF single domain can be magnetoelectrically selected out of two degenerate AF 180 degree domains. First-principles and symmetry considerations provide theoretical insight. Measurements of spin-resolved UPS, magnetometry, and detailed investigations of the unique voltage-controlled EB offer macroscopically averaged information. Laterally resolved X-ray PEEM and temperature dependent MFM reveal microscopic information of the chromia surface magnetization. In concert, our data provide a coherent interpretation of our results on isothermal electric control of EB.

Financial support by NSF through CAREER, MRSEC, SRC/NSF Suppl. to MRSEC, NRI, & Cottrell Research Corp.

A-11.2:L04 **Exchange Biasing of Magnetoelectric Thin Film Composites**

E. LAGE, C. KIRCHHOF, D. MEYNER, **E. QUANDT**, Christian Albrechts University Kiel, Kiel, Germany

This presentation demonstrates the successful implementation of an intrinsic bias field in magnetoelectric magnetic field sensors via exchange bias. This intrinsic biasing allows the operation at the optimum working point without the application of an external magnetic bias field. Thin film magnetoelectric composites were fabricated by magnetron sputtering on Si-cantilever substrates¹. The composites consist of piezoelectric AlN and multilayers with the sequence Ta/Cu/MnIr/FeCo or Ta/Cu/MnIr/FeCoSiB serving as magnetostrictive component of the composite. The layer thickness of the magnetostrictive FeCo or FeCoBSi layers and the angle dependency of the exchange bias field is used to adjust the shift of the magnetostriction curve in a way that the maximum piezomagnetic coefficient is found at zero magnetic bias field. Accordingly, such self-biased composites show a high sensitivity to AC magnetic fields with a ME coefficient of 21 V/cmOe for its mechanical resonance at 1011.5 Hz in the case of the FeCo samples. Consequently, this internal bias field opens the path to individually biased sensor array components and the realization of a three-dimensional vector field sensor.

1. H. Greve et al, *Appl. Phys. Lett.* 96, 182501 (2010).

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A-11.2:L05 **Magnetoelectric Properties of Layered Thin Film Composites**

HEE YOUNG LEE, Yeungnam University, Gyeongsan, Korea

Magnetoelectric properties of PZT-Terfenol-D composite will be reviewed.

The structure of the composite showed a strong impact on magnetoelectric coupling between ferroelectric and magnetostrictive films. The effect of the film processing variables on microstructure, ferroelectric and magnetic properties will be discussed in some detail.

Session A-11.3

Dynamics of Multiferroics & Structural Characterization

A-11.3:IL01 Terahertz Emission from BiFeO₃ Thin Films

M. TONOUCHI, Institute of Laser Engineering, Osaka University, Suita, Japan

Terahertz (THz) radiation has been observed from multiferroic BiFeO₃ (BFO) thin films via ultrafast modulation of spontaneous polarization upon carrier excitation with illumination of femtosecond laser pulses. The radiated THz pulses from BFO thin films were clarified to directly reflect the spontaneous polarization state, giving rise to a memory effect in a unique style and enabling THz radiation even at zero-bias electric field. The emission mechanism is explained by the direct modulation of spontaneous polarization. We also find strong photoassist effect on polarization switching of BFO films. On the basis of our findings, we demonstrate potential approaches to ferroelectric nonvolatile random access memory with nondestructive readability and ferroelectric domain imaging microscopy using THz radiation as a sensitive probe.

A-11.3:IL03 Ferroelectric and Multiferroic Tunnel Junctions

A. CRASSOUS¹, **V. GARCIA**^{1,2}, M. BIBES¹, A. CHANTHBOUALA¹, S. FUSIL¹, K. BOUZEHOUE¹, E. JACQUET¹, L. BOCHER³, A. GLOTER³, C. DERANLOT¹, S. XAVIER⁴, S. ENOUZ-VEDRENNE⁴, N. MATHUR², A. BARTHÉLÉMY¹, ¹Unité Mixte de Physique CNRS/Thales, Palaiseau, France; ²University of Cambridge, Cambridge, UK; ³Laboratoire de Physique des Solides, Université Paris Sud, Orsay, France; ⁴Thales Research and Technology, Palaiseau, France

To overcome the scarcity of multiferroic materials researchs focus on artificial multiferroics obtained by combining ferroelectric and ferromagnetic materials. I will show results on a particular type of artificial multiferroics composed of a magnetic tunnel junction with a ferroelectric barrier (MTJJs). In these ferroelectric tunnel junctions, large changes in the resistance are observed and correlated with the direction of the ferroelectric polarisation of the barrier¹. This give rise to large electroresistance phenomena (TER) that amounts to 75000% for a 3nm BaTiO₃ tunnel barrier. When a ferromagnetic counter electrode of Fe is added to obtain a ferroelectric magnetic tunnel junction, a modulation of tunnel magnetoresistance reflecting changes in the spin polarisation of the electrode when the ferroelectric polarisation is switched have been observed². These junctions provide an interesting opportunity to obtain a robust room temperature magnetoelectric effect and to achieve an electric control of the spin polarisation.

1. V. Garcia et al, *Nature* 460, 81 (2009); A. Gruverman et al, *Nanoletters* 9, 3539 (2009); A. Crassous et al, *Appl. Phys. Lett.* 96, 042901 (2010).
2. V. Garcia et al, *Science* 327, 1106 (2010); S. Valencia et al, *Nat. Mat* 2011 (*Nat. Mat.* 3098).

A-11.3:IL04 Study of Strain-induced Morphotropic Phase Boundary in Multiferroic BiFeO₃ Thin Films

LANG CHEN, School of Materials Science and Engineering, Nanyang Technological University, Singapore

A morphotropic phase boundary driven by epitaxial strain has been observed in a lead-free multiferroic BiFeO₃ thin films and the strain-driven phase transitions were widely reported to be iso-symmetric Cc-Cc ones by recent works. In this talk, we suggest that the tetragonal-like BiFeO₃ phase identified in epitaxial films on (001) LaAlO₃ single crystal substrates is monoclinic MC. This MC phase is different from MA type monoclinic phase reported in BiFeO₃ films grown on low mismatch substrates, such as SrTiO₃. Our recent results also demonstrate that the mixed-phase regions are mainly made up of two highly tilted triclinic

ferroelectric phases. The first principles studies reveal that the piezoelectric responses of these two lowest-symmetry phases are not significantly large, and further suggest that the ease of phase transition between these two energetically close triclinic phases is responsible for the large piezoelectric response in the BiFeO₃ films near its MPB.

Session A-11.4

New Effects

A-11.4:IL01 Electrically-controlled Atomic Spin-valve at a Complex Oxide Interface

J.D. BURTON, **E.Y. TSYMBAL**, Department of Physics and Astronomy, University of Nebraska, Lincoln, NE, USA

Artificial multiferroic materials are interesting, in particular, due to a large magnetoelectric effect which may occur at the ferroelectric-ferromagnetic interfaces. Recently, we have predicted a possibility of the ferroelectric control of the magnetic order within a few atomic layers at the interface between a hole-doped manganite, La_{1-x}A_xMnO₃ (LAMO, A is a divalent cation), and the ferroelectric BaTiO₃ (BTO). [Phys. Rev. B 80, 174406 (2009)]. The effect arises due to "electrostatic doping" associated with the screening charge in LAMO that can be changed by reversing the ferroelectric polarization of BTO. Our first-principles calculations predict that magnetic tunnel junctions with a ferroelectric barrier allow the control of spin transport by ferroelectric polarization. When LAMO is used as one of the electrodes, those few atomic layers near the interface sensitive to the ferroelectric polarization act as an atomic scale spin-valve in series with the ferroelectric tunnel barrier. We find that switching the ferroelectric barrier induces more than an order of magnitude change in the conductance due to the interfacial spin-valve effect in the highly spin-polarized LAMO, constituting a new spin-dependent transport phenomenon. [Phys. Rev. Lett. 106, 157203 (2011)]

A-11.4:IL02 Functionally Graded Magnetoelectric Composites

G. SRINIVASAN, G. SREENIVASULU, V.M. PETROV, Physics Department, Oakland University, Rochester, MI, USA

Novel magnetoelectric (ME) phenomena in multiferroic bilayer composites consisting of functionally graded ferromagnetic and ferroelectric phases are discussed. The grading involves piezomagnetic (q) and piezoelectric (d) coefficients and is achieved with the use of Fe, Co, Ni, Metglas, or ferrites with different q and oppositely poled piezoelectrics. Significant findings include the following. (i) Observation of ME effect under zero-magnetic bias with the ME coefficients as high as 1.6 V/cm Oe at low frequency. (ii) With a biasing field, it is shown that the bending moment due to grading counteracts the asymmetry related flexural strain and enhances the strength of ME coupling. (iii) A factor of 40 increase in the ME voltage is measured at bending resonance. Theoretical estimates of ME coefficients are in general agreement with the data.

S.K. Mandal, G. Sreenivasulu, V.M. Petrov, and G. Srinivasan, *Phys. Rev. B* 84, 014432 (2011).

A-11.4:IL03 Domain Walls and Photovoltaic Effect in BiFeO₃

M. ALEXE, Max Planck Institute of Microstructure Physics, Halle, Germany

BiFeO₃ thin films with periodically ordered ferroelectric domains have shown to generate open circuit photovoltages as large as 15 V by illumination with light having the photon energy above the band gap. Ferroelectric domain walls were playing a major role in a model developed to explain this anomalous photovoltaic effect. In order to closely investigate this nanoscale photovoltaic mechanism, we have developed an AFM-based local measurement of photoelectric and photovoltaic effects. We have shown using photoelectric AFM that, besides a significant tip-enhancement, the photovoltaic currents BFO single crystals are rather uniformly distributed at the crystals surface, suggesting that there is no strong electron-hole recombination within the ferroelectric domains. (M. Alexe and D. Hesse, *Nature Communications* 2011, 2:256) Moreover, to unveil the role of the domain walls we have developed

novel measurement methods such as photo-induced transient spectroscopy (PITS) scanning probe microscopy (SP-PITS), to evaluate and locally map the generation and recombination rates.

The present talk will address general aspects of photovoltaic effect in BFO single crystals and thin films as well as the role of the domain walls in generation mechanism of the anomalous photovoltaic effect.

A-11.4:L04 **Free Charge Contribution to Dielectric Behavior of Oxides**

R. ANAND THEERTHAN, M. MAGLIONE, ICMCB, University Bordeaux 1, Pessac, France

Free charges (electronic or ionic) can influence the dielectric properties of the ferroelectric material to a great extent. Catalan has reported that magnetoresistive artifacts can invoke large magnetodielectric coupling. The interface and core of the dielectric has difference in resistance. This gives rise to Maxwell - Wagner effect and eventually to magnetodielectric effect caused by change of resistance under magnetic field. Here we show that for Fe doped BaTiO₃ domain walls can act as such a interface and electron mobility due to oxygen vacancies as an artifact which can be tuned under magnetic field and give rise to artificial magneto capacitance at high temperature and to magnetodielectric losses at low temperature. Where as in the case of KTiOPO₄(KTP) ionic mobility of potassium ions at low temperature undergoes a drastic change due to superionic transition which eventually influences the mechanical resonance of the system and splits the single piezoresonance at high temperatures into two at 200K and at the same temperature polarization start to appear. Based on these findings we established here a coupling between ionic conductivity and piezoresonance based on buildup of space charges at lower temperature (below 200K).

Session A-11.5 Devices

A-11.5:IL01 **Progress in Magnetoelectric Devices Based on Piezoelectric/piezomagnetic Laminated Composites**

SHUXIANG DONG, Peking University, Beijing, China

Magnetoelectric (ME) effect is a magnetic field-to-electric field coupling via elastic strain in ferroelectric and ferromagnetic composites. Currently, the strongest ME effect observed from ferroelectric and ferromagnetic composites is one type of piezoelectric/piezomagnetic layered laminates. This presentation reviews current progress in ME devices based on piezoelectric/ piezomagnetic laminated composites. ME devices are mainly utilized as high-sensitivity magnetic sensors, current sensors, transformers and gyrators, microwave devices, tunable inductors and filters, energy harvesters, ME actuators, and ME memories, et al. The working principle and properties of ME devices are introduced, and their future development are also discussed in this presentation.

A-11.5:L02 **Tunable BiFeO₃-BaTiO₃ Thin Film Bulk Acoustic Wave Resonators for Microwave Applications**

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The electrically tunable thin film bulk acoustic wave resonators (FBARs), utilizing electric field induced piezoelectric effect in paraelectric phase ferroelectrics have been demonstrated recently. They enable development of novel reconfigurable/adaptable microwave circuit architectures. One may expect enhanced functionalities in the FBARs utilizing multiferroic materials due to the coupling interaction between ferroelectric and ferroelastic order parameters. Additionally, coupling with magnetic phenomenon would allow development of the FBARs tunable by both electric and magnetic field which enable a variety of other advanced applications. In this work the single-phase 0.67BiFeO₃-0.33BaTiO₃ multiferroic thin film solidly mounted FBAR test structures have been fabricated and characterized. The FBAR test structures

reveal resonance at 4.5 GHz, 3% tunability of the resonant frequency and an electromechanical coupling coefficient of 6% at 10 V dc bias. These parameters are highest for the electrically tunable FBARs reported so far. The irreversible changes of the resonant frequency with electric field are less than 0.1%. The relatively low Q-factor, below 100, is associated with wave scattering from rough interfaces and may be improved by the design/technology optimization.

A-11.5:L03 **Strain-dependent Magnetoelectric Properties of Epitaxial CoFe₂O₄/Pb(Zr_{1-x}Ti_x)O₃/SrRuO₃ Heterostructures on PMN-PT Substrates**

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Strong enhancement of magnetoelectric (ME) voltage coefficients at strain-induced transitions between different ferroelectric phases was predicted for epitaxial Pb(Zr_{1-x}Ti_x)O₃ (PZT) films in Phys. Rev. B, vol. 80, art. 054102 (2009). To observe this enhancement experimentally, a precise strain engineering of the film is necessary because the misfit strain has to be adjusted with a high accuracy. This adjustment can be greatly simplified by a post-fabrication fine tuning of misfit strain, which can be realized in films deposited on "active" substrates, such as ferroelectric relaxors PMN-PT and PZN-PT subjected to a bias electric field. In this work, ME epitaxial CoFe₂O₄/PZT/SrRuO₃ composite films were deposited on polished 150-micrometer-thick PMN-PT single crystals by pulsed laser deposition and high-pressure sputtering. The X-ray analysis showed that a tuning of the misfit strain in the range of 0.2% was realized at a bias voltage of 300 V. Strain-dependent ME properties of these heterostructures were investigated for several compositions of PZT films. In addition, we present first results on epitaxial ME heterostructures grown on SrTiO₃-buffered Si substrates. This approach might offer interesting perspectives for CMOS-compatible ME devices based on epitaxial complex oxides.

Poster Presentations

A-11:P52 **Multi-component Oxide Thin Films and Heterostructures for Electronics: Growth Principles**

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In the last years oxide materials for electronics show significant progress. However, many physical details and technological aspects have to be solved. For electronics, thin films and heterostructures are important taking advantage of integration and synergetic concepts leading to new types of devices and functionalities. It is notable that, while fabrication of new devices and materials showing new phenomena are booming, the growth principles and concepts are somehow developing slowly within this general trend. This is because in many cases, growth of materials is very personalized. Understanding of the bi-directional relationship between the general and particular principles deserves attention. The immediate benefit is that knowledge on growth for one material can be transferred to another one. In our work we have analyzed such relationships for some oxide multicomponent perovskites. Materials used in our examples are Bi-Sr-Ca-Cu-O and YBa₂Cu₃O₇, La-Sr-Mn-O, (Ca, Sr)CuO₂, (Ca, Ba)CuO₂ and Bi₄Ti₃O₁₂. Presented thin films or heterostructures are with c-axis and non-c-axis orientations. We discuss film-substrate lattice relationships, control method of growth mechanism, morphology/roughness, uniformity and precipitates/segregates removal, stability domain and inter diffusion.

A-11:P54 **Ferroic and Structural Study of High-dense Polycrystalline TbMnO₃ Ceramics**

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TbMnO₃ is a multiferroic magnetoelectric material at cryogenic temperatures due to a transition between two distinct magnetic states. TbMnO₃ single crystals exhibit a para-antiferromagnetic transition at

TN \sim 41 K. The magnetic wavenumber k is incommensurate at TN, and decreases with the decrease of the temperature until be locked to a constant value where a polarization vector arises in the c - axes direction. In TbMnO₃ single crystals the polarization flops into the a direction when a magnetic field (higher than 4 T) is applied along the a or b directions. In this work, high-dense TbMnO₃ polycrystalline samples were obtained through high-energy ball milling. Microstructural, structural, dielectric and magnetic characterizations were carried out. Dielectric and magnetic transitions, as those reported for single crystals, were not observed in polycrystalline samples, which exhibited three dielectric relaxation processes at distinct temperatures. Two of them, thermally activated, were related to dipolar effects of hopping carriers. A third relaxation process was observed in the temperature range where TbMnO₃ shows magnetic transitions, which could be associated to a distribution of relaxation times due to the formation of ferroelectric domains or clusters.

A-11:P55 Magnetostrictive and Magnetoelectric Properties in Nickel Ferrite - Niobate Relaxor Structures

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Magnetoelectric effect in multiferroic materials is widely studied for its fundamental interest and practical applications. This paper investigates the magnetostrictive and magnetoelectric properties of multilayer structures consisting of 6 nickel ferrite (Ni_{0.3}Zn_{0.62}Cu_{0.08}Fe₂O₄) and 7 relaxor (Pb(Fe_{0.5}Nb_{0.5})O₃) layers. The magnetic properties of composites show a dependence typical of such composite materials, i.e. it consists of a dominating signal from ferrimagnetic (ferrite) and a weak signal from paramagnetic (antiferromagnetic) phase (relaxors). The parallel and perpendicular magnetostriction measurements of the composites were performed at room temperature as a function of the external DC magnetic field, by the standard strain gauge technique. The piezomagnetic coefficient for composites were calculated from the measured magnetostriction. Magnetoelectric effect at room temperature was investigated as a function of static magnetic field (300-7200 Oe) and frequency (10 Hz-10 kHz) of sinusoidal modulation magnetic field. The magnetostriction and magnetoelectric effect increase slightly before reaching a maximum at $H_{DC} = 750$ Oe and then decrease.

A-11:P56 Magnetic Properties of the Bi₉Fe₅Ti₃O₂₇ Aurivillius Phase Doped with Samarium

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Bismuth layer-structured compounds in the Bi₄Ti₃O₁₂-BiFeO₃ system known as Aurivillius phases are single phase multiferroics. It was stated that substitution of some rare earth elements for bismuth ions in such structure can modify its magnetic properties. Powders of Bi₉Fe₅Ti₃O₂₇ and Bi₈.1Sm_{0.9}Fe₅Ti₃O₂₇ were prepared by wet chemical method and then were sintered to dense polycrystalline materials. Low field DC susceptibility was measured in the zero field cooled (ZFC) and field cooled (FC) modes at 10 - 400 K. For selected temperatures magnetisation curves and hysteresis loops were also measured. For the pure sample the FC and ZFC curves diverge at lower temperatures indicating a spin glass-like behaviour. The compound with samarium exhibits one order of magnitude higher low field magnetization. The FC and ZFC curves diverge and the spin glass-like phase appear even at 400 K. The samarium doped sample shows a hysteresis with coercive field of 650 Oe at 100 K. At 10 K the magnetization curve exhibits a nonlinearity similar to paramagnets at low temperatures. The low temperature hysteresis loops are shifted with respect to zero field what can be attributed to "exchange bias" of the samarium sublattice by the iron one, which possibly orders antiferromagnetically at above 300 K.

A-11:P57 Reflection of Electromagnetic Waves from Multiferroic TbMnO₃

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It is known, that in terbium manganite (TbMnO₃) at low temperatures the modulated magnetic structures and the strong magnetoelectric interaction are observed. These are sinusoidal and cycloidal structures. The spectrum of coupled spin and electromagnetic waves and dynamic properties manganites are studied not enough. The spectrum of coupled spin and electromagnetic waves is explored theoretically in our paper.

We use approach when $L \gg a$, where L - period of modulated structures, a - lattice constant. The joint solution of equations of motion for a magnetic subsystem in the form of Lagrange and the Maxwell equations yields us a spectrum of the coupled waves in the multiferroic TbMnO₃. Interaction of spin and electromagnetic waves depends of magnitoelectric interaction magnitude and external fields. In spectrum of coupled waves (segnetomagnons, electromagnons) appears the forbidden band, their width depends on constant of magnitoelectric interaction. Calculations of reflection coefficient R as a function of frequency shows that R vary from 0 to 1. Investigations have shown that forbidden band width in a spectrum of the coupled waves and a reflexion coefficient of electromagnetic waves can change external electrical and a magnetic fields.

A-11:P59 Structural Relationship in BiFeO₃ - Based Compounds

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Multiferroic magnetoelectric are materials that present potential applications where the ferroelectric and magnetic ordered materials have been used. Among these materials, the BiFeO₃ is a very promising candidate. Due to the difficult to synthesize this material, nanometric grains are desirables in a powder preparation route. In this sense, nanostructured powders of the BiFeO₃-XTiO₃ (X = Ba or Pb) compounds were prepared by mechanosynthesis and sol-gel synthesis. Their structural and ferroic properties have been improved by the formation of two-phase compounds and, in some cases, the formation of a monoclinic solid solution (Cm or Cc space group). The crystal structure of the samples was studied by X-ray powder diffraction and sincrotron radiation - high resolution X-ray powder diffraction. Structural parameters were refined through Rietveld analysis (FULLPROF program). The refinements were conducted with a rhombohedral (R3c space group) single phase or a monoclinic (Cc or Cm space group) single phase. Using a model with a single phase, the refinement did not yields good results. However, by using a two phases model (rhombohedral and monoclinic phases) the refinements showed the better agreement between the experimental diffraction pattern and the theoretical one.

FOCUSED SESSION A-12

Progress in Metamaterials Research

Oral Presentations

Session A-12.1

Microwave & THz Metamaterials

A-12.1:IL01 Terahertz Metamaterial Response at High Fields

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Recent developments in the generation of high field terahertz pulses enable new regimes in far-infrared nonlinear optics to be explored. This is of particular interest with regards to metamaterials, since, on the subwavelength scale, dramatic field enhancement occurs. This can, in turn, lead to dramatic nonlinearities up to and including catastrophic irreversible damage. In the talk, I will present our recent results exploring the electrodynamic response of metamaterials excited by THz pulses with peak electric fields of several hundred KV/cm. Within the active

region of split ring resonators - the canonical metamaterial "atom" - the electric field can be enhanced by more than a factor of ten corresponding to local fields of several MV/cm. Several examples will be discussed including the metamaterial enhanced THz field driven insulator to metal transition in the vanadates.

A-12.1:IL02 Analytical Modelling of Microwave/Millimeter Wave 1D and 2D Gratings and Fishnets

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Since the discovery of extraordinary transmission (T.W. Ebbesen et al, Nature, 391, 667, 1998) hundreds of papers have been published in the technical/scientific literature on the topic. They provide physical explanations for many subtle details of the phenomenon or report on a wide variety of structures exhibiting such exotic electromagnetic behavior. Surface plasmon polaritons (SPP) supported by the periodically structured screens (otherwise fully opaque) were identified as the causal agent explaining the phenomenon. However, an alternative, but compatible, interpretation of the observed results has been developed along the last few years. This interpretation is based on the analogy of the actual periodic structures and equivalent waveguide problems (F. Medina et al, IEEE Trans. on Mic. Theory Tech., 56, 3108, 2008; ibid. 58, 105, 2010). The advantage of this point of view is that leads itself to analytical models based on circuit analogs of the electromagnetic phenomenon, which have just a few parameters to be determined. This talk will report on the applications of this model to a number of periodic structures (1D and 2D) that have been solved since the first proposal of this methodology. These include extraordinary transmission, anomalous transmission and fishnet systems.

A-12.1:IL03 On the Lateral Confinement of Surface Waves in the Microwave Regime

E.M.G. BROCK, **E. HENDRY**, **A.P. HIBBINS**, Electromagnetic Materials Group, Physics Building, University of Exeter, Exeter, England

There have been extensive studies into the excitation of surface waves in the optical regime, and in particular of surface plasmon polaritons (SPPs). Extension of this surface wave concept to the microwave regime might seem problematic at first sight, since at these frequencies metals behave as near-perfect conductors, completely screening the incident field. However the addition of a sub-wavelength corrugation introduces an artificial boundary condition, producing a "meta-surface" that supports a strongly bound mode, similar in character to SPPs. We present work undertaken at Exeter investigating the lateral and sub-wavelength confinement of surface waves in the microwave regime. In particular, the experimental validation of a recent theoretical study suggesting that a chain of closely spaced metallic cuboids ("dominos") in contact with a metallic surface can support laterally confined modes ("domino plasmons") is discussed. The dispersive limit of the mode is shown to be insensitive to the lateral width of the chain. The electric field profile is experimentally measured for these modes and the mode supported by a tapered chain of metallic cuboids of comparable periodicity. Furthermore, the group velocity of the domino plasmon is experimentally measured to explore slow waves.

A-12.1:IL04 Design and Optimization of Microwave Triangular Meta-material Resonators in Coplanar Configuration

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Metamaterial (MM) structures exhibit phase and group velocities having opposite sign and negative effective permittivities, making them good candidates for novel applications in microwave sub-systems. Several analytical and experimental results are available concerning the shape optimization of resonating MM configurations. In this paper, a Complementary Sierpinski Triangular Resonator (C-TSR) in coplanar waveguide (CPW) has been studied for C and X Band applications. The peculiarity of the triangular structure to exhibit multiple resonances is proposed for dual and three-band purposes, to obtain efficient unit cells for high performance microwave tunable oscillators. The MM nature of the resonators has been studied deriving the effective dielectric and magnetic permittivity by means of the Y- and Z- electrical parameters. Single and back-to-back triangles, even including the presence of inner small triangular resonators, have been simulated, optimizing the

performances of the notch response in terms of quality factor Q and impedance matching. As a result, a proper shape and number of inner triangles can change the frequency of resonance of the entire structure. Q-values up to 10000 have been predicted, and an isolation better than 30 dB between the resonance peaks has been evaluated.

A-12.1:IL05 Electromagnetic Shielding using Nanoparticles Embedded in Polymer Matrix Composites

N. MORA¹, **F. RACHIDI**, Swiss Federal Institute of Technology-EPFL, Lausanne Switzerland; **M. DADRAS**, Centre Suisse d'Électronique et de Microtechnique - CSEM, Neuchâtel, Switzerland

Composite materials with multifunctional requirements have been developed with increasing demand as a new technique for electromagnetic shielding. In this work we consider an electrically nonconductive polymer matrix that is mixed with conductive nano-reinforcements to form a new dielectric material. In this work we present an experimental evaluation of the complex permittivity of a polymer matrix composite (PMC) material with nickel (Ni) nanoparticles as the conductive reinforcement, between 10 MHz and 1GHz. Particles size distribution and particles density was observed by Transmission Electron Microscopy. The complex effective permittivity of the Ni-PMC was also theoretically estimated by considering a quasistatic approximation. We have measured the complex permittivity of the first fabricated samples from 10MHz to 1GHz. The results show that the complex permittivity of the Ni-PMC is significantly increased. The measured effective complex permittivity was compared with the one obtained from the theory, with a high degree of agreement. The shielding effectiveness of the Ni-PMCs can be estimated from the complex effective permittivity measurement. The effect of the geometrical parameters of the NPMCs on the shielding effectiveness will also be studied in this work.

A-12.1:IL06 Enhanced Microwave Transmission at Microwave Frequencies through Omega Particles

F. BILOTTI, **L. DI PALMA**, **D. RAMACCIA**, **A. TOSCANO**, "Roma Tre" University, Rome, Italy; **D. ATES**, **E. OZBAY**, Bilkent University, Turkey

Enhanced transmission through sub-wavelength apertures is an hot topic in science. This phenomenon is typically obtained by using two different approaches: excitation of either perturbed leaky modes or localized resonances at the aperture. The former approach requires the presence of a large material cover or extended corrugations on top or around the aperture. The latter approach, instead, requires an electrically small resonator placed in close proximity of the aperture. In this talk, we present the results obtained when using single or double, connected or non-connected, omega resonators. We describe the physics behind the operation, present a quasi-static equivalent-circuit model, and, finally, show the validation of the model through proper full-wave numerical simulations and experimental results. Several examples of circuit (e.g. filters, dual-band combiners, power splitters, impedance matching devices, etc.) and radiating components (e.g. sensor antennas, horn antennas) based on the enhanced transmission obtained by using omega particles will be presented and discussed.

A-12.1:IL07 Bulk Millimeter Wave and Terahertz Metamaterial Design

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The terahertz range is gradually becoming one of the most fertile investigation fields. It is the natural limit where two important research topics such as metamaterials and plasmonics converge. Standard metals at terahertz still retain a high conductivity characteristic, so that metamaterial structures designed in the microwave/millimeter-wave range can be easily extrapolated to terahertz. Plasmonic techniques to steer surface currents at a metal dielectric interface can also be successfully applied in terahertz. Therefore, techniques from both branches can coexist at this frequency range to provide a fast development. Nowadays terahertz frequencies are finding a great deal of relevance in important applications such as security, biosensing, material engineering, and communications to cite just a few. In the presentation metamaterials and plasmonics (in particular, extraordinary transmission) will be mixed together to obtain several volumetric devices such as frequency selective surfaces with regular and anomalous extraordinary transmission, polarizers, negative refraction and bi-refracting prisms, metallodielectric lenses, quantum-cascade laser antennas and so on.

A-12.1:L08 **Surface Wave Resonances Supported on a Square Array of Square Metallic Pillars**

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Surface waves have been extensively studied throughout the majority of the electromagnetic spectrum between radio and ultraviolet on both planar metal-dielectric interfaces, structured metal dielectric interfaces and more recently at the surface of a metamaterial. At optical frequencies the unstructured metal surface supports a localised Surface Plasmon Polariton with electromagnetic fields that exponentially decay into both media. However, at microwave frequencies, similarly strong surface wave confinement can only be achieved with subwavelength structuring of the interface. These structured metamaterials are of particular interest at microwave frequencies since they provide tuneability of the bound surface wave dispersion. Here we present results for a metamaterial structure in the form of a square array of subwavelength square cross-section metal pillars on a conducting ground plane which supports a family of surface waves. The nature and dispersion of these surface waves has been explored using a novel experimental technique, involving the use of collimated surface waves, and the results obtained show excellent agreement with finite element method modelling.

A-12.1:L09 **Influence of Dielectric Loss and Permittivity Variation on Metamaterial Performance**

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As an alternative to metal-based metamaterials, magnetodielectric metamaterials have recently been developed using resonant dielectric spheres and cubes of high permittivity microwave ceramics. Conventional approaches for obtaining metamaterial properties ($\pm\epsilon$, $\pm\mu$) are based on orientation-dependent, lossy metallic structures, such as split ring resonator/wire pairs, fishnet- and omega-shaped structures. This alternative dielectric route, via Mie resonances of magnetodielectric structures, provides a mechanism for engineered electrical and magnetic response. In this presentation, experimental results will be presented demonstrating an approach for achieving an isotropic, double negative (DNG) metamaterial composite at Ku band frequencies. In particular, the influence of microwave ceramic resonator properties, including Q, permittivity variation, ceramic microstructure, and dimensional tolerances will be discussed. Microwave ceramic properties and metamaterials comprised of MgTiO₃, (Zr,Sn,Ti)O₂, SrTiO₃ and Ba(Zn,Ta)O₃ will be presented. It is observed that resonator Q tracks closely with dielectric Q, and that low Q materials may prevent useful metamaterial development.

A-12.1:L10 **Reflectionless Ultra-thin Wave-plate Based on Metamaterials**

WUJIONG SUN, **QIONG HE**, JIAMING HAO, LEI ZHOU, State Key Laboratory of Surface Physics and Key Laboratory of Micro and Nano Photonic Structures, Fudan University, Shanghai, China

It is highly desirable to efficiently control the polarization of electromagnetic(EM) waves. Conventional methods to manipulate light polarization suffers the energy loss problem or size issue (which is inconvenient especially for low frequency applications). We design an anisotropic ultrathin metamaterial, which can manipulate EM wave polarizations efficiently in transmission geometry with perfect transmittance, including polarization conversion and rotation. Our system is a laterally anisotropic ABA structure consisting of three metamaterial layers, which allow perfect transmissions of EM waves for two incident polarizations within a common frequency interval. The transparencies are governed by different mechanisms (ABA tunneling effect¹ and EOT mechanism²), resulting in significant differences in transmission phase changes for two polarizations. The proposed device is much thinner than wavelength at the working frequency. Microwave experiments performed on realistic samples are in excellent agreement with numerical simulations³.

1. L. Zhou, W. Wen, C.T. Chan, and P. Sheng, *Phys.Rev.Lett.* 94, 243905 (2005); 2. T.W. Ebbesen, H.J. Lezec, H.F. Ghaemi, T. Thio, and P.A. Wolff, *Nature* 391, 667 (1998); 3. Wujiong Sun, Qiong He, Jiaming Hao, and Lei Zhou, *Opt.Lett.* 36, 927 (2011).

A-12.1:L11 **Tuning Extraordinary Transmission by Meander-lines in Hole Arrays**

V. TORRES, **P. RODRIGUEZ-ULIBARRI**, M. BERUETE, F. FALCONE, M. SOROLLA, Millimeter and Terahertz Waves Lab., Universidad Pública de Navarra, Pamplona, Spain; M. NAVARRO-CÍA, Experimental Solid State Group, Dept. of Physics, Imperial College London, London, UK

In this work we systematically analyze the frequency tuning of the extraordinary transmission peak as we gradually increase the inductance by adding turns to a meander line connecting consecutive holes of a doubly periodic hole array. This brings about three important consequences: the aperture is more subwavelength, which opens novel possibilities for realistic metamaterials, great increment in the fractional bandwidth of the resonance and the phenomenon emerges away from the onset of higher-order modes. The structure is studied from equivalent circuit perspective that fits with a high degree of accuracy with numerical results obtained with a commercial simulator even for structures with non negligible thickness, where two sharp peaks emerge. A discussion on the origin of each lumped element of the equivalent circuit is also done for two different polarizations. Moreover, a parametric study of several design parameters of the structure is performed in order to obtain the electromagnetic features of the meander-line. These results could be useful in the design of frequency selective surfaces, spatial filters, polarizers, etc.

A-12.1:L12 **Novel Pseudo-plasmonic Surfaces in the Microwave Regime**

H.J. RANCE, A.P. HIBBINS, J.R. SAMBLES, Electromagnetic Materials Group, University of Exeter, School of Physics, Exeter, Devon, UK

We present a summary of current microwave studies being undertaken at Exeter, reviewing our work on structurally-dictated surface modes on metals. Employing a combination of experimental, and numerical and analytical techniques, we extend the concept of pseudo-plasmonic surfaces beyond the original 'spoof' plasmon studies¹. The propagation of surface waves on a range of structures will be discussed, including their excitation on ultra-thin substrates formed from printed circuit boards^{2,3} and patterned surfaces with a high degree of surface anisotropy⁴ and low surface symmetry. Furthermore, we investigate a 'zig-zag' geometry with both arrays of slits⁵ and holes, both of which mediate enhanced transmission via diffractively coupled surface waves. High-Q Fano-shaped resonances are observed in the former while the originality of the latter lies in its polarisation-selective excitation of the different surface wave bands.

1. J.B. Pendry et al, *Science* 305, 847 (2004); 2. M.J. Lockyear et al, *Phys. Rev. Lett.* 102, 073901 (2009); 3. A. P. Hibbins et al, *Phys. Rev. B*, 84, 11 (2011); 4. H.J. Rance et al, "Structurally-dictated anisotropic 'designer surface plasmons'", accepted, *Appl. Phys. Lett.* (2011); 5. H.J. Rance et al, *Appl. Phys. Lett.* 95, 4 (2009)

Session A-12.2

Photonic, Nanophotonic, Plasmonic and Infrared Metamaterials

A-12.2:IL01 **Taming the Blackbody with Infrared Metamaterials**

XIANLIANG LIU, **W.J. PADILLA**, Boston College, Newton, MA, USA

Metamaterials have been demonstrated which are able to achieve nearly 100% absorption of incident radiation, over a narrow band. By Kirchhoff's law of Radiation, we demonstrate that these absorbers may also be modified to control the emissivity spectrum of a body at a particular temperature over a bandwidth of 50%. Thus these metamaterial surfaces may be applied as coatings nearly any material to control their blackbody emission spectra. We highlight the theory, simulation and present experimental results of metamaterials controlling both absorption and emission, and present several potential applications.

A-12.2:IL02 Enhancement of Light-matter Interactions in Slow-wave Meta-surfaces

LEI ZHOU, State Key Laboratory of Surface Physics and Physics Department, Fudan University, Shanghai, China

Light-matter interactions (LMIs) have generated lots of fascinating phenomena in condensed matter physics and optics. However, such effects are typically weak in conventional materials due to short LMI time, caused by the fact that light travels too fast. Available approaches to slow down light typically require an optically thick medium. Recently, Metamaterial(MTM)-based slow-wave structures were proposed, including photonic structures with negative-refractive components or Fano-resonance-based MTMs. Still, these systems were built upon bulk slow-wave mechanisms. In addition, using such structures to enhance LMIs has not yet been explicitly demonstrated. In this talk, we show that an ultra-thin metamaterial can trap photons for a long time, with measured effective wave speed $\sim c/382$ in a $\lambda/27$ -thick microwave sample. The slow-wave effect is governed by the anomalous dispersion and surface plasmon excitations, which is more significant in thinner samples owing to stronger mode hybridizations. Light-matter interactions are remarkably enhanced inside the slow-wave structures, leading to perfect omni-directional light absorption and dramatically enhanced nonlinear generations, which are demonstrated by microwave experiments and full wave simulations.

A-12.2:IL04 Active Nanodevices: the Next Challenge for Plasmonics

G. WURTZ, A.V. ZAYATS, Department of Physics, King's College London, London, UK

Plasmonic nanomaterials show promise to revolutionize nanotechnology, in particular in the area of information technology. In particular, their potential in the design of active nanodevices with the speed of photonic devices and the nanoscale dimension of semiconductor electronics, will open a new technological era not constrained by the limitations in size and speed photonics and electronics devices currently show.¹ In this presentation we will discuss the potential of complementary plasmonic structures made of assemblies of strongly interacting nanorods² as well as plasmonic crystals³ in providing effective solutions in the development of active nanodevices.

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2. G.A. Wurtz, R. Pollard, W. Hendren, et al, *Nature Nanotechnology* 6, 107 (2011);
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A-12.2:L07 Imaging the Local Field Enhancements in Metamaterial Unit Cells with Femtosecond Laser Pulses

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The technological challenges of the future can be summarized as follows: energy, transport, nanotechnology, information/communication technology, health care, and environment. All of these can be developed from the bottom-up, by means of nanoengineering suitable metamaterials. Just as natural materials derive their properties from those of their constituent atoms and molecules, artificial metamaterials derive their properties from those of their nanoengineered unit cells. We have developed novel methods for visualizing the localized field-enhancements of metamaterials' unit cells. Based on optical second harmonic generation and ultrafast hydrodynamics of metal nanostructures, these methods combine user-friendliness and high resolution.

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A-12.2:IL09 Controlling Radiation Using Dark Plasmon Modes

N.X. FANG, KIN HUNG FUNG, A. KUMAR, JUN XU, Massachusetts Institute of Technology, Cambridge, MA, USA

In this talk we present our recent progress towards controllable stimulated light emission using plasmonic nanostructures. In particular we are interested in dark plasmon modes associated with to "forbidden" photon transition in nanoantennas and nanolasers. In our approach, a focused electron spot is used to selectively excite bright and dark modes in single metal bowtie nanoantenna with precisions better than 20nm. The measured high resolution spectrum shows unexpected high photon counts associated with signatures of the dark modes, in contrast to common wisdom that such dark modes only couple weakly to the far field. With an eigendecomposition response theory, the phenomena can be successfully explained as a result of hybridization between localized plasmons. These probes could provide brand new insight of solid state lighting with unprecedented fine spectral and spatial resolution.

A-12.2:L11 Ferromagnetism in Cr Doped Indium Oxide for Homogeneous Negative Index Materials

A. AKYURTLU, A.-G. KUSSOW, Electrical and Computer Engineering Department, University of Massachusetts Lowell, MA, USA

Thin films of optically transparent magnetic semiconductor Cr doped Indium Oxide to be used as very low-loss homogeneous negative index of refraction materials are fabricated and characterized. We have experimentally investigated the electric and magnetic properties of thin films of Cr-doped Indium Oxide, $\text{In}_{2-x}\text{Cr}_x\text{O}_{3-\delta}$. The ferromagnetic behavior of Cr-doped indium oxide critically depends on the oxygen deficiency concentration, or parameter, δ , which is supposed to be within narrow range, $1.6\text{e-}4$ to $1\text{e-}2$. These thin films are fabricated by DC-RF sputtering deposition technique. Cr-doped indium oxide thin films were deposited on p-Si(100) substrate at room temperature. Due to narrow range of required oxygen deficiency, δ , it is a challenge to fabricate viable material with ferromagnetic properties. In this work, we demonstrate how one can fabricate Cr-doped IO with desirable stable ferromagnetic properties, with magnetic saturation up to 0.6 mB/Cr .

A-12.2:L12 Strong Coupling Effects in Fabricated Tunable Layers of Metal Nanoparticles

S. MÜHLIG, C. ROCKSTUHL, F. LEDERER, Institute of Condensed Matter Theory and Solid State Optics, Abbe Center of Photonics, Friedrich-Schiller-Universität Jena, Jena, Germany; A. CUNNINGHAM, T. BÜRGEL, Département de Chimie Physique, Université de Genève, Geneva, Switzerland; D. CIALLA, K. WEBER, Institute of Physical Chemistry, Friedrich-Schiller-Universität Jena, Jena, Germany

Bottom-up metamaterials (MMs) have attracted considerable attention, since for their fabrication robust self-assembly processes can be exploited. Here, we introduce a bottom-up MM made of stacks of strongly coupled layers of randomly arranged metallic nanoparticles (NPs). NPs in individual layers are made from gold or silver and the material can vary from layer to layer. Each layer is fabricated by employing electrostatic forces between negatively charged NPs and positively charged polymers. This avoids cluster formation and is the key to achieving high density NP layers. Control over the distance of consecutive layers is achieved by separating them with a discrete number of polymer layers. The minimal distance is in the order of one nm; enabling extraordinary optical properties due to the strongly coupled plasmonic resonances. The emergence of symmetric and asymmetric eigenmodes is revealed and a huge splitting is witnessed. Fabricated samples are used for sensing devices exploiting the huge field enhancement in narrow spatial domains between consecutive layers. Direct evidence for the field enhancement is put forward by measuring surface enhanced Raman scattering signals from molecules adsorbed to the samples. All measurements are entirely supported by numerical simulations.

Session A-12.3

Nonlinear, Tunable & Active Metamaterials

A-12.3:IL01 Shaping of Light in Metamaterials and Plasmonic Structures

Y.S. KIVSHAR, Nonlinear Physics Center, Australian National University, Canberra, Australia

We review our recent theoretical and experimental results on the light shaping in plasmonic structures and nanostructured metamaterials. In particular, we discuss several effects associated with the subwavelength nanofocusing and shaping of light in plasmonic waveguides, nanofocusing of polychromatic plasmon beams, and the generation of Airy plasmons. First, we study nonlinear transverse self-action of plasmon beams propagating in tapered metal-dielectric-metal waveguides with the Kerr-type nonlinear dielectric. We demonstrate that in contrast to light focusing in straight waveguides, an appropriate choice of the taper angle allows an effective compensation of attenuation with the propagation of a spatial plasmon soliton. Next, we introduce the concept of polychromatic plasmonics and demonstrate several functionalities of the so-called broadband plasmonic lens based on a metal-dielectric-metal curved structure. We develop analytical descriptions and employ simulations to show capability of three-dimensional subwavelength manipulations and beam shaping, including nanofocusing, self-collimation, and optical pendulum effects. Finally we demonstrate the generation, shaping, and near-field mapping of the propagating Airy plasmons.

A-12.3:IL03 Making Stable Plasmon Solitons

D. SKRYABIN, A. MARINI, A. GORBACH, C. MILIAN, University of Bath, Bath, UK; B. MALOMED, University of Tel-Aviv, Israel

Using a combination of numerical and analytical techniques we demonstrate that a metal stripe (or arrays of those) surrounded by the active and passive dielectrics supports propagation of stable spatial surface-plasmon solitons and vortices. Our analysis demonstrates existence of both one- and two-dimensional structures. The latter are possible in the regime of slow plasmons with group velocities being far less than speed of light. The solitons we discuss is a substantial qualitative step beyond previously known plasmon-solitons decaying over the distances of only few tens of microns. Our analytical methods are rigorous and based on the multiple scale reduction of the Maxwell's equations and nonlinear boundary conditions to the system of coupled Ginzburg-Landau equations.

A-12.3:IL04 Magnetically Controllable Metamaterials

SHIYANG LIU, Institute of Information Optics, Zhejiang Normal University, Jinhua, Zhejiang, China; ZHIFANG LIN, Surface Physics Laboratory and Department of Physics, Fudan University, Shanghai, China; S.T. CHUI, Bartol Research Institute, University of Delaware, Newark, Delaware, USA

Metamaterials are composite materials composed of sub-wavelength building blocks designed with state-of-the-art configurations, which exhibit novel and unique electromagnetic (EM) properties. For the metamaterials including metallic constituents, the surface plasmon polaritons can also be excited. The building blocks are usually made of metallic materials, accompanied with the drawbacks of intrinsic loss, narrow working frequency, and tunability limitation. We have designed a class of metamaterials composed of building blocks made of ferrite materials, it is accordingly termed as the magnetic metamaterials (MM). In present talk, we are going to demonstrate that with the MM we can construct a magnetically tunable negative index material with the impedance matched to the air. The excitation of the magnetic surface plasmon (MSP) resonance can also be observed in the MM. Due to the MSP resonance and the time reversal symmetry breaking nature of the MM, the unidirectional waveguiding of the EM wave is demonstrated. In the honeycomb lattice consisting of the ferrite rods, the self-guiding unidirectional zigzag edge states can also be induced at the edge of the zigzag ribbon. With the further investigation, we can expect even more interesting phenomenon realized in the MM system.

A-12.3:IL05 Nonlinear Optical Properties of Plasmonics Materials

M. KAURANEN, G. GENTY, R. CZAPLICKI, H. PIETARINEN, H. HUSU, M. ZDANOWICZ, K.O. KOSKINEN, R. SIIKANEN, Department of Physics, Tampere University of Technology, Tampere, Finland; J. LEHTOLAHTI, J. LAUKKANEN, M. KUITTINEN, University of Eastern Finland, Department of Physics and Mathematics, Joensuu, Finland

The optical properties of metal nanoparticles are dominated by the plasmon resonances of conduction electrons. The resonances give rise to strong local fields, which can enhance nonlinear interactions. Defects can also support their own plasmonic modes and lead to highly local nonlinear responses. In earlier work, we have shown that local but mutually retarded nonlinear sources lead to effective quadrupole effects in second-harmonic generation (SHG) from arrays of metal nanoparticles. Here, we show that such higher-multipole effects are suppressed by significantly improved sample quality. This is a prerequisite for metamaterials with tailorable nonlinear properties. We demonstrate tailorable nonlinear properties by ordering L-shaped nanoparticles in a lattice with sub-wavelength period. By varying the mutual orientation of the particles, we modify the symmetry of the structures. We find that the tensorial SHG responses of two samples with similar orientational particle distributions vary by a factor of up to 50 depending on detailed particle ordering. The results are explained by long-range diffractive coupling between the particles. Such resonance-domain effects provide new ways to control the optical responses of metamaterials.

A-12.3:L06 Nonlinear Backward-wave Photonic Metamaterials

A.K. POPOV¹, M.I. SHALAEV²; S.A. MYSLIVETS³; V.V. SLABKO², I.S. NEFEDOV⁴, ¹University of Wisconsin-Stevens Point, Stevens Point, WI, USA; ²Siberian Federal University, Krasnoyarsk, Russian Federation; ³Institute of Physics of Russian Academy of Sciences, Krasnoyarsk, Russian Federation; ⁴Aalto University, Aalto, Finland

Novel concepts of nonlinear-optical photonic metamaterial are proposed. They concern photonic materials that provide coherent nonlinear-optical energy exchange between ordinary and backward waves as applied to three- and four-wave mixing processes. Three different classes of materials which support backward waves will be considered: plasmonic negative-index metamaterials (NIMs), metamaterials with specially engineered spatial dispersion, and crystals that support optical phonons with negative group velocity. The possibility to exploit ordinary crystals instead of plasmonic nonlinear-optical metamaterials that are very challenging to engineer is very attractive. It will be shown that extraordinary nonlinear optical frequency-conversion propagation processes attributed to NIMs can be mimicked in some of the readily available crystals, if optical phonons with negative group velocity are implemented as one of the coupled counterparts instead of backward electromagnetic wave. Comparative review of unparallel properties of coherent energy exchange between ordinary and backward electromagnetic waves in NIMs and between ordinary electromagnetic waves coupled through backward vibration waves will be given. Unique photonic devices will be proposed.

Session A-12.4

Cloaking, Transformation Optics, Antennas, Superlenses

A-12.4:IL02 Transformation Electromagnetics

M. MCCALL, Imperial College, London, UK

Transformation electromagnetics has opened up a multitude of possibilities based around the concept that coordinate transformations can be actualized in real physical space by designing a suitable inhomogeneous electromagnetic medium. The most striking example is the electromagnetic cloak via which light can be caressed around objects to prevent them being seen. Recently we extended the idea of a spatial object cloak to that of a so-called spacetime or event cloak in which light is selectively slowed down and speeded up to prevent certain events from being observed. This requires both spatial and temporal inhomogeneity of the host medium. Both of these generic

cloak types can be described using the mathematics of general relativity. However, the exact relationship between coordinate transformations and curvature has only recently been clarified. Drawing on topical examples, I will show how the connection between coordinate transformations and curvature can be used to define generic device types such as artificial black holes. Prospects for extensions of the formalism beyond electromagnetics will also be discussed.

A-12.4:LO3 **Double-negative Negative Index Metamaterial Composed of a Silver Nanowires Structure at Visible Light Spectrum**

YONGXIANG ZHAO¹, **FEI CHEN**^{1,2}, QIANG SHEN¹, LING LI¹, XIAOGUI WANG¹, ZHIXIONG HUANG², LIANMENG ZHANG^{1,2}, ¹State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, China; ²Key Laboratory of Advanced Technology for Specially Functional Materials, Ministry of Education, Wuhan University of Technology, Wuhan, China

A novel double-negative negative index metamaterial (NIM) composed of silver nanowires structure at visible light spectrum with high FOM and low loss is presented. The geometrical parameters of the proposed NIM of silver nanowires structure were optimized by differential evolution (DE) in order to decrease the transmission loss of material to the greatest degree. By using numerical simulation of a wedge-shaped model and S-parameter retrieval method, we found that the DE-designed silver nanowires structure can exhibit a low loss LH frequency band with simultaneously negative values of effective permittivity and permeability at the yellow-light wavelength of 595 nm. The figure of merit is 45.8 ($n = -0.9993 + 0.0218i$), that means the developed nanomaterial may have practical applications because of its low loss and high transmission.

A-12.4:LO4 **Trapped Rainbow Techniques for Spectroscopy on a Chip and Fluorescence Enhancement**

V.N. SMOLYANINOVA¹, I.I. SMOLYANINOV², A.V. KILDISHEV³, V.M. SHALAEV³, ¹Department of Physics Astronomy and Geosciences, Towson University, Towson, MD, USA; ²Department of Electrical and Computer Engineering, University of Maryland, College Park, MD, USA; ³Birk Nanotechnology Centre, School of Electrical and Computer Engineering, Purdue University, IN, USA

We report on the experimental demonstration of the broadband "trapped rainbow" in the visible range using arrays of adiabatically tapered optical nano waveguides. Being a distinct case of the slow light phenomenon, the trapped rainbow effect could be applied to optical signal processing, and sensing in such applications as spectroscopy on a chip, and to providing enhanced light-matter interactions. As an example of the latter applications, we have fabricated a large area array of tapered nano-waveguides, which exhibit broadband "trapped rainbow" effect. Considerable fluorescence enhancement due to slow light behavior in the array has been observed.

A-12.4:LO5 **To Invisibility and Beyond**

U. LEONHARDT, University of St. Andrews, St. Andrews, UK; **YUNGUI MA**, Zhejiang University, China

In 2010 Science listed metamaterials and transformation optics among the top ten research insights of the last decade. What is special about this research area and how might the story continue? The lecture explains what the characteristic features of transformation optics are and endeavours to make predictions for future directions of research.

A-12.4:LO6 **Dirac-cone Dispersion at $k=0$ and its Implications**

X.Q. HUANG, Y. LAI, Z.H. HANG, F.M. LIU, C.T. CHAN, Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong

We show that by employing accidental degeneracy, dielectric photonic crystals can be designed and fabricated that exhibit Dirac cone dispersion at the centre of the Brillouin zone at a finite frequency. In addition to many interesting properties intrinsic to a Dirac cone dispersion, we can use effective medium theory to relate the photonic crystal to a material with effectively zero permittivity and permeability. We then numerically and experimentally demonstrate in the microwave regime that such dielectric photonic crystals with reasonable dielectric constants can manipulate waves as if they had nearly zero permittivity and zero

permeability at and near the Dirac point frequency. The concept can be extended to acoustic and elastic wave. For the case of elastic waves, we show that Dirac cone dispersion at zone center can be related to a special kind of elastic crystal in which only longitudinal wave is allowed in one direction and only acoustic wave is allowed in some other direction. Such materials may be useful for cloaking which in many cases require certain components of permittivity and permeability to be zero.

A-12.4:LO8 **Superlensing with Arrays of Metallic Nanorods**

P. BELOV, Queen Mary University of London, UK & National Research University ITMO, St. Petersburg, Russia

Tailoring the parameters of silver nanorods array for subwavelength imaging of arbitrary coherent sources has been discussed recently in [Phys. Rev. B 82, 113408 (2010)]. In this paper we examine the performance of the proposed superlens. In particular, we evaluate the operational bandwidth of the device. The impact of source-offset is also investigated and this provides an idea about the level of tolerance offered by the superlens with regard to source location. The performance of device is analyzed numerically both through analysis of transmission and reflection coefficients and by full-wave simulation for a particular sample source arrangement. Also, we analyze capabilities and functionalities of a multi-segment superlens suggested by S. Kawata et al. [Nature Photonics 2, 438 (2008)] for long-distance transport of color images with subwavelength resolution. We study the performance of three- and six-segment nanolens structures by analyzing numerically both transmission and reflection coefficients and by employing the full-wave simulations for a particular source arrangement. We observe that such a stacked structure offers limited subwavelength imaging performance due to operation with coherent sources only within narrow frequency band, typically 3-5% wide.

A-12.4:LO9 **Near-field Mapping of (Slow) Light**

L.(K.) KUIPERS, FOM Institute for Atomic and Molecular Physics (AMOLF), Amsterdam, The Netherlands

Manipulating light at the nanoscale forms the central theme of nanophotonics. Photonic crystals can exert a huge control over light at the nanoscale. In particular, their ability to slow down light over appreciable bandwidth offers the potential to influence light-matter interactions. We have used a phase-sensitive, time-resolved, near-field microscope that is able to distinguish different components of the in-plane electric field to investigate the local properties of light in photonic crystal structures, like waveguides and cavities. We experimentally show the existence of an evanescent mode at the interface of a fast-light to a slow-light section of waveguide. The gradual increase in the width and intensity of the slow mode are fingerprints of the existence, which is confirmed by an detailed modal analysis of the measurements. Interestingly, the near-field probe used is also a metallic nanostructure. We have used its cylindrical symmetry to induce a light-matter interaction mediated by the magnetic field rather than by the electric field, which usually dominates light-matter interaction at optical frequencies. The circular current induced by the magnetic field impinging on the metallic ring in effect results in a "diamagnetic" light matter interaction which allowed the tuning of the resonance frequency of a photonic crystal nanocavity.

A-12.4:L10 **On Conformal Lenses**

HUANYANG CHEN, School of Physical Science and Technology, Soochow University, Suzhou, Jiangsu, China

In this talk, We will present a new class of gradient index lenses from multivalued optical conformal mapping. We shall call them the conformal lenses. Such lenses have several magical properties. For example, they can transform one source into many or many into one. Rather than using negative index materials, implementation here only needs isotropic positive index materials.

Session A-12.5

Acoustic and Seismic Metamaterials

A-12.5:IL01 Acoustic Magnifying Hyperlens

JENSEN LI, Department of Physics and Materials Science, City University of Hong Kong, Hong Kong

In this lecture, we review the basic concepts of using metamaterials for acoustic imaging and wave manipulation. Starting from periodically layered structures, we can easily construct metamaterials with large anisotropy which is very useful to obtain sub-wavelength resolution in acoustic imaging. By geometric scaling the layered structure in the radial direction, an acoustic hyperlens can be obtained so that the image with subwavelength details can be progressively magnified and exit the lens as far-fields. We have further developed different geometric transformations on the periodically layered structures to achieve a variety of wave manipulations including negative refraction in the effective medium regime, acoustic cloaking, and tunneling with a density-near-zero material.

A-12.5:IL02 Zero Acoustic Transmittance through Holey Structures

J.S. BELL, A.R.J. MURRAY, E. HENDRY, A.P. HIBBINS, I.R. SUMMERS, J.R. SAMBLES, University of Exeter, Exeter, UK

The acoustic transmittance of an "acoustic double fishnet", which comprises a pair of closely-spaced, periodically perforated plates, is explored. Experimental measurements are matched with analytical models that show the extraordinary acoustic properties are due to hybridization between the two-dimensional resonance supported in the gap between the plates, and pipe modes within the holes. Complete reflection of sound occurs at a frequency dictated by the periodicity of the holes. At this frequency the input impedance is purely imaginary.

A-12.5:IL03 Negative Effective Gravity in Water Waves

X.H. HU¹, C.T. CHAN², K.M. HO³, J. ZI⁴, ¹Department of Materials Science, Laboratory of Advanced Materials, and Key Laboratory of Micro and Nano Photonic Structures (Ministry of Education), Fudan University, Shanghai, China; ²Department of Physics, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China; ³Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa, USA; ⁴Department of Physics and Key Laboratory of Surface Physics, Fudan University, Shanghai, China

Based on analytic derivations and numerical simulations, we show that near a low resonant frequency water waves cannot propagate through a periodic array of resonators (bottom-mounted split tubes) as if water has a negative effective gravitational acceleration g_e and positive effective depth h_e . This gives rise to a low-frequency resonant band gap in which water waves can be strongly reflected by the resonator array. For a damping resonator array, the resonant gap can also dramatically modify the absorption efficiency of water waves. The results provide a mechanism to block water waves and should find applications in ocean wave energy extraction.

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Session A-12.6

Novel Concepts in Metamaterials

A-12.6:IL02 Generalized Framework for Designing PhoXonic ($x=n,t$) Metamaterial Networks: Defects, Edge, Surfaces and More

CHEONG YANG KOH, DSO National Laboratories, Singapore

The manipulation and control of phoXons ($x=n, t$) is both fundamentally and technologically extremely important, manifesting themselves in different areas such as in probing light-matter interactions, sound insulation, heat management and opto-mechanics. PhoXonic crystals and metamaterials (PnCM) are artificially structured materials (at certain length scales) that provide promise in controlling the propagation of phoXons. For example, the "effective" material constitutive properties now depend on the detailed spatial distributions of the eigenmodes, which are tailorable in these metamaterials. This affords exciting possibilities in tailoring interactions between specific phoXonic eigenmodes and suggests new fundamental limits in performance e.g. generalized selection rules in photon-phonon coupling. However, the vector nature of the phonon makes the development of a governing framework with which to guide the design of these PnCM complicated and no coherent framework currently exists for the design of phononic structures. By utilizing a combination of "global" and "local" governing principles, we present a design framework allowing us to exactly treat the vector nature of phonons, photons and other waves; this unifies the design of PnCM, both finite and infinite, within the same framework. In the first part of the talk, we discuss the fundamental principles, adopted from a combination of group, representation theory, conservation and broken symmetry concepts, governing the framework. In particular, we discuss the choices of physical topography for a particular desired band structure/dispersion relation, demonstrating new structures such as a polychromatic phononic metamaterial possessing multiple complete in-plane spectral gaps (totaling over 100% in normalized gap size) and a phononic metamaterial which exhibits a single complete in-plane spectral gap of 102% and a complete spectral gap of 88%. In the second part of the talk, by generalizing the concept of defect states (cavities, interfaces, edges etc) within the same symmetry framework, we discuss new methods for providing unprecedented control over the manipulation of phoXons via their propagation, spatial interactions and localization, as well as obtain new classes of defects. The generality of the framework allows extension to interactions with other waves, such as in opto-mechanical structures, as well as corrections to intrinsic material constitutive relations, by virtue of the length scales of their interactions. This provides a promising route forward to the development of integrated platforms that allow for the rational manipulation and interactions of phonons with other waves, such as photons, phonons and spin waves.

A-12.6:IL03 Metamaterials with Conformational Nonlinearity and Tunability

M. LAPINE, Nonlinear Physics Centre, Australian National University, Canberra, Australia; Dept. Photonics and Optoinformatics, NRU ITMO, St.Petersburg, Russia

We review the novel concepts for metamaterial design, which were recently developed aiming at nonlinear, tunable and reconfigurable materials. One of the approaches leads to magnetoelastic metamaterials, based on offering a mechanical degree of freedom to metamaterial structure. The nonlinearity arises from elastic displacement of the strongly interacting structural elements. This type of nonlinearity relies on the counterplay between the electromagnetic attraction and the elastic repulsion, and the induced deformation alters the electromagnetic response of the entire structure. Another approach offers self-active conformational changes and nonlinear behaviour within specially designed metamaterial elements. The self-activity results from an interplay between three realms of physics: electrodynamics, mechanics and thermodynamics. We achieve such behaviour by combining the responses of a different nature in a flexible spiral resonator. In addition, this opens a route towards nonlinear chirality. We are certain that the general concepts of magnetoelastic and self-active metamaterials provide a starting platform for the future research on microwaves, THz and optics, as well as for the development of useful applications.

A-12.6:L04 Patterned Ferrimagnetic Thin Films of Spinel Ferrites Directly Obtained by Laser Irradiation: A Way to Prepare Magnonic Crystals?

I. PASQUET, L. PRESMANES, C. BONNINGUE, **PH. TAILHADES**, Université de Toulouse, UPS, INP, Institut Carnot CIRIMAT, Toulouse cedex, France and CNRS, Institut Carnot Cirimat, Toulouse, France

Mixed copper cobalt spinel ferrites can be prepared, by radio frequency sputtering, in the form of thin films made of small crystallites having an average size close to 20 nanometers. Due to their small size, these spinel ferrite crystallites can be quite easily oxidized or sintered by heating. Both oxidation and sintering, can be done locally by a laser beam focused at their surface, for only some tens of nanoseconds. The irradiated zones display different magnetic properties than the other parts of the films. By a proper monitoring of the laser beam it is then possible to prepare periodically structured films, which could display the specific collective properties of a magnonic crystal. Such a magnonic crystal processing could be very interesting because it does not require a conventional photolithographic procedure, to built the periodic structure. Moreover, it was shown that not only micronic, but also submicronic periodic patterns, can be obtained directly with a blue laser spot.

A-12.6:IL05 Quantum Levitation

S. MASLOVSKI, Instituto de Telecomunicações, Universidade de Coimbra, Polo II, Coimbra, Portugal

The Casimir-Lifshitz forces between metal and dielectric bodies in vacuum that originate from quantum fluctuations of electromagnetic field in the space surrounding the bodies are known to be prevalently attractive. Even when metamaterials are involved, flipping the sign of the force and obtaining the so-called Casimir repulsion and stable levitation in air-filled passive metal-dielectric structures is not trivial. In this talk an overview of the current state of art will be given, followed by examples of systems in which stable quantum levitation is achievable. Practical approaches to the calculation of Casimir energy and forces in metamaterials will be also presented. A special attention will be paid to Casimir-Lifshitz interactions in arrays of metallic nanowires in which the fluctuation-induced forces are known to be extremely strong and long range.

A-12.6:IL06 Modeling of Time with Metamaterials

I. SMOLYANINOV, University of Maryland, College Park, MD, USA

Metamaterials have been already used to model various exotic optical spaces. Here we demonstrate that mapping of monochromatic extraordinary light distribution in a hyperbolic metamaterial along some spatial direction may model the flow of time. This idea is illustrated in experiments performed with plasmonic hyperbolic metamaterials. Appearance of the "statistical arrow of time" is examined in an experimental scenario which emulates a Big Bang-like event.

A-12.6:L07 Experimental Evidence of Negative Refractive Index in Homogeneous Cr-doped Indium Oxide

A.-G. KUSSOW^{1,2}, A. AKYURTLU², ¹Department of Physics, University of Connecticut Storrs, Connecticut, USA; ²Electrical and Computer Engineering Department, University of Massachusetts Lowell, MA, USA

Thin films of optically transparent magnetic semiconductor $\text{In}_{2-x}\text{Cr}_x\text{O}_3$ (Cr-doped indium oxide) are fabricated, characterized and ferromagnetic behavior was proven within the specific range of Cr-doping. The accurate measurements of the angle-dependent reflection and transmission behavior, within 20-40 wavelength range, proves, after the extraction, the low-loss refractive index with negative real component $n \approx -5.0$. This effect was theoretically predicted previously within the same infrared frequency range near the boundary of the magnon spectra, with figure of merit $\text{FOM} > \sim 5.0$. Some conclusions regarding the specific usage of the metamaterial in applications are drawn, and similar effects in transition metals, Fe and Ni, are discussed

A-12.6:L08 Use Light to Levitate

CHENG-WEI QIU, Department of Electrical and Computer Engineering, National University of Singapore, Singapore

We demonstrate how light can be manipulated to levitate particles and virtual images. In particular, We have experimentally verified optical

analogue of dynamic elevation, in which the light can be elevated vertically while preserving the optical phase. Using affine transformation and natural crystals, a reflecting sheet can effectively float above the original altitude, making any cutting on the sheet outstanding and hence more visible from the surrounding environment. It is important to note that the phase is verified to be always preserved during the light elevation. We have also observed that a light can levitate a particle and drive it as a levitating "train".

Poster Presentation

A-12:P63 Method of CRLH Antenna Impedance Measurement by Means of On-wafer Characterization Equipment

G.I. SAJIN, National Research Institute for Microtechnologies, IMT Bucharest, Microwave Laboratory, Bucharest, Romania; I.A. MOCANU, Politehnica University of Bucharest, Faculty of Electronics, Telecommunications and Informations Engineering, Bucharest, Romania

This contribution deals with the measuring of CRLH zeroth-order resonating antenna impedance using the transmission line stubs. Antenna structure is placed on the plate of the on-wafer equipment and the probe-tip is moved along the antenna feedline until the minimum S_{11} is reached. Knowing antenna geometrical dimensions, and the position of probe-tip an equivalent open-circuit matching stub are obtained. After S_{11} on-wafer measurement and using relationships derived from the transmission lines theory, real and imaginary parts of the unknown antenna impedance are computed. To illustrate this method we will use a CPW CRLH zeroth-order resonant antenna with the following geometrical dimensions of the CRLH: Interdigital capacitors: width = 8 μm ; space = 7 μm ; length = 250 μm ; number of digits = 10; Inductive stub: length = 212 μm ; width = 42 μm ; space = 10 μm . Antennas were processed on 5 $\text{k}\Omega\text{cm}$ silicon substrate ($\epsilon_{\text{r}} = 11.9$). The technology consists of a wet etching photolithographic process of 0.6 μm Au / 500 Å Cr metallization obtained by evaporation on the silicon wafer surface. The measured values for three samples of antenna structures were: Antenna #1 48.5326 - j×16.9639 Ohms; Antenna #2 48.6053 - j×16.8143 Ohms; Antenna #3 48.1786 - j×16.3707 Ohms.

FOCUSED SESSION A-13

Graphene: From Science to Technology

Oral Presentations

A-13:KL Graphene-based and Graphene-derived Materials

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Graphene-based materials are promising because of their electronic and thermal transport, mechanical properties, high specific surface area, that they can act as an atom thick layer, barrier, or membrane, among other reasons. Our micromechanical exfoliation approaches^{1,2} conceived of in 1998 yielded multilayer graphene and one paper described in detail how monolayer graphene could be obtained¹. We have 3 main areas of research pertaining to graphene: (i) Growth of large area graphene on metal substrates, characterization and physical properties, and studies of devices having graphene as a central component; (ii) Generation, study, and use of graphene-based platelets (to date, typically derived from graphite oxide) including as dispersed in liquids, and powders derived from such colloids or generated by microwave or thermal treatment of graphite oxide; (iii) Generation and study of new types of carbon derived from graphene-based precursors, such as "activated microwave expanded graphite oxide", or 'aMEGO'³. Time permitting, I will briefly present our pioneering studies that have already been published (composites, thin films, transparent conductive films, electrical energy storage, large area monolayer CVD growth on copper, graphene as a protective coating,) as well as discuss our ongoing research in other areas such as thermal transport in isotopically-labeled graphene. A recent talk given at Harvard may be of use to those audience members wanting to familiarize themselves with research from my group; it also provides a (brief) history of the experimental discovery of graphene: http://bucky-central.me.utexas.edu/RuoffsPDFs/Ruoff_Master_2011

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Session A-13.1

Graphene Production, Processing and Chemistry

A-13.1:IL02 Assembly of Graphene-Based Two-dimensional Nanosheets

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Two-dimensional (2D) nanomaterials, which possess nanoscale dimension only in thickness and infinite length in the plane, have attracted tremendous attention owing to their unique properties and potential applications in the fields of electronics, sensors as well as energy storage

and conversion. Recent investigations of graphene, a 2D "aromatic" monolayer of carbon atoms, have demonstrated exceptional physical properties including ultrahigh electron mobility and ballistic charge carrier transport. These have triggered wide interest in 2D nanosheets other than carbons. Here we present a bottom-up assembly approach to the fabrication of 2D nanosheets based on chemically derived graphene. The graphene sheets can be assembled on the surface to make conductive graphene films which can serve as transparent electrodes in a number of organic electronic devices. Other 2D nanosheets based on graphene will be produced to possess the features including a large aspect ratio, mesoporous structure, high surface area and high monodispersity. As the consequence, these 2D nanomaterials may hold great potential in the areas of catalysis, sensors, supercapacitors and batteries.

A-13.1:IL03 Preparation of Graphene and Its Electronic Properties YUNQI LIU, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China

Graphene is currently the most promising potential successor to silicon for use in next-generation electronic devices due to its fascinating physical properties. In this presentation, I will report the preparation of graphene by chemical vapor deposition and its applications in electronic devices.

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A-13.1:IL04 Epitaxial Graphene Grown by High-temperature Sublimation on 3C-SiC

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In this work we explore the properties of epitaxial graphene (EG) grown by high temperature sublimation on the Si face of 3C SiC(111) in relation to the substrate surface status and defects. We used spectroscopic ellipsometry mapping from 0.73 eV to 6 eV on a 0.2 cm² area in order to probe the uniformity of the graphene thickness and properties. Our results revealed that homogeneous large scale 1 to 2 monolayer (ML) graphene can be grown on polished 3C-SiC substrate. The polished surface also enabled elimination of the puckers and reduction of strain in the EG. We also observed few areas where the carbon bunched up on the surface of the substrate and formed islands of multilayer graphene. In these areas the energy of the main van Hove singularity transition at ~ 4.5 eV increased as compared to 1ML graphene. The maps further revealed that low scattering times of the free carriers corresponds to the thick carbon bunches. The reduction of scattering time indicates lower carrier mobility across the graphite-like islands, while the large area of 1 to 2 ML graphene show high mobilities and good graphene-like band energy. We also find correlation between the number of graphene ML and the buffer layer coverage and surface roughness, which may be associated with substrate defects.

A-13.1:IL06 Exploring the Synthesis and Applications of Graphene

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Graphene is the ultimate two-dimensional material consisting of a single layer of sp² hybridized carbon. Here we explore different approaches to synthesize this carbon allotrope, ranging from chemical conversion to vapor phase deposition. Briefly, graphite can be converted into graphene

oxide (GO) sheets, which readily disperse in water, and then can be reduced by various methods.^{1,3} Due to its unique ability to be solution processed and patterned, GO and chemically converted graphene (CCG) hold promise for applications ranging from distributed ignition to transparent conducting electrodes for flexible solar cells, touch screens, etc.^{4,8} Chemical vapor deposition of graphene onto metal substrates enables the growth of continuous, large-area graphene.⁹ The challenges of growing graphene, controlling the number of layers, transferring graphene and some exciting new uses such as flash memory will be discussed.¹⁰ Characterization includes optical microscopy, AFM, SEM, TEM, STM and Raman spectroscopy.

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A-13.1:L07 Graphene Growth on Non-metallic Substrates: Approaches and Perspectives

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The deposition of graphene from the gas phase by CVD is of great interest to develop large scale coatings for electronic applications. So far the CVD routes mainly utilize growth from hydrocarbons on transition metal substrates which reveal a more or less pronounced carbon affinity and solubility as well as a catalytic activity for dehydrogenation reactions. In contrast to these substrates, inorganic glasses and glass like materials are ideal supports for graphene based transparent electrodes, but do reveal a different chemical affinity to carbon films. Therefore CVD approaches towards such coatings have to deal with a different growth chemistry, which will be discussed in this presentation. Also the preparation of other 2D materials will be presented. The controlled growth of graphene based films from selective precursors on nonmetallic substrates, especially on the structural analogue boronitrene films (monolayers of hexagonal boron nitride, BN) resemble an ideal model system for such studies.

A-13.1:L08 Systematic Comparative Study of Thermally and Extreme-UV Reduced Graphene Oxide

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In this work we present a systematic study on graphene oxide (GO) reduced by thermal annealing at different temperatures in ultra-high vacuum (UHV). Standard Optical Microscopy, X-ray Photoemission Spectroscopy (XPS), and micro-Raman Spectroscopy (uRS) have been used to characterize the samples. All the experimental information have been merged using the annealing temperature as a unifying parameter in order to provide an overall view of the mechanisms involved in the GO reduction. The cross-correlation of the collected data allows the use of the optical contrast as an easy-to-use tool to access a more complete information (chemical, electronic and vibrational properties). Furthermore we propose a photolithographic approach operating on large area (100's μm^2) graphene oxide (GO) films via space-resolved photoreduction with 46.9 nm coherent light produced by a table top capillary discharge plasma source. XPS data show that a dose of 200 mJ/cm² UV light significantly reduces pristine GO, with a good spatial modulation investigated by uRS.

A-13.1:L10 Study of Na Intercalation of Ex-situ Grown Graphene on 6H-SiC(0001) by SPELEEM

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Numerous investigations have been done on graphene owing to its peculiar electronic and transport properties. Epitaxially grown graphene on SiC(0001) is considered as one of the most promising methods for fabrication of graphene based electronic-devices. The properties of graphene can be modified by adsorbing, intercalating, atoms/molecules on, or in between, the graphene and the substrate. The interaction of Na with graphene was recently studied using STM and conventional LEED and XPS. Intercalation of Na was proven but no information

about the surface morphology or of local changes in the chemical composition after Na deposition was provided. Therefore, we performed a detailed study of the interaction between Na and graphene using LEEM, μ -LEED, μ -PES and XPEEM. This allowed us to extract information about the surface morphology and changes in the local atomic structure and chemical composition after Na deposition and also after heat treatment at different temperatures. A furnace grown graphene sample prepared on SiC(0001) with mainly monolayer graphene coverage and islands of 2 ML was used. The intercalation of Na could be investigated in detail on the 1ML and 2 ML graphene areas and was found to begin from the domain boundaries. These findings will be presented and discussed.

Session A-13.2

Electronic and Optical Properties

A-13.2:IL01 Electronic Structure of Nanographene; Edge State and Electron Wave Interference

T. ENOKI, Tokyo Institute of Technology, Tokyo, Japan

Graphene edges affect seriously the electronic structure depending on edge chirality. We investigated the edge-inherent electronic features by STM/STS, AFM observations and Raman spectra. STM/STS observations demonstrate the presence of edge states in zigzag edges. In the vicinity of an armchair edge, an STM hexagonal pattern was observed together with a 3-fold symmetry fine structure at the individual superlattice spots. This is understood as a consequence of the intervalley scattering with interference taking place at an armchair edge. The 3-fold symmetry fine structure suggests the antibonding coupling between the adjacent spots in the hexagonal superlattice. The intervalley scattering at an armchair edge gives specific dependence of the Raman G-band intensity on the polarization direction of the incident beam as expressed by $\cos^2(\theta)$. A graphene nanoribbon of 8 nm $> 1 \mu\text{m}$ prepared by heat-treatment of graphite step edges shows this angular dependence, being demonstrated to consist of pure armchair edges. Single sheet graphene oxide is found to form a 2D arrangement of linear corrugations of oxidized lines running along the zigzag direction with an interline spacing of ca. 10 nm. This suggests that zigzag edged graphene nanoribbons with a width of ca. 5 nm are created.

A-13.2:IL02 Molecular Functionalization for Engineering Transport Properties of Graphene

REN-JYE SHIUE¹, HUNG-CHIEH CHENG², SHAO-YU CHEN¹, PO-HSUN HO², CHUN-WEI CHEN², YIT-TSONG CHEN^{1, 2}, WEI-HUA WANG¹, ¹Academia Sinica, Taiwan; ²National Taiwan University, Taiwan

Among all two-dimensional electronic systems, graphene exhibits a unique characteristic that all of its material - carbon atoms - is on its surface. Although it usually means more complexity in practical circumstances, the all-surface property actually provides a rare opportunity to exquisitely engineer electronic transport in graphene by molecular functionalization. First, I will discuss the realization of high-quality graphene p-n junctions by non-covalent chemical functionalization. A generic scheme for the graphene p-n junction fabrication is established by combining the resist-free approach and spatially-selective chemical modification process. The modification is confirmed by surface potential and spatially-resolved Raman imaging. The transport measurements show high quality of graphene p-n junctions with observations of Fermi energy difference and distinct quantum Hall effect. Second, we demonstrate a facile method to achieve high mobility graphene on organic self-assembled monolayer (SAM). Ultrasmooth topography and hydrophobic surface property of the organic SAM are confirmed by surface characterizations. We show high carrier mobility of graphene on organic SAM, which can be attributed to low residual doping, small charge inhomogeneity, and the smoothness of graphene.

A-13.2:IL03 Electronic Structure Calculations of Self-assembled Monolayers on Graphene and Graphene Nanoribbons

D. BELJONNE, S. OSELLA, LIPING CHEN, University of Mons, Mons, Belgium

To take full advantage of the remarkable electronic properties of graphene in semi-conductor applications, different strategies have been applied that aim at opening a suitable bandgap. Among these, chemical doping of graphene can be achieved by decorating the graphene layers with strong electron-withdrawing molecules. We will discuss the results of Density Functional Calculations (DFT) showing hybridization of the frontier molecular orbitals and partial charge transfer between graphene and the molecular acceptors in the hybrids, as a function of the nature of the adlayer and coverage density. Another approach is based on the design of graphene nanoribbons (GNRs) with suitable widths and edge structure. DFT and TDDFT calculations have been performed to assess the electronic structure and optical properties of armchair and zigzag GNRs. These calculations allow the design of GNRs featuring both one-electron energy diagram and light absorption properties compatible with their use as donors in organic solar cells.

A-13.2:IL04 Chemical Potential Jumps, Bistability, and Electron-plasmon Interactions in Bernal-stacked Bilayer Graphene

M. POLINI, NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, Pisa, Italy

In this talk I will review a series of intriguing many-body effects that occur in doped (Bernal-stacked) graphene bilayers including i) chemical potential jumps in heavily-doped samples, which are technologically relevant for the realization of bistable devices, and ii) satellite "plasmarons" bands, which can be detected by angle-resolved photoemission spectroscopy and/or scanning tunneling spectroscopy. If time allows, I will also discuss current-carrying broken symmetry states associated with Pomeranchuk instabilities that might occur in biased bilayer graphene.

A-13.2:IL05 Band Gap Opening by B and N Co-doping in Graphene

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Performance of electronic and photonic devices based on graphene is limited because of its gapless semi-metal nature. To create a band gap, several theoretical studies showed the possibility via doping of B and N atoms into graphene. Here, we report the synthesis and characterizations of large-scale B and N co-doped graphene (BN-G) films grown by low-pressure chemical vapor deposition method. Doping of B and N into graphene lattice has been achieved via in-situ doping during growth. By varying the heating temperature of BN precursor, the doping concentration could be tuned from 3 to 50 atomic percent. As-grown samples were mainly 1-2 layers, and exhibited well-distributed B-N dopants in graphene lattice for BN-G with ~3 at.% BN (low-BN-G), whereas segregation of h-BN domains occurred for BN-G with high BN content (>20 at.% BN). Optical band gap measurement suggests more than one adsorption edge at 2.2 and 3 eV in low-BN-G, and the field-effect characterization supports the band gap opening in BN-graphene.

A-13.2:IL06 Inhomogeneous Electronic Structure and Transport Gap in Disordered Bilayer Graphene

E. ROSSI, Department of Physics, College of William and Mary, Williamsburg, VA, USA

Bilayer graphene is an extremely interesting material from both a fundamental and a technological point of view. This is due to the strictly two-dimensional nature of its charge carriers, its high room-temperature mobility, and the fact that a band-gap can be opened in its band structure via an external electric field. In this talk I will present a transport theory for disordered gapped bilayer graphene. I will show that in graphene and bilayer graphene the disorder can induce strong carrier density inhomogeneities and how these inhomogeneities affect the transport properties of these systems. I will show that in gapped bilayer graphene an increase of the disorder, by increasing the density fluctuations, can drive the system from being an insulator to being a metal. This is the opposite of what happens in conventional two-dimensional electron gases in which an increase of the disorder makes the system more insulating, not less. In recent experiments the activated transport-gap of bilayer graphene has been found to be orders of magnitude smaller than its band-gap. Our results offer an explanation for the large discrepancy between the transport-gap and the band-gap in bilayer graphene providing a compelling resolution to this outstanding puzzle in the physics of graphene.

A-13.2:L07 On the Possibility of Ultra-low Power Switching in Multilayer Graphene Nanostructures

B. DELLABETTA, Micro and Nanotechnology Laboratory, University of Illinois, Urbana, IL, USA; **J. SHUMWAY**, Dept. of Physics, Arizona State University, Tempe, AZ, USA; **M.J. GILBERT**, Dept. of Electrical and Computer Engineering, University of Illinois, Urbana, IL, USA

A particularly attractive way to solve the power consumption problem in next generation logic devices is by harnessing collective motion of electrons. While collective phenomena are normally found at low temperatures, recent work suggests it possible to find spontaneous coherence at and above room temperature in closely spaced monolayers of graphene separated by a thin tunnel dielectric. This occurs when electrons in the top layer bind with vacancies in the bottom layer via a strong Coulomb interaction to form "indirect excitons", which in turn organize into a Bose-Einstein condensate. This type of behavior may be viewed as spontaneous interlayer coherence or a selection of a particular superposition of states in the two layers for the entire system. Despite the potential applications, the superfluid phase of multilayer graphene remains a controversial and poorly understood quantity. In this contribution, we theoretically examine the materials properties, length scales and transport conditions required to realize and manipulate this state at room temperature. Additionally, we present results of static and dynamic quantum Monte Carlo calculations detailing the ability of the exciton condensate to screen the additional fermion flavors found in graphene.

A-13.2:IL08 Raman Spectroscopy of Pristine, Defected and Strained Graphene

C. CASIRAGHI, School of Chemistry and Photon Science Institute, University of Manchester, UK, & Physics Dept., Free University Berlin, Germany

Raman spectroscopy is the most common and informative characterization technique in graphene science and technology. I will discuss the use of Raman spectroscopy to determine the number of layers, doping, strain, defects, functional groups, quality and type of edges¹⁻⁵. In particular, I will show a detailed analysis of the Raman intensities of graphene and their dependence on doping, type of substrate, amount of defects and excitation energy⁶⁻⁸. I will then focus on the effect of biaxial (e.g. isotropic) strain on the Raman spectrum of graphene by using graphene bubbles and balloons⁹. In particular, bi-layer balloons have been used to avoid the effect of the substrate and to study the dependence of the inter-layer interactions on the strain. Finally, I will show the possible use of a graphene bubble as optical element to make an adaptive-focus lens¹⁰.

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A-13.2:IL09 Resonance Raman Scattering in Graphene

M.A. PIMENTA, A. RIGHI, S.D. COSTA, D.L. MAFRA, A.O. COIMBRA, L.M. MALARD, C. FANTINI, L.G. MOURA, E.A. MOUJAES, H. CHACHAM, R.W. NUNES, Departamento de Física, Universidade Federal de Minas Gerais, Belo Horizonte, Brazil

Raman spectroscopy is a very useful tool to study graphene, since it furnishes information about the atomic structure, presence of disorder, number of layers, defects, charges and strain. However, important information about electrons can be also obtained in a resonance Raman investigation, where the energy of the laser excitation can be tuned. We will present experimental results of the dispersion of electrons and phonons in graphene devices, where an applied electric field and changes in the Fermi level can be controlled by an external gate voltage, showing that Raman spectroscopy is useful to quantify the interaction of graphene with its surrounding environment. We will also show that Raman spectroscopy can be useful to characterize Moiré patterns graphene layers, due to the unklapp double resonance (U-DR) Raman process. Finally, we will present results of the electronic dispersion in uniaxial strained bilayer graphene.

A-13.2:IL10 Tailoring the Electronic Properties of Epitaxial Graphene on Metallic Substrates

M. PAPAGNO, C. CARBONE, Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Trieste, Italy

The low energy excitations in graphene behave as massless Dirac fermions and obey the relativistic Dirac equation where the speed of light is replaced by the Fermi velocity. New electronic properties result from epitaxial growth of graphene on metallic surfaces, due to electron hybridization and structural modifications. Selected studies making use of synchrotron radiation-based spectroscopic techniques will illustrate aspects of the electronic interactions of graphene with metal substrates of diverse electronic and crystal structure. We will show how the electron group velocity, chirality, and bandgaps can be tailored by periodic perturbing potential, doping, intercalation, and hybridization with the supporting substrate. Moreover, we will illustrate how the structural and electronic properties of epitaxial graphene are modified by the interaction with magnetic layers and self-assembled magnetic clusters. Finally, the implications of these results and their potential applications for graphene based devices will be discussed.

Session A-13.3

Electronic, Spintronic, Optical and Sensing Applications

A-13.3:IL02 Graphene-based Transistors with Tunable Band Gap **D. NEUMAIER**, AMO GmbH, Aachen, Germany

The emergence of graphene with its unique electrical properties has triggered hopes in the electronic devices community to utilize it as a channel material in field effect transistors. It is especially promising for devices working at frequencies in the 100 GHz range. So far, graphene field effect transistors (GFETs) have shown cut-off frequencies of up to 300 GHz. However, the low on/off ratio and the poor voltage gain are limiting factors utilizing graphene transistors in analog and digital applications. Here an already small band would already help especially for analog high frequency applications. In this talk I will discuss opportunities to introduce a band gap to graphene by using bilayer graphene with a perpendicular applied electric field. Transistors based on bilayer graphene having a rather small band gap of order 100 meV show significantly improved switching behavior and voltage gain compared to monolayer graphene transistors and are therefore ideal suited for analog high frequency electronics. The intrinsic transconductance, defining the cut-off frequency of bilayer graphene transistors is not reduced by the introduction of a band gap.

A-13.3:IL03 Graphene Field Effect Transistors for Bioelectronics **J.A. GARRIDO**, Walter Schottky Institut, Technische Universität München, Garching, Germany

For medical applications in neuroprostheses as well as for fundamental research on neuron communication, it is of utmost importance to develop a new generation of electronic devices which can effectively detect the electrical activity of nerve cells. Due its maturity, most of the work with field effect transistors (FETs) has been done based on Si. However, the high electronic noise and poor stability associated to Si technology have motivated the search for more suitable materials. In this respect, the outstanding electronic and electrochemical performance of graphene holds great promise for bioelectronic applications. Here, we report on arrays of CVD-grown graphene FETs (G-FETs) for cell interfacing. The high carrier mobility in graphene together with the large interfacial capacitance at the graphene/electrolyte interface leads to very high device sensitivities. Furthermore, G-FETs exhibit very low electronic noise with an RMS value that is equivalent to gate signals of less than 8 μ V. Further, the biocompatibility of graphene will be also demonstrated, by showing the healthy growth of several cell cultures on graphene layers. Finally, we will demonstrate the ability of graphene FETs to transduce with high resolution the electrical activity of individual electrogenic cells.

A-13.3:L04 Two Dimensional Graphene/h-BCN Based Devices with Large Ion/Ioff Ratio for Digital Applications

G. FIORI, S. BRUZZONE, G. IANNACCONE, Dipartimento Ingegneria dell'Informazione, University of Pisa, Pisa, Italy

Despite graphene has revealed to be a material with outstanding electrical properties, such peculiarities are hard to be exploited in electronic applications, due to the lack of a band-gap, which prevents to completely switch-off the channel as desired in digital electronics. The scenario would drastically change, if we could find a way to block one of the main stream of the particles, either electrons or holes. Here we propose a new device concept, based on two-dimensional graphene intercalated with h-BCN (hexagonal boron carbon nitrogen), able to suppress the ambipolar behavior and to block one of the type carrier, as well as to fully modulate the current due to the carriers of the other type. The followed approach is based on a multiscale method coupling density functional calculations (DFT) with the Non-equilibrium Green's functions (NEGF) formalism and the 3D Poisson equation. Both two dimensional graphene/h-BCN based devices with in-plane transport, as well as vertical transport through graphene/h-BCN/graphene multilayers will be investigated, in order to assess performance and limits against industry requirements. We will show that the proposed devices manages to comply with technological requirements for next generation transistors.

A-13.3:IL06 Graphene Nanostructures for Building Blocks of Quantum-dot Based Nanodevices

S. MORIYAMA, International Center for Materials Nanoarchitectonics, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, Japan; Y. MORITA, Faculty of Engineering, Gunma University, Kiryu, Gunma, Japan; K. ISHIBASHI, Advanced Device Laboratory, RIKEN, Saitama, Japan; E. WATANABE, D. TSUYA, Nanotechnology Innovation Center, NIMS, Tsukuba, Ibaraki, Japan

Graphene, single atomic-layer of graphite, is one of the attractive two-dimensional conducting materials for building blocks of novel quantum electronics. The corresponding energy dispersion adopts the so-called Dirac cone, which leads to a rich physics inherited from quantum electrodynamics. In terms of applications, 2-dimensional sheet structure and its properties of ballistic transport and high mobility make it a candidate for future quantum devices and even integrated quantum nanodevice systems. Here, we present several methods for fabricating graphene-based quantum dot devices and report an experimental demonstration of their electrical transport properties. Graphene sheets can be carved out to form nanostructures such as quantum wires and quantum dots. The performance of such nanodevices depends on the chemical nature of sample edges, the detail of constrictions, and so on. We fabricated novel graphene nanostructures, and the electrical transport measurements through our single-dot graphene nanostructures indicated single-electron-transistor characteristics at low temperatures in a magnetic field. At the Conference, we will report the details of the fabrication and transport characteristics of the graphene-based nanostructures.

A-13.3:IL07 Graphene Quantum Systems

S. DRÖSCHER, A. JACOBSEN, D. BISCHOF, T. IHN, **K. ENSSLIN**, ETH Zurich, Switzerland

Graphene quantum structures are prepared by electron beam lithography and subsequent dry etching. This way high-quality quantum dots, rings and constrictions have been fabricated. In this talk we study the electronic properties of graphene constrictions and the details of their local potential landscape. Using three-terminal quantum dots the tunnel coupling of graphene to their environment is investigated and the importance of the dot's wave function with respect to resonance in the leads is analyzed.

A-13.3:L09 In-situ CCVD Grown Graphene Transistors with Ultra-high On/Off-Current Ratio in Silicon CMOS Compatible Processing

P.J. WESSELY, F. WESSELY, E. BIRINCI, U. SCHWALKE, Technische Universität Darmstadt, Darmstadt, Germany; B. RIEDINGER, Fraunhofer-Institut für Werkstoffmechanik, Freiburg, Germany

We invented a novel method to fabricate graphene transistors on oxidized silicon wafers without the need to transfer graphene layers. By means of catalytic chemical vapor deposition (CCVD) the in-situ grown monolayer graphene field-effect transistors (MoLGFEs) and bilayer

graphene transistors (BiLGFETs) are realized directly on oxidized silicon substrate, whereby the number of stacked graphene layers is determined by the selected CCVD process parameters. In-situ grown MoLGFETs exhibit the expected Dirac point together with the typical low on/off-current ratios between 16 (hole conduction) and 8 (electron conduction), respectively. In contrast, our BiLGFETs possess unipolar p-type device characteristics with an extremely high on/off-current ratio up to 10^7 exceeding previously reported values by several orders of magnitude. We explain the improved device characteristics by a combination of effects, in particular graphene-substrate interactions, hydrogen doping and Schottky-barrier effects at the source/drain contacts as well. Besides the excellent device characteristics, the complete CCVD fabrication process is silicon CMOS compatible. This will allow the usage of BiLGFETs for digital applications in a hybrid silicon CMOS environment.

A-13.3:IL10 Graphene-based Molecular Spintronics

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We present viable molecular paths to fabricate novel spintronic nano-architectures. As a first step, we explored different strategies to efficiently graft molecular nanomagnets on carbon surfaces¹. We also employed TbPc2 molecules appositely functionalized with pyrene groups that selectively graft to graphene on SiO₂². Secondly, we characterized the low temperature magnetoconductance of pristine graphene devices. Interestingly we found that below 1 K a magnetic hysteresis appears from structural defects when the field is swept at high enough rates ($\text{dB/dt} > 10 \text{ mT}$)³. Finally, we present the design and the realization of hybrid devices made by graphene nano-constrictions with sizes down to 10nm decorated with TbPc2 magnetic molecules. The magnetization reversal of the molecules in proximity with graphene is detected by the magnetoconductivity of these hybrid devices, which shows the uniaxial magnetic anisotropy typical of the TbPc2 SMMs. These results depict the behaviour of multiple-field-effect nano-transistors with sensitivity at the single-molecule level⁴.

1. *Adv. Funct. Mat.* 20, (2010), 1552; 2. *ACS Nano* 4, (2010), 7531; 3. *Physical Review B* 83, (2011), 121401; 4. *Nano Letters* 11 (2011) 2634.

A-13.3:IL11 Efficient Spintronics with Graphene

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Spintronics is a paradigm focusing on spin as the information vector, ranging from quantum information to zero-power non-volatile magnetism. Several spintronics devices (logic gates, spin FET, etc) are based on spin transport in a lateral channel between spin polarized contacts. We will discuss the potential of graphene for such types of devices. We will present magneto-transport experiments on epitaxial graphene multilayers on SiC. The spin signals are in the $\text{M}\Omega$ range in terms of $\Delta R = \Delta V/I$, well above the spin resistance of the graphene channel. The analysis in the frame of drift/diffusion equations leads to spin diffusion length in graphene in the 100 μm range for a series of samples having different lengths and different tunnel resistances. The high spin transport efficiency of graphene can also be acknowledged up to 75% in our devices. The unique combination of long spin life times and large electron velocity of graphene (compared to classical semiconductors and metals) results in long spin diffusion length. It appears as a material of choice for large scale logic circuits and the transport/processing of spin information. Understanding the mechanism of spin relaxation, improving the spin diffusion length and also testing concepts of spin gate are the next challenges.

A-13.3:IL12 Novel Graphene Based Materials in Optics, Optoelectronics and Photovoltaics

CHUN-WEI CHEN, Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan

In this talk, I would like to present the implementation of graphene-based materials in optical, optoelectronic and photovoltaic applications. Graphene oxide (GO) is an atomically thin sheet of graphene and

covalently decorated with oxygen-containing functional groups. GO contains a mixture of sp² and sp³ hybridized carbon atoms. Recently, we are able to vary the sp²/sp³ ratio of GO through reduction by photo or chemical ways. By controlling reduction state of GO, the PL emission of GO can be tuned from blue to red color with a wide spectrum.^{1, 2} In addition, we would also like to demonstrate that chemically derived graphene-oxide (GO) from solution processes or epitaxial graphene obtained from chemical vapor deposition (CVD) to replace the ITO electrode. GO could be also a simple solution processable alternative to PEDOT:PSS as the effective hole transport and electron blocking layer in polymer photovoltaics,³ suggesting that future polymer solar-cell devices could be "all-carbon" by roll-to-roll or solution processes for large area.^{4, 5}

1. *Blue photoluminescence from chemically derived graphene oxide*, *Advanced Materials*, Vol. 22, 505, (2010); 2. *Tunable photoluminescence of graphene oxide*, (submitted); 3. *Solution processable graphene oxide as an efficient hole transport layer in polymer solar cells* *ACS Nano*, Vol. 4, 3169, (2010); 4. *Solution processable nanocarbon platform for polymer solar cells*, *Energy and Environmental Science*, 4.3521. (2011); 5. *Top laminated graphene electrode in a semitransparent polymer solar by simultaneous thermal annealing/releasing method*, *ACS Nano*, 8, 6564, (2011).

A-13.3:L13 Dielectric-tuned Diamondlike Carbon Materials for a Ultrahigh-speed Self-aligned Graphene Channel Field Effect Transistor

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The authors present diamondlike carbon (DLC) films prepared "directly" onto graphene using our original photoemission plasma-enhanced chemical vapor deposition (PA-CVD). We have succeeded to prepare DLC films having different dielectric constants in a large extent from 1 (low-k) to 7 (high-k) by tuning composition ratio, pressure and temperature of the reaction gases. A graphene-channel field effect transistor (GFET) is a promising electronic device because graphene exhibits outstanding carrier transport property. However, the ungated region between the gate electrode and the source/drain electrodes in which the carrier density cannot be controlled by gate modulation has a high resistance because of low intrinsic carrier density of graphene. Thus a GFET having a self-aligned structure which minimizes the ungated regions is desired. Herein using PA-CVD we present a self-aligned graphene-channel field effect transistor (SA-GFET) with a high-k DLC film as a top-gate dielectric and a low-k DLC film as a side-wall to isolate electrodes and to passivate the device. "One carbonaceous material" can realize a SA-GFET suitable for ultrahigh-speed and ultrahigh-frequency applications having a high gate capacitance (a high transconductance) and a low parasitic capacitance.

Session A-13.4

Energy Applications

A-13.4:IL01 Graphene Layers for Hydrogen Storage

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Graphene epitaxially grown on the silicon face of silicon carbide resides on top of a carbon layer, known as zerolayer graphene whose structural properties are controversially debated. In the first part of the talk I shall discuss scanning tunnelling microscopy (STM) studies of the zerolayer and of the zerolayer decoupled from the substrate by hydrogen intercalation, known as quasi-free standing monolayer graphene. Atomically-resolved STM images of the zerolayer reveal that, within the periodic structural corrugation of this interfacial layer, the arrangement of the atoms is topologically identical to that of graphene. In the second part of the talk I will argue that such graphene layers can be used to develop an hydrogen storage device in which storage and release of hydrogen is obtained by exploiting and controlling the corrugation of individual layers of graphene. I'll present simulations of hydrogen chemisorption on corrugated graphene and release under the application of time-dependent mechanical deformations. The

corrugated graphene device can reversibly store and release hydrogen by external control of the local curvature at room conditions and with fast kinetics.

In collaboration with: S. Goler, C. Coletti, V. Tozzini, K. V. Emtsev, U. Starke, S. Heun, F. Beltram

A-13.4:IL02 **Fabrication of Graphene-based Flexible Energy Storage Devices**

FENG LI, WENCAI REN, **HUI-MING CHENG**, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China

Graphene and its composite materials are expected to be used in high-performance energy storage devices. At the same time, the increasing demand for flexible energy storage devices has arisen due to their applications for wearable and portable electronic products, typically roll-up displays, electronic papers, and flexible systems for personal multimedia. Therefore, graphene-based materials (graphene/oxide, graphene/polymer, etc) can be developed for flexible energy storage devices such as lithium ion batteries (LIBs) and electrochemical capacitors (ECs). Synergetic effects between graphene sheets and metal oxides or conductive polymers are found to improve the capacity or capacitance, rate capability, cyclic performance, and flexibility of these energy storage devices. It is demonstrated that, compared to the individual constituents, graphene-based composites as electrode materials for LIBs and ECs have a common and great improvement in their electrochemical properties. In particular, because of the good flexibility of graphene, it can be used to fabricate graphene-based membranes which can be used as free-standing and binder-free electrodes for flexible energy storage devices.

A-13.4:L03 **Enhanced Infrared Light Harvesting of PbS Quantum Dot Photovoltaic and Photodetector on Graphene Electrode**

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We fabricated PbS colloidal quantum dot (QD)-based photovoltaic and photodetector using a transparent graphene as electrode. The high infrared transparency of graphene electrode with respect to indium tin oxide (ITO), so the infrared photoresponse of the graphene-based device is superior to the ITO-based counterpart, in spite of a higher sheet resistance of the graphene electrode. The devices were illuminated at wavelength of 1500 nm (0.368 mW/cm²), the graphene-based PbS solar cell exhibits a PCE of 1.17%, which is higher than the 0.55% of the ITO-based solar cell. The outstanding infrared characteristics of the devices based on the graphene electrode make it a promising candidate for infrared optoelectronic applications such as solar cells, imaging and sensing, or optical communication.

Session A-13.5

Graphene Composites

A-13.5:IL01 **The Potential of Graphene Composites: Interfacial Stress Transfer in an Ideal System**

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Graphene is one of the stiffest and strongest known materials making it an ideal reinforcement in high-performance composites. We have prepared model composites consisting of single graphene flakes (monolayer and thicker) sandwiched between polymer films and employed Raman spectroscopy to monitor stress transfer from the polymer matrix to the graphene during deformation^{1,2}. The rate of peak shift of the G' peak with applied strain is proportional to the effective modulus of the reinforcement and the shift of 60 cm⁻¹/‰ obtained for monolayer graphene corresponds to a modulus of 1 TPa. The polymer-graphene interface was found to fail at high strains but would heal upon

relaxation. Mapping the G' peak shift across the flake showed that the strain in a flake could be modelled using continuum shear-lag theory. The critical length of the graphene required to obtain efficient reinforcement was found to be 30 microns, implying that in order for graphene to be used in structural composite, the graphene flakes either need to be large (>30 microns long) or chemically functionalised to improve the interfacial strength with the matrix.

1. L. Gong *et al*, *Advanced Materials*, DOI: 10.1002/adma.200904264;
2. R.J. Young *et al*, *ACS Nano*, DOI: 10.1021/nn2002079.

A-13.5:L02 **Shape Memory Polyurethane with Graphene-iron Hybrid Nanoparticles for Helical Stents**

JUNG-HWAN JUNG, IL-KWON OH, School of Mechanical, Aerospace and Systems Engineering, KAIST, Daejeon, Republic of Korea

A helical stent capable of controlling the diameter was developed with shape memory polyurethane reinforced with graphene-iron nanoparticles. The graphene nanoflakes decorated with ferromagnetic nanoparticles were synthesized with a foaming agent method integrated with microwave radiation. The ferromagnetic shape memory polymer films were made with the incorporation of graphene-iron nanoparticles into the polyurethane matrix. Also it was actuated with an induction heating system that can generate alternating magnetic fields. The reinforcement of magnetite nano-particles influences the thermo-mechanical properties of the shape memory polymer films and the helical shapes of the bio-medical stents were fabricated through the thermal treatment process. Present results show that the diameter and the length of the shape memory polymer stents with graphene-iron nanoparticles can be controlled by the induction heating system.

A-13.5:L03 **Multifunctional Spark Plasma Sintered Graphene Nanoplatelets / Ceramic Composites**

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The use of carbon nanostructures has opened new possibilities for research in the field of ceramic composite materials. In this work we report the fabrication of dense graphene nanoplatelets (GNPs) /Si₃N₄ composites (1-18 wt% GNPs) by the spark plasma sintering technique without damaging the nanoplatelets. Their particular geometry and the effect of the applied pressure induced the preferential orientation of the platelets. Composites showed different electric/thermal conductivity responses for measurements done under two unlike geometric orientations, namely parallel and perpendicular to the ab plane (graphene plane) of the platelets. The degree of orientation, level of exfoliation of GNPs and the matrix characteristics were determined using SEM, TEM and Raman spectroscopy tools. The electric and thermal conductivities for in-plane measurements showed an enhancement as compared to the cross results. Up to 60% increase over the monolithic for the thermal conductivity was observed and peak electric conductivity of 40 S/cm was obtained for 18 wt% GNP composite. These results are quite relevant as they demonstrate how the addition of relatively low amounts of C nanostructures renders multi-functional ceramic composites, without compromising other properties of these ceramics.

Poster Presentations

A-13:P65 **Breakdown of the Quantum Hall Effect in Graphene**

Y. MORITA, Gunma University, Kiryu, Japan

Our focus is on graphene in the quantum Hall regime with a finite electric field. In our theoretical analysis, this model can be mapped into the problem of the Harper equation, which has a close connection to the physics of quasicrystal. In our theoretical study, we reveal the global phase diagram of the system and the fate/breakdown of the quantum Hall effect. Further, we have discovered a multifractal structure hidden in this system, which can lead to a novel transport property. A possible candidate of this kind of system is a graphene nanotransistor. We shall also discuss on these experimental settings and propose theoretical predictions. It is a generalization of the experimental results which we have reviewed in 'Fabrication of quantum-dot devices in graphene', *Science and Technology of Advanced Materials*, 11, 054601-054605 (2010).

A-13:P67 **Graphene Based Cathode for Dye Sensitized Solar Cells**

L. KAVAN, J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Prague, Czech Republic

Commercial graphene nanoplatelets (GNP) in the form of optically transparent thin films on F-doped SnO₂ (FTO) exhibited fair electrocatalytic activity towards I³/I⁻ redox couple and excellent activity towards Co(III)/(II)-bipyridine complexes. The latter are particularly promising for the next generation of dye sensitized solar cells with high voltage. The cathode exchange current densities scaled linearly with the GNP film's optical absorbance. Depending on optical transmission, the electrocatalytic activity of GNP films is outperforming the activity of platinized FTO. Dye-sensitized solar cells with Y123 dye adsorbed on TiO₂ photoanode and Co-based redox shuttle achieved energy conversion efficiencies between 8 to 10% for both GNP and Pt-based cathodes. However, the cell with GNP cathode is superior to that with Pt-FTO cathode particularly in fill factors and in the efficiency at higher illumination intensities.

A-13:P70 **Graphene-chitosan Nanocomposite Film by Reduction of Graphene Oxide within Chitosan Networks**

CHANG KEE LEE, **JIN KIE SHIM**, **SANG BONG LEE**, Korea Packaging Center, Korea Institute of Industrial Technology, Bucheon, Korea

Dispersion state of graphene in a polymeric matrix has been considered as a key for formation of the composite. Oxide form of graphene has been used to "good dispersion state" however reduction of the oxide form disturbs the graphene's dispersion. It is mean that properties of graphene composite are changed due to the alteration of its internal structure induced by the reduction. In this study, the internal structure of graphene composite was controlled by reduction step during composite preparation and then the effect of the alteration of internal structure was investigated. The graphene-chitosan nanocomposite film was obtained via reduction of graphene oxide that was carried out in the chitosan networks using hydrazine. The GO was dispersed in 2 wt% of chitosan solution prepared by 2 wt% of aqueous acetic acid and then the GO-chitosan mixture was casted into a film. The GO-chitosan composite film was reduced by hydrazine monohydrate at 95°C. We confirmed the reduced GO and alteration of amorphous region in the nanocomposite film using X-ray diffraction. The morphology and internal structure were characterized by scanning electron microscopy and transmission electron microscopy respectively.

hybrid or inorganic component used in our structures is carbon nanotubes. We show that we can obtain enhanced dissociation of excitons, enhanced transport of carriers and evidence for broadband absorption by using the nanotubes to create triple junction structures within the OPV cells. Upto 25% enhancements in the energy conversion parameters such as short circuit currents with respect to virgin OPV cells is demonstrated, with better stability and robustness of devices. Self assembled semiconducting carbon nanotube networks are demonstrated in the hole extraction layer which is believed to present the ideal band alignment for hole collection allowed by the tuning of the electronic and chemical properties through the self assembly process. This is without the need for commonly used hole transport layers. IPCE data is analysed critically for the devices, and compared to the virgin OPV cells.

A-14.1:IL02 **Light Harvesting Schemes for High-performance Polymer Solar Cells**

FANG-CHUNG CHEN, **JYH-LIH WU**, **CHIA-LING LEE**, **YI HONG**, **MING-KAI CHUANG**, **KIM-SHIH TAN**, Department of Photonics and Display Institute, National Chiao Tung University, Hsinchu, Taiwan

Organic photovoltaic devices (OPVs) have received much attention because they are promising alternative tools for harnessing renewable energy. Recently the power conversion efficiencies (PCEs) of these OPV devices have reached as high as 9%, opening up the possibility for their practical use as flexible, light-weight, low-cost energy systems. While the internal quantum efficiency of OPVs can approach almost 100%, efficient light harvesting in OPVs remains one of the major limitations toward realizing high PCEs. In this work, we blended metal nanoparticles (NPs) into the buffer layer to trigger localized surface plasmon resonance for enhancing the device performance. The PCE of the OPV device incorporating the NPs can be improved. The mechanism of the plasmonic-enhanced OPVs will be discussed. Finally, we recently found that the direct excitation of charge-transfer excitons in the donor-acceptor blends of the OPVs can lead to substantially photovoltaic response. The device probably will become a promising wireless electrical source for biological nanodevices. Further, the results might open up new avenues for harvesting the long-wavelength spectrum of solar irradiation to provide even higher-efficiency solar cells.

A-14.1:L03 **Cobalt Doped ZnO Nanorods Fabricated by Chemical Bath Deposition Technique**

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ZnO nanorods are currently studied for a variety optoelectronic applications. Typically, thin film and bulk ZnO show a strong light absorption in the ultra violet range. For devices that operate in the visible and infrared range such as optoelectronic sensors and photovoltaic cells, it is necessary to modify the absorption profile from UV to higher wavelengths in the visible region. In this study we investigate optical absorption of ZnO nanorods doped with cobalt using a modified chemical bath deposition technique. The light absorption properties of Cobalt doped ZnO nanorods were studied using Photoluminescence (PL) and Raman Spectroscopy. For doping of Cobalt ranging from 1 to 5 percentage of the total weight, the PL intensity shows a suppression of the prominent UV peak at 385 nm with increase in doping concentration. This reduction in PL intensity at 385 nm is accompanied by an increase in the PL intensity at 429 nm and 469 nm. Scanning Electron Microscopy measurements of nanorod morphology reveal that, higher level of cobalt doping results in larger diameters for ZnO nanorods ranging from 600nm to 1.5 microns. We will discuss details of ZnO-Cobalt structures using Raman spectroscopy and X-ray analysis on cobalt doped ZnO nanorod samples of 1 -20% doping concentration.

A-14.1:L04 **Effective Harvesting of Photons Using Smart Material Systems for Solar Energy Conversion**

I.M. DHARMADASA, Materials & Engineering Research Institute, Sheffield Hallam University, Sheffield, UK

Various ways to harvest photons from the solar spectrum and energy from the surroundings have been considered and combined according to solid state physics principles. A graded bandgap multi-layer solar cell has been designed to absorb UV, visible and infrared radiation minimizing thermalisation losses, and combining impact-ionisation and impurity photovoltaic effect to enhance number of photo-generated charge carrier generation and collection. The above theoretical device design

SPECIAL SESSION A-14

Multifunctional Smart Materials for Energy Harvesting

Oral Presentations

Session A-14.1

Smart Materials for High Efficiency Solar Cells

A-14.1:IL01 **Carbon Nanotube-organic Hybrid Solar Cells for Energy Harvesting**

S.R.P. SILVA, Nanoelectronics Centre, Advanced Technology Institute, University of Surrey, Guildford, UK

The use of organic-hybrid solar cells for energy harvesting is examined as a route to enhance the performance of the OPV structures. The

was experimentally tested using well researched material, $\text{Al}_x\text{Ga}_{(1-x)}\text{As}$. The highest reported $V_{oc} \sim 1175$ mV together with highest possible fill factor in the mid 80%'s, have been achieved for initial devices. The highest efficiency achieved after two growth runs is over 20%. As expected from this design, impurity PV effect is experimentally observed producing V_{oc} values in the range (600 - 900) mV in complete darkness for $\text{Al}_x\text{Ga}_{(1-x)}\text{As}$ based devices. When this effect is active in solar cell devices, the combination of impurity PV effect and impact-ionization under illumination can enhance the number of photo-generated charge carriers producing large values of J_{sc} .

1. *Third Generation Multi-layer Tandem Solar Cells for Achieving High Conversion Efficiencies*, IM Dharmadasa, *Solar Energy Materials & Solar Cells* 85 (2005) pp 293-300; 2. *Third Generation Multi-layer Graded Bandgap Solar Cells for Achieving High Conversion Efficiencies - II*: IM Dharmadasa, JS Roberts and G Hill, *Solar Energy Materials & Solar Cells*, 88 (2005) pp 413-422; 3. *The reproducibility, Uniformity and Scalability of Multi-layer Graded Bandgap solar cell structures based on GaAs/AlGaAs System*, IM Dharmadasa, GJ Tolan, JS Roberts, G Hill, S Ito, P Liska and M Grätzel, *Proc. of 21st EU photovoltaic conference, Dresden Germany, June-2006*, pp 257-262; 4. *Solar Cells Active in Complete Darkness*, IM Dharmadasa, O Elsherif and GJ Tolan, *Journal of Physics: Conference Series* 286 (2011) 012041, doi:10.1088/1742-6596/286/1/012041.

A-14.1:L05 **Bi2S3 Nanoparticles Supported on CNT-TiO2 Matrices for Photovoltaic Applications: a Comparative Study of Preparation Methods**

M.E. RINCON, J.C. CALVA, M. SOLÍS, Centro de Investigación en Energía- UNAM, Temixco, Morelos, Mexico

Bismuth sulfide (Bi_2S_3) nanoparticles were supported on CNT-TiO₂ matrices to improve both the characteristic of the Bi_2S_3 absorbing layer and the transport and collection of photogenerated carriers. CNT-TiO₂ matrices were prepared by two distinctive methods rendering CNT/TiO₂ composite and CNT-TiO₂ hybrid electrodes, whereas Bi_2S_3 deposition was carried out by chemical bath. The as obtained photoanodes were subjected to thermal annealing previous to their application in a photoelectrochemical cell. Photoelectrochemical performance in both systems was correlated to the microstructural and optical differences observed by various conventional techniques (SEM, TEM, XRD, UV-Vis), while the interfacial interaction between CNT and TiO₂, and the bonding of Bi_2S_3 to TiO₂ was explored by Scanning Kelvin Probe Microscopy. The relevance of these data to explain the best photoactive material for emerging solar cells will be discussed.

A-14.1:IL07 **Organic Solar Cells: How They Work and How to Improve Them**

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During the last two decades several families of small conjugated organic molecules and polymers have been developed in view of photovoltaic (PV) solar energy conversion. When integrated into thin film PV devices these organic materials can either play the role of interfacial layers for charge injection/collection or be constitutive of the heterojunction itself as p- or n-type semiconductors. In both cases, parameters as diverse as the bandgap, energy levels, exciton binding energy, morphology, charge transport, etc, have to be taken into account for a proper molecular design. In this presentation we introduce the basic principles of organic solar cells and draw a state-of-the-art of the main families of organic molecules and polymers that have been synthesized today.

A-14.1:L09 **Influence of the Indium Precursors on ITO Properties Grown by Metal-organic Chemical Vapor Deposition**

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The influence of the deposition parameters on the electrical and optical properties of ITO thin films grown by MOCVD has been studied by the investigation of different indium and tin precursors. Studied indium precursors were two commercially available, $\text{In}(\text{acac})_3$ and $\text{In}(\text{TMHD})_3$, and a new one, 'InAL', produced especially by the industrial partner AirLiquid. For tin precursor we used Dibutyltin diacetate (DBTD) and

$\text{Sn}(\text{acac})_2$. The precursors were solubilized in the same solvent, and the mixed liquid solution was injected in an evaporator by the pulsed injection method [Materials Science and Engineering B 118 (2005) 105-111]. After optimization of the evaporation parameters, growth conditions were varied to establish the deposition kinetics. The studied parameters were deposition temperature, pressure in the reactor and oxygen ratio in the deposition atmosphere. Indium oxide, tin oxide and ITO layers were structurally characterized by XRD, SEM and FTIR. Optimized ITO films from the different precursors were evaluated by measuring their optical and electrical properties.

Acknowledgements: This study has been financially supported by the European funded (FEDER) Preclnov project.

A-14.1:IL11 **All-polymer Solar Cells Based on Perylene-diimide Copolymers: From Material Design to Photovoltaic Performances**

S. LUZZATI, E. KOZMA, D. KOTOWSKI, M. CATELLANI, Istituto per lo Studio delle Macromolecole, CNR, Milano, Italy

Polymer solar cells are attractive in view of their potential application for low-cost solar energy conversion. Polymeric solar cells generally consist of a bulk heterojunction made upon blending a light absorbing donor and hole-conducting conjugated polymer to an acceptor and electron-conducting material. The most successful acceptors to date are soluble fullerene derivatives that are characterised by good accepting properties and high electron mobilities. The replacement of fullerene by a polymer acceptor has raised the attention due to the potential advantages connected to the good absorption and to the easier tailoring of the electronic properties of conjugated polymer materials respect to fullerenes. However the difficulty in designing n-type polymers with good accepting properties and good electron mobilities to compete with fullerene is an issue that is limiting the power conversion efficiencies of all-polymer solar cells. In this contribution we present a series of acceptor perylene-diimide copolymers with good accepting properties and good electron mobilities that we have designed and tested in all-polymer solar cells, in combination to poly-3-hexylthiophene. The solar cells exhibit encouraging power conversion efficiencies (1.6%) and show remarkably good charge transport properties in the active blend, comparable to optimised polymer/fullerene devices.

A-14.1:IL14 **New Catalysts for Production of Solar Fuels**

IB CHORKENDORFF, Danish National Research Foundation's Center for Individual Nanoparticle Functionality (CINF), Department of Physics, Technical University of Denmark, Kongens Lyngby, Denmark

The production of fuels directly or indirectly from sunlight represents one of the major challenges to the development of a sustainable energy system. Hydrogen is the simplest fuel to produce and while platinum and other noble metals are efficient catalysts for photoelectrochemical hydrogen evolution, earth-abundant alternatives are needed for large-scale use. We show that bioinspired molecular clusters based on transition metal sulfides mimics nature's enzymes for hydrogen evolution when deposited on various supports. It will be demonstrated how these catalyst deposited on p-type Si can harvest the red part of the solar spectrum and potentially be coupled to CO₂ hydrogenation. Such a system could constitute the cathode part of a tandem dream device where the red part of the spectrum is utilized for solar fuel evolution, while the blue part is reserved for the more difficult oxygen evolution. Similarly investigation of photocatalysts using a recently developed microreactor platform will be discussed. It will be demonstrated how such devices allows for following the activity for water splitting as a function of relative humidity and how it can be used to investigate for example the undesired effect of back reactions from H₂ and O₂.

A-14.1:L15 **Polarizing Field Effect on Charge Transfer in Hybrid Photovoltaic Cells with Ferroelectric Bi-layers**

SOUMEN DAS, DAAN LIU, YOON BONG HAHN, School of Semiconductor and Chemical Engineering, Chonbuk National University, Jeonju, South Korea

Stoichiometric and polycrystalline ferroelectric $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ and BiFeO_3 thin films were deposited on glass and silicon substrates by wet chemical synthesis method. The qualitative assessment of the solution-processed dielectric layers was performed by concentrating on number of issues such as phase stability, electronic structures, band alignment, transport properties including carrier concentrations and conductivity by X-ray diffractometer, X-ray and ultraviolet photoelectron spectroscopy, Raman spectroscopy and capacitance-voltage measurements. These films

were introduced in the studied hybrid photovoltaic cells to form $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3/\text{ZnO}/\text{P3HT-PCBM}/\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_x$ and $\text{BiFeO}_3/\text{ZnO}/\text{P3HT-PCBM}/\text{BiFeO}_x$ assembly. The effect of these ferroelectric layers on the overall electrical performance of these all solution processed bipolar devices was studied.

Session A-14.2

Smart Materials for Self-power Generators

A-14.2:IL01 **Energy Harvesting on Vibration: A Performance Comparison Between Ferroelectric and Electrostrictive Polymer Material**

D. GUYOMAR, P.-J. COTTINET, M. LALLART, L. LEBRUN, Université de Lyon, INSA-LYON, Villeurbanne, France

The current trend in electronics is its integration in day to day devices or portable equipments in order to extend the number of functions and to improve their reliability. This paper addresses the problem of the electrical to mechanical energy conversion in electroactive materials in a general manner and more specifically on ferroelectric materials and electrostrictive polymers that can be used to design energy harvesters. The ferroelectric are brittle and contain lead. Oppositely the polymers are light, flexible, eco-friendly and their properties can be tuned by introducing nano-particles in the polymer matrix. These polymer composites exhibit a good capability to convert elastic energy into electrical energy once a DC electrical field is applied. The proposed energy conversion improvement is an extension, to polymers, of the so-called "non-linear voltage processing, or "SSH" previously developed for ferroelectric materials which leads to a 1000% increase of the harvesting capability. Due to the bias field, a direct extension of the SSH techniques is not feasible. The needed adaptations will be discussed. The paper will present and discuss experimental and theoretical data.

A-14.2:IL02 **Highly Efficient Power Generation Using Piezoelectric and Semiconducting Coupled Properties**

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Nanopiezotronics is an emerging area of nanotechnology with a variety of applications that include piezoelectric field-effect transistors and diodes, self-powered piezoelectric power generator (nanogenerator), and wireless nano/biosensors. By exploiting coupled piezoelectric and semiconducting characteristics, it is possible for nanowires, nanobelts, or nanorods to generate rectifying current and potential under external mechanical energies such as body movement, muscle stretching, vibrations, and hydraulic forces. Various energy harvesting systems can be designed and developed based on the different physical mechanisms of each energy generator. I will present a flexible hybrid architecture designed to harvest mechanical and solar energies, either separately or simultaneously. By using ZnO with intrinsically coupled piezoelectric and n-type conductive properties, a flexible hybrid energy scavenger is naturally created without any crosstalk and an additional assembling process, thus totally differing from a simple integration of two different energy generators. The piezoelectric output signals from our hybrid cells are originally alternating current (AC) type, but they can be controlled to direct current (DC)-like type by tailoring mechanical straining processes both in a dark and under a light illumination. Based on such controllability of a piezoelectric output behavior, the performance of the hybrid cell is synergistically enhanced by the contribution of piezoelectric generator, compared with the output power generated independently from the solar cell part under normal indoor level of illumination.

A-14.2:IL04 **Thermoelectric Generating Properties of Aurivillius Compounds**

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Thermoelectric generator is expected as an energy converter for co-generation with Refuse Derived Fuel (RDF). Thermoelectric materials were required high Seebeck coefficient, low electrical resistivity and low thermal conductivity. Thermoelectric oxides are suitable at the high temperature range because of chemical stability. Authors focus attention

on Aurivillius compounds. The Aurivillius compounds consist of Perovskite layers and Bi-O layers. It is expected that nanolayered structure shows high Seebeck coefficient due to the quantum confinement of electron in Perovskite layers. It was reported that the Seebeck coefficient of Aurivillius phase Bi_2VO_5 was as high as -28.3 mV/K at 1010 K, and the electrical resistivity of the one was also as high as $0.033 \Omega\text{m}$ at 1010 K. We investigated about element substitution effects at V site on thermoelectric properties. $\text{Bi}_2\text{V}_{1-x}\text{Cu}_x\text{O}_{5.5}$ ($x=0, 0.1, 0.2$) was prepared by solid-state reaction and hot pressing. The resistivities of $\text{Bi}_2\text{V}_{1-x}\text{Cu}_x\text{O}_{5.5}$ ($x=0.1, 0.2$) were one order higher than the one of Bi_2VO_5 . From the results of the resistivities and the Seebeck coefficients, it is presumed that Cu behaves as an acceptor. Thermoelectric generating properties of $\text{Bi}_2\text{V}_{1-x}\text{Cu}_x\text{O}_{5.5}$ ($x=0, 0.1, 0.2$) will be reported in the presentation.

A-14.2:IL06 **Epitaxial $\text{Pb}(\text{Zr,Ti})\text{O}_3$ on Silicon for Energy Harvesting Devices**

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Energy harvesting devices are attractive as an energy source for powering micro-devices, such as small wireless sensors, biomedical implants, environmental condition monitoring systems and structural health monitoring systems. In our work, we focus on energy harvester structures based on epitaxial $\text{Pb}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ (PZT) thin films grown on (001) silicon wafers. The integration on silicon is achieved via a thin buffer layer of epitaxial SrTiO_3 grown through a complex multi-step procedure by molecular beam epitaxy. The physical properties of the PZT layer are investigated by piezoelectric force microscopy and P-E loop measurements, revealing excellent ferroelectric and piezoelectric properties at room temperature. From the structural point of view, TEM investigation reveals the perfect epitaxy of the multilayer, while temperature dependent x-ray diffraction measurements suggest an increase of the ferroelectric critical temperature with respect to the bulk, in agreement with theoretical predictions for two-dimensional clamping. The potential of such epitaxial PZT thin films for energy harvesting devices will also be discussed, by presenting the performances of epitaxial PZT-based harvesters.

A-14.2:IL07 **ZnO Nanowires for Energy Harvesting and Piezotronics**

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Piezoelectricity, a phenomenon known for centuries, is an effect that is about the production of electrical potential in a substance as the pressure on it changes. For wurtzite structures, such as ZnO, GaN, InN and ZnS, due to the polarization of ions in a crystal that has non-central symmetry, a piezoelectric potential (piezopotential) is created in the crystal by applying a stress. For materials such as ZnO, GaN, InN in the wurtzite structure family, the effect of piezopotential to the transport behavior of charge carriers is significant due to their multiple functionalities of piezoelectricity, semiconductor and photon excitation. By utilizing the advantages offered by these properties, a few new fields have been created. Electronics fabricated by using inner-crystal piezopotential as a "gate" voltage to tune/control the charge transport behavior is named piezotronics, with applications in strain/force/pressure triggered/controlled electronic devices, sensors and logic units. Piezo-phototronic effect is a result of three-way coupling among piezoelectricity, photonic excitation and semiconductor transport, which allows tuning and controlling of electro-optical processes by strain induced piezopotential.

A-14.2:IL08 **Highly Efficient, Flexible Thin Film Nanogenerator**

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Energy harvesting technologies converting external sources (such as thermal energy, vibration and mechanical energy from the nature sources of wind, waves or animal movements) into electrical energy is recently a highly demanding issue in the materials science community for making sustainable green environments. In particular, fabrication of usable nanogenerator attract the attention of many researchers because

it can scavenge even the biomechanical energy inside the human body (such as heart beat, blood flow, muscle stretching, or eye blinking) by converging harvesting technology with implantable bio-devices. Herein, we describe procedure suitable for generating and printing a lead-free microstructured BaTiO₃ thin film nanogenerator on plastic substrates to overcome limitations appeared in conventional flexible ferroelectric devices. Flexible BaTiO₃ thin film nanogenerator was fabricated and the piezoelectric properties and mechanically stability of ferroelectric devices were characterized. From the results, we demonstrate the highly efficient and stable performance of BaTiO₃ thin film nanogenerator and the integration of bio-eco-compatible ferroelectric materials may enable innovative opportunities for artificial skin and energy harvesting system.

A-14.2:L10 The Synthesis of In-Se by Vapor Transport Method

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The α and β phase of In₂Se₃ have attracted attention as photovoltaic or thermophotovoltaic (TPV) materials because of the band gap, which is 1.3 eV. We investigated about the deposition of In-Se onto the Si substrate by vapor transport method. The Si substrates were etched by HF solution to remove the surface oxide layer of the one and rinsed by water. The quartz ampoule encapsulated bulk In₂Se₃ and Si substrates was heated in a temperature gradient furnace. During the heating, the bulk In₂Se₃ was placed at the hot side in ampoule, and the Si substrates were placed at alternative side. The temperatures of Si substrates were approximately 850 K and 950 K. The surface morphology was observed by SEM. Phase identification of deposits on the surface was achieved by XRD. The nanoparticles with diameter of 50 nm were sparsely deposited on the substrate surface. The textured surface, which was compactly-arranged square pyramid, was observed at the surface of the substrate. It seems that texture surface formed by etching and eutectic reaction between Si and deposited In. From the results of XRD, the deposits on the substrates were contained β -In₂Se₃, In, Se and InSe. The deposits of other conditions are now under investigation.

A-14.2:L11 Piezoelectric Properties of Crystallized PZT Thin Films on Flexible Substrate for Energy Harvesting

CHONG-YUN KANG, **MIN-GYU KANG**, **YOUNG-HO DO**, **SEUNG-MIN OH**, **SAHN NAHM**, **SEOK-JIN YOON**, Electronic Materials Center, Korea Institute of Science and Technology, Seoul, Korea; Department of Materials Science and engineering, Korea University, Seoul, Korea

The goal of piezoelectric energy harvesting is to improve the power efficiency of devices. One of the approaches for the improvement of power efficiency is to apply a large strain on piezoelectric materials and then many scientists used thin films or nano-structured piezoelectric materials to obtain flexibility. However, the conventional thin film processes available for the fabrication of piezoelectric materials as PbZr_{0.52}Ti_{0.48}O₃ (PZT) are not compatible with flexible electronics because they require high processing temperatures (>700°C) to obtain piezoelectricity. Excimer laser annealing (ELA) is an attractive heat process for low-temperature crystallization, because of its material selectivity and short heating time. In this study, amorphous PZT thin films were deposited on polymer substrate by rf-sputtering. To crystallize the amorphous films, ELA was carried out under various conditions in function of the applied laser energy density, the number of pulse, and the repetition rate. To evaluate the piezoelectric characteristics, piezoelectric force microscopy (PFM) and electrometer are used. As a result, we obtained crystallized PZT thin film on flexible substrate and obtained a flexible piezoelectric energy harvester.

A-14.2:L12 Hybrid Photovoltaic-piezoelectric Flexible Device for Energy Harvesting from Nature

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Photovoltaic energy can be expensive if the solar radiation in a particular region is not abundant. When the solar radiation is scarce in a region, there is presence of winds and rainfall. If flexible solar cells are coupled with flexible piezoelectric films then the hybrid structure can generate energy from solar radiation, wind and rainfall. Hybrid piezoelectric-photovoltaic devices have been developed which are capable of generating electricity from solar as well as wind and rain energy. This work focuses on non-transparent hybrid structure which contains copper

and aluminium electrodes and eliminates the used of costly indium tin oxide (ITO). These hybrid films are made by depositing organic photovoltaic cell based on P3HT and PCBM on a commercial PVDF film. The hybrid piezoelectric-photovoltaic film was first tested under a solar simulator with 1.5 AM filter at one sun solar intensity. The film produced an open circuit voltage, V_{oc} of 0.43V and a short circuit current density, I_{sc} of 4.48mA/cm². It was then subjected to a turbulent wind speed of 10m/sec (36km/hour) in a custom built wind tunnel. A peak voltage of 52V was generated by the PVDF substrate due to the oscillations created by the wind. Peak power was also measured using a variable resistor and was recorded to be 85 μ W. In order to check if the film was not damaged when it was subjected to the turbulent wind speed, the film was again tested under the solar simulator and did not show any changes in its open circuit voltage or short circuit current.

Session A-14.3

Interfacial Characterization

A-14.3:IL01 Interfacial and Electrical Properties of Reliable p-TiO₂ for Optoelectronic Devices Application

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Researches in dye-sensitized-solar-cells (DSSCs) are focused on the sensitization of n-type TiO₂. However, a rational design of efficient solar cells demands understanding the mechanism of p-DSSC as well. Study revealed that wet chemically processed metal ion (Al+3, Cr+3, Ni+2) doped TiO₂ thin films could switch its conducting nature from n-type to extrinsic p-type. The p-type conductivity was examined from Ag/ZnO/p-TiO₂/ITO structures. X-ray photoelectron spectroscopy showed shifting of valence band edges with increasing doping concentrations, and optical absorption spectroscopy showed shifting of the absorption edges, indicating effective doping in TiO₂ lattice. The doped TiO₂ film was employed as active component in bipolar heterojunction devices, which recorded low turn-on voltage and showed rectification behavior. Conclusive results revealed that among various dopants studied, consistent, reliable and reproducible p-type conductivity was obtained in case of Ni+2 ion. The Ni-doped TiO₂ showed mobility of 0.1-2.9 (1/cm²Vs) and hole diffusion coefficient of 0.001-0.1 (cm²/s), better than the previously reported. Further incorporation of p-TiO₂ into solar cells is discussed in terms of conversion efficiency.

A-14.3:L02 Graphene Composite Materials for Supercapacitor Electrodes

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This study presents materials interfacial studies of composite electrode materials of graphene to metal oxide nanostructures. We focus on nanocomposite electrodes combining nanostructures of Co₃O₄ and MnO₂ with graphene. The processing of these electrode materials is based upon a facile, electrophoretic deposition (EPD) process and self-assembled thin film process. Graphene oxide (GO) is deposited onto the nanocomposite layers and then reduced in situ. The presence of the metal oxides Co₃O₄ and MnO₂ allows and graphene layers increase charge storage and transport layer at the electrode/electrolyte interface. The supercapacitor device has increased energy density while still remaining stable after extensive cycling. With the addition of graphene layers to Co₃O₄ and MnO₂ nanowire arrays, we have observed marked increases in electrode conductivity, greatly surpassing that for metal oxides, on the order of 1 S/cm. The cycling stability increased as the mechanical integrity of the metal oxides' phase change during redox reactions by the presence of the graphene layers. The presented process for these nanocomposite electrodes is both scalable and facile. We will demonstrate the interfacial interaction plays critical role in high electrical conductivity of the composite electrode.

Poster Presentations

A-14:P72 **Structural and Photovoltaic Properties of CuO/ZnO Nanocomposite Solar Cells**

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Nanocomposite solar cells of ZnO/CuO 'core-shell' with CuO deposited layers have been fabricated on ITO by electroless deposition (ELD) technique. The ZnO/CuO NRs nanocomposite PVs have wurtzite n-type ZnO (~200 nm) as the 'core' and monoclinic p-type CuO (5-27 nm) as the 'shell' structure. Further ELD CuO layers of 65-205 nm have been deposited onto the nanocomposite 'core-shell' structure. The fabricated nanocomposite structures have been extensively examined by X-ray diffraction (XRD), field emission electron microscope (FESEM), atomic force microscope (AFM) and transmission electron microscopy (TEM). The most significant improved J-V characteristics has observed with a short current (JSC) of 126 $\mu\text{A}/\text{cm}^2$, open circuit voltage (VOC) of 206 mV, fill factor (FF) of 34%, and power conversion efficiency (PCE) of $3.3 \times 10^{-2}\%$ under AM1.5 illumination. Such improvement has been attributed to the quality and uniformity of the CuO/ZnO nanocomposite 'core-shell' with optimized CuO thickness of 178 nm. Such smaller band gap nanocomposite semiconductors with larger absorption coefficients, longer diffusion lengths, and higher mobilities attribute for improved performance of solar cell devices.

A-14:P74 **ITO-free Low-cost Organic Solar Cells with Highly Conductive Poly(3,4 ethylenedioxythiophene): p-toluene Sulfonate Anodes**

KIYEUL YANG, M. ARIFUR RAHMAN, A. RAHIM, MD. MANIRUZZAMAN, C. LEE, H. NAM, H. SOH, J. LEE, Kookmin University, Seoul, South Korea

Currently a significant emerging energy industry has been highlighted. There are various solar cells under development or in mass-production. Among them, flexible organic solar cell (OSC) has attracted significant attentions due to its low cost and flexibility. Consequently, a transparent conductive electrode such as Indium tin oxide (ITO) has its limitation for the use as an electrode due to its brittleness and high cost. Therefore, it needs to be replaced by flexible high conductive electrodes in flexible OSC. We have fabricated an ITO-free OSC by developing highly conductive and transparent tosylate-doped poly(3,4-ethylenedioxythiophene: p-toluene sulfonate) (PEDOT:PTS). The final OSC consisted of Glass/PEDOT:PTS/PEDOT:PSS/P3HT:PCBM/LiF/Al. The PEDOT:PTS was fabricated by vapor-phase oxidative polymerization of EDOT on the patterned UV-exposed octadecyltrichlorosilane (OTS) using Fe(PTS)₃ as an oxidant. The stability of the PEDOT:PTS-PEDOT:PSS interface was analyzed and successfully controlled. In addition, the optimization of the thickness in terms of transmission and conductivity has been done with a power conversion efficiency of 1.4%.

A-14:P76 **The Influence of Anatase Crystal Orientation on its Electro-chemical Properties and Performance in Dye-sensitized Solar Cell**

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The electrochemical behavior of TiO₂ anatase with a predominant (001) face (ANA001) was studied by cyclic voltammetry of Li insertion and chronoamperometry. Both methods proved its higher activity toward Li insertion compared to that of reference materials. The lithium diffusion coefficient of ANA001 calculated from cyclic voltammetry is by 1 order of magnitude higher than those of reference materials with a dominating (101) face. The same tendency, although not so large difference, exhibited the chronoamperometric diffusion coefficients and rate constants of ANA001 and reference samples. The enhanced activity of the anatase (001) face for Li insertion stems from synergic contributions of a faster interfacial charge transfer at this surface and a facile Li

transport within a more open structure of the anatase lattice in the direction parallel to the c-axis. The performance of ANA001 as a photoanode material in dye sensitized solar cells was studied and compared with that of reference material. The anatase (001) face adsorbs smaller amount of the used dye sensitizer (C101) per unit area than the (101) face. The corresponding solar cell with sensitized (001)-nanosheet photoanode exhibits smaller photocurrents and larger open circuit voltage than the reference cell.

FOCUSED SESSION A-15

Actively Moving Polymers

Oral Presentations

Session A-15.1

Shape Memory Polymers

A-15.1:IL01 **Shape Memory Elastomers Based on Ionomer Compounds**

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Shape memory elastomers were prepared from mixtures of a fatty acid or salt (FAS) with a sulfonated EPDM, SEPDM, ionomer. The ionic groups provide compatibility of the FAS with the ionomer, but they also can provide the "permanent" crosslinked network. Strong dipolar interactions between the ionomer and a crystalline FAS provided the thermally reversible, temporary network. Shape fixity of >90% was achieved, but creep recovery of the temporary shape occurred over a 2 week period. The source of the creep was the ionic "permanent" network, not the temporary network, and that problem was resolved by covalently crosslinking the ionomer. High shape recovery efficiencies were achieved. This design of a shape memory polymer (SMP) produced a family of materials, based on a single SEPDM ionomer, with controllable actuation temperature between 20 and 100 °C, depending on melting point of the FAS. The stiffness of the compound can also be controlled, without significantly changing the actuation temperature, by varying the concentration of FAS. Although, this study focused on elastomeric SMP, the design concept has also been demonstrated with thermoplastic and high temperature SMPs.

A-15.1:IL02 **Tunable Shape-Memory Media from Physically Modified Thermoplastic Elastomers**

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Triblock copolymers behave as thermoplastic elastomers when the endblocks are either glassy or semi-crystalline and the midblock is rubbery. Upon microphase separation due to thermodynamic incompatibility between the chemically dissimilar blocks, these materials tend to form rigid microdomains dispersed in a continuous rubbery matrix. Because a fraction of the copolymer midblocks form bridges and connect adjacent microdomains, such copolymers inherently form networks stabilized by physical cross-link sites, or netpoints. Previous studies have established that block, or segmented, copolymers with vitrifiable or crystallizable midblocks can be used as shape-memory polymers (SMPs) insofar as the midblocks serve as the switching segments and the transition temperature corresponds to the glass

transition or melting point, respectively, of the midblock species. Such systems often rely on single macromolecules, in which case variation in shape-memory attributes requires the synthesis of new materials. Building on our previous studies of thermoplastic elastomer gels, we have designed multi-programmable SMPs from commercially available thermoplastic elastomers with a soft midblock. The tunability of these systems, as well as other SMPs developed from similar copolymers, will be presented.

A-15.1:L03 **Multiple Shape-memory Behavior of Polyethylene/Polycyclooctene Blends Cross-linked by Electron Irradiation**

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Comparative investigation was performed on the thermo-induced unconstrained shape-memory (SM) recovery of a multi-phase semi-crystalline covalent network using cross-linked blends of linear (HDPE) and/or short-chain branched polyethylenes (EOC) as well as polycyclooctene (PCO). Different phase morphologies of the blends were generated by means of variation of blend composition and different pathways for sample preparation: Melt mixing of blends, compression molding of films, slowly cooling or quenching of films and subsequent cross-linking by electron irradiation at room temperature. Well developed triple- and partly quadruple SM behavior after one-step programming process was demonstrated for binary and ternary HDPE/EOC/PCO blends, exhibiting a morphology with well segregated phases, where the matrix has the lower melting and correspondingly switching temperature (T_m and T_{sw}) in comparison to the disperse phases. These blends evince pronounced steps of SM strain recovery and modulus as well as distinct DSC melting peaks. The quenching procedure resulted in a better phase separation at nano-level and correspondingly in a more pronounced triple-shape behavior of the blends. All HDPE/EOC/PCO blends showed high values of strain fixing and strain recovery ratios of 95 to 99%.

A-15.1:L04 **Biocompatible and Degradable Polydepsipeptide based Multiblock Copolymers with Shape-memory Capability**

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Recently polydepsipeptides, alternating copolymers of an α -amino acid and an α -hydroxy acid, have gained attention as matrix materials for controlled drug release systems, for TE scaffolds or for biofunctional implants.¹ In contrast to aliphatic polyesters an improved biocompatibility during degradation time period is expected. Thermoplastic phase-segregated multiblock copolymers with polydepsipeptide and poly(ϵ -caprolactone) or poly(p -dioxanone) segments were prepared via coupling of the macrodiols using an aliphatic diisocyanate.^{2,3} The obtained multiblock copolymers showed good elastic properties and combined degradability with shape-memory capability. In the biological evaluation of material samples according to ISO10993 the samples did not show incompatibilities with L929 cells.⁴ The results suggest the investigated copolymers as promising candidates of soft substrates applied in cell culture devices or of in vivo implants.

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A-15.1:L06 **Mechanically-driven Recovery in Amorphous Polymer Networks Programmed for Shape Memory**

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This study proposes a novel method of shape recovery by exploiting the meta-stable programmed state of amorphous shape-memory polymer (SMP) networks and utilizing mechanical stresses to drive shape change. Programming of SMPs can influence the polymer's mechanical

properties via stretching (mechanical anisotropy) and quenching (non-equilibrium structure). This study hypothesized that the programmed samples would experience shape recovery at lower forces compared to non-programmed samples. Three networks were synthesized from tert-butyl acrylate and poly(ethylene glycol) dimethacrylate and were tailored to a glass transition temperature of 52 °C, while varying the crosslinking density. Thin-walled cylindrical samples were programmed to 3.55 mm (25%) axial elongation. A second set of samples was then manufactured to match the geometry of the programmed cylinders to act as non-programmed controls. Both sets of samples were then compressed 3.55 mm at a rate of 1 mm/s at temperatures of 20, 27, 34, and 41 °C. Programmed samples demonstrated compressive strength and deformation energies at 62 and 52% of their non-programmed counterparts, respectively. This study discusses how this mechanism can be used in biomedical devices such as cardiovascular stents and orthopedic fixation devices.

A-15.1:L07 **On the Validity of Time-Temperature Equivalence for Wide Frequency Band Analysis of Shape Memory Polymers**

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Mechanical properties of Shape Memory Polymers (SMP) can exhibit decades of variations for everyday ambient conditions and classical frequency ranges of interest in the context of smart structures. For conventional polymers, the time-temperature equivalence is a very efficient tool to restrain the range of tests to be performed through the use of master curves. Dynamical Mechanical Analyses (DMA) are classically used for testing samples with various frequency and temperature values. The purpose of this study is to validate the time-temperature equivalence on a SMP sample, by performing a wide frequency band analysis combining DMA and modal tests on a structure made from the same material. Modal tests have been performed for various temperature values, and resonance frequencies have been measured and correlated to a finite element model to estimate the material elastic properties. By combining results from both tests, a poor correlation between parameters estimated from DMA and modal tests is observed, which tends to indicate that the time-temperature equivalence is not valid for the material of interest (the whole process has been successfully validated with a PP sample). Several ways are investigated to understand whether the equivalence is valid or not for the tested SMP.

A-15.1:L08 **Synthesis and Characterization of Monofunctionalized Poly(ω -pentadecalactone) with Isocyanato Ethylmethacrylate and Polymers based thereof**

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Multifunctional shape-memory polymers (SMP), which are biodegradable and have a shape-memory capability have attracted interest for biomedical applications.^{1,2} So far only short aliphatic side chains have been used as dangling chain segments contributing to the fixing phase in dual-shape SMP.³ Here we report about the synthesis of a monofunctionalized poly(ω -pentadecalactone)-IEMA (PPDL-IEMA) ($M_n = 2600$ g.mol⁻¹, $T_m = 89$ °C) obtained by ring-opening polymerization of ω -pentadecalactone (PDL) and subsequent reaction of the terminal hydroxyl group with 2-isocyanato ethylmethacrylate (IEMA). When the PPDL-IEMA was polymerized using azobis(isobutyronitrile) (AIBN) as initiator, a polymer with a comb architecture was obtained. The addition of polyethylenglycoldimethacrylate (PEGDMA, $M_n = 370$ g.mol⁻¹) to the reaction mixture enabled formation of a polymer network with PPDL side chains. The obtained polymers were characterized by DSC, NMR, GPC and WAXS. In the case of the polymer networks the shape-memory properties were quantified.

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A-15.1:L09 **Molecular Dynamics Simulations for Micro-vascular Shape Memory Composites**

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Molecular dynamics simulations are used to study the shape memory behavior of a representative amorphous polymer undergoing very large

deformations in the rubbery elastic regime. A physics based micro-macro constitutive model is shown to fit the simulation data under uniaxial, biaxial, and shear loading. The model accounts for nonaffine tube mechanics extended to large deformations by integrating Langevin chain statistics. The model parameters vary consistently with known simulation input parameters. Physical and covalent mechanisms are investigated as sources of shape memory behavior, that is to say, strain fixing and shape recovery. In addition, we introduce a new multifunctional microvascular polymer composite capable of undergoing large deformations. The material is based on the biological concepts of thermo-regulation and muscle activation. The composite is an actively heated and cooled shape memory polymer with embedded microchannels for fluid flow. The active heating/cooling by this local mechanism significantly increases the response time of the material, which to date has been a major drawback. We have successfully fabricated multifunctional microvascular polymer composites with stable hollow channels (100 μm in diameter). Thermomechanical characteristics of the microvascular composite with different fiber architectures will be presented.

Session A-15.2

Shape Changing Polymers

A-15.2:IL01 A Continuous Flow Synthesis of Micrometer Sized Actuators from Liquid Crystalline Elastomers

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Using microfluidics, we realized a continuous flow synthesis of spherically shaped particles from a crosslinked liquid crystalline polymer (LC-elastomer). In this approach, a mixture of a liquid crystalline monomer with crosslinker and UV-initiator is melted and injected through a very thin needle into a co-flowing stream of silicon oil. The size of the particles can be controlled by several parameters, mainly the viscosity of the silicon oil and the flow rate ratio between oil and monomer. Thus we obtained particles with a diameter between 200 and 500 micrometers with a size variation coefficient as low as 1%. Upon heating them into the isotropic phase under a microscope the particles change their shape from a spherical to a rod like conformation. Thereby length changes of more than 70% can be observed. The actuation is completely reversible and very fast, which was shown by rapidly cooling particles in the stretched conformation by a flow of cold air. We also show that the intensity of the shape change strongly depends on the flow rate at which the particles were polymerized. The same conformational change can be achieved by swelling the particles with a suitable solvent, which also induces a phase transition.

A-15.2:IL02 Thermosensitive Helical Shape of Twist Nematic Elastomer Ribbons

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We investigate the thermally induced shape-change of twist nematic elastomer (TNE) ribbons where the local directors continuously rotate by 90 degrees between the top and bottom surfaces¹. In the cases where the director in the midplane is along the long or short axis, the narrow TNE ribbon forms a straight helicoid with Gaussian saddle-like curvature, while the shape in the wide case is a spiral ribbon with cylindrical curvature. In both cases, the temperature (T) variation greatly influences the structural parameters of the ribbons such as twist pitch, helical pitch and diameter, involving a reversal of handedness. The pronounced T effects on the ribbon shape result from a large change in local nematic order induced by T variation. We also show that the TNE ribbons where the midplane director has a finite angle relative to both the long and short axes always form spiral ribbon, even in the narrow case.

1. Y. Sawa, F. Ye, K. Urayama, T. Takigawa, W. Gimenez-Pinto, R.L.B. Selinger, J.V. Selinger, *Proc. Natl. Acad. Sci. USA*, 108, 6364 (2011).

A-15.2:L03 Electro-actuation of Responsive Polyelectrolyte Hydrogel: Role of pH Propagating Front

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Polyelectrolyte gels are able to mimic artificial muscles and act as an accurate valves and active drug delivery systems. Control over swelling, shrinking and bending behavior of a polyelectrolyte gels in response to environmental stimuli enables us to achieve direct conversion of electrostatic energy into a mechanical energy. Although many theoretical models have been proposed to describe actuating phenomena their experimental validation has not been carried out. Here, we present four different models found in the literature which describe the actuating mechanism of hydrolyzed polyacrylamide gels and try to verify them experimentally. The main purpose of this research was to characterize the role of pH changes, originating from water electrolysis occurring on the electrodes, in relation to electroresponsiveness of polyelectrolyte hydrogel. To characterize the contraction or expansion of the gel without affecting it we employed a pH indicator dye as a probe. By using this technique we were able to visualize the dynamics of the pH gradient in situ during actuation, and thereby deduce its role in actuation. In addition we were able to directly visualize ion depletion at cathode facing side of the gel as theoretically predicted.

A-15.2:L04 Plasma Treatment of LCE Affects Thermal Properties of Shape-changing Materials

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Liquid crystalline elastomers (LCE) are a class of actively moving polymers, which have the ability to change their shape caused by an induced disorder in the liquid crystalline structure¹ while the LCE is heated above the phase transition of the mesogens, e.g. from the nematic to the isotropic state (TNI).² Here we report about the influence of plasma treatment on the thermal properties of such LCE's. The mainchain LCE was prepared in a two step reaction of divinyl monomers and 2,4,6,8,10-Pentamethylcycllopentasiloxane acting as crosslinking agent. When the surface of the LCE's was treated with O₂-plasma, we observed a significant decrease of TNI, which was attributed to a disruption of the order of the mesogens due to polymer scission. The length of the time intervals of plasma treatment were varied and the influence on the thermal properties as well as shape change capability was investigated by DSC, WAXS, and cyclic, thermomechanical measurements. This finding might be useful for applications, in which a lower Trans is requested, e.g. biomedical application.

1. M. Bispo et al, *Macromolecules*, 2008, 41, 3098-3108.

2. M. Behl et al, *Adv. Polym. Sci.*, 2010, 226, 1-40.

A-15.2:L05 Shape Memory Polymer Systems with Independent Control of Material Properties Before and After Deployment

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There are distinct advantages to designing shape memory polymer systems that affords two sets of material properties - an intermediate polymer that would enable optimum handling and processing of the material, while maintaining the ability to tune in a set of final properties that would enable the optimal functioning of the polymeric material. We have formulated and characterized shape memory polymer networks that retain the ability to achieve two distinct sets of material properties. By designing a series of non-stoichiometric thiol-acrylate systems, a shape memory polymer network is initially formed via an amine catalyzed Michael addition reaction that proceeds stoichiometrically via the thiol-acrylate 'click' reaction. This self-limiting reaction results in a polymer with excess acrylic functional groups within the network. At a later point in time, the photo-initiated, free radical polymerization of the excess acrylic functional groups results in a highly cross-linked, robust material system. The thiol-acrylate shape memory networks have intermediate rubbery moduli and glass transition temperatures that range from 2 MPa and -10 °C to 20 MPa and 30 °C respectively. The same polymer networks can then attain rubbery moduli of up to 200 MPa.

Session A-15.3

Light-sensitive Polymers

A-15.3:IL01 Photomobile Polymer Materials

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In this presentation we will show photomobile polymer materials that can convert light energy directly into mechanical work and exhibit various 3-dimensional movements by irradiation with light^{1,2}. Large deformations can be generated in the crosslinked liquid-crystalline polymers, contraction, expansion, and bending, by incorporating photochromic molecules, such as an azobenzene, with the aid of photochemical reactions of these chromophores¹⁻⁵. Laminated films fabricated from a crosslinked LC polymer and a polymer film show photomobile properties successfully such as a light-driven plastic motor, inchworm and robotic arms^{6,7}.

1. T. Ikeda, T. Ube, *Mater. Today*, 2011, 14, 480; 2. T. Ikeda, J. Mamiya, Y. Yu, *Angew. Chem. Int. Ed.*, 2007, 46, 506; 3. T. Ikeda, M. Nakano, Y. Yu, O. Tsutsumi, A. Kanazawa, *Adv. Mater.*, 2003, 15, 201; 4. Y. Yu, M. Nakano, T. Ikeda, *Nature*, 2003, 425, 145; 5. M. Kondo, Y. Yu, T. Ikeda, *Angew. Chem. Int. Ed.*, 2006, 45, 1378; 6. M. Yamada, M. Kondo, J. Mamiya, Y. Yu, M. Kinoshita, C.J. Barrett, T. Ikeda, *Angew. Chem. Int. Ed.*, 2008, 47, 4986; 7. M. Yamada, M. Kondo, R. Miyasato, Y. Naka, J. Mamiya, M. Kinoshita, A. Shishido, Y. Yu, C. J. Barrett, T. Ikeda, *J. Mater. Chem.*, 2009, 19, 60.

A-15.3:IL02 Photoresponsive Liquid Crystal Polymer Networks: Glassy Adaptive Materials

T.J. WHITE¹, KYUNG MIN LEE², D.H. WANG³, LOON-SENG TAN¹, M.L. SMITH⁴, H. KOERNER², R.A. VAIA¹, T.J. BUNNING¹, ¹AFRL/RX; ²AFRL/RX, Azimuth Corp.; ³AFRL/RX, UES; ⁴AFRL/RX, NRC, USA

Transducing light energy into mechanical work has profound utility - as a remote actuation source, a quick means to impart a temporary shape (shape memory), or a method to induce spatially varying surface roughness useful in optics. Researchers ranging from Lovrien to Eisenbach to Finkelmann, in addition to a burgeoning present-day community, have realized varying magnitudes of light-to-work transduction in soft materials. This talk will focus on our recent work examining glassy, azobenzene-functionalized liquid crystalline polymer networks (LCNs). The talk will focus on the exploitation of the unique self-organized properties of liquid crystalline polymeric materials to yield compliant, multi-dimensional shape adaptations. Results observed in liquid crystalline systems will be contrasted to those observed in non-liquid crystalline, high performance (T_g ~ 220-350 °C) azobenzene-functionalized polyimides (PIs). The talk will end by contrasting the unique opportunities afforded to each system (LCNs and PIs) with respect to optically fixable shape memory.

A-15.3:L03 Photo-responsive Polymeric Structures Based on Spiropyran

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Spiropyrans are one of the most popular classes of photochromic compounds in science due to their potential applicability in new technologies like data recording and storage and optical switching displays¹. Spiropyrans offer new routes for the fabrication of multifunctional materials that take advantage of their photo-reversible interconversion between two thermodynamically stable states: a spiropyran form, and a merocyanine form, which have dramatically different charge, polarity and molecular conformations². In this work, polymer brushes based on spiropyran were synthesised on the interior of micro-capillaries to study the control of solvent flow through a confined space as well as the spiro-brushes sensing capabilities. We demonstrate that using "grafting from" approach we obtained a 3D arrangement of polymer brushes covalently attach to the inner wall of the micro-capillary where the spiropyran moiety has the freedom to open and close in response to light (ultraviolet, white light). This type of manipulation of capillary surface properties using light aims to develop new modes of

controlling liquid transport in micro-confinements as well as to generate micro-integrated optical sensors.

1. G. Jiang et al, *Adv. Mater.*, 2008, 20, 2888.
2. H. Tian et al, *J. Mater. Chem.*, 2008, 18, 1617.

A-15.3:IL04 Photoresponsive Liquid Crystalline Polymeric Materials

D.J. BROER, Eindhoven University of Technology, Eindhoven, The Netherlands

In-situ photopolymerization of liquid crystalline (LC) monomers has proven to be a valuable technique for the formation of well-ordered polymer networks. Their anisotropic properties led to a variety of applications in optics, electronics and mechanics. The use of light to initiate polymerization enables lithographic approaches for patterning. The LC behavior enables formation of complex morphologies on molecular level. Controlling the director profile of an LC network film in transversal direction gives geometrical morphing upon minor changes in order parameter. Examples of suited profiles of molecular orientation are twisted or splayed director configurations tied up in the network configuration. Reversible order parameter changes can be induced by a variety of means. It can be simply induced by temperature changes resulting in gradients in thermal expansion over the cross-section of the film. But more sophisticated and of interest for applications is a light induced change as a result of the E-Z isomerization of a built-in azo group. In the presentation various complex light-induced morphing figures will be discussed as being controlled by orientation patterns of the LC network molecules. Examples are the formation of surface topologies in thin film coatings, light-source tracking in bending beams and controlled folding and wrinkling of flat films.

A-15.3:L05 Azobenzene-containing, High T_g, Crosslinked & Linear Aromatic Polyimides: Photo-mechanically Bendable and Twistable Cantilevers

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We report the synthesis and photodirected bending and twisting behaviors of amorphous, high glass-transition temperature (T_g: 220-246 °C) polyimides crosslinked by a novel tris(azobenzene-amine) crosslinker (5-30 mol%). In parallel with T_g, the modulus also increases with increasing crosslinker concentration. Cantilevers composed of these azobenzene polyimide networks (azo-CP2), upon exposure to linearly polarized 442 nm light, have shown photodirected bending that is governed by the orientation of polarization, and ranges from +20° to -20°. The polarization-controlled forward/backward, symmetrical/asymmetric bending motions are shown to be strongly dependent on azobenzene/crosslinker concentration as well as thickness and aspect ratio of the cantilevers. Upon removal of the incident light, the cantilevers are photoelastic, restoring to the original vertical position. This is in contrast to the photo-fixing behavior observed for polydomain glassy, azobenzene-containing liquid crystalline network (azo-LCN) polymers when exposed to 442 nm light previously reported. Synthesis and photomechanical properties of several structurally related linear polyimides with varied degree of semicrystallinity will also be presented.

A-15.3:L06 Light Responsive Polyolefins by Post-Reactor Modification

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Smart polyolefins displaying photophysical properties, such as fluorescence emission and response to light stimuli, are very attractive materials for a broad range of applications, as the advanced/functional packaging. Completely apolar matrices like polyolefins are not miscible with the majority of colorant and chromophores, which are polar and/or aromatic molecules. A valuable alternative to the physical mixing is the chemical grafting of the colorant/chromophore onto the polyolefin backbone. Recently, a new radical post-reactor modification method, based on the reaction between nitroxide derivatives and polyolefin macroradicals generated by peroxides, offers the possibility to prepare functionalized polyolefins with a good control of the macromolecular architecture and functionalization degree. The simple esterification of

HO-TEMPO with carboxylic acid derivatives bearing chromophoric groups allows the preparation of smart polyolefins, by transferring the optical properties from the functionality to the polymer. The functionalization of a copolymer ethylene/1-octene with different chromophoric TEMPO derivatives and the photophysical properties of the functional materials are here discussed.

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Session A-15.4

Magneto-sensitive Materials

A-15.4:IL01 **Magnetic Heating of Polymer-SPION Hybrid Materials: From Fundamental Studies to Externally Triggered Drug Delivery**

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Drug release from a polymeric matrix has been externally triggered using an alternating magnetic field in order to develop an on-demand drug delivery implant. Fundamental studies on the heating of superparamagnetic iron oxide nanoparticles (SPION) in an alternating magnetic field have been performed revealing that the Néel relaxation is the predominant heating mechanism for small SPION using an oscillation frequency of 745 kHz. Furthermore, it was demonstrated that a better distribution of SPION in a poly(methyl methacrylate) (PMMA) matrix leads to faster and more efficient heating in an oscillating magnetic field. Finally, a SPION containing PMMA core was coated with a thermo-responsive layer of poly(butyl methacrylate-stat-methyl methacrylate) containing ibuprofen as a model drug. The release rate of ibuprofen reversibly increased upon exposure to the magnetic field and was found to increase with higher iron oxide loading. Finally, magnetically triggered on-demand drug release was demonstrated under physiologically relevant conditions, namely 37 °C in PBS buffer with high ibuprofen content in the implant and only 15 minutes triggering time.

A-15.4:IL02 **Electrically- and Magnetically Induced Motility of Polymer Gels and Smart Composites**

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Electric-, and magnetic field sensitive polymer gels and elastomers are soft smart materials whose elastic- and thermodynamic properties are strong function of the field strength imposed upon them. Colloidal (nano-) particles with special electric and magnetic properties are built into flexible polymer matrix. The particles couple the shape of the gel (or elastomer) to the external fields. Shape distortion occurs instantaneously and disappears abruptly when electric- or magnetic field is applied or removed, respectively. Giant deformational effect, field controlled elastic modulus, non-homogeneous deformation and quick response to magnetic- and electric field open new opportunities for using such materials for various applications. The development of smart polymer composites that show spinning in static uniform field will also be presented. The rotating disk acts like micro sized motors with tuneable angular frequency.

A-15.4:IL03 **Magnetic Ionogels for Fluid Handling in Microfluidic Devices**

B. ZIOLKOWSKI, K.J. FRASER, R. BYRNE, D. DIAMOND, CLARITY: The Centre for Sensor Web Technologies, National Centre for Sensor Research, Dublin City University, Dublin, Ireland

Designing robust, reliable and calibration-free chemical sensors was, and still is, an unrealised dream of for analytical chemistry. Miniaturisation, lower cost and self maintenance of sensors can be achieved by the use of smart, stimuli responsive materials. Such material that actuates only when the desired event occurs would increase the

lifetime of sensors.¹ Those sensors could then be deployed ubiquitously to monitor environment conditions in many places at the same time, building a chemical sensor network. Here we present, novel "ionogels" that respond to magnetic stimuli. Magnetic susceptibility is provided by means of surface-functionalised magnetic particles. This functionalisation allows the particles to be covalently attached to the gel polymeric matrix. Consequently the particles are permanently trapped in the gel. Moreover, due to the hydrophobic nature of the incorporated ionic liquid, the ionogels can swell but do not leach out into water. Mechanical and magnetic properties of the gels are presented. The inherent properties of these "magnetic ionogels" make them an ideal, low-power actuator material for fluid handling in microdevices.

1. R. Byrne, F. Benito-Lopez, D. Diamond, *Materials Today* 2010, 13, 9.

A-15.4:IL04 **Deformation Mechanisms in Iron-particle Magneto-rheological Elastomers: Experiments and Theory**

K. DANAS, N. TRIANTAFYLIDIS, LMS, Ecole Polytechnique, Palaiseau, France; **S.V. KANKANALA**, BD Technologies, Salt Lake City, NC, USA

Magnetorheological elastomers (MREs) of this study are ferromagnetic particle impregnated rubbers whose mechanical properties are altered by the application of external magnetic fields. Due to their coupled magnetoelastic response, MREs are finding an increasing number of engineering applications. In this work, we present a combined experimental, numerical and theoretical study of the response of a particular MRE consisting of a rubber matrix phase with spherical carbonyl iron particles. The MRE specimens used in this work are cured in the presence of strong magnetic fields leading to the formation of particle chain structures and thus to an overall transversely isotropic composite material. The mechanism of deformation in the MRE is studied numerically and experimentally using simple microstructural systems of particles subjected to uniformly applied magnetic fields. The effect of the initial particle chain orientation with respect to the mechanical and magnetic loading direction is analyzed.

Session A-15.5

Degradable, Stimuli-sensitive Polymers

A-15.5:IL01 **Redox-responsive Degradation of Poly(ethylene glycol) (PEG) Based Cryogels**

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Cryogels are macroporous hydrogels that are produced in a partially frozen medium in which the reactants are concentrated in the unfrozen regions and then polymerize to a dense polymeric matrix in between the frozen regions. Compared to hydrogels, cryogels have large interconnected pores with pore sizes ranging from 10-100 micrometer. Cryogels as macromolecular scaffolds have attracted widespread attention from areas in both biology and material sciences. In particular, their similarities to the natural extracellular matrices make them promising materials as synthetic scaffolds for tissue engineering. In this study, redox-responsive degradable poly(ethylene glycol) based cryogels were prepared via a step-growth polymerization process. A Michael addition strategy involving the reaction between maleimide double bond and amine group has been investigated for the synthesis of cryogels. Low molecular weight PEG-based building blocks with amine end groups and disulfide containing building blocks with maleimide end groups were combined to synthesize such cryogels. A toxicologic analysis showed that the degradation products do not have any negative effect on the cell viability. Cell seeding experiments demonstrated the potential of these cryogels as scaffolds in tissue engineering.

A-15.5:IL02 Biodegradable Shape Memory Polymeric Composites
LIN WANG, HONGMEI CHEN, **SHAOBING ZHOU**, School of Materials Science and Engineering, Key Lab. of Advanced Technologies of Materials, Ministry of Education, Southwest Jiaotong University, Chengdu, P.R. China

Shape memory polymeric composite can be defined as that the composite can be fabricated by mixing one filler having some specific functions with the other shape memory polymer via a physical or chemical reaction, and thus the composite possesses not only the original shape memory property of polymer but also some new properties from fillers. They, as emerging active materials, whose shape can be changed in a predefined way under a certain external stimulus, have been drawing more and more attention due to their potential applications in medicine¹⁻³. During the last 5 years, our group have also investigated the shape memory effect of biodegradable polymer composites such as poly(D,L-lactide)/hydroxyapatite (PLA/HA)^{3,4}, crosslinked poly(ϵ -caprolactone) (c-PCL)/Fe₃O₄^{5,6}, and c-PCL/multiwalled carbon nanotubes (MWNTs)^{7,8}. The nature of shape memory effect for these polymer composites belongs to thermal response although the effect was stimulated with heat, alternating magnetic fields and electrical fields.

1. A. Lendlein *et al*, *Science*, 2002, 296: 1673; 2. A. Lendlein *et al*, *Angew Chem. Int. Ed.* 2002.41: 2034; 3. X. Zheng *et al*, *Biomaterials*, 2006, 27, 4288; 4. S. Zhou *et al*, *Chem Mater.* 2007, 19: 247; 5. X. Zheng *et al*, *Colloid Surface B.* 2008, 71: 67.

A-15.5:IL03 Smart Multifunctional Polymers from Polymerisation of Multi-vinyl Monomers

WENXIN WANG, Science Foundation Ireland (SFI), Network of Excellence in Functional Biomaterials, National Centre for Biomedical Engineering Science, Dept. of Mechanical and Biomedical Engineering, National University of Ireland, Galway, Ireland

To develop advanced hydrogel system for tissue engineering application, PEG based in situ crosslinking hybrid hydrogel composed of thermoresponsive copolymer and natural extracellular matrix (ECM) has been developed. A well defined PEG based hyperbranched thermoresponsive copolymer with high content of acrylate vinyl groups was synthesized via a 'one-pot and one-step' deactivation enhanced atom transfer radical polymerisation (DE-ATRP) approach, which provided an injectable and in situ crosslinkable system via Michael-type thiol-ene reaction with a thiol modified Hyaluronan biopolymer. The Lower Critical Solution Temperature (LCST) of this copolymer is close to body temperature, which can result in a rapid thermal gelation at 37 °C. The SEM analysis of crosslinked hydrogel showed the network formation with porous structure and 3D cell culture study demonstrated the good cell viability after the cells were embedded inside the hydrogel. This injectable and in situ crosslinking hybrid hydrogel system offers great promise as a new class of hybrid biomaterials for tissue engineering.

A-15.5:IL04 Tailoring the Thermo-Mechanical Properties of Biodegradable Poly(beta-amino ester) Shape-Memory Polymers

D.L. SAFRANSKI, K. GALL, Georgia Institute of Technology, Atlanta, GA, USA and MedShape Solutions, Atlanta, GA, USA; **D. WEISS**, W.R. TAYLOR, Emory University, Atlanta, GA, USA

A novel class of biodegradable shape memory polymers (SMP) has been developed by combining biodegradable poly(beta-amino ester)s (PBAE) with methacrylate monomers. These networks degrade due to the hydrolytically cleavable PBAE crosslinkers, display shape-memory due to the crosslinked network, and exhibit enhanced stiffness and toughness by adding methyl methacrylate. The objective was to tailor the degradation, shape-memory, and mechanical properties of PBAE networks for specific biomedical applications. The degradation rate is controlled by changing the chemical structure of the PBAE, where increasing the hydrophilicity of the diacrylate increases the degradation rate. The activation temperature (T_g) was tuned by adding methyl methacrylate to the PBAEs, where the T_g can range from -40 °C to 80 °C. The networks displayed near 100% free-strain shape recovery when heated above their T_g. Select networks showed an increase in mechanical properties with time during in vitro degradation due to changes in thermo-mechanical properties. Further in vivo testing has verified the temporally tunable mechanical properties and with favorable biocompatibility. These tailorable biodegradable SMP have potential for cardiovascular and orthopedic applications.

Session A-15.6 Multimaterial Systems

A-15.6:IL01 Shape Memory Polymer Nanocomposites Research and Applications

I.S. GUNES¹, **G.A. JIMENEZ²**, **F. CAO³**, **S.C. JANA⁴**, ¹Currently at 3M, Minneapolis, USA; ²Currently at National University of Costa Rica; ³Currently at Lubrizol, Brecksville, USA; ⁴Department of Polymer Engineering, University of Akron, Akron, OH, USA

Shape memory polymers find numerous applications as surgical sutures, stents and implants, breathable fabrics, packaging materials, and polymeric smart antenna. This talk aims to present a review of recent progress made on shape memory polymers (SMPs), particularly on the development of shape memory polymer nanocomposites. A major drawback of shape memory polymers is low recovery stress, of the order of 10 MPa, compared to 500 MPa for shape memory metal alloys and ceramics. This limits the effectiveness of shape memory polymers in applications requiring shape recovery under constraining stress. In this paper, we exploit nanotechnology to obtain large enhancements in shape recovery stress from shape memory polymer nanocomposites. We capitalize on a set of heuristics that has emerged as the field of polymer nanocomposites matured substantially in last decades. It is now well-established that small quantities - often less than 10 wt% - of nanoscopic inorganic fillers are combined with host polymers to obtain large enhancements in mechanical and thermal properties. This paper evaluates the potential of several nanofillers on enhancement of shape recovery stress of shape memory polyurethanes.

A-15.6:IL02 Laminated Shape Memory Elastomeric Composites

E.D. RODRIGUEZ¹, **D.C. WEED²**, **P.T. MATHER²**, ¹Mechanical and Aerospace Engineering, Syracuse University; ²Biomedical and Chemical Engineering, Syracuse University, Syracuse, NY, USA

Recently, we reported on shape memory elastomeric composites (SMEC) based on thermoplastic nanofibers embedded in a crosslinked elastomeric matrix. In this report, we have prepared anisotropic films of the same materials by orienting the nanofibers prior to matrix incorporation. Moreover, anisotropic shape memory elastomeric composites (A-SMEC) were fabricated using a three step process by electrospinning nanofibers, infiltrating with a rubber matrix, and crosslinking. Mechanical testing was conducted to investigate the change in Young's modulus, strength, and strain-to-failure as functions of fiber orientation direction. Shape memory characterization was conducted, revealing that shape fixing (decreased substantially as the fiber orientation approached the transverse direction. Near complete shape recovery (R_r) for all composites tested, regardless of fiber orientation, was observed. In a second phase of the research, we have prepared laminated shape memory elastomeric composites (L-SMEC) in which stacks of A-SMEC plies are assembled to yield tailored SMPs with quite unique characteristics, including chiral response. We will reveal a number of new shape memory phenomena observed for the L-SMEC materials and suggest applications.

A-15.6:IL03 Multifunctional Shape-memory Polymers

A. LENDLEIN, Center for Biomaterial Development and Berlin-Brandenburg Center for Regenerative Therapies, Institute of Polymer Research, Helmholtz-Zentrum Geesthacht, Teltow, Germany

Shape-memory polymers are an example for converting stimuli-responsive effects on the molecular/morphological level into macroscopic movement. They can be designed to be histo-compatible and biodegradable resulting in multifunctional materials. Potential biomedical applications have been described, as these demand different combinations of properties and functionalities of the applied biomaterials. Polymer systems are developed, which allow tailoring of macroscopic properties by only small changes in molecular parameters. Non-contact triggering of shape changes was realized by incorporating magnetic nanoparticles in shape-memory polymers. These compounds are heated inductively when they are submitted to alternating magnetic fields. Furthermore, triple-shape materials are introduced, which are able to perform two subsequent shape changes. Finally, the temperature-memory polymers and shape-memory polymers, whose apparent switching temperatures can be magnetically adjusted, are presented.

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Med Devic (2010) 7,357; J. Zotzmann et al, *Adv Funct Mater* (2010) 20, 3583; J. Zotzmann, et al, *Adv Mater* (2010) 22, 3424; U. Narendra Kumar et al, *Adv Mater* (2011) 23, 4058; K. Kratz et al, *Adv Mater* (2011) 23, 4058.

A-15.6:IL04 Mechanically Assisted Photolithography

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Mechanophotopatterning (MPP) on a covalent adaptable elastomeric network enables the fabrication of well-defined topographical surface features or textures by exposure to light without the need for solvents, molding, or physical contact¹. MPP is a unique patterning approach whereby deformation is applied to an elastomeric material capable of photoinduced structural modification to alter its equilibrium geometry. This material responds to MPP by continuously and locally deforming via polymer network connectivity rearrangement, enabling three-dimensional control of its geometry. Unlike conventional photolithographic approaches, MPP forgoes any wet chemistry or surface deposition/modification processing and simplifies multi-tiered feature fabrication. Furthermore, in contrast with mechanically assisted patterning techniques that utilize buckling phenomena, MPP on a photoresponsive elastomer allows an arbitrary-sized and designed feature to be written into the material multiple times, while also being able to change the overall shape of the material.

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A-15.6:LO5 Magnetic Field Induced Formation of Magnetic Wires into Thin Elastic Membranes with Controlled Properties

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We present the formation of magnetic polymeric membranes containing periodically aligned magnetic wires. The membranes are formed by spin coating a homogeneous solution containing an elastomeric polymer and colloidal super-paramagnetic nanoparticles on glass substrates. The application of a homogeneous magnetic field during the curing of the polymer, results in the alignment of the nanoparticles parallel to the magnetic lines forming thus wire like structures. The length and the width of the wires and the periodicity between them can be effectively controlled by the external magnetic field, as revealed by detailed microscopy studies. The study of the magnetization of the structured membranes using SQUID, showed a strong directional dependence with the wires, revealing anisotropic magnetic properties with the degree of anisotropy to depend on their dimensions and period. Monte Carlo simulations confirmed the experimental results revealing thus the mechanism of the wires formation. In this way the ability to manipulate the distribution of wires by magnetic field into the polymeric matrix offers significant prospects for the improvement of the properties of this novel class of materials.

A-15.6:IL06 Mechanically Adaptive Polymer Nanocomposites for Biomedical Implants and other Applications

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Motivated by the objective to create mechanically adaptive implants, which are sufficiently rigid to allow for implantation, but soften thereafter to match the stiffness of their environment, we developed a new approach to chemically-responsive, mechanically adaptive polymer nanocomposites. These materials are inspired by the architecture and function of the skin of sea cucumbers, which can change its stiffness "on command". Our artificial nanocomposites adopt the architecture of this adaptive tissue and are comprised of low-modulus polymer matrices and rigid cellulose nanofibers. The non-covalent interactions between the percolating cellulose nanofibers can be mediated by exposure to water. Through modest swelling under physiological conditions the reinforcing cellulose network is disrupted, resulting in a dramatic modulus reduction. A detailed understanding for the structure-property relationships in these materials is being developed and the current

understanding will be discussed. The new materials were used to probe the hypothesis that the formation of a glial scar, which has been identified as a problem for cortical interfacing, is related to the mechanical mismatch between the soft brain tissue and rigid cortical implants.

A-15.6:L07 Thermally-Induced Shape-Memory Effect of Nanocomposites with Poly(omega-pentadecalactone) Switching Segments Under Constant Stress

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Shape-memory polymers (SMP) are stimuli-responsive materials, which change their shape upon application of an external stimulus such as heat or light.¹ Incorporation of magnetite nanoparticle (mNP) in the SMP matrix enables remote actuation of the shape-memory effect by inductive heating.²⁻³ Here, we report on the thermally-induced SMP nanocomposites based on poly(ω -pentadecalactone) and mNP actuated under constant stress conditions. The shape-memory properties of the nanocomposites were quantified after a one step programming procedure in cyclic thermomechanical experiments, in which the stress was held constant during cyclic temperature variation. Here, nanocomposites showed crystallization induced elongation (CIE) and melting-induced contraction (MIC). A restraining effect of the mNP on the chain mobility, which resulted in a decreased CIE with increasing mNP content was observed. This enables SMPs, in which the extent of elongation or contraction caused by temperature change under stress can be controlled by the mNP content.

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Session A-15.7

Applications of Actively Moving Polymers

A-15.7:IL01 Shape Memory Polymers for Biomedical Applications

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Our experience with shape memory polymers (SMP) began with a project to develop an embolic coil release actuator in 1996. This was the first known SMP device to enter human trials. Recent progress with the SMP devices include multiple device applications (stroke treatments, stents, other interventional devices), functional animal studies, synthesis and characterization of new SMP materials, in vivo and in vitro biocompatibility studies and device-tissue interactions for the laser, resistive, or magnetic-field activated actuators. The CIMTEC 2012 paper will highlight our most recent work in SMPs and SMP devices: foam scaffolds for treating aneurysms, healing pathology of implanted foams, clotting dynamics in the foam, new SMP materials, and modeling SMP devices.

A-15.7:IL02 Synthesis of Shape Memory Polymers for Structural Applications

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Epoxy resins are not widely used as shape memory polymers (SMP's) even though their intrinsically advantageous physical properties and ease of processing are conducive to making them promising base materials for highly demanding shape memory (SM) applications. Although proven to show excellent shape memory effect, the main disadvantage of SM epoxies resides in their inherently low ultimate strains, which translates to low deformation strains compared to those reachable by conventional SMP's. Recently developed SM epoxies are discussed with an emphasis on synthetic and engineering routes usable for improving their deformability range, strength while maintaining their intrinsically good thermal and chemical stability, their high thermal transition (i.e., SM transformation temperature), and their excellent SM properties. The shape memory behavior of these epoxies is therefore discussed in lights of their composition, structure and shape memory 'programming'.

A-15.7:L03 Soft Microorigami: Stimuli-responsive Self-folding Polymer Films

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Asymmetry is intrinsic to natural systems and is widely used by living organisms for efficient adaptation, mimicry and movement. Polymer bilayers are the example of synthetic asymmetric systems, which are able to generate macroscopic motion and fold by forming different 3D objects such as tubes and capsules. Similar to bimetal films, the polymer bilayer consists of two substances with different swelling properties. One polymer is non-swellaable and hydrophobic. Another polymer is water-swellaable hydrogel. The folding, which might occur in response to temperature or pH, is caused by swelling of the hydrogel layer. The formed tubes and capsules can be manipulated using magnetic field. Reversible folding and unfolding of the polymer films is applied for reversible capture and release of cells in response to change of temperature and other signals. This novel biomimetic approach can be used for controlled encapsulation and release of microparticles, cells and drugs as well as fabrication of 3D scaffolds for tissue engineering.

A-15.7:IL04 Shape-Memory Polymers as Drug Carrier - Points to be considered

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Novel polymer matrices are demanded in modern medicine such as minimally-invasive procedures, which require implants that can be inserted in a compact shape and acquire their functional shape on demand. Drug release could help to provide the required dose only locally, e.g., to treat infections or to attract specific cells. A well controlled degradation of implants may be desired to allow for a functional tissue regeneration. Degradable shape-memory polymer networks (SMP) exhibit the capability for active movement upon exposition to stimuli such as heat, can incorporate drugs, and can degrade hydrolytically. For combining these capabilities resulting in a multifunctional material, independence of the functionalities has to be shown. Based on examples of semi-crystalline and amorphous copolyester SMP networks, the associated challenges are reported including the effect of drug loading on SMP functionality and degradability as well as the effect of network breakdown on material properties/functions including drug release¹⁻³.

1. Wischke et al, J. Contr. Rel. 138: 243-250 2009; 2. Wischke et al, Macromol. Biosci. 10: 1063-1072 2010; 3. Wischke et al, Eur. J. Pharm. Sci. 41: 136-147 2010

A-15.7:L05 Electrostrictor with Monolithically Integrated CMOS TFT Control

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We present an electrostrictive polymer unimorph controllable with low voltage through an integrated CMOS TFT control system. The electrostrictor material can reach a strain up to 4% with an applied electric field of 150V/μm. We have actuated the device by applying a voltage of 400V to the control system, and can actuate the control with 30V switching. The electrostrictor material was used both as the substrate for the transistors and as the dielectric layer for the control circuitry. The electroactive polymer used has a thickness of 5μm and a relative dielectric constant of 45. The transistors show good performance with mobility of 0.1 cm²/(V*s), and Ion/Ioff=100-1000 (primarily due to gate leakage). The NFET (F16CuPc) had a Vt of approximately 6V, and the PFET (pentacene) had a Vt of approximately -3 V. Using this architecture, we were successfully able to repeatedly actuate a unimorph bender under 30V control, and can scale this architecture to larger systems with more controlled sites.

A-15.7:L06 Ethanol Induced Shape Recovery and Swelling in Poly(methyl methacrylate) and Application in Fabrication of Microlens Array

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Ethanol transportation in pre-deformed poly(methyl methacrylate) (PMMA) is systematically investigated. Two different phenomena occur simultaneously during this process. One is shape recovery, which results from ethanol induced softening and plasticization of PMMA. The other

is swelling, which results from ethanol induced molecular relaxation. Based on this study, a new surface patterning method is proposed to fabricate PMMA microlens arrays in a simple and cost-effective manner.

A-15.7:L07 Self-softening, Self-positioning 3D Flexible Bioelectronics Enabled by Shape Memory Polymers

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Shape memory polymers (SMPs) are shape-changing, stiffness-changing, smart materials that recover imparted strains with tuned recoverable forces at specific, tailorable temperatures. SMPs are utilized as substrates for a new generation of 3D implantable flexible electronics in which devices can be manufactured on a temporarily flat metastable SMP surface. Upon heating the devices above the glass transition temperature (Tg) of the SMP substrate, the devices recover into a predefined 3D shape. To accommodate this shape change, local deformations cannot exceed the strain capacity of the embedded electrodes made from among other materials, gold and chrome, carbon nanotubes (CNTs), and aluminum. For instance, 300 nm gold electrodes with a 50 nm chrome adhesion layer on acrylic SMPs already show permanent structural damage below strains of 15% while the underlying substrate can be tuned to show recoverable strains of 800%. We use photolithography to pattern specific electrode geometries on SMPs to allow for the fabrication of high-strain capacity multi-electrode arrays, cortical brain probes, RFID antennas and cochlear implant electrodes with increased biocompatibility, tailorable mechanical properties, and the ability to respond controllably to a wide variety of stimuli.

A-15.7:L08 Multi-functional Shape-memory Polymers and their Composites

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Shape-memory polymers undergo significant macroscopic deformation upon the application of an external stimulus (e.g., heat, electricity, light, magnetism, solvent and even a change in pH value). These unique characteristics enable Shape-memory polymers to be used in a myriad of fields, including clothing manufacturing, automobile engineering, medical treatment, and aerospace engineering. Shape-memory polymers can be applied in smart textiles and apparels, intelligent medical instruments and auxiliaries, optical reflectors, intravascular delivery system, self-disassembling mobile phones, shape-memory toys, and automobile actuators and many more. This paper presents some recent progress of multi-functional shape memory polymer smart materials and their applications, for aerospace engineering such as space deployable structures and morphing aircraft, which has highlighted the need for development of these materials. A detailed overview of development in these smart materials, of which the undergoing and future applications are used in adaptive structures and active control, is presented. The paper concludes with a short discussion for multi-functional shape memory polymer smart materials and their composites that are expected to extend the range of development and applications available to the related researches and engineers.

Poster Presentations

A-15:P80 Epoxy Based Shape Memory Polymer Composites with Different Textile Reinforcements

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Effects of different reinforcements on the shape memory behaviour of an amine hardened epoxy resin were investigated. As reinforcing materials textile fabrics and plies with unidirectional fiber alignment were used. The reinforcing structures contained glass, carbon and natural fibres. The shape memory behaviour (i.e. shape fixing, recovery stress) of the reinforced epoxy composites was mostly characterized by dynamic mechanical thermal analysis. The project was aimed at contributing to deduce a straightforward reinforcing strategy to enhance the recovery stress of epoxy-base shape memory polymer composites.

A-15:P83 Tailored One-way and Two-way Shape Memory Response of Poly(e-caprolactone)-based Systems for Biomedical Applications

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Towards a potential employ of shape memory polymers in applications, such as smart medical devices and minimally invasive surgery implants, biomaterials studies have focused the attention on biodegradable polymers, like poly(e-caprolactone) (PCL). These researches are typically

aimed at developing materials with tailored properties, such as the activation of the shape memory on desired temperature regions, typically slightly above human body temperature. A series of crosslinked PCL materials were obtained starting from linear, three- and four-arm star PCL functionalized with methacrylate end-groups, allowing to tune the melting temperature (T_m) on a range between 36 and 55 °C. After deforming the specimens at 50% above T_m , the materials are seen to fully restore their original shape by heating them on a narrow region close to T_m ; further, when the shape memory effect is triggered under fixed strain conditions, the materials are able to exert stress on a range between 0.2 and 7 MPa. The materials also display two-way shape memory features, reversibly moving between two shapes when cooled and heated under a fixed load. Finally, to investigate the application of the PCL materials as self-expandable stent, shape memory experiments are currently carried out on tubular specimens.

SYMPOSIUM B

State-of-the-art Research and Application of SMAs Technologies

Oral Presentations

Session B-1 Materials

B-1:IL01 Development of Ni-free Beta-Titanium Shape Memory Alloys

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The Ti-Ni alloys have been successfully applied as biomaterials such as orthodontic arch wires, guide wires and stents in addition to many engineering applications. However, it has been pointed out that pure Ni is a toxic element and causes Ni-hypersensitivity. Although the Ti-Ni alloys are considered as safe in the human body based on experience and scientific consideration, in order to solve the psychological problem on the risk of Ni-hypersensitivity, Ni-free β -Ti SM and SE alloys have been recently developed. There have been many attempts to improve the superelastic properties of β -Ti alloys. Low temperature annealing and aging have been shown to be effective in increasing the critical stress for slip through sub-grain structural refinement and precipitation hardening. Alloying is another useful method to increase the critical stress for plastic deformation. Among various alloying elements the most effective for increasing the critical stress for plastic deformation are interstitial alloying elements such as oxygen and nitrogen. In this presentation, the development of β -Ti SM and SE alloys is reviewed including the basic characteristics such as the martensitic transformation and shape memory properties in addition to recent research results of these alloys.

B-1:IL02 Nanostructured Shape Memory Alloys: Processing, Martensitic Phase Transformations, Properties

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Grain size at the nanoscale can strongly affect the unique thermomechanical properties of shape memory alloys that are based on a martensitic phase transformation. With decreasing grain size the martensitic transformation is hindered; thermally and stress induced transformations might be suppressed completely in grains smaller than a corresponding critical value. On the other hand, the grain size might be optimized to achieve a combination of tailored functional properties and enhanced mechanical strength. Bulk shape memory alloys with grain sizes in the range of several tens to several hundreds of nanometer were processed by methods of severe plastic deformation followed by annealing. The studied nanomaterials include NiTi shape memory alloys, Ni-Ti-Hf high temperature shape memory alloys and Ni-Mn-Ga high temperature ferromagnetic shape memory alloys. Different pathways of the evolution of the small grains that might involve the formation of an intermediate amorphous phase were encountered. The phase stability and the martensitic morphology of the small grains were systematically investigated. Considering a size dependent energy barrier opposing the transformation the results were modeled using the general thermodynamic framework of martensitic phase transformations.

B-1:IL03 High Temperature Shape Memory Alloys

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Since decades ago large research efforts have been devoted to develop SMAs with stable behaviour above 150-200 °C, being of great interest for the automotive, aerospace and energy industries, among others. In the first part of the presentation, the main achievements in different alloy systems will be reviewed, like Cu-Al-Ni-based alloys, ternary Ni-Ti-X (X = Pd, Pt, Hf, Zr) and other systems with ultra-high transformation temperatures (Zr- and Ru-based alloys). The second part will be devoted to the author's recent work on ferromagnetic SMAs, like Ni-Mn-Ga, Ni-Fe-Ga and Co-Ni-Ga. These systems have been worldwide intensively studied for their capabilities in magnetic actuation, but some alloy compositions exhibit a reproducible transformation at elevated temperatures (up to ~620K), which allows to consider them as new and promising HTSMAs. For instance, compositions around Ni₅₁Mn₃₃Ga₁₆ at%, transforming at ~580K, present an excellent stability upon ageing in austenite. Ni-Fe-Ga and Co-Ni-Ga alloys exhibit perfect superelasticity in a wide temperature interval reaching 720K, and a very high strength (stress-induced transformation above 1GPa). Current investigations of superelasticity and shape memory (thermal actuation under stress) in single and polycrystals will be presented.

B-1:IL05 New Trends in Research and Applications of SMA Technologies

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SMA's have found applications in different technologies, but made greatest impact in medicine. Present report reviews modern trends in research and application of SMA's. By method of severe plastic deformation it have appeared possible to obtain nanostructured NiTi which is not only stronger than coarse grained, but has improved functional properties. Thus, a medical implant can be made stronger and thinner at the same time. This can create critical advantages in a number of clinical cases. For example, dental implant can be installed into thin jaw bones < 1 mm. By applying the techniques of modern nanotechnology, the minimal dimensions of machined metal parts can be made < 1 micron. It is demonstrated the design of nanotweezers made of the TiNiCu SMA with overall size 10 microns, with size of manipulated objects, for example CNT being 1000-10 nm. (See on the web: www.snmwsm.org/IL/micropincer.html http://www.youtube.com/watch?v=pEGL_lCxDs). Using nanotools with SME it is possible to solve such fundamental issues in biology as single cell or viruses manipulation, though magnetic control of ferromagnetic SMA at constant temperature would be preferable. The experiments on manifestation of SME in microsamples of NiMnGa and NiMnInCo ferromagnetic SMA's are described.

B-1:IL06 Development of Ni- and Fe-based Magnetic Shape Memory Alloys

R. KAINUMA, Department of Material Science, Graduate School of Engineering, Tohoku University, Sendai, Japan

In the past decade, many kinds of Ni-based magnetic shape memory alloys, such as Ni-Fe-Ga¹, Ni-Co-Mn-In², besides the Ni-Mn-Ga alloy have been found by some research groups including us. Especially, the Ni-Co-Mn-In shows a unique transformation from ferromagnetic austenite to paramagnetic martensite phase and the magnetic-field-induced shape memory effect (SME), namely the metamagnetic SME, has been confirmed. On the other hand, our research group has very recently reported two different kinds of new magnetic shape memory alloys in ferrous alloy systems, Fe-Ni-Co-Al-Ta³ and Fe-Mn-Al-Ni⁴. The Fe-Ni-Co-Al-Ta alloy with the transformation from fcc to bcc martensite shows a huge superelastic (SE) strain over 14%, and the Fe-Mn-Al-Ni alloy transforming from bcc to fcc martensite exhibits a unique SE property in which the SE stress is almost independent of temperature. In the presentation, characteristic features of magnetic, martensitic and mechanical properties for these advanced Ni- and Fe-based magnetic shape memory alloys will be reviewed.

1. K. Oikawa et al, *Appl. Phys. Lett.*, 81 (2002) 5201; 2. R. Kainuma et al, *Nature*, 439 (2006) 957; 3. Y. Tanaka et al, *Science*, 327 (2010) 1488; 4. T. Omori et al, *Science*, 333 (2011) 68.

B-1:IL07 Magnetostructural Transition Related Multifunctionality in Martensitic Heuslers

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The strong coupling of the lattice and magnetic degrees of freedom in martensitic Heusler alloys is the cause of a variety of effects such as magnetic shape memory, magnetocaloric effects, giant magneto-resistance, exchange bias, etc., which are currently being extensively investigated. Among these, magnetic shape memory gives rise to large recoverable strains when a magnetic field is applied and is of particular interest for actuator applications. Large strains (~10%) can be induced by a magnetic field within the martensitic state when high twin mobility is present. Large strains can also be induced when the magnetic field, applied in the martensitic state, causes a reverse transformation to the austenitic state. This occurs when the field can lead to a strong shift of the martensitic transformation temperature. We discuss here the various types of strain in diverse martensitic Heusler systems probed by microscopy, magnetization and neutron diffraction.

B-1:L08 Giant Effects Under High Pressure and High Magnetic Field in Co- and In- Doped NiMnGa Multifunctional Alloys

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Ni₂MnGa ferromagnetic shape memory alloys have drawn a lot of interest for their multifunctional properties due to the occurrence of a martensitic transformation (MT) and ferromagnetic states. We have recently shown that by Co-doping Mn-rich Ni₂MnGa alloys it is possible to obtain a reverse MT between a paramagnetic low temperature phase and a ferromagnetic high temperature one. The magnetization jump between the two phases increases and consequently the possibility to drive the martensitic transformation temperature by a magnetic field is highly enhanced. In the present paper we show that Co-doping is also very effective in increasing the sensitivity of the MT to the applied pressure. A possible explanation to such behavior is related to the huge volume difference between the parent and product phases that is greatly enhanced by Co and is higher than any other NiMnY Heusler alloy are found (Y being a IIIa-Va element). Recently performed magnetostriction measurements in magnetic fields up to 30T confirmed the remarkable structural ($\Delta V/V$) and magnetic (dM/dH) changes related to the MT. Finally, we show how the additional doping of In further improves the aforementioned functional properties, pushing these materials among the most promising candidates for future applications.

B-1:L09 Making Smart Materials Smarter

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Continued advances in shape memory alloys (SMAs) have facilitated their implementation in countless applications including aerospace, automotive, medical and micro-electromechanical systems (MEMS) devices. The ability of SMAs to 'remember' a shape has largely accounted for their popularity and classification as smart materials. The underlying mechanism responsible for the shape memory effect is a reversible thermo-mechanical diffusionless phase transformation. SMAs have been largely limited to 'remembering' a single shape, which has severely limited their application. The current work details how binary NiTi (Nitinol) alloys are made 'smarter' by locally altering phase transformation characteristics. This was achieved by implementing a high power density energy source to locally alter microstructure. Phase characterization facilitated using DSC, XRD and TEM analysis confirmed locally altered transformation temperatures while revealing metallurgical changes. Proof of concept will be demonstrated by embedding additional memories into a monolithic NiTi alloy. Consequently, a novel processing method, called the Multiple Memory Material (MMM) technology was developed.

B-1:L11 Implications of Twinning Kinetics on the Dynamic Magneto-mechanical Response in NiMnGa

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FSMA are a promising family of actuating materials, due to their ability to undergo large magneto-mechanical induced strains, at potentially high rates. Actuation capabilities are determined by the dynamics of twinning reorientation, which is the underlying mechanism responsible for these large strains. Quantitatively, twinning dynamics are described by a fundamental kinetic relation between the applied driving force and the resulted velocity of an individual twin wall. Recently, we quantitatively extracted this relation in FSMA NiMnGa, revealing two distinct kinetic laws for different ranges of the driving force. At velocities lower than about 0.3 m/s, twin motion is a thermally activated process, controlled by few nano-scale properties of the twin wall and by the presence of defects. At higher velocities, twin wall motion is dictated mainly by the crystal's viscosity. Identification of these different governing material parameters and their origins is important for crystal development and optimization. For example, our analysis indicates that the quasi static "twinning stress", commonly used for characterizing the easiness of twin motion in FSMA is relevant only for actuation rates lower than 1 Hz, while at higher frequencies different parameters must be considered.

B-1:L12 From Dual-shape/Temperature Memory Effect to Triple-shape Memory Effect in NiTi Shape Memory Alloys

W.M. HUANG, C. TANG, C.C. WANG, H. PURNAWALI, Nanyang Technological University, Singapore

Triple-shape memory effect (SME), i.e., recovering the original shape through one intermediate shape upon heating, has been demonstrated as an intrinsic feature of thermo-responsive shape memory polymers (SMPs), but yet been achieved in shape memory alloys (SMAs). In this paper, we present two programming approaches to realize the triple-SME in NiTi SMAs. In both approaches, the deformation is uniform throughout the whole length of samples without involving any permanent change in material properties. The requirements/conditions for this phenomenon and the underlying mechanisms are presented, together with experimental verifications. As revealed, with this technique, now we are able to achieve step-by-step motion control in SMAs.

B-1:L13 Alloy Design and Superelasticity in Fe-Mn-Al-Ni Alloy

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Recently, we have reported that Fe-Mn-Al-Ni alloy shows the martensitic transformation from the bcc phase to the fcc phase and superelasticity with small temperature dependence of the critical stress for the martensitic transformation¹. In this paper, the alloy design from the view point of phase stability and superelasticity will be presented. The martensitic transformation in Fe-base alloys is normally from the fcc phase to the bct or bcc phase, but it is estimated from thermodynamic analysis that the bcc phase can martensitically transform to the fcc phase under condition that the stabilization of the bcc phase due to its ferromagnetism is depressed by addition of Mn in Fe-X (X: ferrite stabilizing element) systems. Actually, Fe-Mn-Al alloys with about 30-40%Mn exhibit the non-thermoelastic martensitic transformation from the bcc phase to the fcc phase¹. Furthermore, it was found that the martensitic transformation changes from non-thermoelastic to thermoelastic by addition of Ni because of the formation of fine NiAl-B2 precipitates². Some unique transformation properties in the Fe-Mn-Al-Ni alloys, such as the small temperature dependence of superelastic stress will be discussed.

1. K. Ando *et al*, *APL* 95 (2009) 212504; 2. T. Omori *et al*, *Science* 333 (2011) 68.

Session B-2

Phase Transformation and Microstructure

B-2:IL01 Microstructure, Mechanism and Mesoscopic Modeling of Shape Memory Alloys

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Two perspectives on the modeling of shape memory alloys will be presented. The first one involves a free energy based on the symmetry-adapted strain tensor components as order parameter for the phase transformation. A crystal group-subgroup relationship between the parent and product phase is required in addition to the elastic compatibility constraint. The latter leads to a long-range elastic interaction between the order parameter strains and determines the type of microstructure that is likely to emerge during the phase transformation. Coupling of strain to other functionalities such as magnetism (e.g. in magnetic shape memory alloys) will be considered. The second perspective entails the mechanism of the shape memory phenomenon. In addition to invoking the group-subgroup relationship, an analysis of orientational relationship between the parent and product crystal structures as well as reversible twinning modes will be presented. In particular, it will be critically assessed as to why some alloys (e.g. NiTi, CuAlNi) exhibit good shape memory characteristics while others do not, e.g. ferrous alloys. The intent is to demonstrate that most of the shape memory alloys can be understood consistently within a unified framework.

B-2:IL02 Mechanisms of Twinning and Twin Structures in Ni-Mn-Ga

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Deformation twinning is the lattice-invariant deformation conjunct to martensitic transformations of shape memory alloys. Inter- and intra-variant boundaries form between martensite variants with differently and identically oriented Bain strains respectively. The triple lines of twins with inter- and intra-variant boundaries host disclinations, which have a rotational displacement field. Using TEM imaging, we characterize the disclination structures of inter- and intra-variant boundaries in tetragonal non-modulated martensite of Ni-Mn-Ga. At both boundaries, the disclination arrays of twin stacks impose an ancillary tilt of a few degrees. Inter-variant boundaries are sharp and parallel to {011}. Very thin twins reach these boundaries, some of which taper away from the interface, giving rise to a coarser twin structure in the bulk. At intra-variant boundaries, symmetry-related deformation twins impinge: such boundaries exhibit sub-micron {101} serrations, with overall orientation parallel to {100}. The disclinations mutually screen their long-range strain fields. Bend contours in TEM images reveal the interfacial strain fields. Their periodicity corresponds to the coarser twin arrangement at inter-variant boundaries and the wave length of serrations at intra-variant boundaries.

B-2:IL03 Magnetic Shape Memory Materials: Martensitic Structures and Transformation Behaviour

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Multifunctional ferromagnetic shape memory Heusler Ni-Mn-Ga alloys are frequently characterized by incommensurate structural modulation in martensitic phases. In particular, modulated martensitic phases, showing the higher magnetic field induced strain (MFIS) performance, are the most promising candidates for technological applications. Depending on the alloy composition this periodic structural distortion, consisting of shuffling of atomic layers along defined crystallographic directions, characterizes the martensitic transformation. So far, different types of modulated martensitic structures have been observed and classified depending upon the corresponding ideal nM superstructure. Recently, structural studies based on a new approach provided a clear crystallographic description of such incommensurate distorted martensites. On the other hand martensitic transformation shows a complex behaviour essentially constituted by two levels: lattice deformation with structural modulation and occurrence of a particular microstructure associated to multi-twinning. The detailed knowledge of the martensitic crystal structures and corresponding microstructure actually allows to clarify some fundamental aspects related to the MFIS effect.

B-2:IL04 TEM Analyses of Various Domain Structures in Shape Memory Alloys

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This paper reports on our recent transmission electron microscopy (TEM) studies about complex microstructures observed in shape-memory alloys and compounds. Lorentz microscopy observations revealed the unexpectedly narrow magnetic domain walls observed at the positions of antiphase boundaries (APB) in a Ni₅₀Mn₂₅Al_{12.5}Ga_{12.5} alloy: the observations estimated the wall width at 12 nm, which was substantially smaller than the width at the APB-free position of 48 nm. The result was reasonably explained by the depression of ferromagnetic interaction in the neighborhood of APBs subjected to a chemical disorder. We also mention about the anomalous magnetic phase transformation in a spinel-type compound MnV₂O₄, which exhibits a significant magnetostriction due to the twin boundary motions. Although this compound formed well-defined magnetic domains due to long-range ferrimagnetic order, the magnetic information was dramatically reduced below 42 K. The results provide useful information for understanding of the magnetic anomalies, such as the glassy behavior reported in this temperature range.

These studies were conducted in collaborations with Prof. R. Kainuma, Prof. T. Arima, and Dr. A. Tonomura.

B-2:IL05 Self-accommodation of B19' Martensite in Ti-Ni Shape Memory Alloys

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The microstructure of the martensite in shape memory alloys is characterized by the combination of multiple habit plane variants (HPVs) to minimize the elastic strain energy upon transformation, which is so-called self-accommodation (SA). In the present study, the SA morphology of the B19' martensite is systematically investigated. There are twelve pairs of the minimum SA unit consisting of two HPVs with V-shaped morphology connected to a $\{-1-11\}$ B19' Type-I variant accommodation twin. It is found that an ideal SA morphology consists of three V-shaped units, i.e., a total of six HPVs, clustered around one of the $\{111\}$ B2 traces with hexagonal shape. Triangular and rhombic SA morphologies are also observed. It is revealed that there are four kinds of characteristic HPVs interface to complete the SA morphologies. The proposed models are rationalized by the phenomenological theory of martensite crystallography and the geometrically nonlinear theory. Three dimensional SA morphologies are also discussed on the basis of a novel scanning electron microscopy technique.

B-2:IL06 Elasticity and Damping Characteristics of SMA Single Crystals, Polycrystals and Thin Films

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We discuss the applicability ultrasonic methods for precise determination of elasticity and damping characteristics of ferroelastics in the form of single crystals, polycrystalline materials and thin films. Particular behaviors of SMAs as are strong elastic anisotropy of single crystals, anomalous temperature dependence of elastic coefficients, their change with magnetic field (ferromagnetic SMAs) natural tendency of martensitic (low-symmetry) phase to form twinned structures as well as texture and fine grains structure of polycrystalline materials induced by technological processing are taken into account to the analysis of mechanical properties of SMAs. It is shown that by using a modal resonant ultrasound spectroscopy (RUS), the fully anisotropic elastic tensor (21 independent coefficients) of textured and micro-structured polycrystals can be determined, from which the symmetry class can be estimated with a search method of mirrors in the elastic tensor. The close correlation between the elastic anisotropy and the spatial arrangement of the grain boundaries in the examined materials is evident. The modified RUS and surface wave propagation (SAW) methods are developed for evaluation of elasticity of thin surface layers. The pros and cons of both approaches are summarized.

B-2:IL07 Isothermal Nature of Martensitic Transformations in Some SMAs

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Martensitic transformations have been classified into two groups, athermal and isothermal ones, from the view point of kinetics. Recently, we found that an isothermal transformation changes to an athermal one and vice versa by application of external fields such as magnetic field and hydrostatic pressure. This finding suggests that any martensitic transformation is intrinsically an isothermal one, but appears to be an athermal one in many cases because of undetectably long or short incubation time. In this presentation, we will demonstrate several examples of isothermal nature observed in alloys which are so far considered to exhibit an athermal transformation. That is, we show that thermoelastic transformation in some shape memory alloys (SMAs), such as Cu-Al-Ni, Ni-Co-Mn-In and Ti-Ni-Fe proceed isothermally after some incubation time although each alloy has a so-called martensitic transformation start temperature (M_s) when it is cooled with a constant rate. These results are explained by a statistical thermodynamic model derived by the authors.

B-2:IL08 Twinning in Ni-Mn-Ga Martensites

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Ni-Mn-Ga alloy can show up to 10% strain which is induced by external magnetic field or stress with twinning reorientation mechanism. Macroscopically comprehensive understanding has been obtained for the twin boundary motion, and effecting factors such as twinning morphology, external stress, temperature, and quality of the material. Microscopically the interface structure, and the twinning mechanism, i.e., twinning dislocation nucleation and movement in the atomic scale is still a subject of intensive research. In this paper, the different twinning systems in various martensite structures are outlined and their related crystallography, together with their effect on the material properties are reviewed and discussed.

B-2:IL09 Optimization of Smart Heusler Alloys from First Principles

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The strong structural and magnetic interrelation in ternary X-Y-Z Heusler alloys is responsible for the appearance of magnetostructural phase transitions and related properties. Here, X and Y are transition metal elements and Z is usually an element from the III-V group. In order to discuss the possibilities to optimize the magnetocaloric and magnetic shape-memory effects, we use density functional theory calculations from which the martensitic driving forces can be derived. We find that the electronic contribution arising from the band Jahn-Teller effect is one of the major contribution. The *ab initio* calculations also give a hint of how to design new intermetallics with higher transformations temperatures and higher ductility compared to the prototype alloy system Ni-Mn-Ga. As an example, we discuss the quaternary alloy system Pt-NiMn-Ga with properties very similar compared to Ni-Mn-Ga but with higher maximal eigenstrain of 14% which can be reached in a magnetic field.

B-2:IL10 Highly Mobile Twin Boundary in Ni-Mn-Ga Magnetic Shape Memory Single Crystal

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Magnetic shape memory effect or huge deformation in magnetic field (up to 10% in Ni-Mn-Ga) is mediated by twin boundary motion. Thus the mobility of the boundary is crucial for any application and it determines the efficiency or even the existence of the effect. We investigated mobility of different twin boundaries in modulated 5M martensite of Ni-Mn-Ga in magnetic field. It was speculated that the modulated or adaptive structure is the main reason for the high mobility. We found that extreme high mobility, i.e. movement of twin boundary at external stress below 0.1 MPa or in very low field less than 0.05 T or 500 Oe, can be associated with the twin boundary of Type II. Previously observed lower mobility is connected the most probably with Type I twin boundary. Additionally the temperature dependence of the mobility differs according the type. Type II exhibit rather weak dependence of mobility on temperature whereas the Type I boundary seems to obey exponential increase of twinning stress with decreasing temperature suggesting thermal activation. The reasons for this observed different behaviour is sought and the consequence for applications will be discussed.

B-2:L11 Theoretical Study of Magnetic Properties and Twin Boundary Motion in Heusler Ni-Mn-X Shape Memory Alloys Using First Principles and Monte Carlo Method

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Ferromagnetic Heusler Ni-Mn-X (X=Ga, In, Sn, Sb) alloys and these alloys with addition other elements, for example Fe and Co, have attracted much attention in view of their unique properties such as the shape memory effect, giant magnetocaloric effect, large magnetoresistance and other interesting magnetic properties like a coupled magnetostructural and metamagnetostructural phase transitions¹⁻³. In this work we study by first principles the exchange parameters and density of state of Heusler alloys for different compositions. The

composition dependences of exchange integrals and density of states on Fermi level are obtained. It is shown that on these dependences are peculiarities which agree with ones on the experimental phase diagrams. The obtained ab initio results were used in an microscopic model Hamiltonian for description of magnetic, structural and magnetocaloric properties of Heusler alloys by Monte Carlo method. By the microscopic model and Monte Carlo method we investigated also the twin boundary motion in Ni-Mn-Ga Heusler alloys. It is shown that twin boundary moved at increasing magnetic field.

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B-2:L12 Isothermal Behaviour of the Martensitic Transformation in Ferromagnetic Shape Memory Alloys

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Some ferromagnetic shape memory alloys as Ni-Mn-X (X= In, Sn, Sb) can transform from ferromagnetic austenite to a para-/antiferromagnetic-like martensite. Relaxation phenomena have been found in these first order magnetostructural transformations. Time dependences appear during both direct and reverse transformations in Ni-Mn-In and Ni-Mn-In-Co alloys. DC resistance and AC impedance measurements have shown that their evolution after the interruption of cooling, within the direct martensitic transformation temperature range, follow a logarithmic dependence¹. The same dependence is found in the magnetization vs. temperature cycles at constant field, upon stopping the temperature ramps. The logarithmic kinetics corresponds to the relaxation in a system with a broad distribution of activation energies, as it occurs in the so-called thermal fluctuation magnetic after effect. The slope Z of the logarithmic dependence at different temperatures and fields allow establishing characteristic times (proportional to 1/Z) vs. T and/or field which form pseudo- TTT diagrams with the characteristic C-shape. The above mentioned aspects will be discussed mainly through recent results in Ni-Mn-In and Ni-Mn-In-Co alloys.

1. S. Kustov, I. Golovin, M.L. Corró, E. Cesari, *J. Appl. Phys.* 107 2010 53525.

B-2:L13 Superelastic Behavior in Single Crystals of Cu-Al-Mn Shape Memory Alloy

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Cu-Al-Mn based shape memory alloys (SMAs) are practically attractive because of their excellent ductility and superelasticity. In our previous study, it was found that the Cu-Al-Mn SMA with a coarse grain structure shows an unstable and complicated behavior in the superelastic properties. In this study, to investigate the superelastic behavior in various orientations for single crystals, tensile tests at room temperature were carried out for Cu-17Al-11.4Mn alloy. It was seen that the obtained superelastic strain depends on the crystal orientation, being in good agreement with the calculated value. While the stress hysteresis also shows orientation dependence as expected from the Clausius-Clapeyron relation, that in some particular orientations is abnormally larger than that in the other ones. It was also found from in-situ observation that in the specimens with the large hysteresis multiple martensite variants are always induced during tensile test. This phenomenon can be explained with the Schmid factors of the preferentially induced variants.

B-2:L15 Martensitic Transformation and Shape Memory Effect in TiNi Alloy Subjected to Neutrons Irradiation

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The influence of neutron irradiation on martensitic transformations and shape memory effect in TiNi alloy were studied. Experiments have been carried out in low-temperature helium loop of WWR-M reactor in PNPI RAS. Temperature dependences of resistivity and strain variation in TiNi alloys were measured during the irradiation process directly.

Irradiation of samples by fast neutron was carried out within a wide range of irradiation temperatures (120-450K). It was found that irradiation of TiNi alloy at low-temperature (120-330K) resulted in an increase in resistivity and a decrease in martensitic transformation temperatures. Neutron irradiation at 450K led to a small increase in transformation temperatures and a decrease in resistivity. It was found that these phenomena were due to by two processes - disordering of a TiNi alloy at low temperatures and ordering of alloy at high temperatures. Transformation plasticity and shape memory effect were studied during irradiation by means of a special device. It was found that in spite of strong variation in martensitic transformation kinetics, irradiated alloy kept ability for strain recovery during phase transitions. Moreover, initiation of shape memory effect by neutron irradiation was found in the preliminary deformed TiNi sample.

B-2:L19 Small-scale Transformation Behavior of Pseudoelastic NiTi under Uni- and Multi-axial Loading

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Pseudoelastic NiTi shape memory alloys are finding increasing applications in miniaturised devices. It is important to develop a thorough understanding of the underlying microstructural transformation characteristics at small length scale. In this contribution, we present experimental results from in-situ SEM micro-pillar compression tests and from nanoindentation of single grains of Ti-50.8Ni alloy. The micro-pillar tests reveal unique evolution of stress induced martensite (SIM) plates at a critical transformation stress of ~850 MPa. The deformation behavior is characterized over a wide strain range, covering the pseudoelastic and martensite deformation regime. An attempt is further made to experimentally determine and map in standard stereographic triangles, the orientation dependence of SIM with recourse to nanoindentation using sharp and spherical indenter tips, over a large number of grain orientations. The multi-axial stress state beneath the indenter tip alters the orientation dependence significantly in comparison to that determined experimentally by uniaxial compression of single crystals. Our experimental results are discussed in the light of micromechanical models of correspondent variant pair for SIM, to explain this discrepancy between uni and multi-axial loading.

B-2:L20 Athermal and Isothermal Transformations in Ni-Ti and Ni-Ti-X (X=Fe, Cu) Alloys

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Martensitic transformations (MT) in Ni-Ti alloys are traditionally considered as athermal ones. In this work all possible transformation paths in the Ni-Ti and Ni-Ti-X (X=Fe, Cu) shape memory alloys have been investigated, using resistivity measurements, in order to determine which of them demonstrate isothermal accumulation of martensite/austenite during direct/reverse MTs. The analysis of the experimental data obtained for the entire set of possible transformations in Ni-Ti and Ni-Ti-X alloys shows that all transitions to the B19 $\bar{2}$ phase are isothermal, as well as the reverse B19 $\bar{2}$ -R and B19 $\bar{2}$ -B19 MTs. The direct and reverse B2 \leftrightarrow R and B2 \leftrightarrow B19 MTs are athermal. This regularity is analyzed from the point of view of crystallography and thermodynamics of the MTs. A conclusion is drawn that the isothermal nature of the transitions to/from B19 $\bar{2}$ martensite and athermal nature of all other transitions is related to the easy self accommodation for B2-B19 and B2-R MTs and complex accommodation in the case of the transition to B19 $\bar{2}$ phase. Several experimental observations strongly support the interpretation of the observed isothermal effects in Ni-Ti as due to the diffusionless but thermally activated motion of interfaces during the transformation.

B-2:L21 The Effect of Pressure on Martensitic Phase Transformations

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Stability of the crystal structure is determined by the competition between attractive and repulsive interatomic forces. Using many-body exponential potentials it can be shown that the bcc structure corresponding to

austenitic phases is more stable for low values of the q-parameter characterising the attractive forces for a fixed value of the p-parameter describing the repulsive forces¹. The structural stability can be changed with the acting pressure that may alter the martensitic transformations from the bcc-austenite to a close-packed structure as it can be affected by the internal stresses. The effect of pressure will be examined in a generic model employing many-body potentials and the results will be compared with ab initio calculations for zirconium and sodium representing the structures of hcp and bcc types.

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B-2:L22 Superelasticity in Cu-Al-Mn and Ni-Ti Shape Memory Alloys at Cryogenic Temperature

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Superelasticity in shape memory alloys (SMAs) has been keenly studied for several decades and practically applied in the temperature range near room temperature. On the other hand, there have been less reports on the mechanical properties of SMAs at cryogenic temperatures in spite of their importance in the academic and engineering aspects. In this study, the superelastic behaviors at the temperature ranging from 4.2 to 273 K were investigated in single-crystal Cu-17Al-15Mn (at.%) and polycrystalline Ni-Ti SMAs. In the Cu-17Al-15Mn alloy, the critical stress of stress-induced martensitic transformation decreases with decreasing temperature and its slope becomes gradually smaller at low temperatures of below about 60 K. The molar entropy difference between the parent and martensite phases (ΔS) at 77 K was estimated using the Clausius-Clapeyron equation as being about -0.49 J/(mol·K), which is almost one-third of that at 221 K¹. The superelasticity was also obtained even at 4.2 K. The results in the Ni-Ti SMA will also be presented.

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B-2:L23 Deformation Twinning in Ni₂MnGa

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The ground state of the martensitic phase with composition near Ni₂MnGa is thought to be tetragonal. However, several studies have reported modulated forms with monoclinic symmetry, such as 14M, due to the intrusion of nano-scale twinning. Using TEM imaging, we show that this microstructure results from deformation twinning produced by motion of disconnections with Burgers vector $1/6[100]$ and step height $d(002)$ on the (001) twin plane, where the indexing is referred to the "monoclinic" 2M structure. Kinematical theory is also used to confirm our experimental observation that diffraction patterns vary from being characteristic of the 2M structure at one extreme to the 14M structure at the other extreme, depending on the extent and spatial configuration of the twinning. The origin and extent of twinning is addressed using the topological theory of martensitic transformations. This shows that (001) twinning is the lattice-invariant mode of deformation necessary to accommodate one component of the misfit at the austenite-martensite interface. The other component is accommodated by an array of disconnections whose motion across the interface produces the transformation.

B-2:L24 Magnetic Phase Diagram of NiCoMnGa Metamagnetic Shape Memory Alloy

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Ferromagnetic and metamagnetic shape memory alloys, represented by NiMnGa and Ni(Co)MnIn, have attracted much attention due to their magnetic-field-induced strain and reverse martensitic transformation, respectively. Recently, for Ni(Co)MnIn alloys, the martensitic transformation was reported to be interrupted during field cooling and the two-phases condition is kept up to very low temperatures. This phenomenon was also reported for NiCoMnGa and NiCoMnAl alloys but the reported temperatures of arrested austenite remain below 120 K. Although the addition of Co into NiMnIn was found effective of raising the arrested temperature, an addition of more than 7at% results in precipitation of gamma-fcc phase. Yu et al. have first doped Co into NiMnGa, and Fabbri et al. have also reported the transformation behaviors of Co-doped NiMnGa around Ga=20. However, it is necessary to perform a systematic research for the transformation behaviors of

NiCoMnGa with different Co compositions, including the doping limit of Co. In this research, we report the Ni-_{50-x}Co-_xMn-_{50-y}Ga-_y magnetic phase diagram in large variations of x and y. The detailed results and phase diagrams will be shown in this presentation.

Session B-3

Engineering

B-3:IL01 Thermodynamics of One-way Shape Memory Effect in Alloys under Complex Stress State

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The fundamentals of macroscopic theory rooted in meso-mechanics, employing the notion of phase potentials are discussed, where the coherence energy and the elastic complementary energy are expressed in terms of self-equilibrated stress concentration moduli. On these grounds the specific model is developed. It regards RVE as a three-phase, single-component system and uses the concepts of oriented and self-accommodated martensite compounds. It is conjectured that forward/reverse austenite-martensite phase transitions are initiated at states of unstable phase equilibria - relevant phase potentials being equal. The model reveals yet unknown cross-linking relations between coherence energy coefficients and measurable quantities characterizing SMA material. The sceneries - phase diagrams, of phase equilibria in different subsets of state variables are presented. The special incremental locking rule for the ultimate phase strain is proposed. The model is capable for description of a number of 3D strain/stress, and thermal effects such as pseudoelasticity, hysteresis of quasi-plasticity, fading phase strain effect, quasi-plastic strain history effect and stress recovery under constrained deformation. Some experimental evidence supporting theoretical considerations is presented.

B-3:IL02 Shape Memory Alloys Foams

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Foams and other highly porous metallic materials with cellular structures are known to have many interesting combinations of physical and mechanical properties. That it makes these systems very attractive for both structural and functional applications. Cellular metals can be produced by several methods including liquid infiltration of leachable space holder. In this contribution metal foam production routes will be reviewed with a particular focus on the processing of Cu based shape memory alloys (SMA) by molten metal infiltration of SiO₂ particles. By using this route, highly homogeneous CuZnAl SMA with a spherical open-cell morphologies were manufactured and tested; morphological, calorimetric and thermo-mechanical analyses were reported.

B-3:IL03 Fabrication of Nano-grained Shape Memory Alloys by Severe Plastic Deformation

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Nano-grained TiNi shape memory alloy has been attracting much attention. Reportedly the alloy exhibits the higher shape recovery stress, linear superelasticity and improved fatigue life. Deformation-induced amorphization of TiNi shape memory alloys and post-deformation aging (PDA) lead to the formation of nano-grained structures. This talk introduces the effect of SPD and PDA on microstructure and various performances of processed TiNi. High-pressure torsion deformation produces fully amorphous structures after 10 turns of rotations, and PDA leads to nano-grained samples with grain size ranging from 25 nm to 43 nm. The nano-grained structures stabilize the B2 and R phase with respect to B19' phase. Severe wire drawing produced amorphous/nanocrystalline composite fiber structure. The mechanical properties are characterized by ultra-high tensile strength over 2 GPa and linear superelasticity without stress-plateau. Surface mechanical attrition produced a nano-grained surface layer of ~ 40 micron. Nanoindentation revealed a grain size dependence of elastic modulus, which can be

related to the suppression of martensitic transformation temperatures. The effect of nano-grained structures on biocompatibility will be also presented.

B-3:IL05 Deformation Processes Responsible for Heat Treatment, Shape Setting or Actuation Instability of NiTi

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Superelastic properties and shape of NiTi wires were set using non-conventional electropulse heat treatment. In case of already heat treated superelastic alloy, the shape setting takes place at low temperatures ($< 300\text{ }^{\circ}\text{C}$) only in the martensite phase kept in place by external or internal stress. The process involving simultaneous plastic deformation and reverse martensite to austenite transformation (Low Temperature Shape Setting /LTSS/) leaves the alloy in deformed austenitic state ready for further superelastic cycling. The elevated temperature and stress required to trigger the LTSS process increases with increasing strength of the alloy (cold work, precipitate hardening). Alloy design with respect to LTSS is thus of essential importance not only for the shape setting but also for the cyclic stability of high temperature NiTi (NiTiX) actuators. In the limiting case of cold worked alloy, the LTSS process is suppressed and substituted by dynamic recrystallization of the heavily cold worked microstructure driven mainly by internal stress and energy ($400\text{ }^{\circ}\text{C} - 600\text{ }^{\circ}\text{C}$) which itself provides sufficient plastic deformability at very high strain rates while yielding at the same time nanosized microstructure required for stable superelastic properties of the treated wire.

B-3:IL06 Some Factors Affecting the Shape Recovery Characteristics of NiTi Alloys

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Two-way memory effect is one of the most studied properties of SMAs and one of the least understood properties. Quantitatively, its mechanism is related to the internal stress field associated with dislocations that guides the preferential formation of martensite variants, thus leading to shape change during forward transformation. However, fundamental understanding on the details of the mechanism is missing and there exist various factors that can affect the TWME. In this research, some new experimental observations on the relation between shape memory effect and influencing factors are obtained that provide further insight into the fundamental mechanisms of TWME. Two factors were paid particular attention including initial microstructural condition and the mode of pre-straining. A NiTi bar and a NiTi plate of highly textured and a NiTi ingot of less textured were investigated. Tension, compression, cyclic deformation and constrained thermomechanical cycling were conducted. One-way memory effect, TWME, and transformation characteristics were analyzed with respect to the examined influencing factors. Results show that the shape recovery properties strongly depend on the texture distributions and deformation modes. The mechanism of TWME is further discussed.

B-3:IL07 Mechanical Behaviour of Architected NiTi Materials in Complex Loading

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The aim of the study is to create architected materials constituted of NiTi tubes combining the intrinsic and novel properties of Nickel-Titanium shape memory alloys with purposely engineered topologies. By joining thin-wall tubes by means of electrical resistance welding, we create regular cellular materials. The superelastic behaviour of two architected materials based on identical tubes but with two topologies are modelled using finite element approaches. Large transformations are taken into account or neglected and two constitutive equations are considered; predicted behaviours are compared by simulating complex loading with superelastic loops and subloops. The parameters of the constitutive equations are identified on tensile tests performed on small dog-bone shaped specimens machined from the tubes by spark cutting. The results of the modelling are at last compared with experiments performed on one given architected NiTi material.

B-3:IL08 Modelling of the Coupling Effect Between Phase Transformation and Plastic Gliding on the Thermomechanical Behavior of Iron Based SMA

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A finite element numerical tool adapted to Fe-based SMA structural analysis is proposed. It is based on a developed constitutive model which describes the effect of phase transformation, plastic sliding and their interactions on the thermomechanical behavior. This model is derived from an assumed expression of the Gibbs free energy taking into account, in addition of mechanical and chemical quantities, the non linear interaction related to inter- and intra-granular incompatibilities. Two scalar internal variables are considered to describe phase transformation and plastic sliding effects. Hysteretic and specific behavior of Fe-based SMA during reverse transformation are taken into account by assuming a dissipation expression. Complex thermomechanical loading paths are well described by the proposed model. The numerical tool derived from the implicit resolution of the non linear partial derivative constitutive equations is implemented in the Abaqus finite element code via the UMAT subroutine. After verification tests for homogeneous and heterogeneous thermo-mechanical loading, an example of Fe-based SMA application is studied. It corresponds to an Fe-based SMA tightening system composed of fish plates for crane rails. Obtained results are compared to experimental ones.

B-3:IL09 Nanostructured Ti-Ni SMA: Manufacturing, Microstructure, Static and Fatigue Functional Properties

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Thermomechanical processing of Ti-Ni SMA consisting in cold rolling (CR) and post-deformation annealing (PDA) is used to regulate the alloys' microstructure and functional properties. Low-temperature PDA of the moderately CR alloy results in a polygonized nano-subgrain (NSG) substructure, whereas PDA of the severely CR alloy results in the nanograin (NG) structure. NG alloys are almost free from dislocations, which favor transformation instead of slip, which is macroscopically measured as a significant difference between the transformation and the true yield stresses. NSG alloys with low-angle subboundaries have both slip and transformation stresses increased, as compared to their recrystallized (REC) counterparts. As a result, static performance of Ti-Ni SMA can be ranked as a function of their microstructure as follows: $\text{NG} \gg \text{NSG} \gg \text{REC}$. On the other hand, it appears that NG alloys have higher resistance to fatigue crack nucleation, but lower resistance to crack propagation than NSG alloys, which impacts negatively the overall endurance of the material. That is the rationale beyond our current work on specific sequences of thermomechanical processing with the aim of tailoring Ti-Ni alloys with optimum microstructures, from both the static and fatigue properties points of view.

B-3:L10 Functional Fatigue of NiTi Shape Memory Wires under Assorted Loading Conditions

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Shape memory alloys (SMAs) are increasingly used for the construction of simple solid-state actuators characterized by high power density. The rational design of SMA actuators requires reliable data on the fatigue strength of the alloy under cyclic thermal activation (functional fatigue). The technical literature shows scanty test results on SMAs under functional fatigue and the few data available are mainly limited to the condition of constant stress applied to the alloy. Since the SMA elements used within actuators are normally biased by conventional springs or by another SMA element, their stress condition is far from constant in operation. The mismatch between actual working conditions and laboratory conditions leads to suboptimal designs and undermines the prediction of the actuator lifetime. This paper aims at bridging the gap between experiment and reality. Four test conditions are planned, covering most of the actual situations occurring in practice: constant stress, constant strain, constant stress with prescribed maximum strain and linear stress-strain path. The paper describes the experimental apparatus specifically designed to implement the four loading conditions and presents extensive fatigue results obtained for commercial NiTi wires under those test arrangements.

B-3:L12 Influence of Inclusions on Nitinol Fatigue

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The recent surge of innovative biomedical applications around the world, coupled with strict requirements for proving safety and efficacy of medical devices, has resulted in a push to practically and fundamentally understand the fatigue and fracture of NiTi-based alloys. The fracture - and particularly the fatigue - of Nitinol are relatively poorly understood, even though structural fatigue is the life-limiting behavior of Nitinol medical devices and approval or clearance of such devices depends on adequate fatigue resistance. The fracture and fatigue behavior has been mainly addressed by design improvements. However, it is well known there are several microstructural parameters that can affect the fatigue behavior. This is especially true for Nitinol due to its complex microstructure and material processing cycle. There are a number of results suggesting that, at least at high alternating strains (low cycle fatigue), fatigue is associated with inclusions in the raw material which act as crack initiators. However, there is a general lack of comprehensive works able to demonstrate and definitely confirm this hypothesis. This work is focused on the investigation of the influence of inclusions on fatigue behavior of NiTi pseudoelastic wires. Wires from three different melting approaches were selected and processed in the same conditions of final cold work, annealing treatment, and surface finish, in order to neutralize the main processing effects. Cycling was carried out using a rotary bending fatigue tester and fracture surfaces were investigated by scanning electron microscopy. A robust set of data will be presented, according to the strain-life approach, and analyzed by the most common statistical methods. Type, size and distribution of the inclusions present in the materials seem to have a different, but strong influence on fatigue behavior. Therefore, a general reduction of inclusions may have a beneficial effect in improving lifetime of Nitinol. With the attempt to pursue this goal, some preliminary data and their significance will also be presented and discussed.

B-3:L13 Transformation Behavior of Shape Memory Alloys in Multiaxial Stress State

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Experimental and numerical investigations for the phase transformation behavior of shape memory alloys were conducted. Experimental studies were carried out at room temperature by using a testing machine which was controlled by a hydraulic servo mechanism. Cylindrical specimens of TiNi were examined under axial and torsion loadings. Loadings were applied in strain controlled conditions which were represented by proportional paths or non-proportional paths in the axial and shear strain space. Relations of stress and strain were obtained in the transformation and the reverse transformation conditions. It was revealed that the stress-strain behaviors were very complicated especially in the case of non-proportional loadings. Numerical studies were also performed for the same conditions as those of experiments. A constitutive model which was developed before by the authors considering the accommodation behavior of the transformation strain was used for numerical studies. It was shown that calculated results by the constitutive model were reasonable in comparison with experimental results. But it was left for the future work to analyze the anisotropy nature of the material observed in the experiment.

B-3:L14 Structure and Properties Modification in NiMnGa Single Crystals

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Over the past years considerable effort has been given in the production of single crystalline NiMnGa alloys with magnetic shape memory properties. These alloys have been produced mainly in the laboratory scale, using self-made equipment, thus their wider utilization in practical applications has been limited. Recently, a more industrial type approach towards MSM alloy production has been introduced¹. In the present paper the structure and magnetic shape memory properties of single crystal NiMnGa alloys are described at temperatures from 40 °C until 70 °C. The development of new NiMnGa compositions, towards high temperature structures, the appropriate thermo-mechanical treatment, and the subsequent magneto-mechanical training have also been studied in the present work. In these studies a Design of Experiment (DoE) and various statistical approaches have been introduced. The

first results are very promising, which will help us to better understand the structure-property relationship of this new class of smart materials. This will further improve their acceptance in practical applications.

1. E. Pagounis and M. Laufenberg, Proc. of ACTUATOR 2010, Bremen, 731 (2010)

B-3:L15 Modelling of Shape Memory Alloy Negator Springs for Long-Stroke Constant-Force Actuators

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Shape memory alloys (SMA) are increasingly used for the construction of compact solid-state actuators with high power density. When based on SMA elements of conventional design (wires, helical springs, etc.), the force-displacement curve of SMA actuators is a sloped line ranging from zero to peak force over the stroke of the device. This characteristic does not fit well with the fact that the external load is often constant, which results in reduced stroke and output force of the actuator. This paper contributes to overcoming these drawbacks by envisaging SMA elements in the form of Negator constant-force springs. A Negator spring is a spiral spring made of strip metal wound on the flat with an inherent curvature such that, in repose, each coil wraps tightly on its inner neighbour. In use the strip is extended with the free end loaded and the inner end supported on a drum. The unique characteristic of Negator springs is the nearly-constant force needed to unwind the strip for very large deflections. Moreover the flat shape, having a high area over volume ratio, grants improved bandwidth compared to any solution with solid wires. This paper models mathematically the mechanical behaviour of SMA Negator springs performing as active elements in constant-force, long-stroke actuators.

B-3:L16 Design and Simulation of a Magnetic Shape Memory (MSM) Alloy Energy Harvester

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We present the simulation and development of a vibrational energy harvester based on an active element made of Ni-Mn-Ga Magnetic Shape Memory (MSM) alloy. As the MSM element is subjected to mechanical stress within an external magnetic field, its magnetization changes in proportion to its length, facilitating energy generation in a pick-up coil. Whereas conventional piezo and magnetostrictive devices operate with small (sub-millimeter) stroke at high frequencies (kHz range), the MSM harvester is best suited to longer (millimeter range) stroke at a low frequency (100 Hz or below). Power output of 20 mW has been demonstrated with the prototype device operating at 45 Hz. A description of the magnetic circuit and mechanical design of the harvester is presented along with measured performance data. Time-dependent modelling of the device using Simscape and Matlab software is also described. The effect of various parameters in the magnetic and electrical circuits on the output power is investigated, and experimental findings are compared with predictions produced by the numerical model.

B-3:L18 Influence of Stress on the Work Performance and Plastic Strain Accumulation during Thermal Cycling of TiNi Alloy Under the Stress - symmetrical Scheme

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Influence of stress acting on cooling and heating on the values of shape memory effects, work performance and plastic strain accumulation during thermal cycling of Ti - 51.5 at. % Ni alloy under the stress - symmetrical scheme were studied. Cylindrical samples were cooled under the constant stress of σ_c and heated under the constant stress of σ_h for 60 cycles. The stresses of σ_c and σ_h were applied in positive direction in every odd thermal cycle and in the negative direction in every even cycle. The value of σ_c was varied from 15 MPa to 150 MPa and the value of σ_h was varied from 50 MPa to 400 MPa. It was found that if the value of stress acting on heating was 200 MPa and less, the "training" effect (an increase in values of shape memory effects and work performance) was observed on thermal cycling the TiNi alloy under the stress - symmetric scheme. If the stress acting on heating was higher than 200 MPa, the values of transformation plasticity and shape memory effects and work performance were stable during thermal cycling. It was shown that an increase in stress acting on cooling led to an increase in value of shape memory effect and work performance and a decrease in plastic strain accumulated in the sample during 60 thermal cycles.

B-3:IL19 Phase Field Dynamic Modelling of Shape Memory Alloy Nanowires

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We present several new results on the dynamics of shape memory alloy (SMA) nanowires under multi-axial loading conditions, focusing on FePd samples. First, we develop a phase field model with the Ginzburg-Landau-type free energy describing martensitic transformations in such structures, based on the Landau order parameter theory. We note that the microstructure properties and mechanical behavior of martensitic transformations in SMA nanostructures have been studied before in the literature, mainly for uniaxial loading and under simplifying athermal/isothermal assumptions. Our first example is pertinent to square-to-rectangular phase transformations, studied here with our developed fully coupled thermo-mechanical model. The nanowire response to multi-axial loadings depends critically on the dynamics of loading. In particular, the nanowire behaves in a "stiff" manner in response to the axial loading with complete conversion of the unfavorable martensitic phase. At the same time, the bending load can assist the phase transformation by redistributing the martensitic variants, subject to the local axial stress sign. The nanowire dynamics in response to the multi-axial, combining axial and bending, becomes noticeably "stiffer" compared to the uniaxial loading case. Based on these results, we study the dynamics of microstructure evolution subjected to the multi-axial loading, providing further insight into the mechanical behavior of the nanowire. This new insight is discussed in the context of developing SMA based MEMS and NEMS devices.

Session B-4 Composites

B-4:IL01 From Simple Nitinol Micro-wires Towards Complex Functional NiTi Textiles and Elastomer Composites

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Nitinol micro-wires with diameters in the order of tens of microns exhibit outstanding structural and functional properties in comparison to bulk Nitinol. Moreover, thin metallic wires are nowadays commonly processed by textile technologies allowing to make out of these wires a wide range of 2D/3D structures. Thus, the use of textile technologies to extend Nitinol micro-wires properties to more complex structures appears as a very promising way of engineering novel functional materials with high application potential. To illustrate such an approach, several examples of NiTi textile structures made by weaving, knitting and braiding will be presented. In addition, NiTi textiles embedded into elastomeric matrices will be shown as examples of functional NiTi elastomer composites. Furthermore, experimentally analysed behaviour of NiTi textiles and elastomer composites subjected to complex thermomechanical loads will be described in order to illustrate the wide range of functional thermomechanical properties which can be achieved by integrating NiTi micro-wires into 2D/3D structures using textile processing. Finally, the projection of Nitinol micro-wires' behaviour onto NiTi textiles and elastomer composites will be discussed with regard to the type of internal textile morphology.

B-4:IL02 Recent Achievements of NiMnGa/Polymer Smart Composites

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Although NiMnGa is a fascinating ferromagnetic shape memory alloy, the magnetic motion is obtained only for single crystal state material. And also, the actuation strain is not recovered only by removing magnetic field. In order to solve these problems using low-cost fabrication process, we have proposed a smart composite composed of NiMnGa single crystal particles and polymer matrix composite. The single crystal NiMnGa particles are easily fabricated by mechanical crush using intrinsic intergranular brittleness of polycrystalline NiMnGa ingots. The polymer matrix plays a role of binder between particles, and also the elastic back stress from the matrix polymer induces the reverse reorientation of martensite variants after removing the magnetic field. This stands for shape recovery by removing magnetic field. However, the measurement magnetostrains of the composites are often extremely small in comparison theoretically expected values. In this paper the recent research achievements of NiMnGa/polymer composites are presented in order to reveal the ferromagnetic shape memory effect of the smart composites, from the viewpoint of (1) volume fraction of matrix polymer, (2) elastic modulus of polymer and (3) direction of magnetic field applied.

Session B-5 Low Dimensionality

B-5:IL01 FSMA Thin Films: Recent Developments

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Ferromagnetic shape memory alloys (FSMAs), such as Ni-Mn-Ga alloys, being deposited onto different substrates are of much practical interest for the development of new microactuators for the novel smart systems, such as the magnetic MEMS. In this paper, we present overview giving a glimpse on recent advances made in the FSMAs thin films in the submicron range of thicknesses. Particularly, emphasis is given to the experimental and theoretical studies of magnetic anisotropies exhibited by FSMAs deposited on the cold substrates and subsequently annealed and films epitaxially grown on the hot substrates. A symmetry and value of the magnetic anisotropy of film are important factors to clarify their relationship with the magnetic-field-induced strain (MFIS) and related phenomena. It is shown that magnetic anisotropy is controlled by the film crystallography, martensitic nanodomain structure and film thickness. Generally, the film structural states are dependent on the preparation mode and thoroughly elaborated parameters of deposition. The "cold-substrate" preparation method usually results in the polycrystalline films with 220 out-of-plane fiber texture, while "hot-substrate" method leads to the single crystalline state of films when using appropriate substrates.

B-5:IL02 Shape Memory and Superelastic cycling at Nano-scale

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Shape Memory Alloys (SMA) are widely used for practical applications as sensors and actuators and in particular they are good candidates to be incorporated in Micro Electro-Mechanical Systems (MEMS). However, the characterization of the shape memory and superelastic behavior at micro and nano scale requires new experimental methodologies. In the present work we present a new experimental approach to perform nano-compression tests on micro and nano pillars milled by focused ion beam. Some previous results on shape memory and superelasticity^{1,2} in Cu-Al-Ni single crystals micro pillars will be overviewed and the observed size-effects at nano scale will be discussed. New results concerning the mechanical behavior during cycling at nano scale will be presented, and we will show that Cu-Al-Ni micro-pillars exhibit a perfectly reproducible and reversible superelastic behavior along hundred of cycles. A general discussion on the

martensitic transformation behavior at nano scale will be addressed, and we hope that the presented results can be exploited for microdevices, opening the door for the development of a new generation of Smart MEMS.

1. J. San Juan et al, *Advanced Materials* 20, 272 (2008).
2. J. San Juan et al, *Nature Nanotechnology* 4, 415 (2009).

B-5:IL03 Low Temperature Crystallization of Sputter-Deposited TiNi Films

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The crystallization needed to invest the shape memory property in the TiNi films had been usually realized by high temperature process during and/or after the sputtering deposition. Therefore, the films could not be deposited on temperature-sensitive materials such as polymers. We developed an RF magnetron sputtering system equipped with a ion irradiation system for substrates. This led to the achievement of low-temperature crystallized films [doi: 10.1051/esomat/200902012]. However, the ion irradiation system was not so complete; the ions sometimes were irradiated excessively to the substrate and/or the growing film surface. With the aim of effective working of the system, the circuits for generating the ions in inductively coupled plasma, for supplying pulse bias voltage to substrate, and so on were recomposed. Crystal structures of the films, which are produced by the refined apparatus, are examined by X-ray powder diffraction. The ion fluence is calculated from the plasma density and electron temperature measured by a double probe. The effects of ion fluence on film crystallization were discussed. The crystallized films deposited on a polyimide sheet were patterned to manufacture an electrically excitable actuator and observed a two-way motion.

B-5:IL05 Magnetic Shape Memory Alloys Going Nano

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The high strain of 10% reachable in Magnetic Shape Memory (MSM) alloys makes this class of material of particular interest for the use in microactuators. To understand the difference to bulk materials, here thin films and nanowires made of Fe-Pd are analyzed. In particular the advantages of a well oriented, epitaxial growth are used for a comparison with first principle calculations as well as continuum models. In thin films the epitaxial interface to substrates with different lattice constants is used to stabilize intermediate states during the martensitic transition. The martensitic instability allows covering almost the complete Bain transformation path from an fcc to a bcc structure up to relatively thick films. Straining the films beyond the Bain path induces adaptive nanotwinning, which paves the way to produce novel magnetic nanostructures. As an outlook it is shown that also the preparation of freestanding Fe-Pd nanowires is possible, representing the ideal wrought material for true nanosystems.

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B-5:IL06 Elastocaloric Properties of Sputtered NiTi Thin Films

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In recent years, solid state cooling has been subject to intense scientific research due to it being a potential environmental-friendly alternative to vapor compression technology. Magnetocaloric materials are a prominent material class for this purpose. However, electro-, baro- and elastocaloric materials are also being investigated, since it is not yet clear which effect can be utilized most effectively. The majority of previous publications are concerned with bulk materials, whereas thin films and their inherent properties, e.g. a higher surface to volume ratio, have been investigated less intensively. Here, we present elastocaloric properties of freestanding Ni_{50.4}Ti_{49.6} thin films with thickness between 11 and 44 μm , which were deposited by magnetron sputtering. When strained with high strain rates, a maximum temperature change, $\Delta T = 5\text{ K}$, was measured. With increasing mechanical cycles, ΔT dropped to 2.5 K in cycle 250, but remained constant during further cycling. This trend that was equally observed for the dissipated energy in the

pseudoelastic stress-strain loops. For cycled films, ΔT was found to scale linearly with the width of minor loops, $\Delta\epsilon$, which can be exploited to significantly increase material lifetime.

Session B-6 Applications

B-6:IL01 SMA Dampers for Cable Vibration: An Available Solution for Oscillation Mitigation of Stayed Cables in Bridges

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The wind, rain and traffic induce oscillations in the stayed cables for bridges. One eventual solution relates the use of semi-active devices as magneto-reologic fluids. These devices need guaranteed electrical power and computing and, also, technical attention. The Shape Memory Alloys was studied for their application as passive elements. The study is focused in the required properties of SMA for appropriate reliability of the SMA dampers. The fatigue/fracture life, the thermal effects induced by external temperature and by self-heating and the behavior of the stressed aging SMA wires were studied. The SMA dampers were applied to cables in "facilities": cable No 1 in the ELSA-JRC in Ispra, Italy, the 50 m cable of IFSTTAR near Nantes, France. Furthermore, the behavior of a test cable by localized mass in Pavia, Italy was studied. The experimental results establish a reduction of the oscillation amplitude to a half of less. Moreover, an increase of the oscillatory frequency was observed. Use of windowed Fourier transform or wavelets shows a change of frequency associate of the SMA damping effects associated to changes in pre-stressing.

B-6:IL02 Thermoelastic Cooling

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We are developing thermoelastic cooling devices based on latent heat generated and absorbed during the stress-induced phase transformation in a shape memory alloy (SMA). Compared to other alternative cooling technologies, the coefficient of performance (COP) of SMA-based cooling is among the highest: for a compression based operation, the COP of thermoelastic cooling can be as high as 12. Compared to the vapor compression technology, since thermoelastic cooling completely eliminates the need for high global warming potential greenhouse gases, it has minimal environmental impact. We show that intrinsic ΔT of thermoelastic coolers can be as high as 21 $^{\circ}\text{C}$, which can be effectively used to run air-conditioning or refrigeration cycles. Following an initial demonstration of a small scale 35 W thermoelastic cooler, a number of different designs for implementing SMA wires for cooling cycles have been developed, and prototypes are being constructed. We will address optimizing the SMA compositions for long fatigue life in the context of our previous work on combinatorial optimization of SMAs with minimal hysteresis.

This work is carried out in collaboration with M. Wuttig, R. Radermacher, Y. Hwang, and J. Muehlbauer, and is funded by DoE ARPA-E.

B-6:IL03 Devices for Rehabilitation Applications

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Recent research is showing that Shape Memory Alloys (SMAs) can be advantageously employed for a number of applications in Rehabilitation Medicine and the related field of Neuroscience. This innovative use of SMAs was investigated with the specific aim of improving the treatment approach to neurological patients with sequelae from stroke, traumatic brain injury, cerebral palsy, etc. Several examples of devices built for this purpose will be presented together with an outline of the reasons why the shape-memory and pseudoelastic effects can be regarded as interesting resources on account of scientific, technical and clinical

reasons. In particular the design and functioning of an SMA-based ankle exerciser and pseudoelastic repositioning splints for the upper and lower limbs will be discussed in relation with results of neurophysiological and clinical tests. The main observations so far suggest that this type of devices is able to support patients' physical rehabilitation by adapting to changing conditions and needs during functional recovery. Furthermore, due to their improved tolerability relative to traditional treatments SMA devices can be used for longer times and tend to produce interesting effects in the control of spastic syndromes.

B-6:IL04 Smart Microactuation Devices Based on Shape Memory and Magnetic Effects

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By combining materials and structures showing both, shape memory and magnetic effects, novel smart microsystems can be realized with novel unprecedented functionality. Currently, two major approaches are being pursued, (1) the combination of shape memory alloy (SMAs) and ferromagnetic alloy structures and (2) the development of ferromagnetic SMAs that exhibit shape memory and magnetic effects as intrinsic properties. A prominent example of the first approach is an optical microscanner showing bi-directional actuation in a monolithic SMA cantilever structure¹. The underlying actuation mechanism is currently further explored for use in thermal energy harvesting. Other examples are bistable microswitches with magnetic latching generated by a ferromagnetic disc that is electroplated directly onto an SMA bridge structure². In this way, power consumption can be significantly reduced making SMA actuation much more attractive for applications. The second approach relies on the development of ferromagnetic SMA films or foils showing a bulk-like magnetic shape memory effect. Recently, first magnetic shape memory foil actuators have been developed consisting of a Ni-Mn-Ga stripe and a biasing spring showing reversible linear actuation with 5.5% magnetostrain. In the presentation, the interdisciplinary aspects of materials research, engineering and technology development will be discussed and selected demonstrators will be presented.

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B-6:L06 SMA Applications in Space Engineering: State-of-the-Art

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The use of shape memory alloys in space technology was suggested practically as soon as the first materials of this type had been discovered and investigations of their unique functional and mechanical properties had begun. However, various reasons led to a more than 30-years delay in realization of SMA using in devices and constructions that were really launched to the space. The first appearance of SMA onto the Earth orbit may be considered to occur in 1982, when thermomechanical pipe couplings were tested for sealability in outer space on-the-spot of the Salyut-7 orbital station. Since then, shape memory alloys were applied and tested in some flights. Then were couplings for truss construction, drives and on board of the orbital station Mir, release devices on board of Clementine spacecraft and some other. In the last decade designers of spacecrafts have shown a considerable interest in materials with shape memory effect. As of today, various devices using shape memory alloys are being developed in different space projects. These and other examples will be highlighted in the paper, together with a brief history of shape memory applications in space engineering.

B-6:L07 Design of a Solid State Shape-Memory-Actuator with Guidance Functionality

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Machine tools for small work pieces are characterized by an extensive disproportion between workspace and cross section. This is mainly caused by limitations in the miniaturization of drives and guidance elements. Due to their high specific workloads and relatively small spatial requirements, Shape-Memory-Alloys (SMA) possess an outstanding potential to serve as miniaturized positioning devices in small machines.

However, most of the known SMA drive applications necessitate additional guidance elements to realize a certain mechanical stiffness. In this paper we present a novel SMA actuator design, which does rather not require an additional guidance. The stiffness in directions different from the actuators moving direction is realized by a specific arrangement of the SMA elements. Those are designed regarding geometry, applied load, and control aspects. To evaluate the design of the actuator a multi domain model is developed. That covers not just the mechanical part of the arrangement; but also the transient behaviour of the SMA. Based on that a closed loop control concept for positioning applications is implemented. Furthermore, a sample actuator is built to validate the model and to investigate the capabilities to serve as miniaturized positioning device in small machines.

B-6:L08 An Open-loop Control Approach for Magnetic Shape Memory Actuators Considering Temperature Variations

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Magnetic shape memory alloys (MSMA) show remarkable potentials for actuation purposes because of a large achievable strain and a short response time. But, apart from these advantages, MSMA show a hysteretic behavior between the input and output quantities. Hysteretic phenomena represent an important challenge for the design of control systems for MSMA-based actuators. Furthermore, this hysteretic behavior is sensitive to temperature variations, a situation that arises in many applications. To face the problem of increasing/decreasing temperature during operation, an open-loop control approach considering temperature variations is presented in this paper. For this purpose, an actuator prototype is characterized with particular emphasis on temperature influence concerning the input-output behavior. The presence of a time-varying nonlinearity is addressed by means of a set of hysteresis models and relative compensators to improve the positioning performance of the MSM system. Subsequently, the obtained models are integrated in the control loop and tested experimentally. Finally, the results achieved with the introduced control concept are presented.

B-6:L09 Studies on Internal Friction of a High Temperature Cu-Al-Mn-Zn Shape Memory Alloy

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Materials with high damping capacity for quelling noise and vibration in engineering structures has drawn increasing attention in recent times. Among the different materials that have been attempted so far, shape memory alloys (SMAs) have shown much promise since they exhibit much higher damping due to the occurrence of a thermoelastic martensitic transformation in them. Among the SMAs it is copper-based SMAs that have proven more attractive compared to Ni-Ti SMAs because of their lower cost, higher damping and machining characteristics. In the present work, therefore, the damping properties of a Cu-Al-Mn-Zn alloy, a potential high damping material for high temperature turbomachinery rotor blades, are investigated. The internal friction was studied using a dynamic mechanical analyzer over a range of temperatures (25-300 °C), frequencies (0.5-10Hz) and strain amplitudes (5×10⁻⁶ and 10⁻⁴). The analysis of the results reveals that the damping properties are more sensitive to variation in frequency and strain amplitude, pointing to the suitability of the material for the intended application. The results are presented and discussed in the paper.

Poster Presentations

B:P01 Mechanical, Thermodynamical and Magnetic Properties of Magnetocaloric and Shape Memory Materials Treated by Intensive Plastic Deformation by Cold Rolling

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This work is devoted to investigation of mechanical, thermodynamical and magnetic properties of Gd and Ni-Ti-Cu alloys treated by intensive plastic deformation by cold rolling. The data of XRD, VSM, direct measurements of MCE, AFM, EDX are presented. MCE effect of Gd was measured with the help of direct method of MCE determination. It is shown that intensive plastic treatment allows to produce up to 50 mkm thickness Gd ribbons with magnetocaloric effect comparable to microcrystalline samples. At the same time these ribbons have good mechanical properties. The dependences of magnetisation versus intensive plastic treatment of the samples were measured by SQUID. Also, in this work are discussed some aspects of intensive plastic treatment of Ni-Ti-Cu shape memory nanostructural ribbons. These ribbons are applied by authors to designing of nanotweezers.

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B:P02 Shock Compression of NiTi Powders by One-Stage Gasdynamic Gun

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One-stage gun was designed to compact nanopowders by direct impact of a high speed projectile. By this technique consolidation occurs without significant temperature increase of the powders thus, bulk material maintains the structure of the starting powders. Measurements of the projectile mass and velocity allow to correlate the compaction effect with the projectile energy or momentum in order to find out the operating conditions that guarantee the production of a fully dense product. Samples of compressed nanostructured NiTi powders, featured by an initial relative density between 50-80 %, were prepared and then shock consolidated by using projectiles having masses ranging between 2-8 g and travelling at the velocity of 0.5-1 Km/s. Fully dense NiTi has been obtained by the projectile velocities of 0.6-0.8 Km/s and the corresponding masses of 5-3.8 g. Shock compression technique was also used to obtain a fully dense samples starting from mechanically activated (ball milling) Ni and Ti powders. The obtained compacts have been subsequently reacted following two different ways (controlled synthesis reaction and strong exothermic fast reaction). The obtained results indicate that both methodologies allow to get NiTi alloy but the controlled synthesis reaction gave the best products.

B:P05 Heat-treatment Processing for MnBi in High Magnetic Fields

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The phase diagram for MnBi was investigated in high fields up to 26 T at temperatures ranging from 300 to 730 K. We used the differential thermal analysis (DTA), in order to examine the equilibrium state change of ferromagnetic MnBi by applying high magnetic fields. Ferromagnetic MnBi undergoes a first-order magnetic phase transition to the paramagnetic state at $T_f \sim 628$ K, where the low temperature phase MnBi of NiAs-type hexagonal structure is transformed into the high temperature phase Mn_{1.08}Bi of Ni₂In-type hexagonal structure. It was found that the decomposition temperature T_f increases with increasing magnetic fields at the rate of 2 K/T. This means that the decomposition of MnBi can be controlled by a magnetic field. As a result, T_f on the liquid phase line changes the amount of Mn content from 10 to 20 at.% at the magnetic field of 26 T, and the heat-treatment at 26 T improves the volume fraction of MnBi.

B:P06 Influence of Atomic Order on the Structural and Magnetic Transitions in Ni-Mn-In Metamagnetic Shape Memory Alloys

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Ferromagnetic shape memory alloys (FSMA) have attained a strong attention over the last years due to their peculiar properties as the extremely large magnetic-field-induced-strain and magnetocaloric effect which are related to the martensitic transformation (MT). Among these systems Metamagnetic SMA are a special group of alloys where the MT takes place between a ferromagnetic austenite and a weak magnetic martensite. The MT is a first order diffusionless transformation from a high temperature cubic ordered phase (austenite) to a lower symmetry low temperature phase (martensite). The MT temperature (T_m) strongly depends on composition. Likewise, both T_m and the magnetic properties have a high dependence on the long-range atomic order. By quenching from high temperature a degree of disorder can be retained in a metastable state. In addition, the order degree can be modified by means of post-quenching thermal treatments. The evolution of the metastable retained disorder with thermal treatments in a Ni-Mn-In metamagnetic SMA has been studied by neutron diffraction experiments. This analysis has allowed to determine the dependence of MT characteristics and magnetic properties on the long range atomic order.

B:P07 Composition Dependence of Compatibility in Self-accommodation Microstructure of Beta-titanium Shape Memory Alloy

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Composition dependence of the compatibility condition at junction plane (interface between habit plane variants (HPVs)) was evaluated by geometrically non-linear theory of martensite in Ti-Nb-Al alloys that have cubic to orthorhombic martensitic transformation. The kinematic compatibility condition requires non-zero rotation (θ) of HPV to form stress-free junction plane. This means that the invariant habit plane and the compatible junction plane are not formed simultaneously. There are five types in the morphology of HPV-pair. Two types out of the five have a smaller θ (~ 1 deg.) that is not sensitive to the change in the lattice parameters and/or alloy composition. However, θ of the other three types is a few degrees and has significant composition dependence. The composition dependence of the preferred self-accommodation morphologies is discussed on the basis of the theoretical analysis and transmission electron microscopy observations.

B:P12 Effect of Repeated Heat-treatment under Constrained Strain on Mechanical Properties of Ti-Ni Shape Memory Alloy

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A stent is a flexible tubular device for expansion of the narrow area of human vein. Since the self-expandable stent can be manufactured, a shape memory alloy is often used for materials of the stent. A laser-cut method is used in the manufacture of shape memory alloy stent for an artery. In general, the shape memory alloy stent by laser-cut method is made of shape memory alloy pipe. At first, a laser-cut is performed to the shape memory alloy pipe. The cut shape memory alloy pipe is expanded by insertion of the metal sheath and then is heat-treated for diameter expansion. The heat-treatment for expansion is repeated several times until stent becomes the size of the aim. The effect of heat-treatment condition (for example temperature and time) on mechanical properties was investigated by many researches. However, there are few systematical researches about the effect of heat-treatment under constrained strain on mechanical properties of Ti-Ni shape memory alloy. In this research, the effect of heat-treatment under constrained strain on mechanical properties of Ti-Ni shape memory alloy was investigated.

B:P13 Synthesis of Crystallized TiNi Thin Films by Ion Irradiation
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TiNi is well known as a typical shape-memory alloy, and it is expected to be a promising material for micro actuators. In order to realize micro electro mechanical systems (MEMS) with this material, we have to get thin crystal film of the material, since the shape-memory property appears only when the structure is crystalline. In our previous studies we developed a new apparatus as well as a new deposition process for lowering the crystallization temperature by using ion irradiation. In addition, we have found that the deposited film by the process can be crystallized at very low temperature (below 473K) without annealing but with simultaneous irradiation of Ar ions during sputter-deposition. In this study, we aim at the realization of crystallized TiNi film deposited on polyimide substrate below 373K substrate temperature. In order to realization the purpose, we have revealed the effect of Ar ion energy on lowering the crystallization temperature. The ion energy is measured with a quadrupole mass spectrometer (QMS) having an ion energy analyzer. The deposited TiNi films are examined with an X-ray diffraction (XRD). We discuss the effects of ion energy of ion irradiation on the crystallization temperature of TiNi film.

B:P15 Digital Image-based Method for Quality Control of Residual Bending Deformation in Slender Pseudoelastic NiTi Devices
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Pseudoelastic NiTi-based devices are often required to recover their shape repeatedly and their working performance can be judged from the amount of residual deformation after use. The quality problem in this respect can even be removed from fatigue life or safety issues and impact on the functional and aesthetic value of the product. While linear deformation can be appreciated quantitatively in a straightforward manner, the bending strains are more difficult to assess directly. We devised a very simple digital image-based method to measure the residual bending deformation by comparison of the pristine shape of the device with the one resulting from bending and free recovery. The program was written in LabView and is capable of reporting about the deflection and location of strain concentration along slender pseudoelastic elements in a semi-quantitative way appropriate for quality sample checks. The method is semi-automatic and provides a user-friendly interface for the operator. Apart from simple shapes like straight wires and ribbons, the method was tested on devices as complex as spectacles frames. This application is particularly interesting, where shape recovery and functional and aesthetic value are tightly linked, and deformation by severe handling is a typical effect of use.

SYMPOSIUM C

Electroactive Polymers: Advances in Materials and Devices

Oral Presentations

C:KL Soft Active Polymer and Applications
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Stimulus-active polymers can change their shapes with respect to configuration or dimension upon exposure to a particular stimulus such as heat, electricity, light, magnetic, solvent and pH value. These unique characteristics enable stimulus-active polymers to be used in a myriad of fields, including clothing manufacturing, automobile engineering, medical treatment, and aerospace engineering. Stimulus-active polymers can be applied in smart textiles and apparels, intelligent medical instruments and auxiliaries, artificial muscles, biomimetic devices, heat shrinkable materials for electronics packaging, micro-electro-mechanical systems, self-deployable sun sails in spacecrafts, miniature manipulator, actuators and sensors, and many more. This paper presents some recent progress of soft smart materials and their applications. Special emphasis is focused upon shape memory polymer (SMP), electro-active polymer (EAP) for aerospace engineering such as space deployable structures and morphing aircraft, which has highlighted the need for development of these materials. A detailed overview of development in these smart soft materials, of which the undergoing and future applications are used in adaptive structures and active control, is presented. The paper concludes with a short discussion for multi-functional soft smart materials and their composites that are expected to extend the range of development and applications available to the related researches and engineers.

Session C-1

Advances in EAP Materials

C-1:IL01 Characteristic Electrical Actuation of Plasticized Poly(vinyl chloride) - Various Electrical Functions in Relation with the Dielectric Plasticizers -

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Poly(vinyl chloride) (PVC) has been found to be actuated by applying dc electric field, accompanying colossal strain on the anode surface, particularly when plasticized with large amount of plasticizer. We call the plasticized PVC as PVC gel for convenience in this paper. Impedance spectroscopy revealed recently the some fundamental mechanism of the actuation, that is, the deformation depends on the dielectric nature of the materials. The colossal increase of dielectric constant was induced in the gel, and strongly depends on the nature of the plasticizer and its content. The phenomena observed as electrical actuation of the PVC gels were (1) Creep deformation on the anode surface, (2) Bending motion, (3) Tacking to the anode, (4) Contractile deformation, and (5) Vibrational motion by dc electric field application. Creep deformation and the excellent transparency of the gel can be utilized for focus controllable lens. Tacking force can be applied various in combination with bending deformation. Bending actuator has been successfully

applied micro-finger actuator and passed for hundreds thousands times continuous operation. In this paper, we will introduce not only the various features of the actuation, but also will get into the some detailed mechanism of the deformation.

C-1:IL02 Ferrorelaxor Polymers for Compact and Efficient Electro-mechanical Transducers

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The direct and efficient coupling between the electric signals and the elastic, thermal, optical and magnetic signals in ferroelectric based electroactive polymers makes them attractive for exploiting a broad range of cross-coupling phenomena and applications. This talk will present the recent progresses in my group in advancing the electroactive polymers devices for electromechanical and other applications. Making use of the proximity in energy landscape between different phases which stability can be tuned by introducing "defects" in the polymers, we converted normal ferroelectric P(VDF-TrFE) copolymers into ferroelectric relaxor with a high dielectric constant and PVDF into a dielectric with reversible phase transformation between the polar- and non-polar phases, resulting in high electrostrictive strain with high elastic modulus (>0.5 GPa). I will discuss the molecular mechanism responsible for the large electromechanical responses and further approaches to improve it. Several recent works in developing compact and high efficiency electromechanical devices such as Braille actuators for full page display and micro-pumps for autofocusing will be presented.

C-1:IL03 Microstructured Dielectric Elastomer Stack Actuator Arrays: Technology and Applications

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The mechanical deformation of dielectric elastomer actuators (DEAs) can be increased using multilayer stack actuators, where the driving voltage is reduced using thin dielectric layers. Dielectric elastomer stack actuators (DESA) are efficiently fabricated in an automated process. To produce thin dielectric films, uncured polydimethylsiloxane (PDMS) is spun to a thickness below 50 μm . After curing graphite electrodes are sprayed on the PDMS surface as a liquid suspension through a shadow mask and the next dielectric film can be fabricated on top. The thickness variation within one layer is lower than 4% and the sheet resistance of the electrodes ranges about 10 $\text{k}\Omega/\text{sq}$. The technology presented here is able to produce DESAs with layer thicknesses down to 5 μm . Hence, it is possible to design and fabricate actuators, which are driven only at 150V. Arrays of small actuators with a spatial resolution of 1 mm can be produced as well as single actuator elements with a diameter up to 50 mm. The potential of this technology is demonstrated by different applications with diverse requirements. The first one is a vibrotactile display that generates a perceptible vibration of 250 Hz at a driving voltage of 600V. Other applications are devoted to microfluidics. We show a peristaltic pump with a maximum flow rate of 12 $\mu\text{L}/\text{min}$ and an integrated gas valve with flow rates up to 100 mL/min .

C-1:IL04 Smart Soft Actuators and Energy Harvesters

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Soft materials form the basis of soft machines. Large deformations in soft materials are harnessed in actuators, useful in microfluidics, robotics, biomimetics and adaptive optics, as well as for harvesting biomechanical energy or energy from renewable sources. Actuation mechanisms are manifold, we here concentrate on electrostatic actuation (dielectric elastomers) and phase-change actuation (liquid gaseous phase transition actuator). In the talk a brief overview of materials for actuators and energy harvesters is given. We show that giant area expansions of 1700% can be triggered electrically by suitable actuator design. We discuss area expansions of 120% in phase change actuators working at low operating voltages. We demonstrate energy of conversion up to 200 mJ/g in dielectric elastomer generators based on natural rubber. Coupling of such large deformations with electrostatic fields leads to new phenomenas of failure and instability, pushing the frontiers of smart soft materials. The field is an infant, it is wide open, imagine the possibilities.

C-1:LO5 Flexible and Stretchable Electrodes Based on Wrinkles for Dielectric Elastomer Actuators

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Dielectric elastomer(DE) is one of electro-active polymer(EAP), which has low elastic stiffness, high dielectric constants and high strain energy levels. Recently a lot of researches have been carried out for the actuator and generator applications based on DE. The DE polymers used for such applications usually undergo repetitive tensile strain. Generally, carbon grease is the well known electrode materials for such application. But carbon or silver grease-type electrodes are not allowed for long-time use because of cracks occurrence after some period under repeated extension. To avoid such crack formation, the electrodes should be designed to be flexible and stretchable. In this study, we propose a stretchable electrode by employing wrinkles on the surfaces. Acrylic rubber (AR) sheet was first swollen in silicone rubber(SR) solution with conducting fillers such as carbon nanotubes(CNT) to make the SR and CNTs to be diffused to the surface of AR sheet. After drying, the sheet was stretched to a desired length and crosslinked the SR network. Then the sheet was relaxed then wrinkles were formed on the surface of the AR sheet. The presence of wrinkles was confirmed by SEM and the electric resistance was measured as a function of tensile strain.

C-1:LO6 Synthesis of Stable Polyaniline and Polypyrrole Nanospheres

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One of the major obstacles associated with the synthesis of conducting polymer nanoparticles in water is their unstable nature, which is traditionally overcome through the use of soft or hard templates. Such methods use expensive surfactants, often in large amounts, and require the removal of the template, which adds complexity, expense, and environmental hazard. This study explores a facile, one-pot synthesis of stable polypyrrole and polyaniline nanospheres in water that uses ozone as the oxidant. Multiple variables were investigated in order to study the mechanism of this reaction, including monomer concentration, ozone exposure time, reaction temperature, pH, and the solvent system. Particle size measurements revealed that the size of the nanospheres, ranging from 50 nm to 500 nm in diameter, can be controlled via these reaction conditions. These self-stabilizing nanospheres were also characterized using Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-Vis), scanning electron microscopy (SEM), transmission electron microscopy (TEM), zeta potential, and atomic force microscopy (AFM).

C-1:LO8 One Actuator and Several Sensors in One Device with Only Two Connecting Wires. Mimicking Muscle/brain Feedback

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Artificial muscles based on conducting polymers, fullere derivatives, carbon nanotubes, grahenes or other carbon derivative molecular structures are electrochemomechanical actuators. Electrochemical reactions drive most of the volume variation and the concomitant actuation. Any working or surrounding variable influencing the reaction rate is sensed by the muscle potential, or consumed energy, evolution during actuation. Experimental results and full theoretical description will be presented. The muscle potential is a well defined function of: driving current, volume variation (external pressure or hanged masses), temperature and electrolyte concentration. While working artificial muscles detect any change of whatever those variables by changes on the potential or on the consumed energy evolution. Experimental changes fit those predicted by the theoretical description. Only two connecting wire contain, simultaneously, actuating (current) and sensing (potential) signals. Those constitute new feed back intelligent and biomimetic devices opening new technological borders and mimicking

natural muscles/brain communication. Muscles and actuators; batteries and supercapacitors; smart windows, mirror and screens; smart membranes and electron/ion transducers will sense working conditions.

C-1:L10 Multi-modal Stimuli Responsive Molecular Switches
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Polythiophenes behave as electrochemical molecular switches and this continues to make their synthesis an interesting subject for the development of new materials with switchable functionalities. Spiropyran derivatives can be photonically switched between spiropyran and merocyanine derivatives that manifest dramatically different properties. Herein we present the covalent attachment of a spiropyran derivative to terthiophene to generate a new material capable of multi-mode switching (electrochemical and photochemical) between various isomers.¹ For example, the material's physico-chemical properties can be rapidly switched with complete reversibility by exposure to light or heat sources through mechanisms that can be characterised by first order kinetics. Through the terthiophene moiety, the material can be polymerised without influencing the switching behaviour of the spiropyran moiety. The multi-modal switching behaviour provides additional flexibility for control of the material's properties, for example by using electrochemical switching to assist the reversibility to the system.

1. K. Wagner, R. Byrne, M. Zanoni, S. Gambhir, L. Dennany, R. Breukers, M. Higgins, P. Wagner, D. Diamond, G.G. Wallace, and D.L. Officer, *J. Am. Chem. Soc.*, 2011, 133 (14), 5453-5462.

C-1:L11 Ultra-soft Foam-based Capacitive Sensors
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C-1:L12 Effect of Crack Formation on Stretchable Silver Electrode for Dielectric Elastomer Actuators
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Thin metal films are not commonly used as electrodes for dielectric elastomer actuators (DEAs) as they are presumed to be too stiff to allow large actuated strains. However, they can improve the DEA's reliability due to their ability to self heal, just like they do for metalized plastic film capacitors. Typical DEAs using un-patterned, sputtered metal thin films do not generate more than 10% areal strain. However, this work demonstrated a large areal strain up to 56% of metalized DEA using electrolessly deposited (ELD) silver thin. The large strain of this metalized DEA is attributed to the ultra-thin electrode thickness and crack formation that makes the electrode stretchable. Cracks are observed in the thin silver film electrodes when DEA is activated. In this paper, the cracks in such thin silver electrodes are studied and compared against sputtered silver electrodes. It has been found that the cracks have helped to improve actuated strain, yet did not affect repeatability, as the cracks did not propagate in subsequent activations. Instead, the cracked electrodes had reached a sort of "steady-state".

C-1:IL13 Chitosan/IPMCs Artificial Muscles
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This presentation discusses how biopolymers such as chitosan and ionic polymer metal composites (IPMCs) can be combined to form a new nanocomposite with actuation, energy harvesting and sensing capabilities. Described are biopolymeric and polymeric networks containing conjugated ions that can be redistributed by an imposed electric field and consequently act as distributed nanosensors, nanoactuators and artificial muscles. The presentation briefly discusses the manufacturing methodologies and the fundamental properties and characteristics of such biopolymers/polymers as distributed nanosensors, nanoactuators and artificial muscles. It will further include descriptions of the basic materials' typical molecular structures. A phenomenological model as well as an ionic model of the underlying sensing and actuation mechanisms are also presented based on linear irreversible

thermodynamics with two driving forces, an electric field and a solvent pressure gradient and two fluxes, electric current density and the ionic+plasticizer flux. Intercalation of chitosan biopolymer and ionic polymers such as perfluorinated sulfonic ionomers and subsequent chemical plating of them with a noble metal (IPMCs) is also reported and the properties of the new product are briefly discussed. Chitosan and IPMCs have also been extensively studied for their biomedical applications.

C-1:L15 Properties of a Dielectric Elastomer Actuator Modified by Dispersion of Functionalised Carbon Nanotubes
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Dielectric elastomer actuators, among the broad class of electro-active polymers (EAPs), represent a rapidly growing technology for electromechanical transduction. In order to further develop this applied science, the currently needed high driving voltages must be reduced. For this purpose, one of the most promising and adopted approach is to increase the dielectric constant while maintaining both low dielectric losses and high mechanical compliance. In this work, a dielectric elastomer was prepared by dispersing functionalised carbon nanotubes (FCNTs) into a polyurethane matrix and the effects of filler dispersion into the matrix were studied in terms of dielectric, mechanical and electro-mechanical performance. An interesting increment of the dielectric constant was observed throughout the collected spectrum while the loss factor remained almost unchanged with respect to the simple matrix, indicating that conductive percolation paths did not arise in such a system. Consequences of the chemical functionalisation of the CNTs with respect to the use of unmodified filler were also studied and discussed along with rising benefits and drawbacks for the whole composite material.

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C-1:L16 Bimodal Networks as Candidates for Electroactive Polymers
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An alternative network formulation method was adopted in order to obtain a different type of silicone based elastomeric systems - the so-called bimodal networks - using two vinyl-terminated polydimethylsiloxanes (PDMS) of different molecular weight, a labelled crosslinker (3 or 4-functional), and a platinum-catalyzed hydrosilylation reaction between the three reactants. The crosslinking reaction was initiated by mixing different amounts of short PDMS chains and long PDMS chains with the stoichiometric amount of the crosslinker in a series of mixing schemes. We visualize how the short chains organize themselves between the long chains and show how this leads to unexpectedly good properties for DEAP purposes due both to the low extensibility of the short chains that attach strongly the long chains and to the extensibility of the last ones that retards the rupture process.

Session C-2

Analysis and Physical Mechanisms

C-2:IL01 Visualizing Actuation Mechanisms in Conducting Polymers
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The optical-mechanical-electrochemical coupling in conjugated polymer films can be studied during electrochemical switching by covering the film with a transparent ion barrier, so that the charge-compensating ions must enter and exit only at the edges. The ion concentration is

directly related to the oxidation level and determines the volume of the polymer. The oxidation level also determines the film color. Experiments were conducted with polypyrrole doped with dodecylbenzene sulfonate, a cation-transporting material. When the film was reduced, the edges of the film lightened as the cations began to arrive. At the same time, the height of the film increased in the same areas, proportional to the change in color intensity. As cations were transported further into the film, the oxidized portion travelled as a front to the center. A finite element model based on the Poisson equation and transport equations for both ionic and electronic charge was developed to account for the charge transport. It successfully accounts for the experimentally-observed behaviors, including the emergence of a front and the voltage dependence of the speed of the front. One of the key findings is that during cation ingress, ion movement is dominated by migration, not diffusion.

C-2:IL02 Modeling of Ionic Electroactive Polymers

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Electroactive polymers (EAP) are a very attractive class of actuation materials with remarkable electrical and mechanical properties and with a great similarity to biological contractile tissues. They consist of polymers in various compositions and in variable forms, are lightweight, and fracture-tolerant. Electroactive polymers can be classified in electronic and ionic EAP. In this presentation the actuatoric and sensoric behavior of different ionic electroactive polymers - such as ionic polymer gels, ionomeric polymer metal composites, and carbon nanotubes - is investigated on different scales. For cases in which only the global behavior is of interest, a macroscopic theory can be used. If a more detailed insight is desired, a mesoscopic coupled multi-field formulation can be applied. This formulation comprises chemical, electrical and mechanical fields in order to compute the ion concentrations, the electric potential and the mechanical displacement. By further refining the scale, the whole structure can be investigated on the microscale by the discrete element method. In this model, the material is represented by distributed particles comprising a certain amount of mass; the particles interact with each other mechanically by a truss or beam network of massless elements.

C-2:IL06 Controlling Polymer Crystallization in Functional Nanostructures

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The need to control the crystallization of commodity and engineering plastics is well-established for the fabrication of macroscopic items, in order to optimize their thermo-mechanical properties. This is traditionally done by adding nucleating agents and by playing with processing parameters. The same need emerges when functional polymers are used to fabricate nanostructures, where specific alignment of crystallographic axes and high crystallinity are required for optimal performance. This can be attained by taking advantage of confinement effects that may induce preferential orientation and increased crystallinity. Here, we show that confining electroactive polymers such as conducting, semiconducting, electroluminescent or ferroelectric polymers in the nanocavities of NIL molds or of nanolithographed masks may lead to favored orientation and improved properties. We explain the main principles controlling these effects, including graphoepitaxy and minimization of interfacial energy, and elaborate in more details on the specific case of ferroelectric polymers and on their use for the fabrication of organic memory devices.

C-2:IL07 Interfacial Layer and its Role in Newly Developed High-performance Electroactive Polymers and Composites

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The physics behind the dielectric and electromechanical effects in homogenous materials are well known. Most of the newly developed high-performance electromechanical and dielectric materials, such as electroactive polymers and composites, are inhomogeneous. It is well known that the interaction between different phases/materials is the key to the mechanical property of the materials. Recently, more interest is placed to look the interfacial layer between different phases/materials in these inhomogeneous materials and their role on the dielectric and electromechanical properties. Many of the material responses were

assigned as the results due to the appearance of the interfacial layer. Here, two materials systems are used to study the existence of the interfacial layer. The influence of the interfacial layer on the dielectric, polarization, and electromechanical properties of the materials is studied. It is concluded that although the interfacial layer plays an important role in the materials properties, there are some misunderstanding of the contribution of the interfacial layer onto the materials properties, especially the dielectric and electromechanical properties.

C-2:IL10 Conducting IPN Actuators, from Actuation Mechanism to Applications

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In recent years, many studies on electroactive polymer actuators have been reported. One promising technology is the elaboration of electronic conducting polymers based actuators with Interpenetrating Polymer Networks (IPNs) architecture. This material is thus similar to a layered actuator with the advantage that no adhesive interface is necessary. The IPNs are synthesized from poly(ethylene oxide) and elastomer networks in which the conducting polymer is dispersed, i.e. its content decreases from the outside towards the centre of the film. The conducting IPN morphology was investigated by electrical resistance measurements, DMA and EDS. Aqueous or organic electrolyte solutions were used and actuator performances have been characterized according to the type of salt. However best results were obtained with a room temperature ionic liquid, 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide. We recently synthesized new actuators based on high molecular mass elastomer. The new design of the conducting IPN greatly improves the actuator performances as mechanical resistance, output force, and speed response.

C-2:IL11 Survival Test Experiments for Ionic EAP-s

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In order to consider electromechanically active materials for real-life applications, especially for space technology, an extensive knowledge on how different environmental effects influence the reliability of electroactive polymer (EAP) actuators is required. UV, x-ray, and gamma radiation but also large-scale temperature alterations are examples of such environmental variables that can affect the actuation properties of EAP samples subjected to operate in space. We have designed, constructed, and implemented an intricate experimental setup for measuring electromechanical parameters of bending EAP actuators. This setup allows simultaneous experimentation of over 400 EAP actuators with the size of 5 × 20 mm. The electrical and mechanical parameters used to characterize all the actuators include impedance, current, blocking-force, curvature, displacement, and frequency response. The central objective of these experiments is to obtain understanding about the reliability of different EAP actuators, such as several types of ionic polymer-metal composites (IPMC), carbon-polymer composites (CPC), and conducting polymer actuators. The performance and durability of the actuators is monitored after exposing each type of EAP to the environmental conditions stated above.

C-2:L12 Electrochemical Control of the Memory Properties of Poly(3,4-ethylenedioxythiophene)

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Conducting polymers will be useful for the realization of a non-linear electrochemically controlled hybrid polymeric devices in the framework of a broader program leading to the fabrication of biologically inspired organic networks capable of "intelligent" signal analysis and transduction, i.e. adaptive networks which can be trained to perform sophisticated tasks analogous to those characterizing cognitive processes in biological systems. In this work, we have investigated the memory effect of poly(3,4-ethylenedioxythiophene) (PEDOT) in an electrochemical environment. The memory effect was related to the electromechanical responses and the nucleation and growth mechanisms during the redox switching of PEDOT. By means of cyclic voltammetry, we analyzed the influence

of the waiting time and the holding potential on the memory properties. The effect of electrochemical aging on the electrical properties was explained from the viewpoint of rearrangement of polymer chains, and the electrochemical results were rationalized in terms of a master curve. Because of the interplay of the electrochemical and mechanical properties, a better understanding of the conformational relaxation processes was very helpful for the design of memory devices based on conducting polymers.

C-2:L13 Theoretical Modeling and Numerical Simulation of IPMC Multiphysics

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The modeling of the chemo-electro-mechanical behaviour of IPMC (Ionic Polymer-Metal Composite) bodies is set within the context of the 3-D theory of nonlinear elasticity. It is assumed that a field of chemically induced distortions arise as a consequence of the electrical activation. These mechanical distortions are viewed as inelastic contributions to the mechanical deformation of the body following the point of view presented in ref. 1 and developed in ref. 2 with reference to a linear model of IPMC-like body. As in ref. 2, the derivation of the final PDE equations of the multiphysics problem are thermodynamically consistent according to ref. 3. Standard numerical experiments are performed with focus on the accurate reproduction of the chemo-electrical boundary layers.

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Session C-3

Device Development and Integration Technologies

C-3:IL01 Lab-on-a-chip Applications of Dielectric Elastomer Actuators

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The advent of microfluidics circuits has revolutionized cell biology. Also, it is now recognized that cells modulate their behavior and development in response to mechanical stresses. A device combining the in-vivo-like cellular environment afforded by microfluidic devices with the ability to apply precise mechanical strain to targeted cells would vastly increase the throughput of biology-on-a-chip experiments while enabling in-vitro experimental conditions to closely match in-vivo conditions. We report here on the design, fabrication and characterization of arrays of microfabricated dielectric elastomer actuators for on-chip pumping and for applying strain to single cells. The devices are made from PDMS membranes on which compliant electrodes are deposited by low-energy ion-implantation. Electrodes can be patterned down to 50 μm . We present devices of diameter 500 μm to 2mm that can provide out-of-plane deformation of up to 25% of the diameter, and their use for pumping both conducting and non-conducting liquids. We also report on 100 μm x 100 μm devices that generate up to 80% in-plane strain, used to stretch cells in a larger culture. Our technology is uniquely suited to create chip-scale arrays of miniaturized DEAs: we report on arrays of 72 devices on a 2 cm x 2 cm chip.

C-3:IL02 Actuation of Model Phalanges by Ion Polymer Metal Compound

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We have fabricated a prototype model artificial muscle that drives model phalanges in water. Ion polymer metal compound (IPMC) was used as an artificial muscle type actuator which was fabricated in a shape that bridges two adjoining bones, and controls opening angle of the bones which mimics contraction and expansion motion of the muscle. In fabricating IPMC Nafion R-1100 resin was heat-pressed at 185 °C with 20-30 MPa. The thickness of IPMC can be adjusted by changing the amount of resin, pressure, and time to heat-press. Immersion and reduction process was repeated up to 4 times to thicken the thickness of gold plate surface. Disk-shaped membrane was then immersed to hydrolysis solution using a mixture of dimethyl sulfoxide (DMSO), potassium hydroxide (KOH), and water. The pre-processed membrane was permeated in [Au(phen)Cl₂]⁺ solution. After the immersion, the membrane was reduced with 5% Na₂SO₃ solution to perform gold plating. Fabricated IPMC was then cut in shapes and an electrode was attached on the surface of IPMC. Bipolar power supply and function generators were used to drive IPMC membranes attached to the model phalanges. The model phalanges were successfully activated by IPMC. We have measured generating forces of IPMC by a load cell as well as by an isometric force transducer.

C-3:IL03 Haptic Devices

P. LOTZ, Continental Automotive GmbH, Babenhausen, Germany

Dielectric elastomer actuators are well known for large deformations, high dynamics, light weight and flexibility. Thus, dielectric elastomer actuators are very well suited to generate static and dynamic deformations which can be perceived as haptic informations. Furthermore, the functional principle offers the possibility to sense user input with the same device. Within the last years a lot of developments towards haptic displays and haptic devices with integrated output and input have been made: Elastomer actuators with thicknesses of only a few millimeters or less generate perceivable haptic informations. The geometry of active areas can be designed arbitrarily and is fully integrated into the passive elastomer. Hence, thin and small Braille displays can be built as well as innovative haptic feedback generators and human machine interfaces. All these applications show promising features which can hardly be realized with traditional technologies. This talk will give an overview on the recent developments on haptic devices. These results will be discussed with regard to requirements which have to be fulfilled to commercialize haptic devices based on dielectric elastomer actuators. Driving voltage, durability and lifetime are fundamental issues which have to be considered.

C-3:L04 Dynamic Daylight Redirection for Smart Windows

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Microscale, switchable daylight-redirecting glazings have the potential for widespread application if a low-cost, durable coating can be engineered and manufactured with the proper set of attributes. We will describe here a versatile approach based on microstructured electroactuated polymer thin films. Daylight redirection in these films is externally modulated via an applied voltage to track the angle of incident sunlight, thereby optimizing lighting energy savings over a larger fraction of building floor space and responding to the needs of building occupants. Optical performance characterization as well as quantitative analysis of energy performance potential will be highlighted, as will the role of angular-dependent full-wave simulations in guiding the design of the appropriate thin film microstructure to be employed.

C-3:IL05 New Dielectric Elastomer Actuators for Biomedical and Bioinspired Systems

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ElectroActive Polymers for electromechanical transduction, better referred to as Electromechanically Active Polymers (EAPs), exhibit several functional characteristics in common with natural muscles. Accordingly,

they are increasingly studied as 'artificial muscle materials' for a variety of possible uses. This talk will focus on one of the most versatile and performing EAP technologies, known as dielectric elastomer actuators. The talk will present how combining dielectric elastomer actuation with usage of fluids as a means of hydrostatic transmission allows for new devices that might find application as biomedical and bioinspired systems. Two specific examples will be presented and discussed. The first deals with the development of Braille displays as portable tactile readers for the blind people. The second example consists of new electrically tunable optical lenses, inspired to the architecture of the crystalline lens and ciliary muscle of the human eye.

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C-3:IL06 Integrating Soft Control into Soft Machines

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Dielectric Elastomer (DE) artificial muscles are multi-functional and can be used as capacitive strain sensors, multi-degree-of-freedom actuators and energy harvesters. These functions require the control of charge on the DE membrane through auxiliary electronics. A worthwhile goal would be to find ways of replacing hard and dense electronics with soft and simple components integrated with the DE thus simplifying manufacture and improving portability and wearability. Towards this goal we present two DE devices with integrated control elements: an energy harvester and a motor. Our DE energy harvester includes a passive circuit that passes charge to the stretched membrane to prime it and then harvests the charge at a higher energy on the relaxed membrane. We have used the membrane itself to store charge and piezo-resistive dielectric elastomer switches (DES) to control the distribution of charge. Soft control has vastly improved the overall energy and power density of the system. Our motor that uses antagonistic membrane DE actuators to turn a crank also relies on DES for the control of charge commutation. Both devices consist entirely of dielectric elastomer with flexible electrodes supported in a polymer frame, thus demonstrating the feasibility of integrated soft control.

C-3:L07 Transparent Ionic Polymer Actuators Based on SPI Membranes and Graphene Electrodes

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Transparent electro-active polymer actuators based on sulfonated polyimide electrolytes with graphene electrodes were developed. The SPI membrane shows high optical transmittance for a transparent polyelectrolyte and good electro-chemical properties of ion-exchange capacity, water uptake and proton conductivity required for a high-performance ionic polymer actuator. The transparent graphene electrodes were transferred on the SPI ionic polymer. The actuation performances of the actuators were investigated by electrical excitation tests. Also the electric conductivity of graphene sheets by CVD method was greatly improved through chemical doping techniques, which are responsible for high-actuation performance of transparent polymer actuators. The doping behavior of graphene was confirmed by analyzing the Raman spectra, resulting in great improvements of the actuation performances. Present results show that the transparent artificial muscular EAP actuators were successfully developed with transparent ionic exchangeable membranes and transparent graphene electrodes.

C-3:L08 EAP-Actuators with Improved Actuation Capabilities for Construction Elements with Controllable Stiffness

M. HENKE, J. SORBER, G. GERLACH, TU Dresden, Solid State Electronics Lab, Dresden, Germany

A new kind of actuator based on Electroactive Polymers (EAPs) is developed. The actuator consists of a Danfoss Polypower EAP foil and a supporting structure. The supporting structure applies the necessary pre-straining force to the foil. Usually, such structures have a constant spring stiffness which strongly limits the actuation range. The novel actuator possesses a highly nonlinear spring stiffness for pre-straining the foil. Therefore, the pre-straining force is nearly constant all over the actuation range. This leads to a doubling of the possible actuation range for such an actuator with constant spring stiffness. Such structures are the basis for developing construction elements with variable stiffness.

The contribution shows the basic function of this actuator and its capabilities for the application in new smart, self-sensing and -controlling composite materials for lightweight constructions. The theoretical background of highly nonlinear spring stiffness is discussed and transferred to the developed structures. The theoretical calculations are based on analytic calculations and finite element analyses and are verified by experimental set-ups consisting of different actuators both with constant and highly nonlinear pre-straining spring constant.

C-3:L09 High Performance Flexible Organic Thin Film Transistors with Conducting Polymer Electrodes and Al₂O₃/PVP/Al₂O₃ Multilayer Insulator

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The use of conducting polymer electrode (poly(3,4-ethylenedioxythiophene) (PEDOT)), poly(4-vinyl phenol) (PVP) insulator, polyethersulphone (PES) substrate provided excellent mechanical stability. In addition, the interface between PVP and PEDOT formed during at postannealing at 180 °C caused a leakage current between PVP and PEDOT, which was effectively suppressed by the addition of Al₂O₃. We have fabricated flexible pentacene organic transistors on a PES substrate with PEDOT conducting polymer (conductivity = 650 S/cm) electrode and Al₂O₃(30nm)/PVP(63 nm)/Al₂O₃(10nm) insulator, showing high electrical performances such as threshold voltage of -6V, threshold voltage shift of 1.12V, Ion/Ioff ratio of 1.5E+7, high mobility of 0.41 cm²V⁻¹s⁻¹, that operates after a strain of 2.0% with negligible degradation of hole mobility. In addition, we have measured the long-term stability of the device with an encapsulation layer on it, showing the excellent stability even after 1.5 month of air exposure. The excellent performances of the flexible OTFTS such as high mobility, low threshold voltage shift, low leakage current, high bendability, excellent air stability is attributed to the suppressed interaction between PVP and PEDOT by the Al₂O₃ interlayer.

Session C-4 Applications

C-4:IL01 New Materials Advances for Smart Electro-active Polymers

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Electro-active polymers are a class of smart materials that possess one or more properties that can be altered by electrical stimuli. They are characterized by unique abilities that promise to impact several applications such as biomedical, energy and electronics. This study presents the current and new materials advances for electroactive polymers. In particular, the emphasis will be on conductive polymers and matrices such as polyaniline (PANI), polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT), carbon nanotubes and graphene. In this context, the objectives of this study is the design and selection of conductive polymer and composite materials based on their structure-properties relationships; the design and development of fabrication techniques to manufacture these polymers and composites; the characterization, modeling and optimization of the behaviours and functionality of these new materials to tailor their final properties; the simulation and integration of the final properties of these smart materials into innovatively designed prototypes for diverse applications. This work will lay down the foundations of a design guideline for the development of new smart electro-active polymers.

C-4:IL02 Organic Robotics Based on Conducting Polymers

H. OKUZAKI, University of Yamanashi, Kofu, Japan

Cooperation between the electrical conductivity and hygroscopic nature of conducting polymers can provide an insight into the development of a new class of electro-active polymers (EAPs) or soft actuators working in ambient air. Unlike conducting polymer actuators driven by electrochemical doping and dedoping, this system operated in air without using an electrolyte solution, counter and reference electrodes. Free-

standing films made of poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT/PSS) were prepared by casting water dispersion of its colloidal particles. Upon application of 10 V, the film underwent contraction of 2.4% in air at 50%RH which significantly increased to 4.5% at 90%RH. The principle lays in desorption of water vapor sorbed in the film due to Joule heating, where electric field was capable of controlling the equilibrium of water vapor sorption. Under isometric condition, the film generated contractile stress as high as 17 MPa, which was 50 times larger than skeletal muscle in animals. The work capacity attained 174 kJ/m³, where Young's modulus of the film increased from 1.8 GPa to 2.6 GPa by application of 6 V at 50% RH.

Poster Presentations

C:P01 Adhesion Between Poly(dimethylsiloxane) Layers

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Different adhesion methods of poly(dimethylsiloxane) (PDMS) layers were studied with respect to adhesional force and the resulting rheology of the two-layered PDMS films were investigated. The role of adhesion between PDMS layers on the performances of two-layer structures was studied with peel strength test and by SEM pictures. The rheology of the double-layered compared to the monolayer films changed in some cases which indicates that the adhesion process needs to be carefully introduced in order not to alter the final properties.

C:P02 An Organic Polymeric Material for Electronics

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Polymers based on vinylidene fluoride (VDF) and trifluoroethylene (TrFE), exhibit intrinsic piezo, pyro and ferro-electric properties and are interesting alternative to inorganic materials, particularly for printed electronics. Their solubility in a large class of solvents enables the application of any printing and coating technique, and the low temperatures needed for the process widen the choice of substrates and constructions. Their polymeric mechanical properties allow the complete flexibility of the final devices, and the intrinsic transparency can be exploited for optical applications. While copolymers exhibit a large hysteresis, and are thus suitable for applications exploiting their ferro-electric characteristics, terpolymers behave as ferroelectric relaxors, showing electrostrictive properties useful in actuators and transducers.

C:P04 Development of Polyaniline Nano-particles and Chloroprene Rubbers Blends as Electroactive Materials

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Polymer blends between polyaniline (PANI) nano/large particles and chloroprene rubbers were fabricated and investigated as the electro-responsive materials. The effects of the chloroprene type, the particle size, the particle concentration, and electric field strength on the electrical properties, the storage modulus sensitivity, and the dielectrophoresis force were studied. Chloroprene W provides the highest storage modulus sensitivity at 55% and is chosen as the matrix. The electrical conductivity and the dielectric constant of the blends increase with increasing concentration of PANI nano/large particles. The storage modulus of the blends (with and without electric field) increases linearly with the PANI content. The maximum storage modulus sensitivities of the blends with PANI nano and large particles at $E = 2$ kV/mm are 73% at 0.01%vol and 63% at 0.1%vol, respectively. The dielectrophoresis force of all specimens increases monotonically with increasing electric field strength. The blends with PANI-nano and large particles at 0.01%vol generate higher dielectrophoresis forces than those of the pure chloroprene W. For the 0.1%vol of PANI nano and large particles, the resultant deflection angle and the dielectrophoresis forces are lower than those of the 0.01%vol systems.

C:P05 Electroactive 1-butyl-3-methylimidazolium Chloride Ionic Liquid-microcrystalline Cellulose Gel for Actuator Application

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Actuator is a device that can transform electrical energy to mechanical energy. Electroactive paper (EAPap) is a kind of well-known category, mainly composed of cellulose. Cellulose is a piezoelectric material whose piezoelectric properties are responsible for the internal rotation of polar atomic groups associated with asymmetric carbon atoms based on non-centre symmetry. The 1-Butyl-3-methylimidazolium Chloride (BMIM⁺Cl⁻) is a well-known solvent of micro-crystalline cellulose. The BMIM⁺Cl⁻ - cellulose gels were prepared by the solvent casting method. The electromechanical properties of the cellulose gels were investigated under the oscillatory shear mode at electric field strengths between 0 to 1kV/mm and as function of temperature. In the absence of electric field, the storage moduli (G') linearly increase with temperature up to 333 K at 1 rad/s. This is responsible for increasing the mobility of BMIM⁺-cation, the dipole-dipole interaction, and the cellulose chain alignment via increasing temperature. In the deflection experiments, under the electric field, the deflection distances of the gels linearly increase with increasing electric field strength along with the dielectrophoresis forces beyond the electrical yield strength of 100 V/mm.

C:P06 Crystal Properties Dependence of Dielectric and Piezoelectric Properties of Poly (vinylidene fluoride-co-trifluoroethylene)

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Poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-co-TrFE)) has aroused wide concern because of its attractive ferroelectric and piezoelectric properties. As a semi-crystal copolymer, the dielectric properties of (P(VDF-co-TrFE)) are closely related with its crystallinity and crystal phase structures. In this paper, different physical handling processes were applied to transforming the crystal properties of P(VDF-co-TrFE), and how the crystal properties influence on electric properties of the copolymer were carefully discussed. The results illustrate that the dielectric constants (ϵ_r) decrease and piezoelectric constants (d_{33}) increase as the function of crystallinity of the copolymer. In annealed copolymer, a larger remanent polarization ($P_r > 9 \mu\text{C}/\text{cm}^2$) and piezoelectric constant (> 25) were obtained in 300MV/m electric field. In addition, the larger electromechanical coupling factors (K_t) in thickness direction of this larger d_{33} copolymer films were determined by fitting the resonance behavior to the piezoelectric equation. These results illustrate the potential application of this high crystallinity ferroelectric film in electromechanical components.

C:P07 A Parametric Fractional Model in the Frequency Domain of IPMC Actuators as a Function of Length

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A flourishing literature exists on IPMC actuators, both as it regards device modelling, control and foreseen applications. It is generally accepted that modelling is a main step towards the full exploitation of this novel technology. Also models should be ruled by using parameters that are under the control of designers. Evidence is given in the literature that non integer order transfer functions could be a suitable choice in the modeling of IPMC transducers. The authors propose a non integer order model of IPMC actuators, parameterized as a function of device length, obtained by identification techniques, applied on a set of DUTs. The proposed model successes in describing the behavior of IPMCs, in the investigated frequency range. More specifically, the resonant frequency, a parameter of main interest in mechanical resonant devices, is faithfully estimated and parameterized as a function of the device length. In the paper a comparison with corresponding integer order models will be reported, in the frequency domain. Experimental validation of the proposed models show that non integer order models over perform corresponding integer order models and requires a smaller number of parameters to be used in the transfer functions.

C:P09 Functional Characterisations of Hybrid Nanocomposite Films Based on Polyaniline and Carbon Nanotubes

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The combination of nanoparticles and conducting polymers, known as hybrid conducting nanocomposites, is a new emerging field. The combination of conductive polymers, such as polyaniline (PANI), with carbon nanotubes (CNTs) has already shown some synergistic properties, thanks to the outstanding characteristics of the two single components, PANI and CNTs. As a consequence, PANI-CNTs nanocomposites have a variety of applications, such as sensors, actuators, and supercapacitors. Usually PANI and CNTs are combined by using electrochemical synthesis starting with the monomer aniline. In this work PANI-CNTs nanocomposite films were obtained by using different combinations of two methods, Electrochemical Deposition (ELD) and Electrophoretic Deposition (EPD). The sample prepared by using these alternative methods were compared with the material prepared by the usual electrochemical synthesis. Therefore, all the films so prepared were characterised and their electrochemical properties were investigated, particularly for evaluating their use as supercapacitor components.

C:P10 PVDF Sensors - Research on Foot Pressure Distribution in Dynamic Conditions

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The article presents a dynamic measurement method of the distribution of foot pressure exerted on the ground by a four points shoe insole, developed by authors, which can be placed in any sport footwear. The value of pressure was measured on heel, medial arch, metatarsus and hallux by recording values of a generated voltage by sensors which were made of piezoelectric polymer PVDF film 100 μm thick with printed silver electrodes. As confirmed by scanning microscope studies, the foil applied in the sensors is semi-crystalline. The shoe measurement insert consists of two polyester films without piezoelectric properties. Both films have silver screen printed electrodes. Between them, electroactive polymer sensors were placed. Under the influence of mechanical stress,

the sensor, which is made of piezoelectric polymer film with electrodes, acts like a self-charging capacitor. To conduct correct measurements, it is important to use a restart circuit which ensures recovery to the starting point after execution of each step. Because a PVDF sensor is very sensitive to any mechanical deformation, it is important to make a proper design of the shoe insole to ensure its correct use in pressure distribution measurements. The measuring system allows testing of foot pathology in a dynamic way.

C:P13 Full Polymer Dielectric Elastomer Actuators (DEA) Functionalized with Carbon Nanotubes and High-k Ceramics

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DEAs provide a unique combination of characteristics like large strains, high energy densities, short response times and adjustability of operation speed. These polymer actuators are light-weight, flexible and low-priced. However, DEAs haven't found widespread application in technology so far. This is mainly due to limiting factors like (i) disproportionally high operating voltage (low permittivity of the polymeric dielectric) as well as (ii) the challenging system integration due to the low compatibility of current electrode materials (thin metal layers, graphite suspensions) and the polymeric dielectric. To overcome these limitations, we developed a new actuator platform based on full polymeric DEAs where both electrode and dielectric consist of the same elastomeric matrix. The electrodes were modified with a flexible nano network of highly purified single-walled carbon nanotubes while high-dielectric constant ceramics have been added to the dielectric to increase its permittivity. The mechanical and electrical properties of the composite materials were thoroughly analyzed. Furthermore, defined multi-layer composites were characterized regarding their actuation behavior and robustness.

SYMPOSIUM D

Smart and Interactive Textiles

Oral Presentations

Session D-1

Adaptive/Active Textiles

D-1:IL01 Biomimicry in Textiles: Past, Present and Potential

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The natural world around us provides excellent examples of functional systems built with a handful of materials. Throughout the millennia, nature has evolved to adapt and develop highly sophisticated methods to solve problems. The solutions found in nature include superhydrophobicity, self cleaning, self repair, energy conservation, drag reduction, dry adhesion, adaptive growth, and so on. There are numerous examples of functional surfaces, fibrous structures, structural colours, self-healing, thermal insulation, etc., that offer important lessons for the

textile products of the future. This paper provides a general overview of the potential of bio-inspired textile structures by highlighting a few specific examples of pertinent, inherently sustainable biological systems. Biomimetic research is a rapidly growing field and its true potential can only be realized through interdisciplinary research rooted in a holistic understanding of nature. The paper explores the field of biomimetics as it relates to textiles. The exploration begins with a general overview, followed by a historical perspective; it describes some ongoing efforts in biomimetic textiles. Finally, it explores the potential of use of biomimetic materials and products towards the attainment of sustainable textiles.

D-1:IL02 Photovoltaics go Textile: Fundamental Considerations and Materials Aspects to Realize Dye-sensitized Solar Cells on Textile Electrodes

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Textile-based photovoltaics are of interest for an independent energy supply for a number of textile- integrated electronic applications, mainly in medical and outdoor applications. Preparation of semiconductor films from precursor solutions represents the most promising approach

because of good compatibility of the processes to a low thermal stability of textiles and to the need of a three-dimensional coating process. Dye-sensitized solar cells (DSC) represent a suitable technology since electrolytes can bridge an electrode gap of 10-100 μm typical even in very finely woven fabrics. Thin porous films of ZnO were electrochemically deposited on ELITEX® silver-coated polyamide threads, filaments and knitted fabrics and subsequently sensitized by appropriate dyes¹. The role of deposition conditions, alternative deposition baths and different substrate metals were investigated to improve performance and stability². On textile-compatible corrosion-resistant BEKINOX® stainless steel fibres conversion efficiency close to 1% under AM 1.5 conditions were reached³.

1. T. Loewenstein et al, *Phys. Chem. Chem. Phys.* 10, 1844(2008).
2. M. Rudolph et al, *Phys. Chem. Chem. Phys.* 11, 3313(2009).
3. T. Loewenstein et al, *Chemphyschem* 11, 783(2010).

D-1:L04 Development of Piezoresistive Fibre Sensors, Based on Carbon-thermoplastic Elastomer Compounds, for Textile Application

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The piezoresistive fibre consists of high elastic polymeric matrix and conductive particles, which are homogeneously dispersed inside the matrix. By raw material evaluation (e.g. elastic polymer, conductive particles) fibre properties are investigated considering the project relevant sensor characteristics: change in electrical resistance by dynamic, static and cyclic strain. Textile piezoresistive sensor fibres with tailored electrical response leading to defined strain rates could be developed. As conductive filler two kinds of carbon black, a higher and a lower structured type (Ensaco 250 and 350) were tested successfully. Sample with graphite powder (Timrex HSAG300) reduced the flexibility of the fibres in an unacceptable way and was not further investigated. Additionally the relaxation of the electrical signal under static load was higher than the one of the carbon black compounds. By torque rheometer and DMA analysis it could be verified, that interaction between the different polymers and the carbon black fillers significantly chance. This could be correlated with the sensor behaviour. Therefore the interaction between the both materials should be not too strong and not too weak to achieve good sensing behavior. Selected piezoresistive fibres were successfully integrated into two different demonstrators: into an industrially woven elastic band for tensile measurement and into a none woven matrix sensor for compression measurements. The sensor behaviour in tensile mode for single fibres and woven textile was comparable. With the pressure sensor device, the position of penetration and the amount of deformation can be investigated.

D-1:L06 Integration of OLEDs in Textiles

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Conjugated organic small molecules and polymers, offer the opportunity to produce devices on large area, low-cost and plastic planar substrates. These materials are becoming increase attention also in the field of e-textiles, because they show an interesting combination of electronic and mechanical properties that can be favourably exploited in smart textiles. A key step for the integration of mass production of e-textiles is to completely integrate electronic production with textile productions. In the last years were reached progress in the development of fibers and there processing for application in e-textiles. The application reached from fabric integrated light sources to low cost solid state lighting under the aspect of protection and security. Here are present on the one side the research results concerning the integration of encapsulate solid OLEDs and additionally also OLEDs fabricated on flexible high barrier substrates into textiles. On the other side it will be discussed the first results concerning the realization of an OLED on cylindrical surfaces, based on solution processed technologies to go in direction of low cost processing. It was succeeded to realize a simply, inverted planar construction, based on solution processing. This preliminary work was the precondition for the development of a fiber based OLED. It will be demonstrated that OLEDs were prepared using glass fibers as substrates and solution processed active and hole-transport layers.

D-1:IL07 Application of Melt-blown Technology for Manufacturing the Sensor Non-woven Fabrics Composed of Polymers Loaded with Multi-wall Carbon Nanotubes

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The aim of research was to elaborate the melt - blown technology for manufacturing temperature and chemical vapours sensor non-woven fabrics. In the first case the sensor properties were achieved by application the optimal composition of immiscible polymer blends PCL/PP loaded with multi-wall carbon nanotubes (MWCN). Different polymer compositions were subjected to melt blowing process changing the proportion of matrix polymer PP to dispersed phase PCL/MWCN. Obtained non-woven fabrics were characterised by measuring their electrical properties as a function of changes of temperature in the range of 20-80 °C. As studied, the 70%PP/28,8%PCL/1,2%MWCN non-woven fabrics show the best sensitivity to changes of temperature on the level of 50-60 °C. In the second case the melt blown smart non-wovens were obtained using PLA/MWCN. PLA 4060D delivered by Nature Works Company was melt mixed in two stage process with carbon nanotubes Nanocyl7000 in order to obtain PLA/ 2%MWCN composition. Non-woven fabrics made of this composite were characterised by measuring the changes of their electrical resistance to vapour of benzene, toluene, acetone and methanol. As studied, the PLA/MWNT fabrics manufactured under the optimal conditions show good sensitivity over multiple testing cycle.

D-1:L08 The Concept of Mood Changing Garments Made from Luminescent Woven Fabrics and Flexible Photovoltaics

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A collection of high fashion clothes has been designed and made up which have a number of SMART characteristics. Electric power is provided by an array of flexible photovoltaic strips which have been carefully arranged within the design aesthetic of the garment. They are connected with conductive cloth and their energy is collected via a miniaturized electric circuit and a charged Li battery cell for storage. This energy harvesting capability is two fold; one to charge mobile phones, PDAs, etc and another to provide the necessary energy to an undergarment which is made of a woven luminescent fabric capable of changing colour. The mood changing function of the electroluminescent fabric is provided by another miniaturised circuit which has a microphone incorporated in it. The microphone picks up our voice and by analyzing its characteristics it determines in a logic programmed in the circuitry, whether we are under stress or relaxed and it changes the colour of the garment via LEDs carefully incorporated in the garment design. The garments are made up and form part of a wider collection. Care is particularly given not to use any cabling and everything to form part of the fabric and garment designs.

D-1:L09 Production of PEDOT Coated Conductive Fibers for Smart & Interactive Textile Applications

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Electroactive textile fibers are being widely used for smart textile applications, such as, medical, military and energy generation applications. For integrating electrically conductive fibers in wearable applications and getting better results, fibers should be highly conductive, soft, flexible, durable and resistant to different solvents. We have produced textile based electrically conductive fibers by coating different textile yarn fibers (viscose, polyester) with conjugated polymer, poly (3,4-ethylenedioxythiophene) (PEDOT). We have employed an efficient technique, called oxidative chemical vapor deposition (OCVD) polymerization for this purpose. OCVD is a solvent free technique to form uniform and thin layer of different conjugated polymers on different substrates. It was investigated that relatively good electrical and mechanical properties could be achieved with viscose and polyester yarn fibers and roughly 15 S/cm conductivity was achieved in our initial experiments. Scanning electron microscopy, FT-IR analysis, TGA, and mechanical testing was performed to characterize the PEDOT coated fibers. In order to find out the stretch sensing properties of coated fibers, the knitted structures of these fibers were prepared and variation in electrical properties at tension and relaxation state were investigated. A washing cycle was also performed on knitted structures to determine

the durability of PEDOT coatings on viscose fibers. These PEDOT coated textile fibers could be used in different smart textile applications such as stretch sensors, pressure sensors, and sensors for ECG measurements and as protective clothing for EMI shielding effects. It is also possible that these fibers could be used as solar cells and fuel cells demonstrators.

D-1:IL10 Shape Memory Polymers in Textiles

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This paper highlights the most important areas and directions of shape memory polymers in textiles. The textiles of shape memory polymers involve fibre spinning (including wet-spinning, melt-spinning and electro-spinning), fabric, smart apparel, actively finishing technology and WVP investigation. Based on the molecular structure of shape memory polymer, the shape memory transformation from polymer to textiles and application theory are illustrated and stated. Additionally, the challenges of shape memory polymers in textiles are pointed out and some research directions are also suggested.

D-1:IL11 Interactive Electronic Yarns by Novel Electrochemical and Plasma Treatment

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The number of application fields of micro systems and microelectronic components are increasing continuously. International fairs clearly show smaller and compact circuits on foil substrates. Especially the sensoric and actuatoric sensor systems become more flexible. However, non rigid and extremely loadable and bendable may only be manufactured from textiles. The galvanic and electrochemical finishing of textiles is one way to build textile based micro systems. A concept for the production of electrically highly conductive, functionalized and interactive yarns is proposed. The first step of the concept, the highly conducting yarns, are already transferred into an industrialized production and is commercially available. Silver coated polyamide yarns are already on the market since the end of the seventies. Till now the applications have been limited on the use of their anti-electrostatic and anti-microbial properties. The drawbacks of the yarns can be overcome by an electrochemical treatment to increase the metal layer, to create multi layer systems or functional top layers by anodization and other electrochemical techniques like the electro-polymerisation and electro-deposition of paint. So treated yarns can be processed by any textile technology.

D-1:IL12 Cosmeto-textiles: State of the Art and Future Perspectives

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The skin is the largest human organ. Its care and health are, therefore, essential. The skin can only be healthy and attractive when it is in balance. The pre-requisites for healthy skin are: the moisture content, the protective function, elasticity and cell renewal. All of these parameters are supported by applying pharmaceuticals and wellness substances. The newest movement in beauty is the hybrid of textiles and cosmetics called Cosmeto-Wear: consumers, especially ladies, expect clothing to have a positive effect on the conditions of their skin. Hence, finishers are being asked to create products that offer new and/or improved functions using a limited selection of starting materials. The term "cosmeto-textiles" is a term already in use today encompassing known textiles with coatings/finishes worn close to the body, which makes it possible to provide garments with active therapeutic or cosmetic ingredients that are imparted to the skin of the wearer or released from the finish while the garments are being worn. The objective of this paper is to discuss the state of the art and the future perspectives of cosmeto-textiles products, focusing on the different ways of manufacturing, the choice of active components, the problem of their unwanted loss during washing.

D-1:IL13 Additive Colour Mixing on Textiles with Liquid Crystal Dye Systems

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There are two types of thermochromic dye systems which change colour in reaction to temperature variation that are suitable for application

to textiles; the leuco dye type (which change from coloured to colourless) and the liquid crystal type (which change through a spectrum of colours). The presentation will illustrate selected findings from a practice-led investigation, particularly focusing on the colour change mechanisms of the liquid crystal type, and how, in principle, they can be used to produce colours by additive colour mixing on a fabric surface. The presentation is supported by initial results from a parallel investigation, inspired by the practice-led research, into the scientific basis of the additive colour mixing properties observed. The research highlights that liquid crystals have hidden inspiration on the generation of responsive colour still to offer. In conclusion the presentation will highlight particular design considerations for the use of liquid crystals; for example, they will never offer the permanence or stability of traditional dye stuffs making it necessary to consider non-permanent colour as part of a design function.

D-1:L14 Halochromic Textile Materials as Innovative pH-sensors

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Recently, an increasing interest in pH-sensitive textiles is recognized. These chromic textiles can be used as flexible sensors for various applications. The aim of the current research is to develop textile pH-sensors through the application of pH-sensitive dyes on various textile materials using different techniques. The results of our study show that halochromic dyes can be incorporated into conventional textiles by a standard dyeing technique. Also coating the fabrics with a sol-gel layer containing the halochromic dye proved to be successful. The majority of these developed materials showed a clearly visible colour change with a pH-variation. The response of the sensors was dependent on the density of the fabric but was generally relatively fast, especially for the sol-gel treated fabrics. The halochromic colouration of nanofibres was realized by directly adding the dyes during the fibre formation, which was shown to be highly effective. Again, a clear halochromic shift was observed. The response of these sensors was fast thanks to the high porosity of nanofibrous nonwovens. Yet, it should be kept in mind that the halochromic behaviour of the dyes in the textile matrix altered compared to their behaviour in solution which is most likely attributed to dye-fibre interactions.

D-1:L16 Integration of Small Diameter Wire form SMA for the Creation of Dynamic Shape Memory Textiles

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The integration of Nitinol wire directly into flexible textile structures has seen limited successful research outcomes. This has mainly been due to issues with shape training and the accurate positioning of the Nitinol components. A new approach is investigated here, which utilises small diameter (0.15mm-0.03mm) Nitinol components and the manipulation of the woven structure. This combined approach has the potential to improve the dynamic control of the resulting textiles, giving the textile designer further latitude to adapt a combination of functional and visual properties, as well as expanding application possibilities. This investigation focuses on the development of composite samples that integrate Nitinol directly into woven multifilament polyester and polypropylene textiles, demonstrating the potential for medical and healthcare applications. The prototype composite textiles developed, investigate a range of controlled surface manipulations as well as larger scale shape changes, including the creation of arched forms, pleating, expansion and compression. With supporting data, the evaluation of these samples explores the potential of integrating small diameter Nitinol wires into woven structures and the resultant levels of shape transfer, control and cyclic speed achievable.

Session D-2

e-textiles

D-2:IL01 An Elastomeric Ionic Hydrogel Sensor for Large Strains

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Strain gauges attached to elastic fabric sleeves to monitor body motions could be used in rehabilitation from injury, training and health monitoring. This paper describes a soft hydrogel strain gauge where conduction is via salt solution in the gel. Use of AC sensing eliminates electrochemical effects. An array of 5 sensors on a knitted sleeve around the elbow of a robot arm gives strain readings corresponding to the position of each sensor and the bend of the elbow. The single phase sensor material does not exhibit relaxation and hysteresis effects present in carbon filled elastomers and conducting polymer coated fabric sensors. This makes the hydrogel sensor easier to use in real-time strain monitoring situations. The gauge factor of the sensor is about 2 which results in quite good signal to noise ratio when we are monitoring large strains. The hydrogel sensor does drift due to drying, which could be greatly reduced with an encapsulating film. Connecting the sensors to flexible and stretchable wiring on a soft substrate can also be difficult. These materials and their connections can be printed such that arrays of sensors and connectors could be developed for a disposable sleeve.

D-2:LO3 The Power Conversion Characteristics of Woven Organic Photovoltaic Wire Fabrics

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Recently there has been growing interest in developing smart photovoltaic fabric devices. These devices could be used as a sustainable and ubiquitous power source for wearable and other electronic devices. Three woven photovoltaic fabric structures were constructed with fiber-shaped organic photovoltaic wire (OPW) from Konarka Technologies, Inc. (Lowell, MA, USA). The OPW is flexible, lightweight and wire shaped organic photovoltaic fiber based on bulk hetero-junction nanocomposites. The power conversion characteristics of photovoltaic fabrics developed were thoroughly investigated. It was found that the power conversion efficiency of the photovoltaic fabric depends on the incident light quality; fabric cover factor, swatch size, and fabric weave structure. This study also includes photovoltaic fabric model for understanding the effects of different fabric geometry on power conversion efficiency of photovoltaic fabrics. The model predicts the performance of the photovoltaic fabrics with different shape, size and structures, and it provides design criteria for more efficient photovoltaic fabric device.

D-2:LO4 Textile Sensor Applications with Composite Monofilaments of Polymer / Carbon Nanotubes

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The aim of this work was to develop polymer matrix/carbon nanotube (CNT) composite monofilaments to incorporate in textile products, to be used as sensors. The carbon nanotube polymer composite (CPC) monofilaments were produced with the required electrical and mechanical properties for the development of textile sensors for water vapour and temperature, respectively. The monofilaments selected were formed by poly(lactic acid) (PLA) and polypropylene/polycaprolactone (PP/PCL) blended with CNT, and were incorporated directly into the fabrics. The presence of water or temperature modification induced a variation on the electrical conductivity of the filaments. The sensitivity of the monofilaments to humidity and temperature was demonstrated. The target of these sensors is for textile applications (clothing or home textiles) where there is a need for early detection of humidity or temperature. Also, the application of these sensors in garments for sports or personal protection, among others, can be foreseen. However, the application of these filaments in textile materials is still a difficult stage of the process, due the stiffness of the monofilaments, introducing limitations on their processing on the conventional textile equipments.

D-2:LO5 Feasibility of Printing Woven Humidity and Temperature Sensors for Integration into Electronic Textiles

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We demonstrate a woven textile with integrated humidity and temperature sensors on flexible PET and PI substrates. We discuss the fabrication process of the smart textile and compare two methods of sensor fabrication, first conventional photo lithography and second printing using an ink jet or gravure. The humidity sensor is based on a capacitive transducer covered with a sensing layer while the temperature sensor is made of a resistive metallic line. An encapsulation method protecting the sensors during dicing, weaving and operation has been successfully implemented. The fabricated structures are tested to bending strain, a main source of failure during the fabrication of textiles. We were able to bend bare electrodes and complete sensors down to a minimal bending radius of 100 μm without loss of functionality. The woven temperature sensor has a linear sensitivity of 1.175 $^{\circ}\text{C}$ with a temperature coefficient of 0.0027 $^{\circ}\text{C}$, the humidity sensor shows a repeatable behavior in the tested humidity range between 20 to 70 %RH. The weaving process does not damage or change the behavior of the fabricated sensors. This contribution will highlight the challenges and promises of printed and laminating processes for the large scale fabrication of smart polymeric stripes to be woven into textiles.

D-2:LO6 Novel Fibers as Base Technology for Smart Textile Integration

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The main obstacle of electronic smart textiles to enter a wider market is the still absent total textile integration. This includes desired properties like textile processability (spinning, weaving, embroidery, finishing etc.) as well as customer expectations (textile haptics, ease of use, washability) and finally an increasing need for a sustainable textile life cycle. The potential, however, for novel applications is very large, given the fact that textiles are accepted life-long companions of us. Much effort is thus put into research and development for a better integration of electronic components into the textile substrate. In our undertakings, we have decided to choose a rather different way and go one step back by re-developing simple electrical and electronic elements based on fully textile materials. I will present textile-based e-fibers, which we develop into a textile conducting platform by adding simple electronic functionalities like selective insulation, multi-electrode e-fibers or local sensing. First applications in textile electrodes for ECG and muscle stimulation are shown and future developments given in an outlook.

D-2:LO7 Innovative Smart Materials for Wearable Electronics

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Wearable electronics made of integrated smart fibers are relatively new to the economy and can create high value-added opportunities. These materials play an important role in the development of electrical and electronic devices in which flexibility and rollability are of importance. Insulated micro conductors, which can be served as electrical or data conduits, can be integrated into the flexible substrates and electrical components can be soldered directly onto the substrate. Recently washable micro conductors and connectors have been developed for wearable military applications such as chemical and bio-threat sensors, wound positioning vests, body-borne communication, pressure sensing/ guiding patches for parachutes, and wearable global positioning antennas that map soldiers' whereabouts. Micro conductors based flexible electronics are also being considered in consumer markets. GPS driven shirt for blinds, MP3 player incorporated musical jackets, bodily functions monitoring smart garments, fashionable cloths, and heated jackets have already been successfully tested but not commercialized due to the lack of washable micro conductors. Conductors based on metallized polymers, stainless steel or titanium filaments, and carbon nano tubes have been tested but none of them are suitable for washable electronics due to their price, health hazard, low conductivity, or solderability. Recently EY Technologies together with U.S. Army developed insulated micro conductors (iCon) that are truly flexible, solderable, wearable, and washable. These insulated 25-50 micron conductors are about 4 times smaller than human hair and is only few times resistive than pure gold providing maximum conductivity at minimum power usage. These finer diameter conductors are less prone to bending failures; a major concern in flexible applications. The use of non toxic, ductile metals also minimize fatigue while insulating polymers provide the strength to the conductor. The innovative filaments can be used on commercial equipment and expect to open up new era to numerous intelligent flexible products with improved durability, washability and wearability.

D-2:L08 Novel Flexible Sensors for Smart Clothing to Monitor Vital Signals and Energy Expenditure

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Though during the last decade much attention has been paid to the development of smart clothing for real time vital sensing to monitor the wearer's health conditions, a great commercial success is not achieved yet due to several important reasons. One of the most important reasons is that polymer/textile-based sensors suitable for clothes have not been developed to measure ECG, heart beat rate, and respiration rate. In this study we have developed silver-plated nanofiber web as dry electrode to measure ECG and EMG and physiological sensing belt (PSB) made of a pair of elastic textile bands with a PDMS-coated PVDF film imbedded between them to measure respiration, heart pulse, and energy expenditure during walking, jogging, climbing, running, etc. The ECG and EMG signals measured using our developed dry electrodes were compared to those from the commercial Ag/AgCl gel electrodes. Pulse rate, respiration rate, and physical activity could be accessed simultaneously from the measurement of piezoelectric current signals generated from the deformation of the PSBs wrapped around finger, chest, and thigh, respectively. Thus, by wearing smart apparels with our developed sensors and appropriate electric circuit, the wearer's whole-life health management will be possible in near future.

D-2:L09 Conformable Textile Electronics Comprising Foil Based, Organic Components

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As electronics become more abundant and fulfill an increasing role supporting our life with communication, sensing, etc. integration into our world in an unobtrusive way is necessary. Integration into materials which are surrounding us like textile or thin, foil based, conformable systems, which can even be worn to the body, are possible options. Foil materials are thin and compatible with technologies like printing, laser and (organic) electronic functionalities like light generation (Light Emitting Diodes, OLEDs), detection (organic photodiodes, OPD) can be incorporated) or organic photovoltaic cells, OPV). Interconnection of these elements to textile or stretchable carriers in order to create a conformable system is challenging. This system should withstand the mechanical constraints in dynamic use and demand reliable mechanical and electrical interconnections. The bonding process was studied comprising the boundary conditions in temperature and pressure for the organic components. Reliability was tested for accelerated humidity / temperature conditions as well as dynamic flexing of the composed systems. Inspiring demonstrators will convince the possible applications areas like energy harvesting textiles, phototherapy clothing and smart medical bandages.

D-2:L10 Essential Building Blocks of Fibrous Transistors, Part I: Gate Layer

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During the last decade, research on intelligent textile systems progressed steadily. Today, science is focussing on full integration of electronics into textiles. E-textiles function like their rigid electronic companions but keep their textile properties. To interconnect components within the system, textile structures need to be equipped with electro-conductive properties. For flexible solar cells or fibrous transistors, electro-conductive coatings are applied. Transistors, acting as electrical switches, are essential for realizing fully integrated intelligent textile systems. By electroless deposition of pyrrole and copper on polyester fibres, conductivity is achieved. A DC conductive gate electrode is designed. In this paper, the development of the gate layer within the fibrous transistor is described. Ideal pH and optimal reaction time are determined as well as the effect of variation in fibre diameter is investigated. A reproducible polypyrrole layer has been obtained. Ideal reaction time was 180 minutes at a temperature of 278K. The electroless copper coating process on the polypyrrole layer showed optimal results at a pH of 13. Analysis through SEM and resistance measurements have been completed. Further investigation comprises stability and roughness of the copper layer.

Session D-3

Functionality, Manufacturing, Application

D-3:IL01 Adaptive Textiles for the Home

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This paper introduces a series of design-led investigations exploring the conceptualisation and materialisation of adaptive textiles for the home. As modernism engaged architecture in a redefinition of its boundaries by promoting values of transparency and efficiency, the home became an environment primarily conditioned by technology, more and more disconnected from the exterior. Today, as we realize the consequences of our ability to engineer the world, this paper is asking: can the design of self-actuated textiles contribute to a domestic culture in which technology cultivates a relationship of interconnectivity with nature. By presenting parallel explorations into the material prototyping of light-responsive textiles and design probes into the materialisation of immersive textile environments based on electro-active polymers, the paper will discuss, beyond the purely functional, the cultural and poetic potential of smart technologies, including thin film photovoltaics, light-induced liquid-crystals and dielectric elastomers. Suggesting applications in which adaptive textiles become the medium through which the home reconnects with the multiple rhythmicities of nature, the paper will highlight specific crafting processes in which self-organization and energy-minimization principles play a central role in the shaping of adaptive textiles underpinned with values of interconnectivity while emphasising the significance of interdisciplinary collaborations across science and design.

D-3:IL02 Continuous Multifunctional Carbon Nanotube Yarns

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Continuous weavable multifunctional carbon nanotube yarns are fabricated at one-step by spinning from a catalytic chemical vapor deposition reaction. The CNT yarn is formed through the direct assembling of carbon nanotubes in the gas flow as continuous integrated by mechanical winding. Kilometers of high-quality continuous yarn are spun from this process through the design of the CVD reaction with innovative spinning methods. The CNT yarn consists of high purity carbon nanotubes with single walled or double walled structures with controlled alignments and yarn morphologies. Solid, hollow and multiple layered yarns with interconnected crossed or oriented CNTs are fabricated by controlling spinning. The CNT yarn is strong and flexible which can be manipulated, mechanically engineered and woven into a fabric, potentially for structural and composite applications. It can be infiltrated with polymers or ceramic precursors to form directional nanocomposites with promising reinforcement effects. Moreover, the CNT yarn is highly electrically conductive and thermally conductive potential for functional applications. The use of the CNT yarn as flexible weavable supercapacitors, sensors and solar cells are demonstrated.

D-3:L03 Design and Optimization of an Injection-moldable Force-fit Interconnection Module for Smart Textile Applications

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Integration of electronics into textiles for various applications is gaining more and more interest by research facilities and companies, alike. Recently, different integration and interconnection technologies have been presented. However, most of them have the drawback needing increased temperatures. This work presents a polymer based force-fit interconnection module (Click-Bond) that can be used to establish reliable electrical and mechanical interconnections between electronic components and textile circuit boards at room temperature. It is an extremely fast and cost-efficient process that is able to bring smart textile applications into the mass market. At first, a list of potential polymer materials is generated that can be used in injection-molding, provide the necessary structural and thermo-mechanical properties, and do not include hazardous compounds. The influence of humidity as well as creeping at higher temperatures is analyzed. Besides, models of the module are made and simulated by means of FEA. Material

properties and geometries are varied to find the maximum achievable contact force onto a textile circuit. The design aims at using a single mold to reduce cost. Finally, a model of the mold is made to simulate the injection process before an actual part is produced.

D-3:L04 Challenges for Combining Semiconductor (Thin Film) Technology with Textile Substrates towards Textiles for Energy Production

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In this paper we would like to discuss the challenges of direct fabrication of electronic components onto the textile substrate, e.g. preparing energy harvesting devices by coating on monofilament level or using base coatings. There is an increasing amount of research being done to realise this direct fabrication. This has several advantages over the traditional method where the components were stitched, laminated or fixed by some other means onto the textile. The fixation techniques usually show problems with interconnects, the components used were of the traditional kind, having a rather low flexibility and stretchability, resulting in a loss of the inherent properties of the textile substrate. By depositing the components directly onto the textile substrate its inherent properties can be preserved, since the deposited layers are inherently thin, being on the order of tens of nm, with a maximum of a few μm . The problem is that exactly this primary advantage faces one of the major challenges. The thin layers used in semiconductor technology are as such not compatible with the textile substrate which has an open structure and surface roughness in the order of the fibres or yarns it is made of, being the order of several tens of μm or even more.

D-3:L05 Nanoscience goes Pret-a-Porter: Novel Nanogold-Wool-Composite Fibres

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Professor J.H. Johnston and Dr. K.A. Lucas have recently developed a novel approach for dyeing merino wool with gold nanoparticles by coupling the surface plasmon resonance and the chemistry of gold with that of wool fibres. In a related approach presented here, the research is carried out in three major steps: (a) formation of gold nanoparticles, (b) preparation of wool surface for dyeing process and (c) fabrication of nanogold-wool-composite. The synthesis of red colloidal gold uses reducing agents such as tannic acid. Purple and blue nanogold forms in the presence of other reducing agents and/or surfactants. Seeded-growth-processes allow a wider colour tuning through different particle shapes. Two-phase-processes achieve a beneficial functionalisation of the particle surface. Steps (b) and (c) transfer the outstanding optical properties of nanogold onto wool resulting in durable, non-fading coloured fibres. Characterising studies of all production stages are mainly performed by electron microscopy, visible absorption spectroscopy and dynamic light scattering techniques. Investigations focus on size and shape of nanoparticles, their distribution on the wool surface and the fibre morphology. This novel dyeing process has the potential for colouring wool for high value textiles.

D-3:IL06 Prosys-Laser: Smart Laser Protective Textile Systems

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PROSYS-Laser is dedicated to developing highly innovative "passive" and "active" laser-protective clothing and curtains, hardly available on the market today, for use with hand-held laser processing devices (HLD) and with automated laser machines. Key developments are: passive functional multi-layer technical textiles, providing a high level of laser resistance, active system incorporating functional multi-layer smart fabrics which detect laser exposure and, by means of safety control, deactivate the laser beam automatically and test methods and testing set-ups to qualify passive and active functional technical textiles and tailored PPE. The passive laser-protective textile system will be realized using the best combination of materials, providing, at the same time, laser, fire, and heat protection together with other properties. Designing active system means the realization of functionalized fabrics by using

conductive materials and by exploiting their physical properties. The electronics which interface the active system, providing signal conditioning, acquisition, on-body pre-processing, local data storage and wireless communication, is a major part of the active approach. The electronics will provide alarms and ultimately enforce laser shutdown upon defined conditions.

D-3:IL07 The PASTA project: "Integrating Platform for Advanced Smart Textile Applications"

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PASTA is a FP7 integrated project on integration of electronics into fabrics, with partners from 5 different countries. Until now, many developments in the smart textile field have been focusing on textile technologies (conductive wiring, sensors, connectors,) in a combination with classic printed circuits with classic components. Often, the bottleneck for further integration of electronics into the fabric, is the mismatch of these classic electronic packaging technology with typical textile properties as comfort, drape ability or stretchability, washability and last but not least the manufacturing process. As textile production is essentially a large area roll-to-roll process, any additional production step for smart fabrics should be compatible with that process. Therefore, the PASTA project is focusing on the development of new electronic packaging and interconnection technology for manufacturing large area smart textiles. Three different new electronic packages are being developed: a die-in-yarn solution (for small bare die Si chips), a stretchable carrier as package for bare dies and components, and a crimp flat pack solution for small flexible circuits.

D-3:L08 Application of Flexible Polymer Electrode to Smart Textiles

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Smart textiles used in wearable electric devices such as organic solar cells (OSCs) and organic light emitting diode (OLED) have been attracted wide attention for various benefits, including both easy operation and portability. For applying electric devices on the textiles successfully, it is essential to develop flexible electrodes. Indium tin oxide (ITO) was widely used as an electrode because it has excellent conductivity and transmittance. However, it is not an ideal material for adapting flexible device because propagation of cracks occurs on the ITO surface, under repeated bending cycles, which leads to considerable degradation of its conductivity. To overcome these disadvantages, a polymer based electrode is applied in our study. A low cost and solution processable conducting polymer was prepared and various additives were introduced in order to increase the electric conductivity. Through many experiments, a polymer based electrode was prepared and it was applied to the OSCs anode. As a result, it was confirmed our polymer electrode to show good potential and applicable in smart textiles.

D-3:L09 Two Novel Techniques of Fabric Sensing using Carbon Nanofibres

A. SANTOS, P. ARQUER, B. RUIZ, ITMA Materials Technology, Aviles, Spain

Silver or copper coatings printed in fabric show good conductivity, an essential property for wearable electronics, but also show stretchability problems. On the other hand, carbon nanofibers or nanofibers-silver nanocomposites in dispersed polymeric matrices maintain high conductivity but present very good stretching endurance. The use of carbon nanofibers as smart textile electrodes is demonstrated in this paper applied to two novel sensing methods. The first method achieves a wide range pressure measure, allowing detection from soft caress to hard press. This feature makes it very appropriate to supply a sensation input in toys for children or disabled people. The other interface has been designed for user distinction, enabling permission control, required for military applications. Two easily portable prototypes have been developed to prove the above concepts showing very reliable behavior.

D-3:L10 Improvements of Electronic Contact System in a Smart Garment

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Electro-textile interface is indispensable for the production of smart clothing, but it is rather difficult to integrate electronic components with fabric because their manufacturing processes and their physical properties differ greatly. Due to these differences a number of problems arise in designing smart garments, thus it is necessary to implement unconventional solutions and methods. Different designs of flexible textile interface are investigated, in which bulky wires and solid PCBs are replaced with more clothing-friendly materials. Experiments are carried out with several conductive fabrics and other materials, such as flexible PCBs, which are suitable for designing electronic circuits for smart and interactive clothing. During the study several conductive tracks were constructed, which differ by material composition and geometrical parameters, conductivity, track shape, attaching technology etc. The tests show that the designed flexible tracks are suitable for use and are durable, the tests include wear resistance and washing resistance. Compatibility of flexible circuits with different insulation materials is studied as well. Results of the study are analyzed and compared, evaluating preferable solutions that are suitable for a smart garment system.

D-3:IL11 Bio-inspired Fiber-based Probes

K. KORNEV, Clemson University, Clemson, SC, USA

This talk reviews recent results on fabrication of artificial proboscises for probing and analyses of liquids available in a form of tiny droplets. Depending on the application, the probe can be made ferroelectric or magnetic. We show that ferroelectric and magnetic probes can function as artificial proboscises and can be manipulated remotely to absorb droplets. The chemical composition of this drop can be further analyzed using different techniques. We will show an example of such an analysis based on fluorescence microscopy and PCR assay.

D-3:IL12 MerinoGold - Nanogold as a Novel Colourant and Functional Entity in Wool for High Value Textiles and Fashion Apparel

J.H. JOHNSTON, K.A. Lucas, School of Chemical and Physical Sciences, MacDiarmid Inst. for Advanced Materials and Nanotechnology, Victoria University of Wellington, Wellington, New Zealand

Gold in its yellow metallic form occupies a premier position in the world economy and society representing high value and quality. When the particle size is reduced to nanodimensions different colours can be obtained due to the surface plasmon resonance phenomenon exhibited by gold. The resulting colours depend on the particle size and shape. Small spherical particles are red and with increasing particle size their colour changes to purple and blue-grey. Gold nanorods and shells can be red, yellow, blue or green depending upon the particle shape and dimensions. New Zealand produces fine merino wool for high quality woollen textiles. We have captured an exciting and unique opportunity by linking the prestige and high value of gold with high quality merino wool through the novel use of nanogold as stable colourants in the wool, for high quality fashion apparel, luxury textiles and carpets. The nanogold colourants cannot fade in light, as traditional organic dyes do and provide the textiles with excellent lightfastness and rubfastness qualities. The fibres also show desirable antistatic and antimicrobial properties. Our proprietary goldwool technology is being commercialised thereby providing new market opportunities for high fashion apparel, luxury textiles and premium carpets.

D-3:L13 Durable Self-healing Super-liquid-repellent Fabrics

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In this study, fabrics having a superhydrophobic and superoleophobic surface were prepared by a wet-chemistry coating method using a coating solution containing hydrolyzed fluorinated alkyl silane and fluorinated-alkyl polyhedral oligomeric silsesquioxane. The coating shows remarkable self-healing superhydrophobic and superoleophobic properties and excellent durability against UV light, acid, repeated machine washes, and severe abrasion. The self-healing mechanism is presented. The influence of material type and structure on the surface properties is discussed.

D-3:L14 Improving Colourfastness and Mitigating Photo-degradation in Wool

K. LUCAS, J. JOHNSTON, School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington, New Zealand

Wool is degraded by exposure to sunlight, particularly from the ultra violet (UV) component. Degradation produces numerous changes in its physiochemical properties, notably yellowing, bleaching and loss of tensile strength. Numerous attempts have been made to photostabilise woollen textiles, these traditionally involve the application of organic UV absorbers, anti-oxidants, and thiourea-formaldehyde resins. However none of these treatments offer a high degree of protection in sunlight, especially following repeated laundering. This paper presents a shift in the approach to wool photostability, through the bonding of ZnO quantum dots to wool fibres. Recently ZnO quantum dots have attracted significant attention as inorganic UV absorbers. Their UV absorption can be tuned by changing the particle size and shape and also the nature and level of impurities. Hence ZnO quantum dots have the potential to act as colourless UV and blue light absorbers, thus mitigating the detrimental effect of sunlight on woollen textiles whilst not altering their colour. This paper presents the synthesis of ZnO particles and their attachment to wool fibres. The photostability of the resultant fibres, their physical morphology, and the bonding between the ZnO and wool fibres will be discussed.

D-3:L15 A Classified Catalogue for Textile-based Sensors

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Technical textiles are used primarily for their technical functionality in many different industries today. It is possible to integrate sensors into the textile for monitoring the functionality. Smart textiles are concerned with textile-based sensors integrated mechanically and structurally to a textile. The state of the art in developing textile-based sensors extends from inherent sensor fibers to coated yarns and textiles but without using standardized tools in production. The development of a textile sensor and its interpretation on a specific application has been associated with many investigations into combination of different materials, what is a lengthy and costly developing process. Knowledge has already been generated on textile sensors, which up to now lacks an appropriate classification and structure. A classified catalogue which allows a direct selection of textile-based sensor modules on the basis of measured values and is sorted by application area, is introduced in this article. Setting standards in the field of smart textiles helps companies to produce more focused "smart products".

D-3:IL16 Thigmo-morphogenetic Fiber Composites Embedded with Shape Memory Alloys

M. MINGALLON, Arup & The Architectural Association, London, UK; **S. RAMASWAMY**, KRR & The Architectural Association, London, UK

Thigmo-morphogenesis is the changes in shape, structure and material properties that are produced in response to transient changes in environmental conditions. All plants are capable of movement: petals of flowers which open and close, tracking of the sun by sunflowers, the convolutions of bindweed's around supporting stems, etc. In all these examples, movement and force are generated by a unique interaction of materials, structures, energy sources and sensors. Material experiments were performed to develop a fibre composite material system that has embedded sensing, actuation and control functions. The energy used for the actuation is supplied through a heat source, part of the experimental setup. Nevertheless, the hypothesis is that diurnal variation in the atmospheric temperature would be used as the energy source for actuation. Nitinol shape memory alloys exist in three different crystal structures named martensite, stress-induced martensite and austenite. Strips of nitinol were embedded in a sandwich fibre composite material to aid shape change. Strain gauges and thermocouples were used as sensors and process control units as signals for shape change. The adaptability observed is deployable in a scale that could be proliferated to create large architectural structures.

D-3:IL17 Superhydrophobic Textiles - 75 Years of Smart Textiles

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Seventy six years ago, as reported in his classic 1936 paper, Wenzel was investigating the wetting behavior of light-weight woven and knitted

fabrics. He wished to find a way to make these fabrics both waterproof and preserve their air porosity. Today, we would describe such a material as a smart textile. Since Wenzel's 1936 paper on the effect of roughness on wetting behavior, there have been thousands of papers studying this effect and attempting to apply it to many applications. One of the first extensions was made by Cassie and Baxter (1944) to address porous surfaces, primarily textile materials containing air. This paper will present recent analyses of superhydrophobicity and use of the Cassie-Baxter, Young's and the Laplace equations to explore strategies for producing and quantitatively analyzing superhydrophobic materials. This will allow us to design smart textiles that shed water readily while maintaining an open structure and producing these fabrics using conventional, low cost textile processing techniques.

D-3:IL21 Fabric Optoelectronics Enabling Healthcare Applications
F. VAN ABELEN, K. CHERENACK, S. LUITJENS, G. ZHOU, K. VAN OS, Philips Research, Eindhoven, The Netherlands

Intelligent textiles are placed where technology meets comfort and design. Within the European project PLACE-it we are developing smart textile application into two directions: large area and wearable healthcare applications. For both the textile properties are very promising. However, although concepts and prototypes are easily made, the next steps in getting them towards a commercial success are not obvious. In this contribution the challenges related to commercialization of electronic textiles are presented and illustrated by healthcare application examples. From an industrialization view approach this contribution will highlight the practical differences between electronics and textile industry and the mismatch in requirements for both textiles and electronics. We solved this mismatch by developing a technology platform that is able to combine both worlds. This platform contains a variety of aspects like material selection, design rules for product and processes, test strategy, up to sustainability thinking.

D-3:IL22 Advances in Physiological and Psychological Monitoring with e-textiles
R. PARADISO, Smartex srl, Prato, Italy

Wearable monitoring systems based on Smart Fibers and Interactive Textile (SFIT) platforms combine imperceptible sensing and computing functions with an interactive communication network. The integration into clothes of bio-potential sensors for health monitoring provides daily physiological parameters through a continuous, personalized, self-made detection of vital signs and the tracking of behavioral indicators of the subject. SFIT platforms can be used unobtrusively into the routinely daily activity to perform remote monitoring of persons in different circumstances and situations: during controlled exercises and diagnostic procedures as a biofeedback tool, during the usual daily life, during sleep or even to monitor behavioral indexes and mood disorders. Treatment of stress may include also training in cognitive-behavioral skills. Moreover, physiological signs and behavioral monitoring based on a multivariable approach leads to an enhanced sensitivity and specificity of these systems for the prediction of critical events.

D-3:L23 Respiratory Volume Estimation by a Stretchable Textile Sensor
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E-Textiles using fabric sensor are studied well for respiration monitoring in recent years, for example Wealthy, MyHeart, and MagIC. These can estimate respiratory rate and pattern; however, studies for respiratory VOLUME estimation, which is necessary for inspection and monitoring of Chronic Obstructive Pulmonary Disease (COPD), have not been established. In this paper, we introduce a new stretchable textile sensor and an examination to decide a calculation model for respiratory volume estimation. The sensor will be parts of e-textile wears for COPD inspection and monitoring in our projects. It can stretch up to 172 % (e.g., 11 cm to 19 cm). The stretch can be detected from electronic potential changes between conductive fibers. In the examination, we led a model from comparison between respiratory volumes determined by spirometer and movements of 24 points for each front and back side of torso majored by motion capture. In our evaluation, volumes estimated using

our textile sensor and the proposing calculation model were highly correlated with volumes detected by spirometer ($r = 0.929$, $P = 2.2 \times 10^{-16}$). The residual standard error of the estimated volumes was 5.11 in percentage of VC.

D-3:L24 Structural Conformability and Fluid Uptake Properties of Smart Wound Dressings
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Nowadays, many commercial products have been developed to reduce wound healing times and cost. The complex wound healing phases are still required to develop smarter and more effective dressing products. There are various major requirements that the modern dressings have to meet: maintain a moist environment around the wound; permit diffusion of gases; stimulate the growth factors; provide mechanical protection; prevent the wound desiccation; non-allergenic; minimise pain from the wound; remove excess exudate; control local temperature and pH; be comfortable and easy to remove; cost effective and aesthetically acceptable and biocompatible and elastic. In this study ten commercial smart and modern dressings - CombiDerm®, Versiva® XC®, Sorbsan Plus SA, Opsite® Post-Op, Aquacel™ Surgical, DuoDerm®, Granuflex®, Mepilex® Border, Allevyn Gentle Border and Biatain® - were tested and evaluated. The dressing specimens were obtained from the UK market. The following experimental tests were performed on the dressing specimens; dressing mass and thickness, fluid uptake, conformability, absorption rate, waterproofness, stainless steel (SS) peel test and vertical wicking. It was found that Biatain® had the highest absorbency and fluid handling capacity and also had lower moisture vapour permeability value compared to the other dressings. Versiva® XC® and DuoDerm® had higher extensibility values than other dressings, which are 3.56 (MD) and 3.99 (CD) Ncm-1 for Versiva® XC® and 3.67 (MD) - 3.12 (CD) Ncm-1 for DuoDerm®. The permanent set results were found to be similar pattern to the extensibility results. All tested dressings passed the waterproofness testing. DuoDerm® and Granuflex® showed more than 20 minutes rate of absorption and also their SS Peel values were found to be considerably higher than for the other dressings.

D-3:L25 Washable Screen Printed Textile Antennas
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Wireless communication has become commonly used a variety of applications such as computers, mobile phones and antennas for off-body communication. A lot of efforts has been put in having the antennas in smaller sizes, flat and with better performance. In the last decade research has started into the development of flexible textile antennas for integration into garments (wearable textile system). The textile antennas can find use in medical and military sector or in personal protective clothing. The antenna patch is made out of conductive material, for which in the case of a textile antenna, commercially available conductive coated textile materials, conductive threads for embroidery or conductive inks can be used. When using the conductive coated textile it is necessary to cut the patch in the desired pattern by using a simple cutting tool which sometimes is not very precise and accurate. Therefore, in our study we decide to screen print the antenna patch with two silver conductive inks on Polyester and Cotton/Polyester substrates. The paper describes the influence of several washing cycles on the antenna performance. In order to protect the antennas against the mechanical and chemical action in the washing machine, some of them are covered with an polyurethane layer.

D-3:IL26 Smart Textiles with Biosensing Capabilities
S. PASCHE, B. SCHYRR, B. WENGER, E. SCOLAN, R. ISCHER, G. VOIRIN, CSEM Centre Suisse d'Electronique et de Microtechnique SA, Neuchâtel, Switzerland

Real-time, on-body measurement using minimally invasive biosensors opens up new perspectives for diagnosis and disease monitoring. Wearable sensors are placed in close contact with the body, performing analyses in accessible biological fluids (wound exudates, sweat). In this context, a network of biosensing optical fibres woven in textile enables the fabric to measure biological parameters in the surrounding medium.

Optical fibres are attractive in view of their flexibility and easy integration for on-body monitoring. Biosensing fibres are obtained by modifying standard optical fibres with a sensitive layer specific to biomarkers. Detection is based on colour changes, placing a light source and a detector at both extremities of the fibre. Biosensing optical fibres have been developed for the in situ monitoring of wound healing, measuring pH and the activity of proteases in exudates. Current developments aim at the design of sensing patches based on functionalized, porous sol-gel layers, which can be deposited onto textiles and show optical changes in response to biomarkers. Biosensing textiles present interesting perspectives for innovative healthcare monitoring. Wearable sensors will provide access to new information from the body in real time, to support diagnosis and therapy.

D-3:IL27 Smart Technical Textiles Based on Fibre Optic Sensors: Technologies and Applications

K. KREBBER, BAM Federal Institute for Materials Research and Testing, Berlin, Germany

Technical textiles with embedded fibre optic sensors have been developed for the purposes of the structural health monitoring in geotechnical and civil engineering as well as for healthcare monitoring in the medical sector. The lecture will show selected examples of using such sensor-based smart textiles for different applications and will highlight the results achieved in this innovative field in the framework of several German and European projects.

Poster Presentations

D:P01 Development of "Paper Transistor" using Carbon-nanotube-composite Paper

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We propose a unique transistor based on a carbon-nanotube(CNT)-composite paper(CNTCP). The CNT as an allotrope of carbon with a cylindrical nano-structure has a unique electric character. It can possess both semiconducting- and metallic- characters. In contrast, a normal paper is flexible, and can be fabricated easily. We can make the CNTCP by mixing the normal paper and the CNTs. So the CNTCP has both the CNT's electric character and the paper's flexible character. In this study, we developed a Field-Effect-Transistor(FET) by using only the normal papers and the CNTCPs. This "paper FET" has a Metal-Insulator-Semiconductor structure. The metallic CNTCP was used for gate, source, and drain electrodes as metal layer. In contrast, the normal paper was used for an insulator layer because of its high resistance. Moreover, the semiconducting CNTCP was used as a channel of the FET. Then, the paper FET could be constructed by using these three kinds of the papers. After the construction, we measured electrical conductivity. Then, a drain-to-source current was observed and showed about tens nA. Moreover, we could control the current by controlling the gate voltage. The result indicates that we can develop the paper FET by using only normal papers and two kinds of the CNTCPs.

D:P03 Preparation of Highly Piezoelectric Poly(vinylidene fluoride) Nanofiber Web as a Nanogenerator for Energy Harvesting and Its Power Generating Properties

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As many recently developed mobile and wireless devices are operated with very low electric power, even piezoelectric materials producing very low electric power can be a promising candidate as power source and/or power charger. Inorganic piezoelectric films have a high limitation

in practical application due to hardness, fragility, and difficulty in fabricating in a large area and piezoelectric PVDF film also has some limitations due to relatively small piezoelectric charge constant caused by low content of β -crystal phase in spite of excellent toughness and easy fabrication in a large area. P(VDF-TrFE) film with only β -crystal phase is also limited in practical use due to very high cost. So, PVDF could be a good candidate due to cost effectiveness if one developed the process via which PVDF film has as much β -crystal content as P(VDF-TrFE) has. In this study, we report the power generating, energy harvesting, and charging ability of PVDF nanofiber web with very high content of β -crystal prepared through electrospinning the DMAc-acetone mixture solution of PVDF in the presence of several additives. This PVDF nanoweb can surely be used practically as power source or charger for operating electric circuit embedded into smart apparel in near future due to cost effectiveness.

D:P04 Electrically Conductive Polyacrylonitrile Films with High Temperature Performance

H.J. PARK, YOUNG HO KIM, H.T. CHO, Department of Organic Materials and Fiber Engineering, Soongsil University, Seoul, Korea

Highly electroconductive acrylic films that maintain their electroconductivity at high temperatures (above 200 °C) were prepared by electroless plating of modified polyacrylonitrile (PAN) films with copper sulfate solution. First, the PAN films were modified with hydroxylamine (HA) and/or a hydrazine solution in order to introduce crosslinking and ligands for the copper ions. The characteristics of the modified films were investigated using FT-IR spectroscopy, DSC, EA, and SEM. The results indicate that a simultaneous treatment of HA and hydrazine was the most effective method for achieving the goals of high temperature electroconductivity while keeping the required levels of dimensional stability. The resultant tPAN (HA- and hydrazine-treated PAN) films were subjected to electroless plating with CuSO₄/Na₂S₂O₃ in order to form a CuS coating on the film, and thereby imparting electroconductivity to the film. The CuS-tPAN films exhibited better electrical conductivity than the CuS-PAN films which were prepared from an unmodified PAN. In addition, the CuS-tPAN films maintained their conductivity at temperatures up to 240 °C while the CuS-PAN films did not. EDS analysis revealed that the loss of electrical conductivity arose from the oxidation of the samples.

D:P07 An Eco-friendly Regenerated Cellulose Fiber Spun from Cotton Linter Pulp in NMMO Monohydrate by Lyocell Process

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Lyocell is a new regenerated cellulose fiber produced by a novel simple route. Compared to viscose rayon process polluting the air due to H₂S and CS₂ release, Lyocell is environmentally friendly, since it is manufactured by a closed-loop method which enables almost complete recovery of the non-toxic organic solvent. The process involves dissolving wood pulp in a solution of N-methylmorpholine-N-oxide (NMMO) monohydrate and extruding the filaments into an aqueous NMMO spinning bath. Wood pulp based Lyocell, however, has several fatal demerits such as forest destruction and easy fibrillation in the wet state. To improve these problems, development of Lyocell from different cellulosic sources is actually demanded. Cotton linter is a promising candidate to obtain a novel regenerated cellulose fiber which is not only eco-friendly, but also is found to be much less fibrillated. So in this study we prepared the cotton linter Lyocell by dry jet-wet spinning of cotton linter/NMMO solution, investigated the effects of spinning conditions such as the dope concentration, spin draw ratio, air gap distance, and composition of the coagulation bath etc on physical properties and fibrillation of the fibers, and compared the fibers with wood pulp Lyocell with physico-chemical aspects.

SYMPOSIUM E

Next Generation Micro/Nano Systems

Oral Presentations

Session E-1

Physical MEMS / NEMS

E-1:IL01 Wet Process Innovation in MEMS 3-D Structuring on a Silicon Wafer

K. SATO, Nagoya University, Nagoya, Japan

The limitations of anisotropic chemical wet etching of single crystal silicon have been eliminated by our recent research. The etching properties such as etch rate and its anisotropy are quite variable by a small amount of additives or contaminants in etching solutions. Contrary to the common sense that rectangular recesses are etched on a Si (100) wafer, arbitrary round etch profiles are available with minimal mask undercut when etched using a TMAH solution containing a surfactant as an additive. Curved V-grooves for fluidic systems, 45-degree tilted mirrors for optical use, and suspending curved structures are newly fabricated on Si (100) only by wet alkaline etching. The mechanism of the striking change in etching anisotropy by the surfactant is first clarified by in-situ FTIR analysis at liquid-solid interface. The change in anisotropy occurs due to the selective adsorption of the surfactant molecule for those orientations; (110), (331), (221), and (111), where the etching reactions are selectively suppressed by the surfactant molecules.

E-1:IL02 GaN Resonant MEMS

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We present the design, fabrication, and characterization of GaN MEMS resonators with fully integrated electrical transducers. These devices benefit from III-N as a semi-conducting crystal and piezoelectric material simultaneously. They are the first step toward sensors where AlGaIn/GaN heterostructures are used for their transducers and co-integration with High-Electron Mobility Transistors (HEMTs). The added values for applications are expected in harsh environment sensors thanks to robustness and high temperature operability of epitaxial nitrides. Here, we use the flexural modes on GaN beams with integrated actuation and where the detection is performed by a HEMT device located near the clamping point (Resonant-HEMT). Thank to the 2-DEG modulation that arises under piezoelectric field, detection of resonant nanoscale motion is possible with transmission measurement up to 80MHz on small resonators. The transducer output is strongly controlled by the gate bias. Moreover, an efficient control of actuation is performed by choosing appropriate bias near the depletion regime at the actuator side.

E-1:IL03 History and Recent Progress of MEMS Physical Sensors

H. MURO, Chiba Institute of Technology, Narashino, Japan

Recently various electronic control systems for automotive, industrial and consumer-electronic applications have been developed using advanced semiconductor technologies including MEMS sensors. This paper reviews the history of the development of the MEMS physical sensors and highlights their recent progress where their research trends are categorized into the following 4 items: i) Incorporation of heterogeneous sensors: A typical example of this item is the incorporation of accelerometers and a pressure for TPMS. ii) Integration with advanced CMOS circuitry: As CMOS devices are more miniaturized, more metal layers and the resultant inter-metal via layers have been stacked on the

silicon substrate, which are used as structural and sacrificial layers of MEMS devices. iii) Improvement on wafer-level packaging technology: In order to protect micro mechanical parts of MEMS devices during fabrication and in market wafer-level encapsulation techniques are essential for the stable production and in-wafer sealing or wafer bonding techniques are studied. iv) Adoption of new materials: In addition to the LSI materials, some new materials such as CNT, SiC or AlN are applied to MEMS devices for specific applications. Several research examples of each item are introduced in this paper.

E-1:IL04 Towards Flexible Integrated Systems over Large Areas

R.S. DAHIYA, Centre for Materials and Microsystems, Fondazione Bruno Kessler, Trento, Italy

The birth of microelectronics and subsequent advances have revolutionized computing and communications. Yet, as revolutionary as it has been, applications such as electronic skin are not well addressed by it, as they require spreading sensors and electronics over large and flexible substrates. The early efforts to meet these requirements include flexible printed circuit boards having distinct and stiff sub circuit islands of electronic components connected to each other by metal interconnects. Advancing the research towards bendable and multifunctional electronic systems, new solutions based on organic and inorganic materials are currently being explored. A new trend in this direction is the printable electronics using high-performance materials based micro-/nano-structures such as micro-/nano-wires. This is an interesting development as it may enable high-performance and cost-effective integrated systems over large and flexible substrates. This work presents the developments in the area of flexible electronics systems, covering range of solutions starting from flexible printing circuit boards to the recent micro-/nano-structures based large area flexible electronics. The discussion is centred on how electronic skin has evolved with advances in the area of flexible electronics.

Session E-2

Chemical Micro / Nano-sensors and Systems

E-2:IL01 Gas Sensors: Status and Future Trends

M. FLEISCHER, Siemens AG - Corporate Research & Technology, München, Germany

Gas Sensors are about to conquer a large variety of applications that include e.g. the optimisation of combustion processes, the monitoring of room air to reduce the energy consumption of the HVAC, the detection of fires or monitoring of human activities, the inspection of human breath to detect diseases up to environmental monitoring applications. The key of high performing sensors is the integration of intelligent material technologies and the usage of nano structures for the chemical reception layers. Several functional principles and selected key material will be discussed. These include semiconducting metal oxide sensors where ceramic elements have to be integrated into Si based MEMS structures, sensors based on the readout of work function where a large variety of detection materials can be combined with CMOS based transducers, electrochemical sensors which require an integration of electrochemical and gas catalytic elements, CNT based sensors where the CNTs need to be aligned to MEMS structures up to future living cell based detection units. All these approaches are commonly characterised by the usage of appropriate receptor material with an adequate transducer that is usually done in a combination of heterogeneous material integration and a support from nanotechnology.

E-2:IL02 Semiconductor Nanowire Battery-less Chemical Sensors
Y.(M.) WANG, Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, CA, USA

Battery-less chemical detection, i.e., sensing without the need for an external power source, has instant advantages over the existent sensing nanotechnology, where the detection of chemical species often hinges on the shift of electrical resistance. Here we present a novel sensing platform that is based on the dynamic interactions of chemical species with semiconductor nanowire/nanotube surfaces. The platform takes advantage of special electrical signatures associated with various molecules that allow us to sense and distinguish molecular type and concentration. The nanosensor has the advantages of simplicity, cheapness, and fast response-time. More importantly, these nanosensors do not require any external power sources. We demonstrate several protocol sensing platforms that can be fabricated from different types of semiconductor nanowires/nanotubes. The potentials and limitations of these nanosensors are discussed.

E-2:IL03 Smart Electrochemical Microdevices
H. SUZUKI, University of Tsukuba, Tsukuba, Japan

Electrochemical devices have advantages in miniaturization, batch-fabrication, and integration with other components. Although a major application of electrochemistry has been chemical sensing, the range of applications covers other auxiliary functions such as the control of microfluidic transport and pH regulation. To control the transport of solutions in a microfluidic network, electrowetting is a useful technique. A simple valve can be constructed by forming a gold electrode in a hydrophobic constricted region of a flow channel. Solutions can be injected into selected flow channels or extracted from a solution reservoir when necessary. A reference electrode used as a switch can control the opening of the valves sensing the movement of a solution. A valve electrode used in a three-electrode system with a pH-sensitive reference electrode functions as a pH responsive valve. The idea can also be used to construct a pH filter that passes solutions of a limited pH range. Furthermore, by using a one-electrode system consisting of gold and zinc, valves that work autonomously sensing the arrival of solutions can be realized. Other than these, a pH regulator has been fabricated using a nonstandard three-electrode system with a pH-sensitive reference electrode. The devices have been used in microsystems for the detection of important molecules and for monitoring of the state of cells. Recent progress of the electrochemical devices and their applications to biochemical analyses will be presented.

E-2:IL04 Stimuli Responsive Materials and Next Generation Chemical Sensors
D. DIAMOND, CLARITY Centre for Sensor Web Technologies, National Centre for Sensor research, Dublin City University, Dublin, Ireland

The futuristic vision of the sensor web calls for billions of autonomous sensing devices that feed real-time data into the 'cloud' to contribute to the sensed globe or world. However, there are major impediments that will inhibit the degree to which chemical sensors and biosensors can meet the expectations of this vision, particularly for remote, widely distributed environmental monitoring. In order to realise massive scalability, sensing devices must effectively be 'deploy and forget', in that they must function autonomously for years, providing reliable data into the networked world. In this talk, I will highlight the issue of fluid handling as a major impediment, and suggest ways in which materials with advanced functionalities may provide a way to overcome this hurdle. In particular, I will focus on the role of stimuli responsive materials to provide actuating and sensing capabilities for next generation microfluidics platforms - the key component to provide scale up and widely distributed deployments.

E-2:IL05 Micro and Nanocantilevers: Technology and Application
P. DATSKOS, Oak Ridge National Laboratory, Oak Ridge, TN, USA

In this talk we discuss technology and applications of micro and nanocantilever. Over the past three decades there have been spectacular developments in nano-electro-mechanical systems (NEMS) and micro-electro-mechanical systems (MEMS). As a result, many innovative applications have emerged and particularly a family of chemical and biological sensors. While MEMS/NEMS represents a diverse family of designs, devices with simple cantilever configurations are especially attractive as transducers for physical, chemical and biological sensors. A nano/microcantilever transducer converts physical

or chemical changes into mechanical response. Specific binding sites present in chemically selective layers deposited on a cantilever provide affinity of targeted analytes to the sensor active area. Highly selective receptor layers can be designed using concepts of molecular and biomolecular recognition. Furthermore, transducers based on arrays of bimaterial microcantilevers offer a promising technological platform for uncooled IR imaging. Finally, the use of nonlinear MEMS/NEMS offer new possibilities in both technology and applications.

E-2:L06 Novel Plasmonic Bio-sensing System Based on Two-dimensional Gold Patch Arrays for Linear and Nonlinear Regimes
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We propose a novel bio-sensing platform based on the observation of the shift of the leaky surface plasmon mode that occurs at the edge of the plasmonic band gap of metal gratings when an analyte is deposited on the top of the metallic structure. We detail the numerical analysis, the fabrication and the characterization of these two-dimensional arrangements of gold patches in linear regime showing that sensitivity of our device approaches a value of 1000 nm/RIU with a corresponding Figure of Merit (FOM) of 222 RIU-1. We provide experimental proof of the sensing capabilities of the device by observing colour variations in the diffracted field when the air overlayer is replaced with a small quantity of Isopropyl Alcohol (IPA). Effects of technological tolerance such as rounded corners and surface imperfections are also discussed. We also report proof of changes in colour intensities as a function of the air/filling ratio ad periodicity and discuss how they can be obtained by diffracted spectra. Finally we report the numerical investigation of the non-linear behaviour of the device highlighting the Surface Enhanced Raman Scattering (SERS) performance.

E-2:L07 Fabrication of Gas Sensing Devices from Nanowires: Techniques and Integration
R. JIMÉNEZ-DÍAZ¹, J.D. PRADES¹, F. HERNÁNDEZ-RAMÍREZ², J. SANTANDER³, C. CALAZA³, L. FONSECA³, C. CANÉ³, **A. ROMANO-RODRÍGUEZ**¹, ¹MIND-IN2UB, Departament d'Electrònica, Universitat de Barcelona (UB), Barcelona, Spain; ²IREC, Catalonia Institute for Energy Research, Barcelona, and Departament d'Electrònica, Universitat de Barcelona (UB), Barcelona, Spain; ³Institut de Microelectrònica de Barcelona, IMB-CNM-CSIC, Bellaterra, Spain

In the last years, nanomaterials, such as nanowires, nanoparticles, nanotubes, ..., have emerged as potential building blocks of new devices and circuit architectures due to their enhanced properties derived from their reduced size and well-controlled chemical and physical properties. Large efforts have been devoted to the fabrication of these materials, which can be nowadays obtained in well controlled manners. Furthermore, their functional properties have been studied bearing in mind their potential applications. The development and testing of these nanodevices, as well as their integration with a control and read-out electronics that enables their incorporation into real life applications, however, is very scarce. Few successful case studies have been presented so far. Here we will present how we have developed gas nanosensors from individual nanowires integrating them with semiconducting substrates. We will show how the basic characterisation of these nanowires can be carried out, how to manipulate them to achieve their integration with substrates with electrodes and heaters and their use as gas sensors in front of different gases. The combination of these devices with an ad-hoc designed and fabricated electronics that allows the readout will also be presented.

E-2:L08 Wafer-level Fabrication and Gas Sensing Properties of Miniaturized Gas Sensors Based on Inductively Coupled Plasma Deposited Tin Oxide Nanorods

A. FORLEO, L. FRANCIOSO, S. CAPONE, F. CASINO, P. SICILIANO, CNR-Istituto per la Microelettronica ed i Microsistemi, via Monteroni, Lecce, Italy; H. HUANG, O.K. TAN, Sensors and Actuators Lab, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore

The recent research effort has focused on the development and the synthesis of various 1-D and quasi 1-D nanostructures due to their promising properties. The development of nanomaterials and nanostructures has led to the realization of a variety of micro and nano chemical sensors. The advantages connected to employ the nanostructures is due to their very high surface-to-volume ratio and the possibility to realize single crystalline structures (with expected high stability). Different approaches are used in order to realize 1D nanostructures. In this work, SnO₂ nanorods were successfully deposited on 3" Si/SiO₂ wafers by inductively coupled plasma-enhanced chemical vapour deposition (PECVD) and a wafer-level patterning of nanorods layer for miniaturized solid state gas sensor fabrication were performed. Uniform needle-shape SnO₂ nanorods in situ grown were obtained under catalyst- and high temperature treatment-free growth condition. These nanorods have an average diameter between 5 and 15 nm and a length of 160 to 300 nm. The sensing properties of SnO₂-nanorods based gas sensors were evaluated by exposing them to NH₃ and CH₃OH. The gas sensing tests show remarkable responses to NH₃ even at very low operating temperatures and good responses towards CH₃OH. These performances are attributed to the preparation of highly nanosized material and to the processing for the device realization. The integration of SnO₂ nanorods into micromachined hotplates-based gas sensors tests is in progress.

Session E-3

MOEMS / NOEMS

E-3:IL01 Micromachined Devices for Use in Terahertz Applications

D. WOOD, J.M. CHAMBERLAIN, A.J. GALLANT, A.J. BARAGWANATH, L.E. DODD, C.K.A. HILL, School of Engineering and Computing Sciences, Durham University, Durham, UK

This talk presents results from three aspects of our interest in using micromachined devices in the THz region. First, our early work on making filters from lattice work fences or pillars of gold coated SU8 is described. Pass (up to 97%) and stop bands can be observed, and associated simulations and calculations will be presented to explain the phenomenon. As a follow on, how THz radiation passes through two-dimensional periodic arrays of sub-wavelength apertures has been investigated. In particular, the geometry of the arrays has been studied with time-domain spectroscopy. A time-of-flight model will be presented which can also show how to engineer resonances in other structures: this has major implications in the design of THz sensors. As a result of a parallel but separate development, the use of metal-oxide-metal (MOM) diodes as rectifiers of THz radiation will be discussed. The correct combination of metallisation, oxide and geometry is crucial to success, and how the electrical results can be understood via physical analysis will be presented. In terms of their asymmetry, these diodes show world-leading performance. We have also used nanoimprint lithography to shrink the device size, and how this technology moves the performance towards THz frequencies will be described.

E-3:IL02 Micro and Nanophotonics in Silicon

I. RENDINA, G. COPPOLA, M. GIOFFRE, M. IODICE, L. DE STEFANO, V. MOCELLA, L. SIRLETO, M. CASALINO, P. DARDANO, E. DE TOMMASI, A. FERRARA, I. REA, National Council of Research, Institute for Microelectronics and Microsystems, Napoli, Italy

Up to about ten years ago, the use of silicon in photonics was considered an eccentric and unsuccessful attempt of running after the results already carried out with III-V semiconductors. Pioneer works started because of the possibility of exploiting the well developed and

inexpensive microelectronic techniques for the realization of chips where optical and electronic components were effectively integrated. Nowadays, also thanks to micromachining technologies, silicon photonics is a main research field showing tremendous potential applications in the realization of low-cost, high-performance opto-electronic and opto-fluidic circuits, sensing and micro-opto-electro-mechanical systems. In this communication, new results carried out in the field of silicon micro- and nano-photonics, also exploiting the advance in sub-lithographic technologies and nanosciences, will be presented and discussed. They are allowing the realization of new families of photonic components and systems characterized by unexpected behaviours and performance, such as light amplifiers, sensors and photonic crystal structures for light manipulation at the sub-wavelength scale. Main applications are expected in bio-medicine, as well as in optical communications and on-chip interconnections.

E-3:L03 Powerful Polymer/Silicon Composite Thermal Microactuator for MOEMS Applications

B. THUBTHIMTHONG, **G.K. LAU**, V.M. MURUKESHAN, School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore

Recent advances in micro-opto-electromechanical systems (MOEMS) have seen the development of mechanically-tunable photonic crystals, tunable polymeric micro-lenses, waveguide positioners. These active MOEMS require powerful micro-actuators that deliver a large displacement and a large force at a fast speed. These stringent requirements on actuators have all been met by a recently developed class of thermal micro-actuator based on polymer/silicon composite. This composite thermal micro-actuator is made by deep reactive ion etching of silicon and selectively molding SU-8 polymer into high aspect-ratio silicon structures. In this paper, we demonstrated a powerful polymer composite thermal micro-actuator in a clamped-clamped beam for applications to a tunable 1-D photonic crystal. This actuator configuration has the advantages of precise linear actuation and high actuator stiffness. Anchored to substrate, the micro-actuator has a silicon beam (15 $\mu\text{m} \times 60 \mu\text{m} \times 1440 \mu\text{m}$) integrated with SU-8/Si composite thermal micro-actuator and thin-film heater. By applying a voltage up to 11 V to heat the composite by 160 °C, an actuation stroke up to 23 μm was observed at the center of the beam, which agrees well with finite element analysis and theory.

Session E-4

Smart Micro-nano Systems and Components Integration

E-4:IL01 Integration of Carbon Nanotubes into MEMS for Ultra-low Power Sensors

C. HIEROLD, C. ROMAN, M. MUOTH, K. CHIKKADI, S.-W. LEE, E. CAGIN, M. HALUSKA, ETH Zurich, Department of Mechanical and Process Engineering, Micro and Nanosystems, Zurich, Switzerland

Carbon nanotubes exhibit a number of excellent mechanical and electronic properties as functional materials in sensors. In particular single walled carbon nanotubes (SWNT) are known for their band gap modulation due to mechanical strain, or electronic property-changes due to interaction with surrounding molecules, but also for their ultra-low power consumption requirements. However, successful technology transfer to production and development of affordable products based on CNTs is threatened by the lack of solutions for fabrication and integration of these materials. We present results on individual SWNTs as functional material in field effect transistors, mechanical and chemical sensors. We discuss the influence of process variations on the properties of SWNT devices, and options for sensor fabrication. In a second part we discuss limits in sensor systems as captured by the signal-to-noise ratio (SNR). SNR incorporates sensitivity, bandwidth and noise spectral density, and thus determines limit of detection and resolution. It has been observed that electronic noise - in particular 1/f noise - increases with decreasing device dimensions. We discuss the influence of noise on the performance of SWNT sensors.

E-4:IL02 Combined Top-down and Bottom-up Approach for Next-generation 3D MEMS

M. SUGIYAMA, School of Engineering, The University of Tokyo 3D BEANS Center, BEANS Project, Japan

Integration of functional materials and nanostructures on a 3-dimensional silicon template is a promising direction of development in MEMS. For next-generation MEMS, we are developing a novel framework of fabrication technology: elaborate preparation of 3-dimensional (3D) template, the surface of which should be smooth in nanometer scale, by top-down approach and self-assembled surface modification of the 3-dimensional surface with functional materials such as carbon nanotubes (CNTs) and nanoparticles. Several examples will be presented. Self assembly of nanoparticles, when it is applied to 3D trenches rather than a planar surface, provides a widespread potential for the fabrication of a structure with large surface-to-volume ratio. Closed-packed self assembly of nanoparticles is possible either on the inner surface of a trench or in the whole volume inside the trench, leading to applications such as bio-assay and high-sensitivity gas sensor. CNTs can be introduced to a selected part of a 3D structure using dielectrophoresis at room temperature, in which a special kind of peptide with a binding capability between specific materials acts as material-selective "glue". CNT-based sensors on a Si platform will be developed on the bases of this technology.

E-4:LO5 Modeling of Piezo-actuated Stick-slip Micro-drives: An Overview

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This paper gives an overview about problem of modeling of piezo-actuated stick-slip micro-drives. The drives are effectively used in micro- and nanopositioning systems due to their simplification in design and very good working properties. It has been found that there exist numerous prototypes of such devices. However, they have been investigated empirically. There are few researches dealing with the theory behind this kind of drives. By analyzing the current research activities in this field, it is understood that the model depends strongly on the friction model in that the influences of the guiding system play an important role and were mostly neglected. These analyses are of fundamental importance for an integrated model combining friction and mechanical model offering promising future results. After an introduction section, the paper presents briefly the state-of-the-art of existing prototypes which have been known not only in research but also in commercial field. The problems of mechanical modeling of the drives are deeply analyzed. After that, some main points for the future research are discussed.

E-4:LO6 Controlled Connectivity in Random Nanowire Networks

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Nanowire networks (NW) are promising candidates for a range of material and device applications. NW-polymer composites have found applications in the area of mechanical reinforcement while NW networks themselves are beginning to find uses as transparent conductors. Although much is known about the percolation behaviour of nanowire systems in polymer composites, the inherent connectivity in high density NWNs is not at all understood. Such networks are comprised of wires that are well connected but individual wires are frequently separated by solvent residue or surface passivation that impeded conduction. We begin by visualising the connectivity in NWNs and show that the voltage, spatial and thickness dependences can be understood in terms of a distribution of junction properties. We introduce a universal scaling relationship that is a fundamental property of NWNs and show it is consistent with the presence of locally connected regions or pockets within the network that ultimately lead to conduction. Finally we demonstrate that by controlling the connectivity in NWNs it is possible to create new classes of materials with well controlled conductivity, and which in the case of certain metal nanowires system allows for the fabrication of novel and inexpensive memory devices.

Session E-5 Radio Frequency MEMS

E-5:IL01 Reliability of RF MEMS

W.M. VAN SPENGEN, TU Delft / Falco Systems, Delft, The Netherlands

Despite their excellent RF performance, the success of RF MEMS switches in the marketplace has until now been very limited. The reason is that it has proven to be far more difficult than originally envisioned to ascertain a high level of reliability of these devices. Apart from common MEMS failure mechanisms, the fact that RF MEMS switches contain functional contacting microscopic surfaces poses an extra set of challenges. Metal-to-metal contact switches suffer from contact degradation like macroscopic relays, while capacitive switches suffer from dielectric charging due to the high actuation voltages. Solutions to the charging effect can go in four directions: (1) very leaky dielectrics where the parasitic charge cannot stay on the switch but is rapidly dissipated, (2) perfecting the dielectric for low charging behavior, (3) separating actuation electrodes and the capacitive switch contact, and (4) dispensing with the dielectric altogether, and make the bridge halt just above the other conductor by mechanical stoppers. Recently, a new reason for developing very robust and reliable MEMS switches has appeared. The 'MEMSamp' is a harsh environment class-D PWM (pulse width modulation) amplifier where the traditional semiconductor switches have been replaced by MEMS switches.

E-5:IL02 RF-MEMS Components and Networks for High-performance Reconfigurable Telecommunication and Wireless Systems

J. IANNACCI, Fondazione Bruno Kessler - FBK, Center for Materials and Microsystems - CMM, MEMS Research Unit, Povo, Trento, Italy

MEMS (MicroElectroMechanical-Systems) technology applied to the field of Radio Frequency systems (i.e. RF-MEMS) has emerged in the last 10-15 years as a valuable and viable solution to manufacture low-cost and very high-performance passive components, like variable capacitors, inductors and micro-relays, as well as complex networks, like tunable filters, reconfigurable impedance matching networks and phase shifters, and so on. The availability of such components and their integration within RF systems (e.g. radio transceivers, radars, satellites, etc.) enables boosting the characteristics and performance of telecommunication systems, addressing for instance a significant increase of their reconfigurability. The benefits resulting from the employment of RF-MEMS technology are paramount, being some of them the reduction of hardware redundancy and power consumption, and the operability of the same RF system according to multiple standards. The talk will firstly provide a brief introduction on RF-MEMS technology, covering both technology aspects and also highlighting the working principles of RF-MEMS components. Subsequently, the integration of RF-MEMS components within RF circuits in standard technology will be addressed, reporting some significant examples.

E-5:IL03 Integrated Microsystems

M. ESASHI, S. TANAKA, Tohoku University, Sendai, Japan

MEMS as switches and filters fabricated on LSI are required for multi-band wireless systems, in which good mechanical properties are required for the MEMS and small feature size for the LSI. Such MEMS on LSI can be implemented by following three methods. The first method is a surface micromachining and AlN Lamb wave resonators are fabricated for on-chip multi-frequency oscillators. The second method is a MEMS fabrication after wafer adhesive bonding on a LSI wafer. MEMS micromechanical resonators and FBAR are fabricated using AlN. The third method is a bonding of MEMS wafer to LSI wafer. SAW filter is fabricated on a LSI. This method does not require the damage-free MEMS fabrication to LSI, however the density of MEMS is limited and stray capacitance is increased because of the bonding pads. The MEMS should be encapsulated on a wafer because the moving MEMS are damaged by a direct plastic molding. Wafer level packaging has been developed for this purpose. LTCC (Low Temperature Co-fired Ceramics) which have electrical feedthrough for interconnections has been developed. Owing to the matched thermal expansion of the LTCC with that of the Si the LTCC can be anodically bonded to the MEMS-on-Si wafer for the purpose of the wafer level packaging.

Session E-6

Energy Harvesting and Power Supply MEMS

E-6:IL01 Nanogenerators for Self Powered Sensors and Systems

Z.L. WANG, Wang School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, USA

Ever since the wide range applications of laptop computers and cell phones, seeking of power sources for driving portable electronics is becoming increasingly important. The current technology mainly relies on rechargeable batteries. But for the near future, micro/nano-systems will be widely used in health monitoring, infrastructure and environmental monitoring, internet of things and defense technologies; the traditional batteries may not meet or may not be the choice as power sources for the following reasons. First, with the increasingly shrinkage in size, the size of the total micro/nano-systems could be largely dominated by the size of the battery rather than the devices. Second, the number and density of micro/nano-systems to be used for sensor network could be large, thus, replacing batteries for these mobile devices becoming challenging and even impractical. Lastly, the power needed to drive a micro/nano-system is rather small, in the range of micro- to milli-Watt range. To meet these technological challenges, the author proposed the self-powering nanotechnology in 2005, aiming at harvesting energy from the environment to power the micro/nano-systems based sensor network. This talk will introduce the nanogenerator as a sustainable self-sufficient power source for MEMS.

E-6:IL02 Development of Microscale Thermoelectric Modules for Energy Conversion

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Thermoelectric devices have received increasing attention because of their potential applications as portable energy sources, accurate temperature controllers in infrared detectors, and sophisticated electro-optic and telecommunications components. So far, the fabrication and integration processes of thermoelectric microdevices have been one of the major topics of thermoelectric research, and some microfabrication processes had been proposed and studied to reduce the scales of thermoelectric devices even to a micrometer order. In this talk, we will present two kinds of fabrication processes for thermoelectric micro-modules. The first one is based on our previous MEMS process using a micromachined silicon mold. For this process, we invented a facile method to fabricate glass micromolds with multiply microchannels, into which high-aspect-ratio Bi₂Te₃ micropillars are formed by patterned electrodeposition. The second one to be introduced is basically a mechanical cutting process combined with photolithograph techniques, by which miniaturized modules with high aspect-ratio thermoelectric micro-pillars were fabricated. The thermoelectric performance of the fabricated module was evaluated, whose maximum open output voltage was about 20 mV when heated under a 100 W lamp.

E-6:IL03 Advances in Micromachined Vibration Energy Harvesting Using Piezoelectric Materials

D.-J. KIM, S.-B. KIM, H.C. WIKLE, Auburn University, AL, USA; J.-H. PARK, Argonne National Lab, IL, USA; S.-H. KIM, Brown University, RI, USA

Recent efforts have been made toward developing autonomous, self-powered remote sensor systems that can offer enhanced applicability and performance with cost savings. The technological challenge of realizing such a system lies in the construction and fabrication of a miniaturized energy harvesting device. This work focuses on the development of microscale piezoelectric devices to achieve maximum efficiency of power conversion. In this work, MEMS-scale devices were designed and fabricated based on the modeling of macroscale PZT devices. The current design of MEMS-scale devices comprises a seismic mass made of silicon connected to the substrate by a thin PZT cantilever beam. Factors relating to power improvement and reliability of the device are discussed by addressing the shape of the cantilever, piezoelectric mode, piezoelectric materials, and environmental temperature. Tapering a beam shape resulted in higher power due to uniform strain along the beam direction compared with a rectangular shape. Two modes in piezoelectric coefficients, i.e. d₃₃ and d₃₁, are compared by

constructing PZT MEMS devices using interdigitated and planar electrodes. Lead-free piezoelectric materials and PZT on flexible substrates were also explored for the devices. Current progress of MEMS and macroscale piezoelectric vibration harvesters are summarized with the discussion of future vision.

E-6:IL04 Energy Harvesting from Air Flow

A.S. HOLMES, Imperial College London, London, UK

Energy harvesting from gas flows has potential applications in wireless condition monitoring, for example in air conditioning systems or gas pipelines. This talk will open with a brief review of the various flow-driven energy harvesters reported in the literature. Recent work at Imperial College on energy harvesting from low-speed air flows will then be described. We have developed a cm-scale energy harvester aimed at power delivery for wireless sensors in air conditioning ducts. The device comprises a 2 cm-diameter shrouded wind turbine with an axial-flux permanent magnet generator built into the shroud and a cavity in the exit diffuser to accommodate sensor electronics. The turbine operates at flow speeds down to 3 m/s and delivers between 80 μ W and 2.5 mW of electrical power at air speeds in the range 3-7 m/s. The harvester has been integrated with low-power sensor electronics and an ultra low-power radio to form a complete, battery-less wireless sensor. The design, fabrication and performance of the overall device will be discussed.

E-6:IL05 Novel Energy Harvesting Systems with Dual Micro-nano Structures

HAIXIA ZHANG, Institute of Microelectronics, Peking University, Beijing, China

MEMS energy harvester is a promising substitute of battery, specially in low power consumption applications, such as sensor networks nodes or biomedical implantable devices. The micro vibration power is almost available everywhere and easily converted to electrical power with MEMS energy harvester. For electromagnetic energy harvester, the efficiency is low in low frequency environment and system integration is a problem because of the high temperature in microfabrication of magnet. We developed a novel harvesting system with integrated microelectromagnetic harvester. Special folded beams were designed for 3D harvesting as well as magnet array for frequency up-conversion at low frequency applications. The electrodeposition of permanent magnet was developed to integrate CoNiMnP permanent magnet in the device. The volume of harvester was scaled down to 32mm³. The tested maximum output voltage is 74.4mV at 48Hz and 1g. The maximum output power is 51 μ W at 50Hz and 1g with 21ohms load resist. The harvesting system also includes power rectify units and stroge units. It is favorable in low frequency applications.

Session E-7

Micro(nano)fluidics / Lab on Chip / Bio-MEMS

E-7:IL01 Integrated Photonics for Bioanalytical Microsystems

J.S. WILKINSON, Optoelectronics Research Centre, University of Southampton, Southampton, Hampshire, UK

Microfabricated optical waveguides enable low-cost mass-production of compact, robust, bioanalysis chips, and are ideal for the integration of optical functions in microsystems. Fabrication techniques which revolutionised electronics are enabling a similar transformation in photonics, and optical circuits are particularly well suited to mass-produced bio/chemical sensor arrays exploiting surface chemistry, optical cell-sorters and for integration in microfluidic systems for advanced micro-cytometry. Highly sensitive and specific waveguide biosensors have been successfully demonstrated, and biosensors based on SPR and on fluorescence will be described. Recently, interest has grown in optical manipulation at surfaces as part of the toolbox of the "lab-on-a-chip" and advances in trapping and propulsion of biological cells in the evanescent fields of optical waveguides will be considered. In applications where the volume of a liquid or of a micron-scale object such as a biological cell is to be interrogated, non-evanescent in-plane optofluidic

approaches must be adopted. A key component is the in-plane lens, which can be used for trapping, scattering, fluorescence or Raman measurements. Advances in technologies incorporating integrated lenses for microcytometry will be described.

E-7:IL02 Labs-on-a-Chip for Medical Applications

A. VAN DEN BERG, University of Twente, The Netherlands

Labs-on-a-Chip will play an important role in future medicine, both in point-of-care devices for drug or biomarker monitoring, as well as in early diagnostic devices. We developed a pre-filled ready-to-use capillary electrophoresis platform for measuring ions in blood. It is used to monitor lithium in finger-prick blood of manic-depressive patients, but can also be used for measuring calcium in blood for prevention of milk fever, or for measuring creatinine in blood or sodium in urine for early detection of ESRD. Another device was developed for analyzing male fertility by determining sperm concentration in semen. For early detection of colon cancer, nanowire sensors for detection of hypermethylated DNA will be presented, showing label-free DNA detection. Finally, a microelectrochemical Lab-on-a-Chip will be presented to mimic drug metabolism by CYP450 in liver microsomes.

E-7:L04 Microfluidic Microchemomechanical Systems

R. GREINER, M. ALLERDISSEN, A. RICHTER, TU Dresden/Heisenberg, Polymere Mikrosysteme, Dresden, Germany

The lab-on-a-chip (LOC) technology was expected to influence our every day live in a similarly fundamental way as integrated circuits have. Unfortunately this demand was not met yet. The cause therefore lies in the complexity of microelectromechanical systems (MEMS), which form the base of the current LOC technology. We present a new concept of LOC which are based on fluidic microchemomechanical systems (μ CMS). During the fabrication process these μ CMS are preprogrammed by monolithic integration of special active components. These active components are holding chemical energy that can be transformed at least once into mechanical energy and thus provide a timed and quantitative exactly defined fluidic function. As one application we present a microchip integrated with 2.096 active components. Through an intelligent combination of opening and closing valves and dissolvable membranes this chip is able to perform autonomously a repetitive and equidistant analysis of various fluids. In a second chip designed for kinetic investigations we demonstrate the ability of our system to repetitively control enzyme kinetics. With our simple and inexpensive fabrication method combined with the above mentioned advantages of the invented μ CMS new and better LOC technology can be developed.

E-7:L05 Micro Electrode Arrays for Single Site Electroporation

C. COLLINI, E. MORGANTI, L. LORENZELLI, FBK-CMM, Trento, Italy; **L. VIDALINO, P. MACCHI, CIBIO** - University of Trento, Italy

The in-vitro monitoring of the interaction of cells with engineered nanomaterials is attracting increasing attention in the research community, mainly in the field of toxicity screening or drug development. Nanomaterials are being incorporated into several industrial products, so the study of the impact of these products with the environmental health and safety is becoming more and more important. On the other sides, nanoparticles can be used as a vector to deliver drugs, heat, light or other substances to specific types of cells (such as cancer cells). Particles are engineered so that they are attracted to diseased cells, which allows direct treatment of those cells. This technique reduces damage to healthy cells in the body and allows for earlier detection of disease. In this scenario we realized a platform for single site electroporation of cell consisting of planar high-density microelectrode arrays (MEAs) enclosed in a microfluidics system. The designed configuration allows controlled cell transfection and targeted nanoparticle injection for the traceability and the identification of individual pathogenic mutations.

E-7:L08 Hydrogel-based Microfluidic Systems

M. ALLERDISSEN, S. KLATT, R. KÖRBITZ, A. RICHTER, Chair of Polymeric Microsystems, Dresden University of Technology, Germany

Over the last ten years, microfluidic technologies have gained considerable importance. However, realising highly integrated microsystems is a major challenge, which so far has only been solved insufficiently. Here, we present an innovative approach to fabricate

low-cost, highly integratable microfluidic platforms. As active elements photopolymerized hydrogels based on Poly(N-isopropylacrylamide) (PNIPAAm) are introduced. PNIPAAm is temperature-sensitive. Heated in water above its lower critical solution temperature (LCST), it reversibly changes from a swollen to a shrunken state (volume change in the order of 90%) and can, via an electrothermic interface, be employed as electrothermally switchable actuator. Varying specific parameters in the swelling agent, for example varying its alcohol concentration, can shift the LCST. So not only micropumps or microvalves, but also valves with an appointed threshold value, so-called chemostats or chemical transistors, can be realized. Using the example of a microchip performing enzymatic endpoint analyses, we investigate characteristic behaviour of active elements based on PNIPAAm and show the ability of integrating different fluidic operations like fluid transportation, metering, valving and mixing into one fully polymeric microchip.

E-7:L09 Superhydrophilic PDMS and PET for Microfluidic Devices

R. BARTALI, L. LORENZELLI, N. LAIDANI, M. SCARPA, V. MICHELI, A. PEDRANA, A. GAMBETTI, G. GAMBETTI, R. PANDIYAN, S. ROWLEY, I. LUCIU, Fondazione Bruno Kessler, Trento, Italy

PDMS and PET are materials widely used in the construction of microfluidic devices. Both materials have good chemical and physical properties such as optical transparency, chemical stability and good permeability to gases, but they have low surface energies. Therefore is crucial to enhance the hydrophilic behavior to increase the capillary flow in the microchannel. In this study we compare how oxygen and air plasma treatments change the wetting behavior of PET and PDMS. In particular we study the effect of plasma working pressure on the water surface contact angle. We correlate the contact angle results with the chemical properties of the plasma, roughness and surface chemistry. The plasma parameters, morphology and surface chemistry have been studied by means of optical emission spectroscopy, atomic force microscopy and Auger electron spectroscopy, respectively. Moreover we investigate how the wetting behavior effects the microchannel capillary flow. A super-hydrophilic surface (contact angle less $< 5^\circ$) for both polymers and using both gasses can be obtained by optimizing the working pressure of the plasma treatments. Microchannels realized with polymers with superhydrophilic surfaces show an extraordinary capillary flow with an estimated flow speed of 1m/min.

Session E-8

Flexible MEMS Technology

E-8:IL02 Continuous Process for Large-area Flexible MEMS

T. ITOH, AIST, Tsukuba, Japan

A novel fabrication process for large area flexible MEMS, having been developed in BEANS (Bio Electromechanical Autonomous Nano Systems) project, is introduced. The process consists of continuously high-speed coating for functional film materials, 3-D micro/nano-machining of the films on fibers, and weaving the functional fibers into large-area integration. In the coating process, functional materials, e.g., organic semiconductor (P3HT), piezoelectric (PVDF), conductor (PEDOT:PSS) and insulator (PMMA) films could be formed on fibers with a speed of 10 m/min. In the 3-D micro/nano-machining, a compound reel-to-reel process system including both thermal roller imprint and photolithography mechanism was developed. In addition, the microfabrication of the 3-D exposure module and the spray deposition of thin resist films on the fiber were demonstrated. For the weaving assembly, a cantilever-type microspring contact array was developed for the electrical contact between fibers. Evaluation of the durability showed that the microspring array structures made of PEDOT:PSS are applicable to a movable contact. Weaving assembly process was verified by developing an automatic weaving assembly machine and prototyping a 1.2 x 3 m² flexible sheet of touch sensors.

E-8:IL03 The Potential and Challenges of Printing Sensors and MEMS on Flexible Foil

D. BRIAND, F. MOLINA LOPEZ, A. VASQUEZ QUINTERO, G. MATTANA, N.F. DE ROOIJ, Ecole Polytechnique Fédérale de Lausanne (EPFL), Institute of Microengineering (IMT), Sensors, Actuators and Microsystems Laboratory (SAMLAB), Neuchâtel, Switzerland

MEMS fabrication processes are well established and standard photolithographic and micromachining approaches can be used to make different types of flexible MEMS devices using polyimides, SU-8, PDMS and parylene films, among others. In this communication, we will introduce printing as an alternative method for the technological realization of flexible devices by fabricating them directly on flexible foil (plastic, paper) using as much as possible additives processes. Using flexible foil as substrate in combination with printing/transfer of inorganic and especially organic materials bring different advantages compared to the conventional silicon processing. Thin, lightweight, flexible, conformal and even transparent devices can be foreseen with their production at large scale and low-cost. With a special care in the choice of materials and processes, a new generation of environmental friendly sensors and MEMS will emerge: Green MEMS. However, printing remains challenging and organic electronics cannot in major cases replace its silicon counterpart. Different issues related to the printing processes and to the co-integration of printing devices with silicon devices will be addressed. The technology will be highlighted through some concrete examples focusing on sensors and MEMS.

E-8:IL04 Smart Tubes for Smart Systems

O.G. SCHMIDT, Institute for Integrative Nanosciences, IFW Dresden, Dresden, Germany

Smart tubes consist of strain engineered and highly flexible rolled-up nanomembranes. They can be made out of virtually any material and material combination. They are size scalable and rely on fully on-chip integratable processing techniques. Photonic, optofluidic, magnetic, electronic and chemical functionalities are demonstrated. SiO₂ based smart tubes operated in emission mode reveal highest Q-factors and extremely large sensitivity. The path towards an integrated lab-in-a-tube is envisioned and discussed. Smart tubes are ideally suited to provide a 2D confined transparent scaffold in which behaviour and mitosis of single cells can be studied in great detail. Catalytically active tubes are used as smallest ever made jet engines to act as autonomous smart systems.

Session E-9

Emerging MEMS / NEMS Technologies

E-9:IL01 Atomic Layer Deposition for MEMS & NEMS

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Atomic Layer Deposition (ALD) of thin films is becoming increasingly relevant for micro and nano-electronics applications. The accuracy on the thickness of the deposited layers, the highly conformal deposition on three-dimensional micro- and nano-structures, the possibility to tune optical and mechanical properties and the relatively low temperature of this process make ALD a very interesting technique for Micro and Nano-Electro-Mechanical Systems (MEMS and NEMS). The very thin ALD layers, mostly oxides and nitrides and more recently even metals, can be used either as supporting structures or as sensing elements. In addition, they provide excellent coating or passivation layers for CNTs or nanodevices. Further, they can be employed to define large arrays of nanostructures, without the need of nanolithography and while maintaining compatibility to conventional integrated circuit (IC) processes. In this paper a brief review of the results achieved so far will be given and a few examples illustrating the potential and applicability of this technique for MEMS and NEMS will be presented.

E-9:IL02 Functional RF Devices Powered by MEMS Technologies

K. HASHIMOTO, Chiba University, Chiba, Japan; **S. TANAKA**, M. ESASHI, Tohoku University, Sendai, Japan

In mobile communication equipment, most of all functionalities are implemented in CMOS ICs. One exception is the RF front-end, where low noise (low loss) and high linearity are required, and use of high Q passive components is necessary. For example, a number of RF filters/duplexers using surface and bulk acoustic wave (SAW/BAW) technologies and oscillators using quartz resonators are used in current mobile phones to support multi-band and multi-standard operation. It seems very difficult to support further standards and/or frequency bands, although current ICs are powerful enough to support them. One possible solution for this problem is to give tunability to such devices. Since ultimate down-sizing is also required, use of MEMS technologies is mandatory not only for realization of tunable passive components but also for their hetero-integration with SAW/BAW devices and/or RF ICs. Such tunable front-end is also demanded for the current trend called the software defined radio. In collaboration with leading-edge research labs in Japan, we started a project to develop a really flexible RF front-end using MEMS technologies applicable to present and/or future communication systems such as the cognitive radio. This paper reviews current status and future prospects of this project.

Poster Presentations

E:P01 Electrical and Geometrical Analysis of Molybdenum Microcoils as Magnetic Microgenerators

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We present the fabrication and the electrical characterization of molybdenum (Mo) planar microcoils for magnetic field generation. The bottom electrode consists of a bilayer copper (Cu) - chrome (Cr), deposited by thermal evaporation on a standard silicon substrate. Mo microcoils are patterned by optical lithography and lift off. The inner turn of each microgenerator is connected with the ground contact by vias in a spin-coated polyimide layer, as electrical insulator between bottom electrode and coils. Being electrical performances derived by the geometrical layout, different physical designs of the inductors have been investigated, keeping constant the total footprint area (1 mm²). The effects of different coil parameters as shape, number of windings, width of the track and spacing between them have been experimentally studied in order to improve inductance and quality factor of the device. Preliminary studies on Cu microcoils achieved values of series resistance R_s of 120 ohm, self inductance L_s of 10 uH and quality factor Q of about 50. Similar results are expected for Mo microcoils, being the conductivity of two metals significantly close. An array of these microgenerators can be very promisingly applied to actuate magnetic nanocomposite PDMS membrane in tactile displays.

E:P04 Micro Thermoelectric Energy Harvester Using Bi-Te and Sb-Te Thin Films

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Micro thermoelectric technology is usually applicable for harvesting smaller amounts waste heat in the order of micro watts to a few watts. Thermal energy harvesting using micro-scale thermoelectric generators is a promising approach to alleviate the power supply challenge in ultra low power systems. In this study we have developed micro thermoelectric energy harvester using thermoelectric thin films. The Bi-Te and Sb-Te alloys are known as the best semiconductor materials currently available for thermoelectric applications near room temperature. The Bi-Te (N type) and Sb-Te (P type) thin films were deposited on silicon substrate by using co-evaporating. Bi-Te and Sb-Te thin films were analyzed using X-ray diffraction, field emission-scanning electron microscopy and energy dispersive X-ray spectroscopy. The

thin films were measured electrical properties and Seebeck coefficient. In order to improve that performance of a micro thermoelectric energy harvester, we made thermoelectric legs having the height of more than 10 μm using metal masks. Deposition and patterning of electrode was carried out. Fabrication of a micro thermoelectric device was completed by using dicing. Output power and current-voltage curves of the micro energy harvester were measured.

E:P05 Flexible Thermoelectric Generator with High Thermal Efficiency Kapton/PDMS Package

L. FRANCIOSO, C. DE PASCALI, P. SICILIANO, CNR-IMM, Institute for Microelectronics and Microsystems, Lecce, Italy

In this work we proposed fabrication and high thermal efficiency package of a very low cost energy autonomous, maintenance free, flexible and wearable micro thermoelectric generator (μTG), finalized to power very low consumption electronics Ambient Assisted Living (AAL) applications. The prototype, integrating an array of thin films thermocouples of Sb_2Te_3 and Bi_2Te_3 . Main aim of the work is the complete package of a microfabricated large area array of thermocouples within a Kapton/PDMS 3D assembly characterized by high topography and thermal conductivity modification of PDMS.

E:P07 New Viscosity Data for CuO-water Nanofluid - The Hysteresis Phenomenon Revisited

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Recent experimental data have shown the hysteresis behaviour for Al_2O_3 -water and CuO-water nanofluids when submitted to a heating effect^{1,2}. This phenomenon was recently revisited. New viscosity data were obtained for a 29nm particle size CuO-water nanofluid by a new and innovative technique, which consists of maintaining a forced flow of nanofluid through the measuring chamber of a 'piston-type'

viscometer³. Data show that for a low particle volume concentration (1.6%) the hysteresis observed before^{1,2} did not occur for the temperature range considered. For a higher particle concentration, 5% in particular, the hysteresis behaviour was observed when fluid temperature exceeded 51 °C approximately. Beyond this critical temperature, nanofluid viscosity increases and such an increase even continued with a decrease of temperature during a cooling phase. The effects due to successive heating/cooling cycles were also investigated. In order to determine the effects due to this heating/cooling on the morphological characteristics of the nanofluid studied, granulometry tests are carried out on original and after-heating fluid samples.

1. *Int. J. Heat Fluid Flow*, 28 (6), 1492-1506, 2007; 2. *Int. J. Therm. Sci.*, 47 (2), 103-111, 2008; 3. *Cambridge Viscosity Inc.*

E:P08 Wet-etching Characteristic of SiCN Film Deposited by the HWCVD Method

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SiCN film is known as an insulating film with dielectric constant as high as about 7. The film has also high transparency, high hardness and high wear resistance. Therefore, SiCN is very attractive as an insulating film in ULSI and MEMS. SiCN films have been generally expected in various applications. We can also use them for general industrial uses such as a coating material for stainless steel. In general, SiH_4 is required for deposition of SiCN films, but SiH_4 is so dangerous that industry cannot use these films for safety issue. Recently, we have deposited SiCN films by hot-wire CVD (HWCVD) using Hexamethyldisilazane (HMDS) which is a non-explosion organic liquid source instead of SiH_4 . As a result, it is possible to use the SiCN films even by general industries. In order to apply a SiCN film to ULSI, MEMS or other purposes, a SiCN removal process is needed. In this report, we investigate the wet-etching properties for SiCN films. We evaluated the wet-etching properties for the SiCN films using various kind of chemical agents. It turned out that potassium hydrate, sodium hydroxide and phosphate etch SiCN films. On the other hand, it turned out that sulfuric acid, chloride, acetic acid, and ammonium chloride do not etch SiCN films.

SYMPOSIUM F

Smart & Adaptive Optics

Oral Presentations

Session F-1

Nanophotonics and Smart Optical Nanostructures

F-1:IL01 Nonlinear and Switchable Plasmonic Metamaterials

N.I. ZHELUDEV, **K. MacDONALD**, Optoelectronics Research Centre & Centre for Photonic Metamaterials, University of Southampton, Southampton, UK

The next stage of photonic technological revolution will be the development of active, controllable and nonlinear metamaterials surpassing natural media as platforms for optical data processing with THz bandwidth and quantum information applications. We report an overview on our recent results on achieving new functionalities in nanostructured photonic metamaterials containing nonlinear and active media such as NEMS switchable metamaterials, hybrid metamaterials containing chalcogenide glass, carbon nanotubes, graphene, semiconductor quantum dots and report on exciting plasmonic properties

of superconducting and toroidal metamaterials and on using metamaterials for digitally controlled light localization.

F-1:IL03 Realization of Optical Components and Planar-light-wave-circuits with CMOS Technology

G. PUCKER, Y. JESTIN, M. GHULINYAN, Advanced Photonics and Photovoltaics Unit, Bruno Kessler Foundation, Trento, Italy

Silicon based CMOS technology proved to be an extremely powerful tool for applications in microelectronics and is now the basis of complex microprocessors, large memory circuits, and other digital and analog devices. In the early 1980's it was realized that silicon is also a good optical material for light transmission. Due to the existence of a cost effective mass-manufacturing technology, which allows to control nowadays dimensions in the nanometer range, engineering of silicon and other materials used in CMOS technology allowed to overcome physical limitations of bulk silicon and to realize active optical components such as light emitting diodes, Raman laser or high speed optical modulator. In this lecture we will demonstrate the potential of silicon fabrication technology for realization of different optical devices and circuits based on examples from our own work. It will be shown how controlling size and distance between silicon nanostructures allows the realization of stable LED's, how strain engineering allows the realization of optical non-linear waveguides and how 3-dimensional optical circuits can be realized by combinations of waveguides and microresonators on different planes.

F-1:IL04 Gas Cluster Ion Beam Technology for Nanofabrication
N. TOYODA, I. YAMADA, Graduate School of Engineering, University of Hyogo, Himeji, Japan

Gas cluster ions are ionized aggregates of thousands of gaseous atoms or molecules. In contrast to atomic or molecular ion beams, gas cluster ion beams (GCIB) realize low-energy-per-atom characteristics (energy as low as several eV per atom), which helps to process a solid surface without severe damage. Moreover, reactive GCIBs enhance chemical reactions without heating the substrates owing to their dense energy deposition. In addition, ejections of surface atoms or molecules are enhanced by GCIB bombardment, which causes high yield of sputtering or etching. Lastly, when GCIB bombards a target surface, it induces lateral motion of surface atoms. This lateral motion is referred to as "lateral sputtering," and it induces surface smoothing. These irradiation effects are quite useful for nanofabrication of various materials. In this report, we will focus on our recent study regarding nanofabrication with GCIB for semiconductor, optical devices, storage device and organic materials.

F-1:IL05 Enhanced Broadband Light-matter Interaction with Quantum Dots
B.D. GERARDOT, Department of Physics, Heriot-Watt University, Edinburgh, UK

Efficient light-matter interaction is paramount for quantum emitters such as quantum dots, single molecules, and defect centres in diamond as well as traditional devices such as light-emitting diodes, detectors, photovoltaic solar cells, and lasers. At the heart of extreme light-matter interaction efficiency is a grand engineering challenge: to physically sculpt a material so that the emitter's radiation pattern is entirely directed toward a single mode, and likewise every photon directed at the emitter is absorbed/scattered. Significant progress has been made using high-Q cavities, but these are restrictive in the sense that enhancement is both spectrally and spatially limited. An alternative approach is to develop broadband optical antennas which enhance the light-matter interaction at the single photon level. Examples of this technology include broadband planar dielectric antennas, waveguides, and solid-immersion lenses. Here I will present recent advances in the coupling of optically efficient quantum dots to broadband optical antennas.

F-1:IL06 Diffractive Control of Femtosecond Pulses with Programmable Spatial Light Modulators
P. ANDRES, Departamento de Óptica, Universitat de Valencia, Burjassot, Spain; **J. LANCIS**, Instituto de Nuevas Tecnologías de la Imagen, Universitat Jaume I de Castellón, Castellón, Spain

Many essential processes and interactions on atomic and molecular scales occur at ultrafast timescales. Generation, measurement, and manipulation of ultrashort pulses is challenging since most experiments depend on the electric field amplitude rather than the pulse intensity envelope thereby requiring control over the electric field structure itself. In this work we will introduce some all-optical devices to manipulate femtosecond pulses in a controlled fashion by means of diffractive optical elements as well as their application to optical imaging and material processing. Diffractive optical elements offer some unique features in this scenario. On the one hand, chromatic dispersion of diffractive optical elements is opposite and comparatively large to that of refractive materials that offers an invaluable tool for dispersion management. Diffractive surfaces can be computed and traced to cancel or minimize the impact of wave aberrations and, in general, to sculpt user-defined pulsed beams with full control over the spatio-temporal structure of the electric field. Further, programmable spatial light modulators will be used to codify diffractive optical components that, in this way, will be ready to be integrated in dynamical devices.

F-1:IL07 Passive and Active Nanophotonics
Y. FAINMAN, D. TAN, S. ZAMEK, O. BONDARENKO, A. SIMIC, A. MIZRAHI, M. NEZHAD, V. LOMAKIN, Q. GU, J. LEE, M. KHAJAVIKHAN, B. SLUTSKY, Dept. of Electrical and Computer Engineering, University of California, San Diego, La Jolla, CA, USA

Dense photonic integration requires miniaturization of materials, devices and subsystems, including passive components (e.g., engineered composite metamaterials, filters, etc.) and active components (e.g., lasers, modulators, detectors). This has been made possible by the advances in nanofabrication, integrated with design and testing tools.

Arranged in a regular pattern, sub-wavelength features act as a metamaterial whose optical properties are controlled by the density and geometry of the pattern and its constituent materials. To advance this technology we created design, fabrication and testing tools. The design needs to incorporate not only the electromagnetic equations, but also the material and quantum physics equations to enable the investigation and analysis of near field interactions. These studies need to be integrated with device fabrication and characterization to validate the device concepts and optimize their performance. In this talk, we discuss passive and active devices that recently have been demonstrated in our lab. These include monolithically integrated short pulse compressor utilized with SOI material platform and design, fabrication and testing of nanolasers constructed using metal-dielectric-semiconductor resonators confined in all three dimensions.

F-1:LO8 Magneto-optical and Plasmonic Properties of Thin Film Ternary Alloy Sensors
J.R. SKUZA, National Institute of Aerospace, Hampton, VA, USA; **S.H. CHOI**, NASA Langley Research Center, Hampton, VA, USA

Improvements to magneto-optical (MO) and plasmonic sensors have been sought through new materials and molecular architectures. For example, incorporation of a ferromagnetic material into a noble metal plasmonic sensor increases the sensitivity of the device by coupling the MO and plasmonic properties. These devices have typically been fabricated using segregated noble metal / ferromagnetic multilayers where interfacial effects hinder the sensitivity. A suitable single-layered material would eliminate these interfacial effects. Certain ternary alloys exhibit a ferromagnetic phase with plasmonic properties under specific deposition conditions and these MO and plasmonic properties will be discussed within the context of MO and plasmonic sensors.

F-1:IL09 Towards Three-dimensional Isotropic Metamaterials
T. TANAKA, RIKEN Metamaterials Laboratory, Wako, Saitama, Japan

Metamaterial is an artificially designed material that consists of metal resonator array. Designing resonator array structure so that it is smaller than the wavelength of the light, metamaterials work as a homogeneous material whose electromagnetic properties inherited from its structure. By engineering such materials, we can design and control their magnetic permeability even in the optical frequency region in which all materials in nature lose magnetic response and their relative permeability is fixed at unity. In this talk, we report on the theoretical investigations of the electromagnetic properties and design principle of three-dimensional metamaterials. The laser fabrication techniques for the three-dimensional metal structures are presented. Three-dimensional nano-scale silver or gold structures are demonstrated. Moreover, we report a bottom-up approach with the aid of DNA-template to form cyclic assemblies of gold nanoparticles as the simplest ring resonator structure of metamaterials.

F-1:IL10 THz Switchable Metamaterials
H.-T. CHEN, **A.K. AZAD**, **J.F. O'HARA**, **R. SINGH**, **J. ZHOU**, **M.T. REITEN**, **D.R. CHOWDHURY**, **L. HUANG**, **S. RAMANI**, **Q. JIA**, **S.A. TRUGMAN**, **A.J. TAYLOR**, Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, NM, USA

In recent years terahertz (THz) technology has become an optimistic candidate for numerous sensing, imaging, and diagnostic applications. Yet, THz technology still suffers from a deficiency in sources, detectors, modulators and other functional elements ubiquitous in neighboring microwave and infrared frequency bands. One of the greatest obstacles in this progress is the lack of materials that naturally respond well to THz radiation. The potential of metamaterials for THz applications originates from their resonant electromagnetic response, which significantly enhances their interaction with THz radiation. Thus, metamaterials offer a route towards helping to fill the so-called "THz gap". Here, we present a series of novel THz metamaterials with designed active functionality, enabling dynamic tuning of the amplitude, frequency and polarization state of a THz wave. In these materials the critical dependence of the resonant response on the supporting substrate and/or the fabricated structure enables the creation of active THz metamaterial devices. We show that the resonant response can be controlled using optical or electrical excitation and thermal tuning, enabling efficient THz devices which will be of importance for advancing numerous real-world THz applications.

F-1:L11 Controlling Plasmonic Coupling: Highly Organized Structures for Biodiagnosis

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Plasmonic nanoparticles are excellent candidates for their potential use in microelectronic, optical, biomedical applications or to develop new metamaterial properties. Their electromagnetic behaviour is for sure highly dependent on their specific particle size, shape, and surrounding environment. There are different methods which allow us to fine tune the control over the particle shape and size thus, the materials properties. However, the lack of capability to form reproducible organized structures is still a very important challenge to solve in order to control the plasmonic intercoupling between particles. Therefore, it is clear that their controlled organization in 2D and 3D structures is of key importance. In this work we report novel methods to produce organized structures of plasmonic nanoparticles. These can be done either in a macroscale range, forming linear parallel arrays or, at the nanoscale regime through the controllable cluster formation with high coordination numbers. The plasmonic behaviour of these organizations was theoretically and experimentally investigated. Moreover, these structures, were effectively use for biodetection using Surface-enhanced Raman scattering (SERS) spectroscopy.

F-1:L12 Surface Topography Effect on Plasmonic Characteristics

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The key interest of this study is to understand the physics of plasmonic behavior within quantum-confined domains. To experimentally observe the plasmonic behavior, a series of arrayed nanometer-sized aperture configurations will be fabricated in thin silver films on a quartz substrate using a focused ion beam instrument. Nano-scaled symmetrical features built around each aperture cause the plasmon to undergo a topography-dependent momentum change which is uniquely represented by artificially created electromagnetic dipole radiation. This study also examines exploitation of the surface plasmon polariton phenomenon to permit phase modulation and controlled variation in intensity and spectral response of the transmitted light. The electromagnetic dipole radiation losses will be determined from the changes in transmitted light between the apertures built on the plain surface and the surface with topographical features. Applying a varying electrical field to the array allows control of the transmitted light. Laser light of several wavelengths, both with and without an applied electrical field will be analyzed with the near field scanning optical microscope and a spectrometer.

Session F-2

Active and Responsive Optical Materials and Devices

F-2:IL01 Magnetic Properties of All-organic Nitroxide Radical Ferroelectric Liquid Crystals

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Since 2004, we have reported the preparation and magnetic properties of prototypic, paramagnetic all-organic rod-like liquid crystalline (LC) compounds **1** with negative dielectric anisotropy, which contain a chiral cyclic nitroxide unit in the mesogen core and show a chiral smectic C (SmC*) phase over a wide temperature range¹. Notably, a sort of spin glass (SG)-like inhomogeneous magnetic interactions (the average spin-spin interaction constant, $J > 0$) were found to be generated in the SmC* phase of compounds **1** at high temperatures ($> 25^\circ\text{C}$) in weak magnetic fields². We referred to this unusual magnetic phenomenon as positive "Magneto-LC Effects" ($J > 0$). In fact, these LC droplets floating on water were attracted by a permanent magnet and moved freely on water under the influence of this magnet. Here I talk about i) the origin of strong Magneto-LC Effects and ii) the electric field dependence of the paramagnetic susceptibility in the ferroelectric SmC* phase of

compounds **1**, which were measured at high temperatures ($> 25^\circ\text{C}$) by EPR spectroscopy (0.34 T).

1. N. Ikuma et al, *Angew. Chem. Int. Ed.*, 2004, 43, 3677; N. Ikuma et al, *Adv. Mater.*, 2006, 18, 477; R. Tamura et al, *J. Mater. Chem.*, 2008, 18, 2872. 2. Y. Uchida et al, *J. Am. Chem. Soc.*, 2010, 132, 9746.

F-2:IL02 Raman Gain in Nanostructured and Nanocomposites Materials

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Nonlinear Raman scattering in electrons-confined and photons confined materials is a fascinating research field of great importance from both fundamental and applicative point of view. Concerning the fundamental one, there have been a number of investigations both experimental and theoretical, but some issues remain 'open', while from an applicative point of view there are some important perspectives, for example to realize micro/nano sources with improved performances. In this paper, experimental investigations of stimulated Raman scattering in silicon quantum dots and nanocomposites based Si-materials are reported. Two Raman amplifiers were realized, and amplifications due to stimulated Raman scattering were measured. For both of them, a significant enhancement of Raman gain and a significant reduction in threshold power are demonstrated. In addition, the investigation of spontaneous and stimulated Raman scattering in a nanocomposite material obtained by a high niobium content glass belonging to the K₂O-Nb₂O₅-SiO₂(KNS) glass-forming system is described. Strong changes of Raman spectra in nanocomposite material with respect to the bulk sample are discussed, while a significant enhancement of Raman gain (up to 25 times higher) and of its bandwidth with respect to SiO₂ is proved.

F-2:IL03 Flying with Optical Lift

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Optical lift is a transverse radiation pressure force imparted to an asymmetrical object, e.g., an "optical wing". Lift forces may exceed the forward scattering forces, providing large steering angles. In general, the wing also experiences a torque. However, there are positions of stable rotational equilibrium that allow the wing to exhibit uniform motion. This phenomenon has been observed in our laboratory using micrometer scale particles in water. We are now exploring its use on macroscopic objects such as solar sails. Steering solar sails via optical lift will lessen the mass of the sail, thereby affording lower launch costs and greater accelerations.

F-2:L05 Spodumene Used as Thermoluminescent Dosimeter for High Doses

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Spodumene (LiAlSi₂O₆) is a silicate of technological interest. Studies about the electronic structure of α -spodumene showed that its gap is indirect, with 5.5 eV. We have also synthesized these materials doped with Mn. On exciting the samples by ionizing radiation, electrons and holes can be trapped by sites inside the gap. The thermoluminescent dosimetry is the measurement of radiation doses of through materials that emit energy in the form of light for your heating and this energy can be related to the radiation dose received previously. The importance of these materials, called thermoluminescent dosimeters (TLDs), is related to the degree of complexity involving the various applications. We can mention the dosimetry of high doses, for monitoring in nuclear reactors or during the sterilization of food. In this work we study the properties of spodumene to characterize it as a dosimeter for high doses of gamma radiation. The porosity and microstructure morphology of this TLDs were observed by using scanning electron microscopy. The results based on glow curves, emission spectrum, kinetic parameters and dose response show the feasibility of using this material for application in dosimetry of gamma radiation doses in the region of between 100 and 5 kGy.

F-2:IL06 Liquid-crystals-plasmonic (LCP) Nanostructures for Advanced Electro- and Nonlinear Optics

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We will delve into several LCP nano-structures and describe how the properties of plasmonics and liquid crystals could enhance one other to enable emergent properties and construction of various multifunctional compact electro- and nonlinear- optical switches, filters and modulators. Owing to the broadband birefringence of LC, these processes can function in an extremely broad spectral range from visible - far infrared - terahertz, with greatly improved efficiency. Besides conventional electro-optical modulation of the LC birefringence, we will also explore nonlinear all-optical or self-action mechanisms, in which the desired index or birefringence changes are generated by the light itself. Such processes do not require any electrode, and the incident light can impinge at almost any desired angle for complex geometries/structures. We also report on recent successes in obtaining ultrafast switching speed using pulsed laser modulation of the liquid crystal order parameter/birefringence.

Ref: (1) I.C. Khoo, *Physics Report* 471, p. 221-267 [2009]; J. Smalley et al, *Opt. Exp.* 19, pp. 15265-15274 (2011); I.C. Khoo et al, *Mol. Cryst. Liq. Cryst.* 527, p.109-118 (2010); I.C. Khoo et al, *J. Opt. Soc. Am. B25*, pp. 1931-1937 (2008).

F-2:IL07 White Light Generation in Rare-earth-doped Amorphous Films Produced by Ultrasonic Spray Pyrolysis

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Nowadays, the processing of white light emitting materials is of relevant interest to the optoelectronic industry for application in both liquid crystal monitor screens and high brightness white-light-emitting diodes (WLEDs). One of the most common approaches to develop WLEDs is to couple a near UV emitting LED with a frequency converting phosphor. Hafnium (HfO₂) and aluminum (Al₂O₃) oxides have attracted considerable attention due to their excellent physical and chemical properties, such as their high dielectric constant and insulating characteristics, which allow their application as dielectric materials with relatively high refractive index and wide band gap, as well in the field of optical coatings and metal-oxide semiconductor devices of the next generation. HfO₂ and Al₂O₃ films doped with CeCl₃, TbCl₃ and MnCl₂ were deposited at 300 °C by ultrasonic spray pyrolysis. It is demonstrated that these films can generate cold white light emission upon near UV excitation at wavelengths of AlGaIn/GaN-based LEDs emission. The high efficiency of energy transfer from Ce³⁺ to Tb³⁺ and Mn²⁺, resulting in cold white light emission makes the Ce³⁺, Tb³⁺ and Mn²⁺ doped HfO₂ and Al₂O₃ films interesting materials for the design of efficient near UV pumped phosphors for white light generation.

F-2:IL08 Linear and Nonlinear Optical Properties of Sol-gel-derived Microstructured Fibers Doped with Active Optical Ions and Metallic Nanoparticles

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Microstructured optical fibers, also known as photonic crystal fibers (PCFs) or holey fibers, have attracted growing interest during the last decade, owing to their wide range of optical properties accessible thanks to a freedom of designs that cannot be achieved with conventional fibers. Due to these characteristics, they found a large variety of applications ranging from optical communication to light sources or sensing. As an example, one can cite the broad and powerful supercontinuum sources used for fluorescence imaging, flow cytometry or characterization of optical components. This talk will show that the use of the sol-gel polymeric route can be applied to the preparation of high purity silica glass rods for the achievement of PCF cores with conventional and unconventional composition. As an example, results on the synthesis of Erbium-doped rods and their characterization will be presented. These rods have been used to fabricate a PCF with an Erbium-doped pure silica core. Effects of this synthesis on the spectroscopic properties of Erbium will be discussed together with the performance of the Erbium-doped PCF in amplification regime¹. Bismuth ions are also very interesting optical active elements, due to their potential

applications in fiber lasers and amplifiers in the spectral range 1150 - 1500 nm. The luminescent properties of a Bismuth-doped silica PCF, with a core achieved by the sol-gel technique, will be presented². Besides this, we recently combined the benefit of the PCF geometry to the increased optical nonlinearity induced by gold nanoparticles in order to fabricate a nonlinear silica fiber. This PCF, with a core synthesized by the sol-gel technique and doped with gold nanoparticles, presents a resonant nonlinear absorption characterized by an optical limiting effect³.

1. "From molecular precursors in solution to microstructured optical fiber: a sol-gel polymeric route", H. El Hamzaoui, L. Bigot, G. Bouwmans, I. Razdobreev, M. Bouzaoui and B. Capoen. *Optical Materials Express* 1 234-242 (2011); 2. "Optical properties of Bismuth-doped silica core photonic crystal fiber", I. Razdobreev, H. El Hamzaoui, L. Bigot, V. Arion, G. Bouwmans, A. Le Rouge, M. Bouzaoui. *Opt. Express* 18 19479-19484 (2010); 3. "Linear and nonlinear optical properties of gold nanoparticle-doped photonic crystal fiber", L. Bigot, H. El Hamzaoui, A. Le Rouge, G. Bouwmans, F. Chassagneux, B. Capoen and M. Bouzaoui. *Optics Express* 19 19061-19066 (2011)

F-2:L09 Hybrid Organic-inorganic Photo-driven Nanoimpellers for Drug Release

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Mesostructured SiO₂ films functionalized with the azo-chromophore Disperse Red 1 were synthesized by sol-gel method. The mesostructured long-range order in the films was determined by X-Ray Diffraction. The azo-chromophores in the films work as nano-impellers through their photo-induced trans-cis reversible isomerization. When the films are doped, they are able to control the release of the dopant by all-optical processes. We used the dye laser Rhodamine 6G as dopant, its very distinctive luminescence around 570 nm allows to follow the release. Polarized green and infrared laser light were used as pump sources to direct the movement of the nano-impellers. 532 nm light was used as a probe to induce the Rhodamine 6G luminescence, which was measured as function of the pumping time with a photomultiplier coupled to a monochromator. The results corresponding to the green and to the infrared pumping sources are compared in order to determine the feasibility to photo-control the nano-impellers movement through a two-photon absorption process.

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F-2:L10 ZnO-based Thin Film Double Heterostructured-ultraviolet Light-emitting Diodes Grown by Vapor Cooling Condensation Technique

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Recently, with the increasing demands for ultraviolet light applications, low coast and high performance ultraviolet light-emitting diodes (ULEDs) have been intensively investigated. Zinc oxide (ZnO)-based semiconductors were promising candidate for ULEDs due to their wide direct band gap and large exciton binding energy. Furthermore, the energy bandgap of ZnO-based semiconductors can be modulated by doping various magnesium contents as magnesium-zinc-oxide (MgZnO) film to construct heterostructured devices. In this work, the vapor cooling condensation system was proposed to deposit high quality ZnO and MgZnO films, and to fabricate high performance MgZnO/ZnO/MgZnO double heterostructured-p-i-n ULEDs. By measuring the electroluminescence (EL) spectra of the double heterostructured-p-i-n ULEDs, the peak intensity and total emission power of the double heterostructured-p-i-n ULEDs were 3.08 times and 1.82 times higher than the conventional p-i-n ULEDs. Besides, the EL emission intensity at the visible region induced by the oxygen vacancy in the i-ZnO layer was negligible. It was attributed to the very low defect concentration resided in the i-ZnO active layer deposited by the vapor cooling condensation system. The associated mechanisms will be presented.

F-2:L11 Morphology Control in Luminescent Cadmium Silicate-based Nanostructures

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We report the synthesis of luminescent, single-phase, crystalline CdSiO₃ nanostructures at 580 °C. To the best of our knowledge, this is the lowest temperature at which this material is reported to form. The desired phase is confirmed by comparison to JDPDS Card N. 85-0310. The source of silicon has strong influence on the product morphology: Na₂SiO₃ yields single-phase CdSiO₃ in the form of needle-shaped nanostructures; high surface area (1140 m²/g) mesostructured SiO₂ yields coralloid-shaped nanostructures. Low angle X-ray diffraction reveals that the mesostructured nature of the precursor silica is not maintained in the resulting CdSiO₃. Electron microscopy suggests that in this case a transition occurs between the spherical morphology of the precursor and the needle-shape morphology of the material prepared from Na₂SiO₃. The surface area of the silica precursor has a strong influence in the reaction, since the use of commercial silica with a lower surface area (200 m²/g) does not yield the desired product. Doping with Mn²⁺ and/or Pr³⁺ ions leads to materials with long lasting phosphorescence, with possible uses in emergency lighting, luminescent paints and, with appropriate morphology control and surface modification, in materials for in-vivo sensors.

F-3:L04 Multimodal, High-resolution Imaging Systems Based on Stimuli-responsive Polymers

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One of the core challenges of modern imaging system technology is to provide realistic impressions about a virtual ambient by interaction with the human's auditory, visual, and tactile perception. However, particularly tactile displays with high spatial resolution in form of large-scale integrated microelectromechanical systems are not yet realized. Here, we report on a multimodal display with thousands of actuator pixels, which generates both visual and tactile impressions of a virtual surface. The fully polymeric, monolithically integrated device consists of an actuator array made from poly(N-isopropylacrylamide). This material is a stimuli-responsive, particularly temperature-sensitive hydrogel. Controlling the actuator temperature via a optoelectrothermic interface between an upper and lower temperature (the difference between these states is only 6K) the actuator can be switched from the fully swollen to the fully shrunken state (change in volume up to 90%) in several hundred milliseconds. For tactile impressions we deploy the change in actuator altitude and elasticity. For a monochrome visual functionality we take advantage of another hydrogel effect: During the phase transition occurs a change of the optical properties from transparent to opaque.

Session F-3

Smart Optical Systems and Devices

F-3:IL02 Purely Nonlinear Photonic Crystals

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Ferroelectric materials such as LiNbO₃ provide the unique possibility to structure the optical nonlinearity by means of so-called 'poling' techniques. This enables a new class of purely nonlinear photonic crystals, in which the optical response is engineered by modulating in space the nonlinear optical properties of the substrate, while leaving the refractive index (linear properties) unaffected. Such nonlinear photonic crystals can host a variety of new phenomena, providing a fertile ground for fundamental studies as well as for novel photonic devices. This talk will describe the technology involved in the fabrication of nonlinear lattices in LiNbO₃ and LiTaO₃ and its current challenges. It will also provide examples of novel optical functionalities afforded by purely nonlinear photonic crystals, ranging from optically tunable solitonic switches to multi-beam parametric generators.

F-3:L03 Development of Field-controlled Smart Optic Materials (ScN, AlN) with Rare Earth Dopants

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The purpose of this investigation is to develop the fundamental materials and fabrication technology for field-controlled spectrally active optics that are essential for industry, NASA, and DOD applications such as: membrane optics, filters for LIDARs, windows for sensors, telescopes, spectroscopes, cameras, etc. ScN and AlN thin films were fabricated on c-axis Sapphire or quartz substrate by magnetron sputtering. The background n-type conductivity of as-grown ScN has enough free electrons that can readily interact with the photons. The high density of free electrons and relatively low mobility indicate that these films contain a high level of shallow donors as well as deep levels. Also, the UV-Vis spectrum of ScN and AlN thin films with rare earth elements (Er or Ho) were measured. The red-shifted absorption onset gives direct evidence for the decrease of band gap (E_g) and the energy broadening of valence band states are attributable to the doping. As the doped elements enter the ScN crystal lattices, localized band edge states form at the doped sites with a reduction of E_g. Using a variable angle spectroscopic ellipsometer, a decrease in refractive index with applied field is observed with a smaller shift in absorption coefficient.

Session F-4

Adaptive Optics

F-4:IL01 Intelligent Optical Systems using Adaptive Optics

N. CLARK, NASA Langley Research Center, Hampton, VA, USA

Until recently, the phrase adaptive optics generally conjured images of large deformable mirrors being integrated into telescopes to compensate for atmospheric turbulence. However, the development of smaller, cheaper devices has sparked interest for other aerospace and commercial applications. Variable focal length lenses, liquid crystal spatial light modulators, tunable filters, phase compensators, polarization compensation, and deformable mirrors are becoming increasingly useful for other imaging applications included guidance navigation and control (GNC), coronagraphs, foveated imaging, situational awareness, autonomous rendezvous and docking, non-mechanical zoom, phase diversity, and enhanced multi-spectral imaging. Active components presented allow flexibility in the optical design, increasing performance. In addition, the intelligent optical systems presented offer advantages in size and weight and radiation tolerance

F-4:IL02 Adaptive Optics for Extremely High Power Lasers

A. KUDRYASHOV, Moscow State Open University and Active Optics NightN (Ltd), Russia

Adaptive optics is considered to be an instrument that is used to correct for the wavefront of any incident light. Key element of any adaptive optical system is a deformable mirror. Moreover the property and ability to correct for the wavefront is determined by deformable mirror. At the same time in case of correction of the radiation of high power lasers another important element - wavefront sensor start playing a very significant role. In general in order to correct something one needs at first to measure what need to be corrected. So, in this presentation we shall consider the application of Shack-Hartmann wavefront sensors to measure the aberrations of the high power laser beams and different problems that occur on the way of the use of such sensors as a part of the whole closed loop adaptive system. Also, we shall discuss the efficiency of the use of bimorph mirrors as a perfect wavefront corrector for high power lasers.

F-4:IL03 Testbed for Adaptive Optics Testing

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Adaptive Optics systems are complex and their performances can be hard to establish in field conditions. In addition trying to compare on equal footing different components or algorithms for inclusion in a final system is also a hard proposition. For all these reasons our group at the Naval Research Laboratory (NRL) has developed a test-bed that can be used to test both full AO systems and subcomponents. The test-bed is based on a Liquid Crystal Device (LCD) that can be easily programmed to generate wavefront profiles in a very accurate way. The current device is a Holoeye device with $\sim 600 \times 400$ pixels and a refresh rate up to 33 Hz. These parameters are the hardware limits to the wavefront resolution that can be generated and the temporal evolution of such wavefronts. Of course newer devices are available that allow much higher spatial and temporal resolutions. The most important aspect of the test-bed is the ability of accurate calibration and thus the comparison between theoretical expectation and measured performances.

F-4:IL04 Adaptive Optics at the Large Binocular Telescope
S. ESPOSITO, Osservatorio di Arcetri, Firenze, Italy

The LBT is a unique telescope featuring two co-mounted optical trains with 8.4m primary mirrors. The telescope has been designed to be the first adaptive telescope featuring two adaptive secondary mirrors. The talk gives first an overview of the different AO systems of the LBT telescope in terms of their design and present status of development. Then it describes the main results achieved by first LBT AO system working on sky. During on sky commissioning such a system reached performance never achieved before on a ground based 8m optical telescope. Images with 40mas resolution and Strehl-Ratio (SR) > 90% has been acquired in H band (1.6 μm). Such images showed a contrast as high as 10^{-4} . Finally the talk presents the data reduction of the first scientific images showing the extremely high quality of the telescope performance, in some cases higher than what achieved by the Hubble Space Telescope.

F-4:IL05 Adaptive Optical Systems in Russian Federal Nuclear Center- VNIIEF with Different Control Principles

S.G. GARANIN, **S.V. KHOKHLOV**, **A.N. MANACHINSKY**, **F.A. STARIKOV**, Russian Federal Nuclear Center - VNIIEF, Institute of Laser Physics Research, Sarov, Russia

We report the results of performance of closed-loop adaptive optical systems intended for phase correction of the pulsed and cw laser beams. In the adaptive systems we employ the piezoceramic-based flexible adaptive mirrors of bimorph and pusher type with various aperture size. The conventional control of adaptive system is based on wavefront sensing data (e.g., of Hartmann-Shack type) and following deformation of adaptive mirror surface in the closed loop. We demonstrate the results of such static phase correction in the case of a vortex Laguerre-Gaussian laser beam and a laser beam of Nd:glass Luch powerful laser facility in RFNC-VNIIEF. But owing to local character of measurements of phase gradients their result is very sensitive to presence of phase small-scale noise fluctuations. Besides, additional problems appear at weak signal, at significant background, etc. In this case the sensor-less iterative approaches for control of adaptive mirrors can be more efficient. We demonstrate the dynamic phase correction of tip-tilts and higher phase aberrations of laser beams in the closed loop using the stochastic parallel gradient algorithm embedded into the special control units with microcontrollers.

F-4:IL06 An Optical Vortex Coronagraph for the 3.5 m Galileo National Telescope (TNG)

T. OCCHIPINTI, Adaptica Srl, Italy; **C. BARBIERI**, **E. MARI**, **G. NALETTO**, **F. ROMANATO**, **A. SPONSELLI**, **F. TAMBURINI**, University of Padova, Italy; **E. DIOLAITI**, INAF Astronomical Observatory Bologna, Italy; **A. GHEDINA**, INAF Telescopio Nazionale Galileo, Spain; **G. SWARTZLANDER**, Rochester Institute of Technology, USA; **B. THIDÉ**, Swedish Institute of Space Physics, Sweden

We have designed an innovative coronagraph for the 3.5m Telescopio Nazionale Galileo (TNG) for visible light based on the high contrast granted by the diffractive properties of optical vortexes. Our approach makes use of a Spiral Phase Plate (SPP) with even topological charge in a Lyot type coronagraph and of adaptive optics corrector (AdOpt) to overcome the nuisances of atmospheric turbulence. The TNG is particularly suitable to coronagraphic applications, because the telescope provides two large off-axis unobstructed subapertures. Additionally, the excellent quality of the site grants a considerable fraction of nights with very good atmospheric seeing. The scientific capabilities of the

combination of telescope plus such coronagraph are better and the solutions are simpler than those allowed by coronagraphs not employing OV's, and will span a very wide range of hot astrophysical topics, from the discovery and characterization of brown dwarfs to exoplanets.

F-4:LO7 High Resolution Wavefront Control Using a Photocontrolled Deformable Mirror in Closed Loop

S. BONORA, CNR-IFN, Laboratory for Ultraviolet and X-ray Optical Research, LUXOR, Padova, Italy; **U. BORTOLOZZO**, **S. RESIDORI**, INLN, Université de Nice-Sophia Antipolis, CNRS, Valbonne, France; **D. COBURN**, **C. DAINY**, National University of Ireland, Applied Optics Group, Galway, Ireland

Using a photocontrolled membrane deformable mirror it is possible to control and correct the wavefront with unprecedented resolution. Our novel design of deformable mirror is an electrostatic membrane mirror actuated through the change of resistivity of a photoconductor substrate rather than using a matrix of segmented pads where each of them is connected to an high voltage amplifier. The Optically addressable Deformable Mirror (ODM) is composed by a Bismuth Silicon Oxide (BSO) photoconductive crystal, and a nitrocellulose metallized membrane. The auxiliary light source is a blue Light Emitting Diode modulated by a high resolution LCD panel. The main advantages of this device are the extreme reduction of hardware complexity, since just one high voltage line is used and the high resolution addressing of the DM. We demonstrated those advantages through its use in a closed loop system, by the Zernike characterization exploiting a flexible light addressing up to an equivalent of 15×15 actuators.

Session F-5

Advances in Diagnostic Techniques

F-5:IL01 Neutron Scattering in Optical Materials

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Neutron scattering, despite not being an in-house technique, is widely used for material characterization. Differently from other techniques, neutron scattering, because of the intrinsic properties of the probe, enables for a simultaneous characterization of the atomic scale structure and the THz dynamics of a very wide class of materials. With wavelengths ranging from 0.01 to 100 nm, elastic scattering reveals the spacing of constituent atoms or the size of molecules in crystalline materials like functional ceramics, in polymers and biological macromolecules, up to strain-scanning of metals and alloys in engineering components. Neutrons are also particularly sensitive to light atoms like hydrogen. Further, neutron also possesses a magnetic moment and it can also probe structure and excitations of electronic spins in magnetic materials. Here, the fundamentals of neutron scattering will be presented, together with an overview of the experimental technique and instrumentation. The major achievements in structural and dynamic characterization of optical materials will be presented, with special focus on chalcogenide glasses, ferroelectric nonlinear optical and stimuli-responsive materials, such as shape memory alloys, dielectric polymers, electro-active polymers, polymer hydrogels.

F-5:IL02 Versatile Smart Optical Materials Characterizer

YEONJOON PARK, **HYUNJUNG KIM**, National Institute of Aerospace, Hampton, VA, USA; **GLEN KING**, **SANG CHOI**, NASA Langley Research Center, USA

A new versatile smart optical material characterization system is invented. The system which is based on Michelson interferometer is powered by advanced analysis software algorithm for multi-pixel array type device and various materials. The system measures the intensity, phase, and polarization while applying voltage, current, electric field, magnetic field, pressure, temperature, and chemicals. An innovative "Phase Ripple Map" shows the time evolution of phase & intensity information of the lights thru multi pixels of the materials and devices including liquid crystal, non-linear optical crystal, ferroelectric materials, magneto-optical

materials, thermal expansion coefficients, pressure coefficients, and so on. The hardware and software design of this characterization machine will be discussed.

F-5:IL03 Ultrasensitive SERS Analysis

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Surface-enhanced Raman scattering (SERS) is gaining prominence as an ultrasensitive and ultrarapid detection technique. In the recent years many applications involving both direct and indirect sensing has been developed in biomedicine, biolabelling, medical imaging, multiplex high-throughput screening, pollutant monitoring or molecular and material characterization. Notwithstanding, several aspects such as colloidal stability, plasmon tunability, detection of molecular species with low affinity for gold or silver surfaces, low SERS cross-sections of aliphatic molecules or transition metals detection are still challenging. Here we demonstrate how the rational design in materials from controlling shape, size and composition of the initial colloidal nanoparticles, that will act as optical enhancers, to their integration into hybrid materials for advanced sensing, may resolve most of those SERS shortcomings. Furthermore we discuss the advantages or disadvantages of the different SERS approaches (direct sensing with single particles, generation of hot spots and indirect sensing with biological interfaces and encoded nanoparticles) to the different analytical and bioanalytical problems.

variation.

This work have been done in collaboration with: S. Berneschi, A. Giannetti, F. Baldini, A. Barucci, D. Farnesi, G. Nunzi Conti, F. Cosi, M. Brenici, S. Pelli, D. Ristic, M. Ferrari and G.C. Righini from CNR; and L. Pasquardini, C. Potrich, L. Lunelli and C. Pederzoli from Fondazione Bruno Kessler, Via Sommarive 18, 38123 Povo (Tn) Trento, Italy

F-6:IL03 Development of a Micro-spectrometer for Neural Probe-pin Devices

SANG H. CHOI, NASA Langley Research Center Hampton, VA, USA; **KYO D. SONG**, HARGSOON YOON, Department of Engineering, Norfolk State University, Norfolk, VA, USA; **YEONJOON PARK**, National Institute of Aerospace Hampton, VA, USA; **UHN LEE**, Gachon University of Medicine and Science, Incheon, Korea

Currently available devices for treatment of neurological deficits, invasive or not, generally offer very limited functionality. Recent advances in micro and nano-scale devices and wireless power technology (WPT) have allowed many medical devices to be much more capable and adaptable. The development of implantable probe-pin devices (PPD) as neural probes, combined with a neural electronics interface and WPT enable real-time measurement and control/feedback for remediation of neural anomalies. The PPD was designed to have an embedded expert system that performs semi-autonomous neural functions through a routine of sensing, processing, and control. The PPD uses a micro-spectrometer with a miniature Fresnel grating to differentiate the emission spectra from brain tissue for monitoring neurochemistry. The present work describes the required micro-spectrometer design and performance characteristics and PPD capability needed for this application.

Session F-6

Smart Optics Applications

F-6:IL01 In-vivo Electrical Sensing of Neural Activity and Smart Optics Application in the Brain

HARGSOON YOON, Norfolk State University, Norfolk, VA, USA

Sensing of electro-physiological activity from single units and synchronized neural cells within functional networks are essential to interpret neural processes that govern our behavior such as perception, learning, memory, and emotion. Many investigations have been carried out on the development of in-vivo bioelectric sensing systems which can measure electro-physiological neural functions and assess activity in neural networks from freely moving subjects. Even though a number of techniques are available for neural sensing or imaging, there are limitations, either in terms of available time and space resolution, physical constraints of a subject, or the amount of tissue that can be accessed simultaneously. Electrical neural sensing methods integrated with wireless communication technology are considered to overcome many limitations of existing technologies. This presentation will introduce the in-vivo electrical neural sensing research which can measure neural functions inside the brain engaged in spontaneous or elicited activity. In addition, optical sensing and smart optics applications will be discussed including recent trials utilizing optical interaction with neural potentials and the dynamics of neural cells and membranes in response to optical inputs.

F-6:IL02 WGM Microresonators for Biosensing

S. SORIA, CNR-IFAC Istituto di Fisica Applicata "N. Carrara", Sesto Fiorentino (FI), Italy

In the field of sensing, WGM microresonators are receiving a growing interest as optical structures suitable for the realization of miniature sensors with high sensitivity. When properly excited, WGM microresonators are able to strongly confine light, by means of total internal reflection, along the equatorial plane near their spherical surface. The corresponding supported resonances show low losses and a high quality factor Q (107-109). These high values of the Q factor make possible the detection of any minute event that occurs on the surface of the spherical microcavity. In fact, any minimum change in the surface of the sphere or in the physical and optical properties of the surrounding environment reduces the Q factor value and modifies the position of the resonances inside the dielectric microcavity. From a direct measurement of this resonance shift, one can infer the amount of analyte that produces this

Session F-7

Adaptive Optics for Biological Applications

F-7:IL01 Adaptive Optics for Microscopic Imaging of the Eye

A. ROORDA, University of California, Berkeley, CA, USA

Unlike a microscope which relies on a high quality objective lens, an ophthalmoscope uses the optics of the eye - which have evolved to focus light onto the retina - as the objective. Given the size of the pupil (up to 7 mm) and its distance from the retina (about 20 mm) the eye offers a numerical aperture of just over 0.2, but the optics are so fraught with aberrations that the imaging benefits of this modest NA is not realizable. Adaptive optics can be used effectively to compensate these aberrations and have been producing microscopic views of the retina for just over 15 years. This microscopic imaging has driven a paradigm shift in how we use ophthalmoscopy for vision science. New applications are emerging for the eye, from two-photon imaging of living retina, to microscopic tracking of retinal disease, to testing of human vision on the scale of single cone photoreceptors.

F-7:IL02 Implementation of Adaptive Optics of Non-linear Microscopy to Biological Samples Using Optimisation Algorithms

J.M. GIRKIN, Biophysical Sciences Institute, Department of Physics, Durham University, Durham, UK

Non-linear optical microscopy is now established as the imaging mode of choice for sub-cellular resolution in vivo and deep tissue imaging. The initial two-photon fluorescence excitation has now expanded to include multiphoton fluorescence, second and third harmonic imaging and more recently Coherent Anti-Stokes Raman Scattering. In all of these imaging modalities a crucial feature is that the optical resolution is determined by the excitation volume and as one images more deeply into samples this increases due to sample induced aberrations caused predominantly by local refractive index mismatches. Adaptive optics have now been demonstrated to significantly improve the imaging resolution and signal level, at depth, in a range of biological samples and non-linear imaging modalities. This paper will look at the strategies that can be employed to determine the best mirror shape to minimize

the focal volume and maximize signal level and resolution in the so called "sensor less" approach. Consideration will be given to speed of optimization, the use of look-up tables and pre-determined search patterns.

F-7:IL03 Adaptive Optics for High Resolution Scanning Optical Microscopy

M.J. BOOTH, Department of Engineering Science, University of Oxford, Oxford, UK

Specimen-induced aberrations are frequently encountered in high resolution microscopy, particularly when high numerical aperture lenses are used to image deep into biological specimens. These aberrations distort the focal spot causing a reduction in resolution and, often more importantly, reduced signal level and contrast. The techniques of adaptive optics have been used to measure and correct the aberrations, usually with a deformable mirror, restoring image quality. We have developed wavefront sensorless adaptive optics systems for a range of scanning laser microscopes, including confocal, two-photon and harmonic generation microscopes, for application in biomedical imaging. These microscopes have been used in the imaging of thick tissue specimens, ensuring that image quality is maintained over a range of focusing depths. Most implementations so far have used single aberration correction settings for each image. However, for many specimens, aberrations vary across the image field. We consider the challenges this presents for the measurement and adaptive correction of aberrations.

F-7:IL04 Use Sensor-less Adaptive Optics to Extend Imaging Depth

YAOPENG ZHOU, Abbott Laboratories, Princeton, NJ, USA

Adaptive Optics (AO) has been widely used to correct the optical aberration to improve imaging resolution and contrast in biological applications. In the application of fluorescence imaging, we use AO to improve the fluorescence signal intensity in sub-surface imaging, and subsequently extend the imaging depth, limited by light absorption, scattering, and optical aberration. In our experiment, we applied sensorless AO in a two-photon microscope for mouse bone marrow imaging. The sensorless AO uses the fluorescence signal intensity as a metric to optimize the Deformable Mirror (DM). The iterative process allows DM to form an optimized shape for correcting the optical aberration inherited in the illumination beam path. The AO system is able to significantly improve the fluorescence intensity at the depth hundreds of micrometers below the bone surface.

F-7:IL05 Measuring and Correcting Aberrations in the Rat Brain

J. WANG^{1,2}, **J.-F. LEGER**¹, **J. BINDING**^{1,2}, **C. BOCCARA**², **S. GIGAN**², **L. BOURDIEU**¹, ¹Ecole Normale Supérieure, Institut de Biologie de l'ENS, IBENS, Paris, France. Inserm, U1024, Paris, France. CNRS, UMR 8197, Paris, France; ²Institut Langevin, ESPCI ParisTech, CNRS UMR 7587, ESPCI, Paris, France

Aberrations due to refractive index mismatch and tissue inhomogeneities may limit the resolution, signal intensity and achievable imaging depth in microscopy. Coherence-gated wavefront sensing (CGWS) allows the fast measurement of aberrations in scattering samples and therefore the implementation of adaptive corrections. We have demonstrated a new CGWS scheme based on a Linnik interferometer and a SLED light source. Compared to previously described CGWS, its main advantages are automatic dispersion compensation and possible implementation on any microscope. With it, we have measured a known aberration up to a depth of 400µm (resp. 80µm) into fresh rat brain slices for objectives of NA 0.5 (resp. 0.9). I will also show some results on deep imaging with aberration correction in the rat brain in-vivo.

F-7:IL06 How a Microscope in a Needle can Image Cancer in Humans at High Resolution

D.A. SAMPSON, **R.A. MC LAUGHLIN**, **R.W. KIRK**, **B.C. QUIRK**, **A. CURATOLO**, **X. YANG**, **K.M. KENNEDY**, **B.Y. YEO**, **D. LORENSER**, Optical+Biomedical Engineering Laboratory, School of Electrical, Electronic and Computer Engineering, and Centre for Microscopy, Characterisation and Analysis, University of Western Australia, Perth, Western Australia, Australia

A microscopic view of cancer in situ in the living human has many benefits. High resolution can improve the certainty with which cancer is

detected – this could improve diagnosis, guide procedures and aid in treatment. Ensuring full clearance of tumours during their surgical removal is of particular importance. The accurate detection of tumour margins remains a highly imperfect aspect of cancer surgery with a major negative impact on patient outcomes. Of the available medical imaging modalities, only optics has so far achieved the necessary high resolution in the living human, but only at very superficial depths in tissues – from the surface to a few millimetres at most. Endoscopes and catheters are enabling optics to access tissue surfaces in hollow organ systems inside the body, including in the gastrointestinal tract, in the arteries and in the lungs. Wider access to solid tissues, though, has not been achievable. We have developed the capacity to miniaturize the optics and associated scanning systems to fit into hypodermic needles as small as 30 gauge (310 micrometre outer diameter) to provide such access whilst retaining high resolution. Our work has mainly been based on optical coherence tomography, including three-dimensional imaging. A key aspect is the development of tracking and guidance technologies to ensure the microscopic imaging takes place at the correct site. Our current main target is breast cancer tumour margin identification during surgery. In this talk, I will describe our microscope-in-a-needle technology, and its application in breast cancer surgery.

Poster Presentations

F:P02 Observation of Electric Field Dependence of Molecular Orientation and Anisotropic Magnetic Interactions of All-organic Radical Liquid Crystals by EPR Spectroscopy

K. SUZUKI, **Y. UCHIDA**, **R. TAMURA**, Kyoto University, Kyoto, Japan

We have reported the synthesis of chiral all-organic radical liquid crystalline (LC) compounds, which contain a cyclic nitroxide unit in the mesogen core and show the chiral nematic (N*) and smectic C (SmC*) phases over a wide temperature range¹⁻³. By measuring the temperature dependence of magnetic susceptibility by SQUID magnetometer and variable-temperature EPR spectroscopy, we observed an anomalous increase in paramagnetic susceptibility at the crystal-to-SmC* phase transition of the LC compounds, indicating the generation of a sort of spin-glass-like inhomogeneous magnetic interactions (the average spin-spin interaction constant $J > 0$) in the LC state under weak magnetic fields⁴. We refer to this unusual magnetic phenomenon as positive "Magneto-LC effects". Here we report the electric field dependence of g-value and relative paramagnetic susceptibility in the ferroelectric SmC* phase of the LC compounds to evaluate the influence of external electric fields to the Magneto-LC effects by EPR spectroscopy.

1. N. Ikuma et al, *Angew. Chem. Int. Ed.*, 2004, 43, 3677-3682; 2. N. Ikuma et al, *Adv. Mater.*, 2006, 18, 477-480; 3. R. Tamura et al, *J. Mater. Chem.*, 2008, 18, 2872-2876; 4. Y. Uchida et al, *J. Amer. Chem. Soc.*, 2010, 132, 9746-9752.

F:P03 PLZT:Nd3+ Ceramics for Photonic Applications

M. PLONSKA¹, **W.A. PISARSKI**², ¹University of Silesia, Faculty of Computer and Materials Science, Department of Materials Science, Sosnowiec, Poland; ²University of Silesia, Faculty of Mathematics, Physics and Chemistry, Institute of Chemistry, Katowice, Poland

Neodymium-doped solid-state systems belong to the well known laser material, which emit near-infrared radiation. Optical properties of Nd3+ ions in several host matrices such as glasses and transparent glass-ceramics depends on chemical composition, heat treatment conditions and the preparation method. In present work the influence of neodymium concentration (0-1at-%) and sintering conditions on PLZT:Nd3+ ceramics were studied. Ceramic powders were synthesized by conventional MOM technique, from high purity raw materials (>99.9%), and subsequently sintered by free sintering and hot uniaxial pressing method. To analyze the powders and ceramics TA, XRD, SEM, EDS and dielectric measurements were performed. Optical spectra were examined for all prepared samples, and their optical properties were analyzed using reflectance, excitation and luminescence measurements. The study gives a detailed account of the relationships between doping and preparing conditions on the basic physical and dielectric measurements were performed. Optical spectra were examined for all prepared samples, and their optical properties were analyzed using reflectance, excitation and luminescence measurements.

F:P05 LED Adjustable Spotlight by Using Photo Controllable PVDF-TrFE Copolymer Deformable Mirror

S. BONORA, CNR-IFN, Laboratory for Ultraviolet and X-ray Optical Research, Padova, Italy; **A. MARRANI**, **M. BASSI**, **I. FALCO**, Solvay-Solexis R&D Center, Bollate, (MI), Italy; **M. MENEGHINI**, **E. ZANONI**, Dipartimento di Information Engineering, University of Padova, Padova, Italy

We present the control of the illumination properties of a LED spotlight with a photostrictive PVDF-TrFE copolymer deformable mirror. The divergence of the LED light is controlled by the shape of a gold coated PVDF-TrFE copolymer mirror which is driven by the light given by a low power secondary LED source. Our prototype can change the divergence of the LED source from 10° to 20° thus enabling a controlled focusing of the LED source. This layout has the advantages, with respect to other deformable mirror technologies based on piezoelectricity, to avoid the use of high voltages and to achieve larger deformations. Moreover PVDF-TrFE copolymer, with respect to PVDF homopolymer, does not require drawing or stretching followed by annealing and poling process to show ferroelectric properties and it spontaneously crystallizes to beta phase. We present a detailed description of the copolymer actuator and a optomechanical model of its deformation under light illumination.

F:P08 Peculiarities of Adaptive Laser Location of Debris with Rough Surface

V.A. BOGACHEV, **S.G. GARANIN**, **N.V. MASLOV**, **F.A. STARIKOV**, **V.A. VOLKOV**, Russian Federal Nuclear Center - VNIIEF, Institute of Laser Physics Research, Sarov, Russia

In the interests of the problem of debris search and detection we present the results of numerical simulation of projection of an outgoing laser beam through turbulent atmosphere onto the rough surface of a debris object using an adaptive mirror. For this purpose we analyze the wavefront vortex structure of the radiation, which is backscattered from the object surface and propagates through the turbulent atmosphere into a receiving aperture. Analysis shows that perfect phase conjugation does not ensure the maximal concentration of outgoing beam power on the object if the topological charge of backscattered radiation differs from zero in the receiving aperture. It is shown that the efficiency of focusing the outgoing laser beam onto the object can be enhanced by special control of a flexible adaptive mirror.

SYMPOSIUM G

Embodying Intelligence in Structures and Integrated Systems

Oral Presentations

Session G-1

Smart Materials, Sensors, Actuators

G-1:IL01 Development of Some Smart Sensors for Monitoring Civil Infrastructures

XINCHUN GUAN, **HUI LI**, **JINPING OU**, Harbin Institute of Technology, Harbin, China

Sensors that can detect the changing of the structure and satisfy the requirement of civil structure are one of the key technologies of the monitoring systems that should be developed. In this paper, some smart sensors or material used to make the smart sensors developed by Harbin Institute of Technology are introduced: piezoresistance composite, piezoelectric polymer, piezoelectric cement and corrosion monitoring sensor. Piezoresistance composite is made with carbon nanotube and resin. One character of the work is the carbon nanotube oriented by magnetic field. Piezoelectric polymer is made with PZT particles and PVDF. In order to improve its performance a few carbon nanotubes are also mixed in the composite. Piezoelectric cement is one kind of sensing material whose primary raw materials are cement and piezoelectric ceramic particles (or fiber). The sensing performance of piezoelectric cement is coming from its functional phase, the piezoelectric ceramic. The corrosion monitoring sensor is made with solid-state reference electrode, whose surface is one kind of binary alloy membrane produced by physical vapor deposition. The main producing technology, performance and applications of above sensors are introduced in this paper.

G-1:IL03 Optimal Sensor Placement for Parameter Estimation in Dynamic Systems

C. PAPADIMITRIOU, **D.-C. PAPADIOTI**, University of Thessaly, Volos, Greece

Theoretical and computational issues arising in the selection of optimal sensor configuration for parameter estimation in dynamic systems are addressed. The information entropy is used as a performance measure of a sensor configuration. Asymptotic estimates are used to provide valuable insight into the dependence of the information entropy on the number and location of sensors. The optimal sensor location is formulated as an optimization problem, involving discrete-valued variables, which is often solved using computationally efficient genetic algorithms or heuristic sequential sensor placement algorithms. For continuous structures modeled by finite elements, the problem is alternatively reformulated as an optimization problem over the continuous physical space. Each design variable, indicating the location of a sensor, varies along a one dimensional or two dimensional physical surface of the finite element mesh. Transformations are used to map an irregular surface into a regular parent surface and the optimization is conveniently carried out in the regular parent space. The CMA method is used to carry out the non-convex optimization. The developments and the computational efficiency of the proposed algorithm are illustrated for structural dynamics applications.

G-1:IL04 Wavefront Control of Future Large Thin Shell Space Telescopes

A. PREUMONT, **R. BASTAITS**, **E. ROMNEE**, **I. SURDEJ**, ULB, Active Structures Laboratory, Brussels, Belgium; **G. RODRIGUES**, ESA-ESTEC, Structures Section, Noordwijk, The Netherlands

Large aperture space reflectors are necessary to collect more light and to achieve higher resolution. Applications include astronomy, earth observation, lidar, laser communication and spectroscopy. There is a need for future reflectors with diameters of 10 m and more. The tight weight and volume constraints of current launchers call for a change of paradigm in terms of stowability and areal density; diameters up to 20 m will only be possible if an areal density of 3 kg/m² or less may be achieved. This change of paradigm is offered by the so-called gossamer spacecrafts and membrane optics. The use of adaptive doubly curved elastic shells is one option; the reflector is molded in its final shape and rolled for stowage. Once released in orbit, the reflector will unfold on its own strain energy. The sources of surface figure error are: manufacturing, creep in rolled configuration, thermal gradients and gravity gradients.

This paper consists of two parts. The first part examines numerically the morphing capability of adaptive doubly curved elastic thin shells provided with various orthotropic layers of active materials with strain actuation capability (e.g. piezoelectric). The control capability of various layered architectures on the optical modes (Zernike) is examined. The second part describes a concept of secondary wavefront corrector based on segmented flexible mirrors. The segments consist of Silicon wafers covered by a thick layer of PZT on their back side. The morphing capability of the concept is demonstrated.

G-1:IL05 **Fatigue of NiTi for Dampers and Actuators**

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The application of Shape Memory Alloy devices to practical uses needs well established performance and life. The reliable application in some areas, as dampers in engineering, needs a long fatigue life (some million oscillations). The present work reviews results on fatigue, and points the possibility to apply NiTi to dampers and actuators. Due to size effects and to the fact that fatigue failure usually comes from a surface defect inducing crack growth, fatigue has to be studied for concrete applications. It is revealed that NiTi is useful to effectively damp vibrations even at relatively low stresses and strains. The experimental results from facilities (cable 1 in ELSA-JRC, Ispra, Italy, and IFSTTAR test cable, Nantes, France) are analyzed, and confirm that NiTi wire is able to damp stayed cables. Testing machine experiments indicate that the main parameter controlling fatigue life is the stress on the NiTi wire. Long wire life (in the million cycle regime) can be achieved under limited stresses (under 200 MPa). Also, experiments have been done on thermal actuation of NiTi wire under traction at constant load. The results demonstrate that long actuator life (larger than 150000 cycles) can be achieved at low stresses (around 100 MPa), coherently with the mechanical cycling.

G-1:IL06 **Smart, Active Fiber Devices and Approaches to Realizing Textile Composites for Sensing and Energy Harvesting**

M. SHTEIN, K. PIPE, S. MORRIS, S. BISWAS, B. O'CONNOR¹, A. YADAV¹, University of Michigan, Ann Arbor, MI, USA; ¹Currently at North Carolina State University, USA

Traditional energy harvesting and sensing devices have rigid form factors that limit the ability to integrate their functionality into other structures, particularly when covering large areas. For example, the cost of installation is a significant fraction of the total cost of electricity from photovoltaic panels. If thin-film semiconductor devices could be integrated more pervasively and seamlessly in multi-functional structures and smart materials, their payback period potentially could be shortened and novel capabilities could be realized. Motivated by these and other reasons, we have investigated photovoltaic, light-emitting, antenna, and other devices in the form of fibers that could be woven into large area, multi-functional textiles and composites. We also investigated novel methods of fabricating these devices on non-planar substrates and directly on arbitrary surfaces. In this talk, we will review recent progress in organic-based energy conversion devices, antennas, and deposition methods potentially enabling pervasive and cost-effective multi-functional composites with sensing and energy harvesting capability.

G-1:IL07 **Modeling of Multifunctional Hybrid SMA-ceramic Composites**

D.C. LAGOUDAS, B.T. LESTER, Y. CHEMISKY, A. PARRINELLO, Texas A&M University, Dept. of Aerospace Engineering, College Station, TX, USA

A new hybrid Shape Memory Alloy (SMA)-MAX phase ceramic composite is being developed. By using an SMA the phase, it is expected that this composite will show effective transformation behaviors and that the martensitic transformation of the SMA phase will be able to generate a residual stress state in the composite which results in a compressive loading on the ceramic phase which will then take advantage of the improved mechanical properties of ceramics under compression. Both of these effects are explored in this work. First, a micromechanical scheme is developed to determine the effective transformation characteristics of the composite. Analysis demonstrates that a stress redistribution due to transformation results in a reduction of the effective transformation strain and a shift in transformation temperatures. To explore the capability of transformation to induce a residual stress state

in the composite, Finite Element methodologies are implemented. To capture the effects of the microstructure, a numerical model is developed based off of tomography. By considering an elasto-plastic approximation of the MAX phase ceramic response, it is shown that the desired residual stress state is developed and the cause of such a stress state is shown to be transformation.

G-1:L10 **On Characteristic Properties of a Layered Packet Base-foundation on the Base of the Analysis of the Solutions of the Corresponding Three-dimensional Dynamic Problems of Elasticity Theory**

L.A. AGHALOVYAN, M.L. AGHALOVYAN, Institute of Mechanics of NAS of Armenia, Yerevan, Armenia

Two-dimensional, three-dimensional and multilayered packets from plates, simulating base-foundation, base-seismoisolator-foundation of constructions, are considered. The cases, when the contact between all the layers is complete, i.e. on the surface of the contact all the components of the displacement vector and the corresponding components of the stresses tensor are continuous and the case, when between part of the layers the contact is complete and between the rest of the layers the contact is incomplete (Coulomb friction), are studied in detail. It is considered that on the foot of packet seismic effect acts (the value of the displacement vector is given, changing harmonically in time). A general asymptotic solution of three-dimensional dynamic problem of elasticity theory for n-layered packet is built. It is shown that the solution becomes mathematically exact, when entering in the boundary conditions functions are polynomial. The character of the stress-strain state of a three-dimensional packet, when the contact between the layers is complete, is studied in detail. On the base of the mathematically exact solution it is established that when there is a middle layer made of softer material of rubber type, the amplitudes of vibrations on the upper layer decrease sharply. By the same taken the application of seismoisolators is theoretically justified. The analysis of the exact solution of another class of problems, when the contact between the separate layers is incomplete, brought to the conclusion that the tangential displacements informed to the lower layer practically do not influence on the stress-strain states of the above standing layers with complete contact between the layers. The detected phenomena may be applied in the calculations of bases-foundations of constructions in seismosteady building for diminishing the negative influence of the seismic forces.

G-1:L11 **Advanced Smart Materials to Enable Adaptive Structural Composites**

M.R. MASCHMANN, G. EHLERT, A. McCCLUNG, G.P. TANDON, D. PHILLIPS, R. JUSTICE, **J.W. BAUR**, Air Force Research Laboratory, Materials and Manufacturing Directorate, AFRL/RX, WPAFB, OH, USA

Shape control of aero components has the potential to optimize the agility, versatility, and propulsion efficiency of current and future vehicles. Actively, or autonomously, optimizing the shape of an aero component can be enabled by distributed air flow sensing and controlled morphing. This presentation will discuss materials and materials concepts involved in efforts to create sensitive artificial hair flow sensors and shape changing composites. The artificial hair sensors are fabricated from small diameter structural fibers and mechanoresistive carbon nanotube (CNT) arrays. The detailed mechanics of CNT arrays are investigated through the novel application of digital image correlation to CNTs tested in-situ under compression within an electron microscope. Strain mapping of the entire arrays with resolution on the order of the individual tubes could be obtained. Shape changing composites are fabricated from reinforced, thermally-activated shape memory polymers (SMP). The shape memory properties of a series of commercially available and internally synthesized high temperature polymers are characterized. Composites were also constructed with networks of microchannels to provide improved control of the activation and deactivation of the shape memory composite during shape change.

G-1:L12 **Nonlinear Viscoelastic Model of Isotropic and Anisotropic Magnetorheological Elastomers**

K. SAPOUNA, Y.P. XIONG, R.A. SHENOI, Faculty of Engineering and the Environment, University of Southampton, Southampton, UK

Magnetorheological Elastomers (MREs) is a promising smart material that can adjust its mechanical and dynamic properties instantly and irreversibly when an external magnetic field is applied. Our recent research showed that MREs is governed by a nonlinear stress strain

relationship where both stiffness and damping depend nonlinearly on the magnetic field. However, the majority of the researches on MREs relevant publications are limited to linear domain assuming the material behaves linearly in a specific strain range. This paper focuses on the characterization and development of a nonlinear general viscoelastic model that can predict the variation of damping and stiffens with the magnetic field for both types of MRE (anisotropic and isotropic). For this purpose static and dynamic compression tests are performed first for a range of strain amplitudes and magnetic fields. Then a parameter extraction method is developed. An application of the developed MRE model is demonstrated by simulating an active vibration isolator and its isolation effectiveness is predicted numerically using Matlab and Simulink. MRE isolators can be an attractive solution to the complicated active mechanical isolation systems present in many engineering applications in the industry today.

Session G-2

Integration Technologies

G-2:IL01 Actuator & Sensor Integration for Adaptronic Applications **THILO BEIN**, Fraunhofer LBF, Darmstadt, Germany

Adaptive structural systems enable new and innovative approaches to optimise engineered structures with increased functionality in all fields of mechanical engineering. Over the last decades, adaptronics are mostly applied to noise and vibration control in high-cost markets whereas the research was focussing on the actuator design, control concepts and simulation. Nowadays a trend can be observed towards system integration of the actuators and sensors, manufacturing and system reliability. Since 2008 these topics are being addressed within the state-funded LOEWE-Center AdRIA (Adaptronics - Research, Innovation, Application). Among others, new multifunctional materials, miniaturisation of actuators and sensors, manufacturing using rapid prototyping technologies, structural health monitoring as well as self-sustaining systems are being developed for highly integrated adaptive structural systems. In this context, an important aspect is the system integration into the overall application ensuring the reliability over the defined life-time of the system. This paper discusses the specific requirements of the actuator and sensor integration with respect to adaptive structural systems and outlines recent developments made in manufacturing highly integrated adaptive structures.

G-2:IL02 Digital Implementation for Active Control **L. FARAVELLI**, ZHICONG CHEN, Dept. Structural Mechanics, University of Pavia, Pavia, Italy

Active structural control sought its first implementations in the age of transistors (if not valves), wires and huge elaboration machines. The evolution, as recorded along the last fifty years, is evident not only to scientists and designers but also, and perhaps mainly, to the end-users, to whom an always lower insight is required to manage the resulting control systems. But the basic revolution was developing in the last few years, when all instrumentation, as well as control boards, moved from the analog to the digital format. In Civil Engineering such a revolution is visible, at the moment, in the world of the testing laboratories, where large shaking tables have been updated to the new format. This paper approaches the features of the integration of digital control in structural engineering, with focus on the way to drive an active mass damper system. Laboratory experiments and numerical simulations are reported to support such a contribution to an ongoing task in Structural Control.

G-2:IL03 A Mathematical Framework for Structural Control Integration **F. PALACIOS-QUINONERO**, **J. RODELLAR**, J.M. ROSSELL, J. RUBIÓ-MASSEGÚ, Department of Applied Mathematics III, Universitat Politècnica de Catalunya, Barcelona, Spain

The latest trends in structural vibration control of large structures, such as tall buildings, consider control systems of increasing complexity, which typically involve a large number of sensors and actuation devices, together with a wide and sophisticated wireless communication network.

In this context, semidecentralized control strategies, which can operate using partial state information, are specially interesting. The semidecentralized approach reduces computational costs and information exchange, and increases robustness with respect to interconnection degradation. Overlapping decompositions and the Inclusion Principle have proved to be a suitable theoretical framework to design effective semidecentralized overlapping controllers for a variety of large-scale and complex systems, such as electric power networks, automated highways, civil and space structures, and communication networks. These ideas have also been successfully applied to design controllers for vibration control of buildings under dynamic excitations. The paper will present the conceptual and mathematical framework and some examples to illustrate its potential to design control systems for large scale structures within a variety of information exchange and actuation scenarios.

G-2:IL04 Dynamic Sensor Data Fusion: Developments for Structural and Mechanical Systems using Dual State Parameter Estimation Techniques

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It is well recognized, although not frequently exploited, that some sensors capture certain structural response properties better than others and therefore the intelligent use of a variety of sensor types in combination may provide for a higher fidelity picture of the system dynamics. The simplest example to illustrate the point of sensor performance is that an accelerometer performs better in the higher frequency range than in the lower frequency range simply because, at a given level of displacement, the level of acceleration is higher than if it were at a low frequency. In contrast, a displacement sensor such as an LVDT or even a differential GPS antenna could potentially perform better than the accelerometer at very low frequencies because the associated acceleration would be very low. These very low frequency dynamics are extremely important in the modeling of nonlinear hysteresis and permanent damage for civil structural systems. This presentation will review some recent developments in the development and use of algorithms which combine the relative strengths of different sensors, and through information redundancy to simultaneously provide enhanced measurements and highly accurate nonlinear models of the underlying structural behaviors. The process of exploiting data redundancies from different sensors type, often popularly called "Data Fusion" can be envisioned in a number of contexts. Three common scenarios are a) when the heterogeneous sensors are collocated and no information about the underlying structural model is needed in order to enhance the measurements through a fusion process, or b) when the sensors are not collocated, but the underlying structural mechanics is known with a high degree of confidence, or finally, c) when the sensors are not necessarily collocated and the underlying structural mechanics are also unknown. The presentation will review some theoretical and field application of the scenario described in case (a) using a Kalman filter based approach to combine accelerometer and dynamic differential GPS displacement data from a major NYC long-span bridge. While this comparatively simple case of collocated sensing has many applications for dynamic measurement enhancement and de-noising, and case (b) can be formulated as a simple extension of case (a), case (c) is perhaps the most interesting and challenging case. In this case the sensors may not be collocated and the structural model itself is also to be identified. Using assumptions about the topology of the structure and subsequently assuming the mathematical form of the dynamic model, dual state and parameter estimation techniques can be used to simultaneously estimate the system parameters as well as estimating unmeasured states and de-noising measured data. To date, this approach has been pursued with the use of the assumption that the model can capture the system dynamics with time-invariant parameters. Particular success has been achieved with the Unscented Kalman Filter (UKF) and variants of the Particle Filter methods.

G-2:IL05 Insight and Applications in Energy Harvesting from Bullets to Birds **E. GARCIA**, Laboratory of Intelligent Machine Systems, Cornell University, Ithaca, NY, USA

The creation of self-powered monitoring systems is possible only through the harvesting of energy from the environment. The proliferation in semiconductor technology, and their dependence on batteries has led to a growing need to tap into ambient sources of energy. Energy in the environment can be converted to stored electrical energy by a variety of

means, such as solar energy collection and mechanical power harvesting. Solar power is the most established technique, and can generate low voltage, moderate current (for North America we can expect approximately 10 mW/cm²). The drawbacks of solar are its dependence on direct sunlight. Hence the design and development of a multi-source system becomes important. Garcia's Laboratory at Cornell University in USA has fabricated small mechanical and solar harvesting system for operating yaw control circuit on the moth as well as for self-powered bird tagging systems. While most energy harvesting literature has focused on extracting energy from vibrating structures, several previous studies have addressed harvesting energy from flowing fluids. Garcia's lab has been working to find the link between structural dynamics of a piezo-composite structure and aerodynamics for energy harvesting systems, hence directing the research toward energy and the environment. Piezoelectric composite structures are used as transducers and coupled to nonlinear impedance matching circuits to maximize energy transfer. In order for such a system to operate effectively it is important to understand the aerodynamic interaction between neighboring power harvesters including downstream wake effects, and how these interactions can be leveraged to maximize the output of the system. The study to experimentally investigate the changes in steady state power output and oscillation frequency due to aerodynamic wake effects when a pair of flutter energy harvesters are placed in various two dimensional configurations has given insight into the maximum power regions bested on flapper location. The Garcia Group has also developed a new concept in nonlinear switching circuit design that can increase the theoretical power harvested from a piezoelectric by 400%, where actual power is less because of dissipation in the circuit. To date, Garcia's group have achieved increases of 280%. The switching approach simulation and data, also shows that our ability to store power remains nearly constant, even though the storage capacitor voltage is increasing. Also a peak detection scheme for switching circuit is developed that is based on a passive differentiator and a low power zero crossing detector.

G-2:IL06 Design of Energy-harvesting and Storage Systems (EHSS) for Future Aero-vehicles

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We have been working since 2006 on AFOSR MURI :design of airborne EHSS and their integration to load-bearing aerospace structures. In this MURI project several US universities are teaming, University of Washington (UW), University of Colorado(CU), University of California at Los Angeles (UCLA), Virginia Tech (VT) and University of Illinois at Urbana-Champaigne (UIUC). UW is working mainly on airborne EHSS components, namely, dye-sensitized solar cells (DSSC), organic PV, thermoelectrics and Li-ion battery, and also characterization of composite structure with EHSS. CU is working on modeling of selected EHSS components, namely, piezoelectric energy harvester for mechanical energy and Li-ion battery. UCLA is working on integration of EHSS components into load-bearing composite structures. VT has been working on the piezoelectrics based mechanical harvesting devices and their integration into composite panels. UIUC has been working on the nanostructure characterization of EHSS embedded in a composite panel. I will discuss selected research progress on the current AFOSR MURI on EHSS, mainly focusing on UW work, namely dye-sensitized solar cells based on both glass and PET substrates, their integration in composite structural member, thermoelectric module based on light metallic semiconductors and their integrations to UAV engine.

G-2:L07 A Fractal-inspired Multi-frequency Piezoelectric Energy Converter: Computational and Experimental Characterization

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This paper deals with the computational analysis and experimental characterization of a fractal inspired, multi-frequency, piezoelectric energy converter. In order to develop self-powered wireless sensor nodes, many energy harvesting devices, able to convert freely available ambient energy into electrical energy, have been proposed in the literature. A promising technique, in terms of simplicity and high conversion efficiency, is the harvesting of ambient kinetic energy through piezoelectric materials. The aim of this work is to investigate the power output and the efficiency of a fractal-inspired, multi-frequency, piezoelectric energy converter. This converter, previously presented by the author, has the peculiarity of a broadband frequency response in the range between 0 and 100 Hz. The converter is a square, thin sheet

structure, characterized by a fractal geometry obtained through a pattern of cuts in the plate. The work is organized in two steps. First, we analyze computationally the modal response and the power output of the energy converter, by minimizing the amount of piezoelectric material used. Second, we investigate experimentally a prototype of the converter. Both the computational analysis and the experimental tests are performed in the range between 0 and 100 Hz.

G-2:L09 Vibroacoustic Optimization and Implementation of Adaptive Metacomposite Based on Periodically Distributed Shunted Piezoelectric Patches

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In the last few years, a technological revolution has occurred in the fields of integrated MEMS that offers new opportunities for smart structures design and optimization. We know today that the mechanical integration of active smart materials, electronics, chipsets and power supply systems is possible for the next generation of smart composite structures that can be considered as a new class of adaptive metamaterials. By using integrated distributed set of electromechanical transducers, one can attain new functionalities. In this paper, we present an application of the Floquet-Bloch theorem in the context of electrodynamics for vibroacoustic power flow optimization by mean of distributed shunted piezoelectric material. The main purpose is to present a numerical approach able to compute the multi-modal wave dispersions curves into the whole first Brillouin zone for periodically distributed damped 2D mechanical systems. In a second time, we optimize the piezoelectric shunting electrical impedance for controlling energy diffusion into the proposed semi-active distributed set of cells. Particular implantation problems are also addressed for taking into consideration electromechanical lack of robustness due to electronic coupling and patches electrostatic parasitic behavior.

Session G-3

Smart Structures and Integrated Systems

G-3:IL01 Seismic Protection of Structures with Resettable Tuned Mass Dampers

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Vibration control of civil engineering structures using tuned mass dampers(TMD) is now a widely accepted control strategy. Although the design and application of traditional linear TMD systems are well developed, nonlinear TMD systems that may lead to better control performance are still in the development stage. There are two main problems associated with linear TMD systems: (1) detuning effect and (2) excessive TMD stroke. In order to improve the performance of TMD systems, some researchers have proposed using semi-active TMD systems, which are usually TMDs with semi-active control devices. The semi-active device can be in one of several forms, such as an MR damper, a variable friction damper, or a variable stiffness device(VSD). Among them, VSD is a relatively new concept. The VSDs can be divided into two types: on-off type and continuous type. The continuous type is effective in reducing detuning effect while the on-off type is effective in reducing TMD stroke. In this study, a resettable variable stiffness TMD (RVS-TMD) is proposed to combine the advantages of the continuous and the on-off types. The RVS-TMD consists of a TMD together with a resettable variable stiffness damper(RVSD). The seismic performance of this system is investigated numerically in this study.

G-3:IL04 Mechanics and Model-based Control of Structures

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The present contribution gives an overview on research that has been performed since 2008 in Area 2, Mechanics and Model Based Control, of the COMET K2 Austrian Center of Competence in Mechatronics (ACCM). ACCM is a peer-reviewed research center funded by the Austrian government, in which scientific and industrial partners from

Austria and abroad are jointly performing research in multi-firm and strategic research projects, grouped into six interconnecting Areas. Area 2 is motivated by the fact that mechanics and control both are rapidly expanding scientific fields, which share demanding mathematical and/or system-theoretic formulations and methods. The goal is to utilize and extend these relations, with special emphasis on solid mechanics and control methods based on physical models. In the present contribution, results concerning the following topics are reviewed in some detail: - Mechanical Modelling of structures, robots and machines: Model based reduced order approximation; Multi-physics actuation and sensing; Structural control and health monitoring; - Model based control for linear/non-linear lumped/distributed parameter systems: Geometric modelling of distributed parameter physical networks; Integrated control loop design; Parameter identification for non-linear systems.

G-3:IL05 Structural Damage Identification by Finite Element Model Updating

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Many researchers are looking for methods to exploit the differences in dynamic signatures to identify possibly occurred damage. Increasingly popular is operational modal analysis delivering natural frequencies, (non scaled) mode shapes and modal strains, representing a dynamic signature free from influences of the not measured (in many cases not measurable) dynamic excitation. Different methods are proposed that further translate the modal differences in a more or less refined representation of damage. Still the most versatile and powerful method is based on finite element updating (or more generally: inverse modeling). For updating (which is in fact a problem of minimizing differences between measured and calculated quantities) many powerful numerical optimization methods (local or global) are at disposal. A possibility that allows to incorporate measurement and model uncertainties is Bayesian based updating. Guidelines are presented for a successful damage identification by finite element model updating which also incorporates the experimental setup of the operational vibration test. Finally, a real case will be presented. On a prestressed concrete viaduct of the E313 highway at Boirs, Belgium, tendons of some of the outer girders were seriously corroded. Operational modal analysis with exogenous (OMAX) input tests were conducted on one of the seriously damaged spans and modal parameters were successfully extracted. Without any measurement of the viaduct in its intact state, damage identification became very challenging. A detailed finite element model based on the blueprints was constructed. To improve the efficiency while performing model updating, an equivalent orthotropic plate model with similar dynamic behavior as a refined volume model was constructed. This simplified model was treated as the baseline model for model updating using the measured modal parameters. Although the residuals of this optimization problem represents both modeling error and damage effects, the results of model updating match the trend caused by the damage.

G-3:IL06 Vibration-based Damage Detection under Changing Environmental and Operational Conditions

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Structural Health Monitoring (SHM) allows to perform a diagnosis on demand which assists the operator to plan his future maintenance or repair activities. Using structural vibrations to extract damage sensitive features, problems can arise due to variations of the dynamical properties with changing environmental and operational conditions (EOC). The dynamic changes due to changing EOCs (like variations in (temperature, rotational speed, wind speed, ...) may be of the same order of magnitude as the variations due to damage making a reliable damage detection impossible. In this paper, we show a method for the compensation of changing EOC. The well-known null space based fault detection (NSFD) is used for damage detection. In the first stage, a training is performed using data from the undamaged structure under varying EOC. For the compensation of the EOC-effects the undamaged state is modelled by different reference data corresponding to different representative EOC conditions. Finally, in the application, the influences of one or other EOC on each incoming data is weighted separately by means of a fuzzy-classification algorithm. The theory and algorithm is successfully tested with data sets from a real wind turbine and with data from a laboratory model.

G-3:IL07 Monitoring, Evaluation and Control for Life-cycle Performance of Intelligent Civil Structures

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The civil structures are subjected to various loads and harsh environmental actions for their operation period. The intelligent civil structures, integrated with sensing technology and control technology, can self-sense their status and control their behaviors. The wave propagation-based sensing technology is developed for local damage detection of composite materials, corrosion monitoring of reinforcement and scour monitoring for bridge piers. The compressive sensing sampling technique is employed to compress the monitored data in SHM and wireless network nodes, and to recovery loss data in wireless nodes to base station. The damage detection approaches for gradually developing damage of linear structure system (damage caused by sustaining loading, fatigue loading and durability), and nonlinear structure system (seismic damage) have been proposed. The monitored wind effects from long-span bridges are also and control methods based on aerodynamics are investigated. Finally, the modeling approaches for ultimate value estimation and fatigue damage estimation of applied loads and structural response based on monitoring technology are also presented.

G-3:IL09 High Precision Adaptive and Morphing Structures

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Using actuators and sensors in structures might be essential for high functionality. But "integration" per se is no added value. For example, actuators have to be then sufficiently small and material weakening has to be avoided. So such concepts are specifically apt for actuating and controlling small displacements or low mass / low damping vibrating systems e.g. in opto-mechanical systems or space structures such as large reflectors, solar arrays or telescopes. Structurally integrated fiber optic sensors used for (health) monitoring and deformed shape reconstruction will be discussed first. Active damping of large solar arrays via piezo-ceramic actuators can be quite beneficial for reducing limits of the satellite attitude control system. For large reflectors with high dimensional stability requirements, post-manufacturing improvement of shape accuracy via shape memory polymers or a certain compensation of in-orbit disturbances is of interest. A further challenge comes into play when such structures have to be drastically morphed in their shapes in order to adapt to modified mission needs, which then calls for micro-actuators with relatively large displacement strokes. Presented results are based on simulations and experimental data derived from laboratory models.

G-3:IL10 Bistable Structures for Use in Morphing Applications

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There has been increasing interest in the possibility of creating morphing structures in the recent research literature. One way to achieve this is to use structures which have multiple stable static shapes, and then to actuate the structure between these shapes to achieve the required morphing task. In this paper, we examine the use of plate structures to try and achieve this task. In particular we will consider composite plates which can be manufactured to have bistable characteristics which can then be used to switch between two stable states. We will discuss the issues of the plate stiffness and subsequent dynamics and control of the plate. We will also discuss the modelling of the plate vibration, and how this affects the potential performance of a morphing structure.

G-3:IL11 Deployable Structures

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Deployable structures have been developed for many different applications from space to mechanical and civil engineering. In the paper the general concepts of deployable structures, combining static and kinematic behaviour are presented first, also discussing their relationships with adaptive and variable geometry structures. Reported applications to civil engineering and architecture are then reviewed and categorized. The characteristics of the following systems are summarized: 1. Pneumatic Structures, 2. Tensegrity Structures, 3.

Scissor-like Structures, 4. Rigid Foldable Origami, 5. Mutually Supported Structures. The problems of form finding, direct and inverse kinematics, actuation and self-deployability for some of the most interesting among the above structural types are then discussed in the paper. Some examples involving rigid foldable origami and mutually supported structures are finally presented.

G-3:IL12 Integration of Piezoelectric Components in Composite Structures

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Composite materials are currently being used instead of classical metal ones even for load carrying structural functions in aeronautic, aerospace, marine, automotive and railway transportation structures. This tendency is expected to grow rapidly and, for some applications, composite materials may be dominant in a near future. Although composite materials have undeniable advantages over classical materials, they are known to be sensitive to vibrations and damages. This explains the current big research interests in vibration control and damage identification techniques that might be integrated in composites. These require surface-bonded or preferably embedded sensors and actuators working either passively (without input energy) or actively (with input energy). The integration of the so-called smart or active materials, such as piezoceramics, shape memory alloys, magneto-strictives, electro-strictives, optical fibres, etc., in composites renders them *multifunctional* in the sense that they can assure integrated sensing, actuation, vibration damping, noise reduction and health monitoring. This leads to the so-called smart composites. This invited lecture will focus on the (i) adequate choice of the host and piezoelectric transducer for effectively coupled integrated smart mono-morph, bimorph and multi-morph composite structures. Both Carbon and Glass Fiber Reinforced Plastic (CFRP & GFRP) host composites will be investigated for adhesively bonded monolithic d_{31} and d_{15} PZT or d_{31} Macro-Fiber Composite (MFC) patches; (ii) integrated piezoelectric smart composites characteristics (properties, coupling and response) under bending vibration, shear(d_{15})-induced torsion and d_{15} -shear static actuation. Emphasis will be put on their effective properties identification, patch positioning, adhesives influence on the simulated response, and the experimental non linear responses of these smart systems.

G-3:L13 SHM System for Monitoring and Prediction of Cracks Development in Concrete Structures

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This paper describes the concept of monitoring massive concrete structures based on the inverse problem solution. Properties of young concrete are changing very intensively in the early stage of hydration process, and therefore it is very important to know material constants as a function of age of concrete in order to accurately modeling the phenomena occurring in it. The main idea is to determine the time-dependent thermal properties of concrete on the basis of point temperature measurements in a small laboratory molds. Then, based on these parameters, the coupled thermo-mechanical equations are solved to describe the maturation and aging of concrete. This allows to specify (at the design stage) the potential risk of structural damage (e.g. thermal cracking) and thus prevent them e.g. through the use of intelligent cooling systems. Own, based on finite element method, software TMC (Thermal & Mechanical modeling of Concrete) gives also the possibility of predicting the formation of cracks during the aging of structure, which will be verified by means of electric sensor networks (so called ELGRID). This integration will enable to provide a complete system for monitoring and prediction of the structural stress state and damage development.

G-3:L14 The ELGRID System for Monitoring of Cracks in Massive Concrete Structures

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A system for monitoring propagation of cracks in aging concrete structures using an electrical sensor network is presented. Based on the data from the independent software modeling thermo-mechanical process in concrete (so called TMC), the areas of high risk of damage in massive concrete structures are specified. Arrays of surface-mounted conductive strips which break under local damage-induced strains are

then deposited to detect the onset and to track the growth of cracks. Lengths and plane arrangement of the strips are chosen to the anticipated size and direction of crack propagation. Additional electrical circuit connects the strips in a compact network of pre-designed topology and parameters. Crack occurrences indicated by broken branches within the network are located by measuring network responses on dynamic test signal and solving the inverse problem using the methods of gradient-based optimization.

G-3:L16 Smart Composite Device for Structural Health Monitoring

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Composite materials are increasingly used in civil field for structural strengthening. Besides, monitoring the structure during its lifetime is very important, in order to detect possible anomalous situations and to reduce maintenance and inspection costs. Optical fibers represent a promising and increasingly used technique for long-term health monitoring of structures. The aim of this research is to assess the feasibility and reliability of strain measurements by utilizing FBG (Fiber Bragg Grating) optical sensors embedded in FRP (Fiber Reinforced Plastic) packaging. The resulting device is conceived to be applied on the external surface of the structure. The packaging provides the optical fiber with the necessary protection against accidental damage during handling and installation. The mechanical characteristics of the packaging allow the device to be used as a sensorized reinforcement as well. The paper discusses the technology set-up, the physical and the mechanical characterization and the in situ validation.

G-3:L18 Real-time Smart Abstract Shape Identifiers

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Smart structural systems are emerging as a vehicle for implementing semi active control algorithms. Sensors, processors and actuators are the generic basic components of any smart structural system. Sensors are employed in gathering information that could be used by a smart shape identifier in order to define a real-time abstract deformed shape of the system at any given point in time. This information could be employed in proposing a suitable smart control algorithm to suppress the vibration of a given structural system. In this paper, two real-time smart shape identifiers are presented. The proposed algorithms employ neural network and fuzzy logic as two potential smart technologies. Both models are capable of identifying and/or classifying the abstract deformed shape of a three degree-of-freedom structural system in real-time. The neural network model was developed and trained by a single earthquake record then tested using five unseen earthquake records. The fuzzy inference system employed a rule-base that was developed to capture all potential combinations of inter-story deformations then tested using all six earthquake records. The performance of both models was measured by the statistical and geometrical properties of a linear compliance graph.

G-3:L21 A Coupled Electro-mechanical System for Damage Detection and Energy Harvesting

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Recent trends in structural health monitoring refer to vibration-based methods as a suitable tool for real time checking the integrity of structures. From a technological point of view, PZT sensors represent reliable and efficient means to measure the structural response, in particular the mechanical curvature. In this context, a coupled electro-mechanical system constituted by PZT sensors glued to the surface of a beam structure is studied. This system is used to illustrate a novel technique for damage identification and, at the same time, to investigate the possibility of energy harvesting. The identification procedure is based on measurements of both eigenfrequencies and eigenvectors curvatures. It consists of a model independent localization of damage, which reduces the computational effort to a one-dimensional minimization problem of a non-convex functional, and a minimization of this functional based on the comparison between analytical and measured frequencies. The same coupled system is exploited for energy harvesting purposes. Once the mechanical energy is transformed into electrical energy through direct piezoelectric effect, it can be employed for self-powering electrical circuits and sensor electronics.

Session G-4

Bio-inspired Materials and Structures

G-4:IL01 What We Can Learn from Nature's Flyers for Better Flapping Air Vehicle?

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Studies on flapping-wing flight have focused on the aerodynamic enhancement mechanisms of hovering insects such as leading-edge vortex formation and stabilization. Recently our curiosity has gradually moved on how complex combinations of insects' wing motion affect not only aerodynamic loads generation but also flight stability and control. Nature's flyers have evolved and adopted flapping-wing flight to be aerodynamically efficient; this applies to wing morphology and kinematics and also to how flying animals maintain their flight stability. Flight behaviors and control principles of nature's flyers have inspired us to build better flapping wing air vehicles. This talk introduces a feedforward tail control for the longitudinal stability of flapping air vehicle flight, which is motivated by biological examples. This control method was examined using an integrative ornithopter flight simulator and experimental platforms. The numerical and experimental results showed that phasic relationship between wing and tail activation signals might act to improve longitudinal flight stability in terms of a reduction of the amplitude of body pitch oscillation. The simplicity of the link between tail and wing motion described here could lead to novel ways to automate the ornithopter.

G-4:IL02 Mussel-inspired Technology for Microfluidics and Stem Cell Culture

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The nonwetting properties of superhydrophobic surfaces have allowed a variety of applications. Despite the large effort to develop methods to prepare superhydrophobic surfaces, few strategies to tailor the superhydrophobic surface properties have been developed. However, polydopamine (pD), a mussel-inspired polymer, could successfully modify the superhydrophobic surfaces. Through the pD-coating on the superhydrophobic surfaces, a new type of microfluidic system is reported. It is a pump-free, two-dimensional microfluidic system, energy efficiently operated with gravity. The device is fabricated by hydrophilic pD-micropatterns on superhydrophobic anodized aluminum oxide surfaces on which liquid droplets move along the predetermined paths of pD with no residuary liquid trace. A rapid mixing device to monitor structural changes of a protein and a micro-reactor for the synthesis of nanoparticles were fabricated. The pD-coating on superhydrophobic surfaces was also applied to controlled formation of stem cell (SC) aggregates (spheroids). To produce homogeneous SC spheroids, hanging drop culture system by using dot-shaped, pD-patterned superhydrophobic surface was hired. Through this culture system, homogeneous spheroids of mesenchymal stem cells (MSCs) were produced.

G-4:IL04 Mechanical Model of Bio-inspired Ultra-sensitive Infrasound Sensor for Landslide

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Landslides are a widespread hazard in many mountainous and hilly regions. Field evidence has shown that geo-hazardous events such as landslide can radiate infrasonic waves in the form of both acoustical and motion signals. Thus, hazard assessment and even early detection of imminent landslides is achievable through advancements in ultra-sensitive infrasound motion sensors. However, current sensors for infrasound motion detection are not sensitive enough. In this paper, a mechanical model of hair cell is established based on the sensitivity of fish's inner ear to infrasound. Through numerical analysis by OpenSees, responses the model subject to static loading show that the amplification of displacement response of gated model is highly sensitive to weak loading and lowly sensitive to larger loading due to the negative stiffness effect of whole pendulum bundles caused by the opening of gating spring. Responses of the model subject to dynamic loading show that gated model is acute sensitive to low-frequency loading and lowly

sensitive to high-frequency loading due to the negative stiffness of gating spring. The proposed gated model can be used as the theoretical basis for the design of new ultra-sensitive bio-inspired infrasound sensors for landslide monitoring.

G-4:IL07 Learning from Plants – Biologically-Inspired Adaptive Structural Systems

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This research is an interdisciplinary study to create a multifunctional adaptive structure concept through investigating the characteristics of plants. We explore new ideas building upon innovations inspired by the mechanical, chemical, and electrical properties of plant cells. It has been observed that plant nastic actuations (e.g., rapid plant motions of mimosa) occur due to directional changes in plant cell shape facilitated by internal hydrostatic pressure, achieving actuations with large force and stroke. It is also known that plants can adapt to the direction/magnitude of external loads and damage, and reconfigure or heal themselves via cell growth. The ability to concurrently achieve distributed large stroke/force actuation, significant property change, self-reconfiguration, and self-healing has long been the dream of the adaptive structure researchers. The features of plants can provide engineers with valuable knowledge and opportunities for interdisciplinary intellectual advancements that could lead to a new paradigm of adaptive structures. In this research, building upon and advancing from the fluidic flexible matrix composite (F2MC) concept, F2MC cells are created that emulate functions of plant cells based on our understanding of the cell response to pressure and loading. Through structural analysis and synthesis, F2MC cells are to be assembled to form a hypercellular topology resembling a circulatory network for potential global structural control. The outcome of this research could become the building blocks of future systems with enhanced functionality and performance. The next generation's air, marine, and land vehicles, intelligent machines and infrastructures could benefit from the knowledge discovered.

Session G-5

Ongoing and Perspective Applications

G-5:IL01 Recent Advances in Active Structural Control Strategies for Civil Engineering Applications

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With the increasing demand on structural safety, the concept of structural control is conceived to protect the controlled structure by reducing its response to external excitation, such as earthquake and strong wind. In this paper, wireless sensors and a fuzzy controller are introduced to update an active mass damper (AMD) for a scaled three-storey steel frame. One of the main obstacles to the spread of active structural control strategies in civil engineering was associated with the cables connecting the sensor units (necessary to provide the control feedback) to the managing computer (where the sensor signals are processed and elaborated) and from here to the actuators. These physical connections among parts far away across the building are often in conflict with the architectural constraints. Furthermore, their vulnerability to mechanical damage may cause the control system to be put out of service. Therefore, the adoption of wireless sensors adequately designed and tailored to the application aims to eliminate the high costs of installation and maintenance due to the cables. With respect to the classical control solutions, which are based on the modelling of the controlled object, the main advantages offered by a fuzzy controller are: (1) its robustness; (2) the ability to handle the non-linear behaviour of the structure; (3) the easiness of implementation. The whole controlled structural system consists of the three-storey steel frame, four single-axis wireless accelerometers mounted on each floor of the frame, a mass cart driven by a direct current (DC) motor, the DC motor position controller and a Fuzzy controller. The frame is mounted on a single-axis shaking table whose motion is used to simulate the excitation. The whole controlled structural system will be tested and the results will be analysed.

G-5:IL02 On the Use of Statistical Pattern Recognition Methods for Structural Health Monitoring

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In this paper the authors discuss the merits of using statistical pattern recognition and classification methods in comparison to the more traditional model based methods for structural health monitoring. Brief summaries of methods using autoregressive models, wavelet transforms and simple rotation measurements are presented. The use for each of these methods will vary with the load and the type of structure. For example, the autoregressive models are used for long term deterioration where ambient vibrations are measured; wavelet transforms are used with non-stationary earthquake response motions, and rotation algorithms are used for non-ductile concrete frames experiencing large permanent deformations. Example applications are shown for a single column, four story steel frame structure and for low rise concrete frame. In addition, it is shown how fragility functions can be developed using features from the wavelet transform and can be embedded in a sensing node for rapid damage estimation after an earthquake event.

G-5:IL03 Structural Control Issues in New Generation Offshore Wind Energy Plants

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Offshore wind energy is one of the fastest growing powers in the field of renewable energy. An offshore wind farm situated sufficiently far away from the coast can generate more wind power and will have a longer operation life since the winds are stronger and more consistent than those on or near the coast. It can also avoid some major problems of the traditional wind farms like the visual and noise impacts and potential damage to wildlife. From the technical point of view, it is difficult to anchor the wind turbines directly on the seabed in deep water. Thus, new constructive solutions based on floating support structures are proposed. One of the main challenges is to reduce the fatigue of a floating offshore wind turbine so as to guarantee its proper functioning under the constraints imposed by the floating support structures subject to a greater range of motion than that of the fixed-bottom support structures. This paper will analyze the dynamic loads and response of the wind turbine components (blades, drive-train, nacelle and tower) and the mooring systems for the floating support platform and will address the (passive, active and semiactive) structural control issues concerning about the mitigation of the dynamic wind and wave loads on floating wind turbines.

G-5:IL05 Assistive Knee Braces with Multifunctional Actuators

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Assistive knee braces are a kind of wearable lower extremity exoskeletons that can enhance people's strength and provide desired locomotion. It is possible to use knee braces to assist elderly or disabled people on improving their mobility in order to solve many daily life problems, such as going up and down stairs and crossing over obstacles. With a continually aging world population, devices that help elderly with mobility problems are in great need. By using assistive knee braces, patients may avoid being bedridden and will be able to maintain their physical activities. They will be able to benefit from the positive effects of exercise and enjoy an active lifestyle. Studies have been conducted in the development of exoskeletons. The commonly used actuation devices in assistive knee braces are electric motors. For such actuators, the brake function would consume much power to maintain posture and might cause safety problems. Some researchers adopted smart fluids in actuation mechanisms. The developed knee braces using smart fluids could provide controllable torque as assistive devices in passive and semi-active means while only little power is consumed. However, in some situations for the wearer going upstairs or stepping over obstacles, such knee braces would not be able to help in active ways. To combine the advantages of electric motors and smart fluids, we have developed an assistive knee brace by integrating a magneto-rheological (MR) actuator with electric motor. The MR actuator could function as brake when adjustable torque is preferred; or work as clutch to transfer torque from motor to the brace. With adaptive control, the actuation system worked well and could provide desired torque with better safety and energy efficiency. However, the actuator seemed a bit bulky to be used on human body. A more compact actuator is desired

for assistive knee braces. With this motivation, a multifunctional actuator integrating motor, clutch and brake functions into a single device was designed. We developed two kinds of multifunctional actuators with inner armatures and input/output plates. The assistive knee brace using the multifunctional actuator combines the advantages of electric motor and MR fluids into one single device, and it has the advantages of less power consumption, improved safety and better controllability. We evaluated the kinematic and kinetic changes of walking while wearing the assistive knee brace. Temporal and spatial gait parameters, joint kinematics, and joint kinetic parameters during walking with the developed assistive knee brace were compared with normal walking.

G-5:IL07 Structural Health Monitoring of a Tall Building with Huge Floating Platform

YI-QING NI, Y.X. XIA, H.F. ZHOU, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

The New Headquarters of Shenzhen Stock Exchange (NHSSE) is a tall building with a height of 228m. One outstanding feature of NHSSE is its huge floating platform which is a steel truss structure assembled with a total of 14 steel trusses. It overhangs from the main tower 36m along the long axis and 22m along the short axis at a height of 36m above the ground. As a result, the huge floating platform has an overall plan dimension of 98m×162m and a total height of 24m, making it the largest cantilever structure in the world. In view of the uniqueness of the floating platform, a structural health monitoring system has been devised and implemented on NHSSE by The Hong Kong Polytechnic University. A total of 224 vibrating-wire strain gauges have been installed to measure the strain while a novel vision-based displacement tracking system has been employed to monitor the deflection. In addition, accelerometers and a wireless sensing board are implemented to monitor dynamic responses of the structure. This paper reports the monitoring results of stresses and deflections of NHSSE during the construction process of dismantling the shoring and modal parameters of NHSSE under ambient vibration excitations, and their comparison with the prediction results obtained by a finite element model.

G-5:L08 Development of a Visualized Data Management System for Life-cycle Health Monitoring of Civil Structures

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The data management system (DMS) is an essential part of the structural health monitoring (SHM) system, which stores a pool of monitoring data for various applications. A robust database within a DMS is generally used to archive, manage and update life-cycle information of civil structures. However, many applications especially those to large-scale structures provide little support for visualizing the long-term monitoring data. This paper presents the development of an effective visualized DMS by integrating 4-dimension (4D) model technology, nested relational database, and virtual reality (VR) technology. Spatial data of the 4D model is organized in nested tables; while static monitoring data and dynamic monitoring data are linked to the 4D model. The model is then reconstructed by use of an OpenSceneGraph 3D engine. A user interface is developed to query the database and display the data via the 4D model. To demonstrate its efficiency, the proposed method has been applied to the Canton Tower, a supertall tower-like structure instrumented with a long-term SHM system.

G-5:L09 Magnetic Shape Memory Actuators and their Applications for Rotor Systems

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In recent years a considerable increase in the scientific interest has been observed in the properties, development and applications of various structural materials of controllable mechanical properties. Because of their controllable properties smart materials like: piezoelectrics, electro- and magnetorheological fluids, and most of all classical and magnetic shape memory alloys (SMAs, MSMAs) are of the highest interest. Exceptional physical properties of smart materials allow them to be integrated with other materials in order to obtain characteristics which cannot be reproduced in any other way. In such a way new multifunctional

materials of fully controllable properties can be made which next integrated within elements of structures enable one to control their static or dynamic characteristics. In this papers the authors focus on two subjects. The first one is connected with MSM alloy, modelling of MSM effect as well as properties and certain application possibilities of a MSM actuator. The second subject results from lack of practical applications for MSM actuators. An experiment on a special rotor rig with smart bearing has been carried out by the authors. The smart bearing assembly utilises an MSM actuator with the magnetic shape memory effect. The experimental results reveal the influence of the MSM actuator and showed that this kind of actuator can be successfully applied for vibration reduction, tuning and control in the case of rotor systems. Additionally the authors prepared a finite element method model of the rotor and MSM actuator and simulated successfully the observed phenomena numerically.

SPECIAL SESSION G-6

Advances and Challenges in the SHM of Civil and Aerospace Structures

G-6:IL01 Ultrasonic Guided Wave Monitoring of Railroad Tracks
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The potential of ultrasonic guided waves for the structural health monitoring of railroad tracks will be presented. Two applications will be discussed: rail flaw detection and rail thermal stress detection. Both topics are relevant to ensuring the safety of rail transportation systems. Numerical and experimental results of ultrasonic guided wave behavior that is pertinent to the two aforementioned applications will be presented.

G-6:IL02 NDE/SHM of Underwater Structures: A Review
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Subsea infrastructures and broadly speaking any structure containing or surrounded by water such as water mains represent an important element of modern civilization. An arbitrary classification could consist of five groups: offshore structures that serve to extract oil or natural gas from the sea bed; communication cables; pipelines that carry oil and natural gas; naval vessels (ships and submarines); waterfront facilities such as piers, retaining walls, and docks. The occurrence of structural failure of any of these systems can have serious consequences for the people, the environment, and the economy. In this paper we describe the most important nondestructive techniques adopted to assess the health of offshore structures, pipelines, and marine facilities.

G-6:L03 Autonomous Hybrid SHM System for Cable-stayed Bridges by Solar Powered Multiscale Sensor Nodes
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In this study, solar-powered hybrid sensor nodes are developed for vibration and impedance monitoring in cable-stayed bridges. The following approaches are proposed to achieve the objective. Firstly, vibration and impedance monitoring methods are briefly outlined. Secondly, the solar-powered hybrid sensor nodes are described on the design of hardware components and embedded software for vibration and impedance monitoring. In this approach, a solar-powered harvesting system is designed for autonomous operation of the hybrid sensor nodes. Finally, the performance of the hybrid sensor nodes integrated with solar-powered system is evaluated for long-term monitoring on on-site cable-stayed bridges. Some parameters (e.g., temperature, supply

voltage, acceleration and impedance signatures) of operating system are analyzed to examine the performance of the hybrid sensor nodes under various weather conditions.

G-6:L04 Magnetic Flux Leakage (MFL) Sensing-based Steel Cable NDE Technique Incorporated on a Cable Climbing Robot for Bridge Structures
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This study applies an E/M (Electro-Magnetic) sensor based MFL (Magnetic Flux Leakage) inspection system which is incorporated into the cable climbing robot to monitor the condition of steel cables. While the robot moves along the cable, this inspection system measures the MFL to detect the cross-sectional loss of steel. To verify the feasibility of the proposed damage detection technique, a steel cable bunch specimen which has several types of damages were fabricated, and it was scanned by proposed robotic MFL inspection system to measure the magnetic flux density of specimen. LMA (Loss of Metallic Cross Section Area) and LF (Local Fault) signals were extracted by using the signal filtering technique. To interpret the condition of the wire rope, some kinds of features are extracted from LMA and LF signals by the signal process techniques, and the SVM (Support vector machine) based pattern recognition technique classify the conditions using the extracted features. Finally, the results were compared with the information of actual inflicted damages to confirm the accuracy and effectiveness of the proposed cable monitoring system.

G-6:L05 Structural Element with Non-homogeneous Fiberconcrete Distribution in the Volume Building Technology Process and Strength
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Non-homogeneous fiberconcrete structure building process consists of: concrete components mixture preparation (without fibers) placing it in a mould and mix compaction. After that, precise amount of fibers is non-uniformly strew on the upper surface of the concrete construction member and after that is pressing into the concrete till the necessary (may be diverse within one construction) depth. This operation is executing by lattice type device. Device has vertical cells, with larger cross-section size smaller than the length of fiber, and smaller cross-section size bigger than concrete aggregate largest linear size. Vibration can be applied to device during pressing process. Another option for above-mentioned device is parallel strips connected with plane plate or cylindrical shell. In this case fiber pressing into concrete must be done by two motions orienting device in orthogonal directions. Structural non-homogeneous fiberconcrete fracture model was created; material fracture process was modeled, based on single fiber pull-out law, which was determined experimentally. Depending on crack size and opening, different crack parts are bearing different loads across the thickness. The load is carried by each fiber at a constant crack opening is known from micro-mechanical investigations, then the total bending load P was obtained through equilibrium conditions. Modeling results compared with experiments were done.

G-6:IL06 Laser Ultrasonic Techniques for Structural Health Monitoring Applications
HOON SOHN, YUN KYU AN, BYEONGJIN PARK, TROUNG THANH CHUNG, CHUL MIN YEUM, JIN YEOL YANG, HYEON SEOK LEE, KAIST, Yuseong-gu, Republic of Korea

In this overview paper, we present a suite of laser ultrasonic techniques that have great potentials for structural health monitoring (SHM) of various structures such as aircraft, nuclear power plants, wind turbine blades, and underground/underwater pipelines. First, the basic working principle of laser ultrasonic excitation and sensing is briefly discussed and a full noncontact laser scanning system is developed with integrations with an autonomous inspection robot, wirelessly excited piezoceramic transducers, and optical fibers for embedded sensing. Then, various SHM examples using laser ultrasonic techniques are presented, and associated challenges are discussed. These examples include but are not limited to: (1) delamination and debonding detection in composites, (2) fatigue and fracture crack characterization in metals,

(3) impact/acoustic source localization, (4) ultrasonic measurement from rotating/moving objects, (5) optical fiber guided ultrasonic measurement under high temperature and radioactive environments and (6) underwater ultrasonic generation and measurement.

G-6:IL07 Sensor Location in Nonlinear Acoustics Used for Damage Detection in Composite Chiral Sandwich Panels

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This paper demonstrates damage detection in a smart sandwich panel with integrated transducers. The panel is built from a chiral honeycomb and two composite skins. A low-profile, surface-bonded piezoceramic transducer is used for high-frequency ultrasonic excitation. Low-frequency excitation is performed using an electromagnetic shaker. Ultrasonic sensing is performed using laser vibrometry. Nonlinear acoustics is applied for damage detection. The study is focused on sensor location analysis with respect to vibro-acoustic wave modulations. The paper demonstrates that when structure is damaged, the high-frequency "weak" ultrasonic wave is modulated by the low-frequency "strong" vibration wave. As a result frequency sidebands can be observed around the main acoustic harmonic in the spectrum of the ultrasonic signal. However, intensity of modulation strongly depends on sensor location.

G-6:L09 Vibration Control of Chimney Using Tuned Mass Damper

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Many tall and overhanging structures are susceptible to vibrations. Most of industrial chimneys and steel towers are structures particularly sensitive to the dynamic effect of wind and earthquake. This vibration of structure is controlled by various damping devices or dissipation methods. The tuned mass damper (TMD) is widely used for passive vibration damping treatment. These devices are viscously damped to 2nd order systems appended to a vibrating structure. Proper selection of the parameters of these appendages, tunes the TMD to one of the natural frequencies of the under damped flexible structure. The TMD is placed at the structure's location with the corresponding maximum of the vibration amplitude of the natural frequency. A TMD is connected to the structure at the location where a significant or the biggest vibration is occurring. The device is consisting of a moving mass, springs and a damping element. The aim of this paper is to get vibration control of chimney using Tuned Mass Damper. In this paper response spectral analysis of chimney is done and displacements are calculated, then TMD is attached at the top of chimney to control displacement at top of chimney.

G-6:L10 On Line Material Parameters Assessment for SHM Application

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Precise information on material properties of a structure is important starting from its designing process to further monitoring tasks. In the paper authors propose a method of Young's modulus estimation of thin plates based on the inverse problem solution of Lamb waves propagation. In the method a 2D array of sensors is employed to measure the dispersion characteristics of materials which is used for tested object manufacturing. Solution of inverse problem for dispersion curves using updating procedure of a tested object model simulated using LISA algorithm. Formulation of the method and case studies for different object geometry will be presented.

G-6:L11 Experimental Dynamic System Identification of Damaged Reinforced Beam

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Identification of dynamic characteristics of any structural system is known as dynamic system identification. Due to the special role of the beams in most of the civil engineering structures, dynamic system identification of beams, especially during service time, is of high

importance. A phase space in classic mechanics is represented as a multidimensional space. The number of measured values for a phase space is equal to the doubled number of degrees of freedom of the system being investigated. As it has been shown by the investigations of several authors, the expansion of a phase space by taking into account the phase planes "acceleration-displacement" and "acceleration-velocity" substantially promotes the efficiency in analyzing a dynamic system behaviour. Hereby, we pass on to a three-dimensional phase space confined with three co-ordinate axes, i.e. displacement, velocity and acceleration. An interest taken into accelerations in dynamic systems is conditioned by the fact that these accelerations are more sensitive to high-frequency components in oscillating processes. The article presents the results of experimental and analytical investigations of an essentially non-linear dynamic system. The author proposes to expand the phase space by taking into account the phase planes, namely, "acceleration – displacement" and "acceleration – speed". It has performed the structural analysis of the phase trajectories obtained in the test records for oscillations of cracked beam in the expanded phase space.

G-6:L12 A Comparative Assessment of Two SHM Damage Detection Methods in a Laboratory Tower

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We present a comparative study of two statistical damage detection methods applied to Structural Health Monitoring in smart structures. The first method is based on autoregressive techniques. The second one is based on stochastic subspace identification. Both methods are examples of time domain algorithms, which only use output signals. They will be used to detect damage on a laboratory tower simulating a wind turbine tower. The output signals from the structure will be measured using seven accelerometers. In order to excite the tower a modal shaker will be used. In a first stage the algorithms will learn how the structure behaves in the healthy state. In a second stage the methods will be given a new signal, which they will have to identify as healthy or damaged by comparing some characteristic from the healthy state with the new unknown state. The result of this comparison will be a metric, telling us that there is damage if it is above an indicated threshold. There are four bolted joints, each one with four bolts. The damage will be simulated by loosening one or two bolts in one of the joints. A ninth type of damage will be considered by loosening one bolt in each joint. Both methods are able to correctly detect the presence or absence of damage in nearly all the cases.

G-6:L13 Characterization of CFRP Composites Using Electromechanical Impedance Technique

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In this paper electromechanical impedance method was described. This method was used in order to diagnose surface state and to characterize adhesive bonds of CFRP composites (Carbon Fibre Reinforcement Polymer). Measurements have been conducted for referential and weak bonds in CFRP composites. Principle of electromechanical impedance method is the measurement of basic electric parameters of piezoelectric transducer, e.g. resistance, reactance, impedance, phase angle. The sensor is mounted on or embedded in the host structure and supplied by low voltage source (usually in range 1 V - 5 V). Due to electromechanical coupling of piezoelectric transducers, glue layer and host structure mechanical resonances are visible in the electric impedance spectrum of transducer. Appearance of additional resonance peaks, their shift in frequency or magnitude change can be treated as indicator of damage of host structure. A CeramTec SONOX P5 transducer was mounted on each sample using epoxy glue. Measurements were conducted using HIOKI Impedance Analyzer IM3570. Investigations were executed in wide range of frequencies (4 Hz - 5 MHz), but only few intervals contains valuable information. Results of investigation showed clear differences between reference samples and samples with anomalies.

Poster Presentations

G:P01 Reliability of Stretchable Mould Interconnect in a Conformable Matrix Application

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Soft and conformable, stretchable circuits are the gateway for development of friendly human/device interfaces (e.g. robotic skins, "on skin" medical applications, textile-combined wearable devices), hence meeting high scientific and industrial interest. SMI (Stretchable Mold Interconnect) technology developed at CMST/IMEC allows for manufacturing of stretchable, electrical interconnects by processing very similar to PCB practice. So far the SMI interconnect had been well characterized only as a stand-alone building block. Current work embarks on targeting and overcoming potential challenges in incorporating the interconnect into more complex, functional structures such as large area electronic matrices. In this study a vehicle comprised of silicone and copper conductor is evaluated with respect to mechanical robustness by means of FEM and life, stretching, endurance tests. FEM and empirical results are compared. Both modeling and experimental output is used to investigate appearance of new critical zones. An impact of Poisson effect on reliability is revealed.

G:P02 Optical Fiber Based Structural Health Monitoring Systems in Electric Power Plants

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This work presents application of SHM systems based on optical fiber sensors for structural monitoring in different areas of electric power plant. A modern fluid boiler and installations of environmental protection included in power plant were considered. In the first case it was

necessary to make sure that replace of so called pre-heaters would not menace the safety of the whole construction. Possible dangers could arise from the fact that additional openings in the main combustion chamber walls were made. In the second case SHM system was implemented in the range of composite pipelines with big diameters of sorbent circulation system which was a part of the installation of flue gas desulphurization. The main task of the system was to locally measure a deformation of the construction, to give information about emerging threats as well as to run if necessary alarms. For this purpose a system based on SOFO® and FBG sensors was applied. The arrangement of the sensors was supported by FEM analysis of the whole construction made by boiler and absorber producer. The measured values were compared with the design as well as with calculated values. It enabled evaluation of the inhomogeneous loads distribution and increased safety of the construction during its repair and operation.

G:P03 Polydopamine Microfluidics

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A new type of microfluidic system called polydopamine microfluidics is reported. It is a pump-free, two-dimensional microfluidic system, energy efficiently operated with gravity. The device is fabricated by hydrophilic polydopamine micro-patterns on nanostructured, superhydrophobic anodized aluminum oxide (AAO) surfaces on which liquid droplets move along the predetermined paths of polydopamine with no residuary liquid trace. Polydopamine coating, inspired by mussels' robust adhesion on versatile substrates, was utilized to stably modify the superhydrophobic AAO surface. The flow rate of polydopamine microfluidics was about 30 $\mu\text{L/s}$, faster than that used in conventional microfluidic systems ($\sim 0.5 \mu\text{L/s}$), which is suitable for large volume applications. A rapid mixing device to monitor structural changes of photoactive yellow protein (PYP) and a micro-reactor for the synthesis of gold nanoparticles were fabricated to demonstrate the utility of the polydopamine microfluidic device. The polydopamine microfluidic device is a promising candidate for a new type of microfluidic systems that is potable with extremely low energy consumption for operation.

SYMPOSIUM H

Mining Smartness from Nature

Oral Presentations

H:KL Biomimetics: Lessons from Nature

B. BHUSHAN, Ohio Eminent Scholar and The Howard D. Winbiger Professor Director, Nanoprobe Laboratory for Bio- & Nanotechnology and Biomimetics The Ohio State University, OH, USA

Nature has developed materials, objects, and processes which function from the macroscale to the nanoscale. These have gone through evolution over 3.8 billion years. The emerging field of biomimetics allows one to mimic biology or nature to develop nanomaterials, nanodevices, and processes^{1,2}. Properties of biological materials and surfaces result from a complex interplay between surface morphology and physical and chemical properties. Hierarchical structures with dimensions of features ranging from macroscale to the nanoscale are extremely common in nature to provide properties of interest. Molecular scale devices, superhydrophobicity, self-cleaning, drag reduction in fluid flow, energy conversion and conservation, high adhesion, reversible adhesion, aerodynamic lift, materials and fibers with high mechanical strength, biological self-assembly, anti-reflection, structural coloration, thermal insulation, self-healing, and sensory aid mechanisms are some of the examples found in nature which are of commercial interest. This talk will provide a broad overview of four selected objects of interest found in

nature and applications under development or available in the marketplace. These will include Lotus Effect used to develop superhydrophobic and self-cleaning surfaces with low adhesion^{3,5}, Rose Petal Effect used to develop superhydrophobic surfaces with high adhesion⁶, Gecko Adhesion to develop surfaces with reversible adhesion⁷, and Shark Skin to develop surfaces with low fluid drag⁸.

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Session H-1

Algorithms, Mechanisms and Structures in Nature as an Inspiration for Mimicking

H-1:IL01 Biologically-inspired Reversible Adhesives: Where are we now?

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Biological hairy attachment systems demonstrate their excellent adhesion and high reliability of contact. Based on the broad structural and experimental studies of biological attachment devices, the first industrial bioinspired reversible adhesive foil was developed, which adhesive properties were characterised using variety of measurement techniques and compared with the flat surface made of the same polymer. The microstructured foil demonstrates considerably higher pull off force per unit contact area. The foil is less sensitive to contamination by dust particles, and after washing with water, its adhesive properties can be completely recovered. This glue-free, reversible adhesive is applicable in dynamic pick-and-drop processes, climbing robots, and other systems even under water or vacuum conditions. The foil represents therefore a considerable step towards development of industrial dry adhesives based on the combination of several principles previously found in biological attachment devices.

H-1:IL05 How to Control Bacteria to Act like Microrobots

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Modern technologies have failed so far at providing the resources necessary for the implementations of self-propelled microrobots built entirely from artificial or synthetic parts with the capability to perform practical tasks. As such, in recent years, the uses of natural entities acting as microrobots have been considered. Among these, bacteria have been a primary choice for several reasons including but not limited to the overall size that is at the lower end of the micrometer range, the flagellated motors used for self-propulsion that are similar in design to modern engineered motors, and the multiple sensory means that can be exploited for control purpose and for the execution of tasks that must be performed autonomously. Here, the MC-1 magnetotactic bacterium is considered as an excellent substitute to artificial microrobots. Indeed, this type of bacteria already proved to be capable to perform micro-assembly tasks and to target tumors for future drug deliveries. More specifically, it will be shown that magnetotaxis can be used to not only control accurately the motion of these bacteria but also to increase their level of autonomy while exploiting other embedded sensory means in situation where information is lacking for proper feedback external control.

H-1:IL06 Cellulose Nanowhiskers: Orienting, Assembling and Interfacial Control

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The deformation micromechanics of interfaces in cellulose nanowhiskers (CNWs)-based nanocomposites will be presented. The use of a Raman spectroscopy technique for following the local interactions between CNWs and between the nanowhiskers and resin materials is introduced. This technique relies on the monitoring of a shift in the position of a characteristic Raman band associated with the main chain vibrations of the cellulose molecules within the CNWs. Upon applying tensile deformation to the CNWs, via stress transfer within a composite, it is shown that the band located at 1095 cm⁻¹, corresponding to C-O stretch modes, shifts towards a lower wavenumber position; shifts in the opposite direction for samples deformed in compression are also reported. It is shown that the effects of orientation, surface charge and aspect ratio can be interrogated using this method. It is further demonstrated that the mechanics of the components of all-cellulose composites comprising a matrix phase of cellulose reinforced with cellulose nanowhiskers are also distinguishable using this approach. A model is also introduced, derived from the micromechanics data from model composites, that shows that it is possible to determine the energy required to break-down the interfaces in these materials.

H-1:IL07 Hydro-actuated Plant Organs as Prototypes for Convertible Devices

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Various plants are able to activate organ movements upon humidity changes. These hydration-based movements can be conducted even by non-living organs as they originate from water-swellaable polymers in the cell walls. The specific deformation pattern is controlled by a sophisticated hierarchical organization from the molecular level to the entire plant organ. Among various hydro-responsive movements, a specific focus will be laid on ice plant seed capsules. The honeycomb-like tissues in their valves direct the water-actuated polymer shrinking and swelling into an almost unidirectional deformation, which facilitates a hydro-responsive opening and closing of the capsule. Further, the in-plane curvature of the valve backing constitutes an efficient locking and packing mechanism as it impedes the opening until it is straightened in the wetting process. The general principle indicates that control of movement is mediated by directing active gels via a specific structural organization. This concept may inspire biomimetic materials research for the development of self-sustaining convertible structures.

H-1:IL09 Innovative Biomimetic Materials Inspired by Plants

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Bio-inspired materials are becoming of major interest in light-weight constructions, enhanced materials, functionalized surfaces and interfaces as well as in architecture. Transferring the inspirations from biology into technical applications includes several levels of abstraction and modification. An example of this is the Flectofin®, a new façade-shading system based on the opening mechanism of the perch in the flower of *Strelitzia reginae*, which is able to induce a major shape change by only a minute deformation of the backbone. For self-repairing materials the repair of fissures caused by internal growth stresses in *Aristolochia macrophylla* using pressurized cells inspired the development of PU-foam coatings for self-repairing membranes of pneumatic structures. To reduce external damage caused by impact is a major challenge for light weight materials which are used for protection and packaging. The pomello, *Citrus maxima*, has evolved a fruit wall providing an excellent damping system which is able to dissipate more than 90% of the initial potential energy of the fruit with only negligible damage. Structural features of the peel have been transferred in a first approach to a technical prototype to provide enhanced protection systems.

Session H-2

Biomimetic Materials

H-2.1 Bioinspired and Bioenabled Materials and Manufacturing

H-2.1:IL01 Shape-preserving Chemical Transformation of 3-D Biogenic and Synthetic Templates

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The precise and scalable fabrication of functional assemblies with complex 3-D morphologies, well-controlled micro/meso/nanoscale structures, and tailorable chemistries remains a difficult technological challenge. Nature provides stunning examples of organisms (e.g., diatoms, brittlestars, sponges, butterflies) capable of fabricating hierarchical 3-D structures with a wide variety of shapes and patterned features. However, the chemistries of such intricate biogenic structures are of limited range and generally not tailored for man-made applications. The functional chemistries of self-replicating biogenic 3-D assemblies

can be appreciably expanded, while preserving biogenic morphologies, through patented BASIC* (Biological Assembly and Shape-preserving Inorganic Conversion) processes. In this presentation, fluid/solid displacement reactions and conformal coating approaches for converting bio-inorganic and bio-organic templates into 3-D replicas for optical, electrical, and chemical applications (e.g., energy harvesting/storage, sensing, water purification) will be described. Adaptation to self-assembled synthetic structures will also be discussed.

*K.H. Sandhage, et al, U.S. Patents No. 7,067,104 (6/27/06), No. 7,204,971 (4/17/07), and No. 7,615,206 (11/10/09).

H-2.1:IL02 **Materials Inspired by Nature: Design and Fabrication of Biocomposites from Cellulose Nanofibers**

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Bioinspired nanostructure engineering represents an important emerging field whose principles based on low-energy methodologies can be exploited to considerably expand the range of properties of composite materials. Cellulose nanofibers with lateral dimensions three orders of magnitude smaller than plant cellulosic fibers are ideal materials for the construction of strong and tough materials. We have developed a low-energy biosynthetic system for the production of high-strength composite materials consisting of self-assembled and nanostructured cellulosic nanofibers through the exploitation of cultures of *Acetobacter acetii* grown in the presence of hydroxyethylcellulose (HEC). This achievement is the result of a novel biomimetic nanostructural composite design based on cellulose nanofibrils compartmentalized by thin coatings of a hydrated amorphous HEC. Further, nanostructured layered biocomposites have been prepared from nanofibrillated wood cellulose (NFC) and HEC by applying our previously developed paper-making approach. The stiff wood cellulose nanofiber network in a soft HEC matrix results in biocomposites with a unique combination of low yield stress, high ultimate strength, high toughness, thermomechanical stability, limited moisture adsorption and high creep resistance.

H-2.1:IL04 **Bio-inspired Silk-based Materials**

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Proteins reflect one fascinating class of natural hierarchically structured substances. The interplay between the polymeric building blocks is intriguing, and for long researchers tried to unravel the underlying concepts. One well-known example is spider silk with excellent mechanical properties such as strength and toughness. Most spider silks are used for building the web, which reflects an optimized trap for flying prey. In order to analyze the potential of the underlying spider silk proteins, we have developed a recombinant system using bacteria as hosts which produce silk proteins mimicking the natural spider silks. Recombinant proteins enable detailed analysis of the fiber formation process. Additionally, silk proteins can be processed into other morphologies such as hydrogels, spheres or films with tailored properties for biomedical applications.

H-2.1:IL05 **Non-canonical Base Pairs in DNA Crystal Design**

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DNA has proved to be a successful material for creation of nanoscale structures because of its inherent programmability and predictable structural features. However, the creation of periodic three-dimensional (3D) DNA arrays is hampered by the inherent linearity of the Watson-Crick duplex. Here, we describe how predictable non-canonical base pairing motifs can be used in conjunction with Watson-Crick duplexes to assemble macroscopic 3D crystals with useful nanoscale features. Parallel-stranded homopurine 5'-GGA base pairs serve as a junction region in a continuously base paired 13-mer DNA crystal. This motif is predictable and has been used in different sequence contexts to rationally design DNA crystals with different lattice dimensions. A structurally similar homoparallel region, 5'-CGAA, has also been observed in a 9-mer DNA crystal structure, and we have crystallized and determined the structure of a DNA 19-mer that contains a variant of this 5'-CGAA motif. Identification of new non-canonical motifs will further expand the DNA construction kit to create 3D DNA crystals, and we have initiated

a high-throughput crystallization screen of short DNA oligonucleotides to identify new motifs.

H-2.1:IL07 **Self-assembled Polymeric Supramolecular Frameworks**

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Polypeptides offer a rich toolbox to tune self-assemblies and hierarchies vs synthetic polymers, still not incorporating the full biomaterials complexity of proteins. Functional hierarchical self-assemblies were demonstrated already early by complexing small molecular weight surfactants to block copolymers (Science 295 2407 2002). DNA-like oligomers are more functional oligomers due to their hydrogen bonds. Deoxyguanosine monophosphate (dGMP) complexes ionically with polylysine (PLL) (Soft Matter 2 329 2006). Upon ionic complexation of dGMP with a triblock copolypeptide polylysine-b-polybenzylglutamate-b-polylysine (PLL-b-PBLG-b-PLL), nanoribbons are formed with several length scales of order, where dGMPs form quadruplexes. (Adv Funct Mat 18 2041 2008) By contrast, for dGMP complexed with a diblock copolypeptide PLL-b-PBLG, space filling self-assemblies are formed instead of ribbons. (Angew Chem 50 2516 2011) Lamellar assembly is obtained with alternating PBLG and PLL/dGMP domains. The dGMPs form hydrogen bonded ribbons within the PLL/dGMP domains, stabilizing porosity. The concept allows the first polymeric supramolecular framework materials and robust and quick preparation of nanoscale cages. Finally we will describe recent developments on functional macromolecular porosity.

H-2.1:IL07b **Biomimetic ceramic and hybrid nanofibers**

YOU-LO HSIEH, University of California, Davis, CA, USA

Nanofibers and nanofilm-nanofiber hybrids have been assembled from biological and synthetic polymer precursors. The ability of biopolymer nanocrystals to assemble has been further enhanced by further tuning their dimensional characteristics and surface functionalities. The formation of ultra-porous and super-hydrophilic structures and functional ligand-binding capabilities of these nanocrystals have been demonstrated by varied derivation methods, chemical reactions and processing conditions. Synthetic polymer precursors to ceramic and carbon have been fabricated into ultra-fine fibers and hybrids with varied nano-scale structures, including nanowires, nanoparticle-filled porous core-sheath and segmented morphologies. These ceramic and carbon nanofibers exhibited unique properties such as dual super-hydrophilicity and super-oleophilicity, capacitor and ductile behaviors. The chemical and structural versatility of these nanofibers and hybrids have potential in applications for catalysis, separation, sensors, bioactive agent carriers, drug-delivery and diagnosis.

H-2.1:IL08 **Bio-inspired Chiral Nanostructures with Plasmon and Exciton Resonances**

A. GOVOROV, Department of Physics and Astronomy, Ohio University, Athens, OH, USA

Hybrid nanostructures are assembled from metal nanocrystals and molecules. They exhibit both plasmonic and excitonic features. This talk will discuss our recent results on the optical chirality of hybrid nanomaterials. If a nanostructure incorporates chiral molecules, the exciton-plasmon interaction is able to alter and enhance the circular dichroism (CD) of chiral components^{1,2}. In particular, the exciton-plasmon interaction creates new chiral plasmonic lines in the CD spectra of a biomolecule-nanocrystal complex^{1,2}. Strong CD signals also appears in purely plasmonic systems with a chiral geometry and a strong particle-particle interaction^{3,4}. Recent experiments on the protein-nanocrystal and multi-nanocrystal complexes have shown the presence of new chiral plasmonic lines in the CD spectra^{2,4}. Potential applications of chiral hybrid nanostructures studied by us are in sensors and optical devices.

1. A.O. Govorov, Z. Fan, P. Hernandez, J.M. Slocik, R.R. Naik, *Nano Letters* 10, 1374 (2010); 2. J.M. Slocik, A.O. Govorov, and R.R. Naik, *Nano Letters* 11, 701 (2011); 3. Z. Fan, A.O. Govorov, *Nano Letters* 10, 2580 (2010); 4. A. Kuzyk, R. Schreiber, Z. Fan, G. Pardatscher, E.-M. Roller, A. Högele, F.C. Simmel, A.O. Govorov, T. Liedl, *cond-mat arXiv:1108.3752*.

H-2.1:IL10 Study Concerning 3D Collagen Grafts for Wound Dressing and Controlled Release

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Collagen, one of the most common biomaterials, has been found diverse applications in biomedical field such as wound dressing, drug and gene carrier, and tissue engineering for its excellent biocompatibility and controllable biodegradability. The main subject of interest throughout this report is to extract and optimize the parameters of the extraction for acid-soluble collagen from calf skin, chick skin, calf ligamentum nuchae, bovine patellas and jellyfish and to produce collagen fibers using electrospinning technique together with collagen films for the construction of 3D scaffolds for wound dressing and treatment. The technique will fabricate fibrous collagen constructs composed of fiber diameters ranging from several microns down to 100 nm or less to obtain an alternative, cheap and safer collagen scaffolds through the electrospinning process, with good biocompatibility and improvement of the cellular environment to assist in cells adhesion and proliferation. It was proved that the cannonball jellyfish contains large amounts of collagen, and that its toxicity can be removed in the same process used to prepare the jellyfish as a food product. Formation of films is biomimetically carried.

H-2.1:IL11 Mimicking the Anisotropic Behavior of Natural Porous Structures by Controlling the Reinforcing Particles Distribution in Polymeric Foams

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Natural porous materials, like wood or bone, are multiscale composite structures exhibiting mechanical (such as elasticity and strength) and functional (such as the thermal or acoustic insulating properties) behaviors dependent on the measuring direction. They show the best performance/weight ratio among all materials because their response is optimized in the needed direction by removing matter where not strictly functional, giving as a result a strong morphological anisotropy. A new approach has been developed to mimic this behavior in polymeric foams, in which the mechanical and/or functional response of a polymeric foam is tailored in a specific direction or pattern through the control of the spatial distribution and configuration of reinforcing particles. In order to demonstrate the concept, a polymeric foam was produced with micro- or nano-magnetic fillers distributed along specific directions or patterns by means of the magnetic field. The effects of particles dimension and content, production process, and magnetic field configuration were investigated and related to the mechanical (both elastic and magnetoelastic) and functional performances.

H-2.1:IL12 Templated Mineral Growth - A Pathway to Synthetic Nacre Biomineralisation

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Biominerals are a major area of research as they often differ in their structure and properties compared with their geological counterparts. Replication of the hierarchical structures of biominerals produced under ambient conditions in under-saturated aqueous solution, poses a significant synthetic challenge. By understanding the key parameters and components involved in, and responsible for, in vivo synthesis, improved design of synthetic materials is possible through direct replication and manipulation of these design features. Our research focuses on understanding how the organic framework mediates the inorganic crystal growth. One thrust pertains to developing synthetic nacre and its analogues. The insoluble organic matrix of nacre is the carbohydrate chitin. While present in low amounts in the final biomineral it plays an important role in both the nucleation and growth of the calcium carbonate and also the final characteristics of the material. With this in mind we have investigated the use of biopolymer self-assembly and have developed a responsive biopolymer scaffold that enables control of calcium carbonate platelet formation and association. The final material has a structure and length scale comparable to that seen for the aragonitic plates of paua shell/nacre.

H-2.1:IL16 Novel Interpenetrating Nylon-acrylic Polymer Composite Thin Films: Towards Improving Nylon's Resistance to Water

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The hygroscopic nature of polyamide (PA), known as nylon, restricts its use in waterproof applications. Therefore, the intent of this study was to develop nylon-based hydrophobic thin film composites. We present an inexpensive method to tune nylon's wettability from super-water absorbant to hydrophobic creating rough surfaces inspired by natural surfaces exhibiting hydrophobicity. The process doesn't require harsh conditions and allows wettability control by semi-interpenetrating composite generation. These composites combine nylon's performances with polyethylcyanoacrylate (PECA) biodegradability and have remarkable hydrophobicity. Controlling ethylcyanoacrylate (ECA) monomers polymerization in PA we fine tuned surface topography to create suitable roughness to improve water resistance. Water contact angle tests showed a stable hydrophobic response using at least 30% of PECA with angles reaching 132°. Pure PA was highly absorbent and pure PECA slightly hydrophilic so a significant roughness-induced wettability effect was established for the composites. Their morphology was investigated by Scanning Electron and Atomic Force Microscopy indicating existence of a dual-scale roughness surface covered with crosslinked sub-micro PECA particles which inhibit water penetration.

H-2.2 Functional Bio-inspired Surfaces

H-2.2:IL01 Reconstructing Synthetic Cellular Compartments on a Surface

R. BAR-ZIV, Department of Materials and Interfaces, The Weizmann Institute of Science, Rehovot, Israel

A light-directed approach has been developed for the immobilization of entire genes, encoded on long DNA polymers, which are end-attached to a surface. The DNA can be packed to form spatially varying, highly dense polymer brushes, in which the local DNA concentration is comparable to that in a bacterium. Carrying out directional transcription in these DNA brushes such as reveals interesting features not present in dilute bulk solution reactions, such as effect of DNA density and gene orientation on transcription. These observations lead us to suggest a scenario in which dense DNA brushes form boundary-free compartments that are partitioned from the surrounding reservoir. We propose implications for the assembly of synthetic multi-component genetic systems on a surface.

Selected references: S.S. Daube, D. Bracha, A. Buxboim and R. Bar-Ziv, Proc. Natl. Acad. Sci. USA 107(7):2836-2841 (2010); M. Bar and R. Bar-Ziv, Nano Lett. 9(12): 4462 (2009); A. Buxboim, S. Daube and R. Bar-Ziv, Nano Lett. 9(2): 909-913 (2009); A. Buxboim, S. Daube and R. Bar-Ziv, Molecular Systems Biology, 4: 181, 1-8, (2008); S. Daube, T. Arad and R. Bar-Ziv, Nano Lett. Mar;7(3):638-41, (2007); A. Buxboim, M. Bar-Dagan, V. Frydman, D. Zbaida, M. Morpurgo and R. Bar-Ziv Small, Mar;3(3):500-10, cover article, (2007).

H-2.2:IL03 Bioinspired Assembly of Superparamagnetic Nanoparticle Membranes

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Nanoparticles with ultrastable and carefully controlled core-shell structures can be used in biomedical applications, e.g., as biomedical imaging contrast agents or in hyperthermia. Exquisite control allows further applications through assembly into biomimetic membrane and vesicular structures for which permeability can be externally controlled by applied magnetic fields. The intrinsic size range of core-shell nanoparticles from that of proteins to viruses makes biomimetic approaches to their assembly into membranes interesting from both an applied and fundamental point of view. I will describe a new synthetic toolkit built on nitrocatechol dispersants and the monodisperse synthesis of Fe₃O₄ cores to investigate membrane assembly of superparamagnetic nanoparticles at liquid interfaces, including into lipid membranes. The relationship between nanoparticle structure and the assembled membrane structure and the release of model drugs from

the formed nanoparticle actuated vesicles will be highlighted. Additionally, new methods to characterize nanoparticles at liquid (membrane) interfaces will be introduced.

H-2.2:IL04 Biomimetic Self-organized Functional Surface Materials

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In the world of insects simply repeated structures generate functions. For example, the moth-eye, whose surface is covered by regularly arranged sub-cellular size dots pattern, is a "micro device" that enables high-speed night flight of its owner. In this report, anti-reflective silicon surfaces have been simply prepared by using self-organized honeycomb-patterned polymer films as masks for dry etching process. Simple casting of polymer solutions under highly humid condition can provide "honeycomb-patterned" polymer films. Self-packed surface monolayer of mono-dispersed water droplets formed by evaporation cooling on the solution surface acts as a temporary template of micropores. The "honeycomb-patterned" film has a double-layered structure with pillars supporting the two porous layers on each vertex of the hexagons. Regular arrayed pillar-structure, like a "pincushion", was formed when the "honeycomb-patterned" film was cleaved into halves by peeling with an adhesive tape. The polystyrene honeycomb-patterned film was fixed on silicon substrate as a pincushion-structured porous mask for the reactive ion etching. After dry etching, pincushion-like silicon structures with hierarchy were formed. The surface showed very small light reflectance and super-hydrophobic nature.

H-2.2:LO5 Smart Skin Pattern of Springtails - Robust Omniphobic Surfaces in Nature

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The objective of our research was to investigate the major role of the nanoscopic cavities formed by the primary granules (PG) of springtails with respect to the omniphobic wetting behavior to improve recently described suggestions in (Helbig, et al PloS one, 6(9): e25105, 2011). To achieve this, model surfaces were performed by a versatile replication process using the hierarchical cuticle structure of the Collembola species *Tetradontophora bielensis* as the biological model. We tuned the replication process to get on the one hand faithful replicas featured by all present structure elements of the cuticle including the nanoscopic PGs and on the other hand smoothed replicas excluding the PGs. We performed static contact angle measurements and determined the hydrostatic pressure resistance using both types of replicas with and without PGs, respectively, in reference to the biological model. Furthermore, we elaborated the wetting transition from heterogeneous to homogeneous wetting state at elevated pressures using a combination of numerical simulation and analytical calculations that impressively demonstrated the slip-stick propagation of the advancing liquid front inside the grooves whereas the "macro-plastron" disappears, but a "nano-plastron" inside the nanocavities remains.

H-2.2:LO6 Bio-inspired Surface Structures to Control Wettability and Ice Accumulation

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Natural surfaces such as plant leaves, feathers, and insect cuticle cause a superhydrophobic effect by combining a rough surface structure with a hydrophobic surface chemistry. We have developed a wide range of high aspect ratio post and closed-cell wall arrays to control wettability, and thereby control the kinetics of ice nucleation for supercooled water droplets bouncing off cold substrate surfaces. We have demonstrated that there can be a relatively large range of cold temperatures (to around -30°C) for which the surface area and time of contact are too small to allow ice nucleation and accumulation¹. Recent results show that hydrophilic tip structures can be used to control water condensation and freezing morphologies in novel ways. An altogether new approach we have developed is to take inspiration from the pitcher plant, which uses a confined surface layer of water along a series of parallel grooves to produce an ultra-slippery surface for insects. We have developed a surface called SLIPS (slippery liquid-infused porous surface) which we have shown to be repellant to a very wide range of liquids, and has ultra-low adhesion properties for ice².

1. L. Mishchenko, B.D. Hatton, V. Bahadur, J.A. Taylor, T. Krupenkin, J. Aizenberg, "Design of Ice-free Nanostructured Surfaces Based on Repulsion of Impacting Water Droplets", *ACS Nano* 4, (2010).
2. T.-S. Wong, S.H. Kang, S.K.Y. Tang, E.J. Smythe, B.D. Hatton, A. Grinthal, J. Aizenberg, "Bioinspired self-repairing slippery surfaces with pressure-stable omniphobicity", *Nature* (2011) 477, 443-447.

Session H-3

Bio-inspired Sensors and Actuators

H-3:IL02 Development of an Odorant Sensor Using Living Cells Expressing Insect Odorant Receptors

H. MITSUNO, **T. SAKURAI**, **H. MITSUHASHI**, **R. KANZAKI**, Research Center for Advanced Science and Technology, The University of Tokyo, Meguro-ku, Tokyo, Japan; Graduate School of Information Science and Technology, The University of Tokyo, Bunkyo-ku, Tokyo, Japan

Existing odorant sensors are mainly fabricated based on metal-oxide semiconductor devices or quartz crystal microbalances. These sensors have been studied for improving on various parameters, such as sensitivity, selectivity, and portability. However, it has been difficult to develop odorant sensors that incorporate a combination of desirable properties. In contrast, living organisms, especially insects, use numerous olfactory sensory cells, which express different odorant receptors, to sensitively detect the environmental odorants in real time. Therefore, focusing on the olfactory transduction of insects, we developed two odorant sensor systems that consist of a fluidic device and living cells expressing insect odorant receptors. One sensor system using *Xenopus laevis* oocytes was able to detect odorant components at a few ppb in solution and integrate with a robot without any noise reduction systems. The other sensor system using insect cultured cells, Sf21 cells, enabled us to acquire odorant response measurements for a long period of time. These results show that our proposed sensor system can be applied to detect various kinds of odorants with high sensitivity, selectivity, and portability, and provide an innovative platform to develop odorant sensors with high performance.

H-3:IL03 Imitating the Cricket Cercal System: the Beauty of the Beast with a Twist of the Engineer

G. KRIJNEN, MESA + Research Institute, University of Twente, Enschede, The Netherlands

MEMS offers exciting possibilities for the fabrication of bio-inspired mechanosensors. Over the last years we have been working on cricket inspired hair-sensor arrays for spatio-temporal flow-field observations (i.e flow-camera) and source localization. Whereas making flow-sensors as energy efficient as cricket hair-sensors appears to be a real challenge we have managed to fabricate capacitively interrogated sensors with sub millimeter per second flow sensing thresholds, use them in lateral line experiments, address them individually while in arrays tracking transient flows, and use nonlinear effects to achieve parametric filtering and amplification. During these developments we have been working in close collaboration with insect biologists, generating a bidirectional flow of information and knowledge, beneficial to both parties. E.g. where the engineering has greatly benefitted from the insights derived from biology and bio-physical models, the biologist have been able to take advantage of MEMS structures allowing for the sort of analysis that is hard to do on living material (e.g. the study of viscous coupling between closely spaced hair-sensors). In the presentation the important insights, developments and results will be highlighted.

H-3:IL04 Mimicking Insect Ultrastructures for Vision

KI-HUN JEONG, Korea Advanced Institute of Science and Technology (KAIST), Daejeon, Korea

Insects provide diverse ultrastructures for vision such as imaging, illumination, or camouflages to overcome the scaling limit in optics. For example, natural compound eyes realize wide field-of-view with a single lens platform by hemi-spherically arranging ten thousands of of ommatidia in a single eyelet. Recently micro and nanofabrication enable the emulation of three dimensional structures as well as the optical

functions. This work reports some engineering efforts for mining the smartness from insect vision organs by using multi-dimensional micro- and nanofabrications.

H-3:L06 Material Properties and Evaluation of Sensitivity of Photomechanic Infrared Receptors in Pyrophilous Insects

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Jewel beetles of the genus *Melanophila* are well-known to approach forest fires. The same so-called pyrophilous behaviour has been observed in a few flat bug species of the genus *Aradus* (Heteroptera, Aradidae). In both groups so called photomechanic IR receptors have been found. A miniaturized spherical IR sensillum is innervated by a mechanosensitive cell and is strikingly similar in beetles and bugs. Because the thermo-/mechanical properties are crucial for translation of IR radiation into mechanical displacement the Young modulus and hardness of the relevant cuticular components of an IR sensillum were measured by nanoindentation. Results show that a compliant microfluidic core is enclosed in a hard and rigid outer shell which supports the current model of photomechanic stimulus translation. Using the results of simulations of the thermal and optical conditions of a historic oil-tank fire in Coalinga, California in 1925, we calculated the detectable radiation flux in dependence of the distance to the fire. For the calculation we used different approved models used in risk and safety analysis and extended the models for larger distances. It turned out that *Melanophila* beetles should be able to detect a large fire by IR radiation from distances of 130 km.

H-3:L08 Detection of Salmonella Using Bio-inspired Autonomous Sentinels

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An investigation of a bio-inspired autonomous pathogen detection system that mimics the function of natural immune systems, such as white blood cells, is presented. In this detection system, magnetoelastic (ME) sentinels are used to seek out, capture, and signal intelligence of target pathogens in liquid environments. A sentinel is constructed of a freestanding ME resonator (transducer platform) coated with a biorecognition layer that specifically binds the target pathogen. Due to their magnetic nature, ME sentinels may be wirelessly driven to move through an analyte using a magnetic field. Upon contact with the target pathogen, a sentinel binds with the target cell, increasing the sentinel's mass, resulting in an instantaneous decrease of the sentinel's resonant frequency. By wirelessly monitoring the resonant frequency, a sentinel can signal the presence and concentration of target pathogens, imitating the function of white blood cells. In this study, E2 phage (specifically binding with *Salmonella*) coated ME sentinels were fabricated. The detection of *Salmonella* in analytes containing different pathogen concentrations is presented, demonstrating proof-in-principal of autonomous ME sentinels.

H-3:IL09 Actuator-like Hydrogels Based on Conductive Chitosan

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Intrinsically conducting polymers are of great interest for a large number of applications. But among the major drawbacks are their low solubility in common solvents and their poor mechanical properties. Elaboration of composites associating a matrix, bringing its mechanical properties, and polyaniline (PANI), as the conducting polymer, is a way of overcoming these disadvantages. To obtain an hydrogel in which PANI was homogeneously dispersed and to avoid its migration, the idea was to incorporate PANI onto a polymer, the chitosan, which is able to be cross-linked. Grafting reaction was optimized: more than 99% PANI is grafted onto polymer and chitosan keeps his coating properties after grafting. Then, the cross-linking conditions between copolymer and glutaraldehyde will be discussed. Conductivities values as high as the precursor graft copolymer were obtained after dehydration and drying of hydrogel. Hydrogels of Chitosan-graft-PANI exhibit rheological, swelling and mechano-electric properties. They were actually used like actuators. In this work, we studied the ability of the composite hydrogel to convert mechanical work into electrical energy. Experiments demonstrated the feasibility of a mechano-electric actuator using our new composite hydrogel as sensing material.

H-3:L11 Use of Textile Friction to Mimic Hill's Model in Dynamic Contraction of Braided Artificial Muscles

B. TONDU, CNRS-LAAS and University of Toulouse, Toulouse, France

Several types of artificial muscles are actually able to mimic the active spring-like behaviour characterizing the tension-length diagram of the skeletal muscle but the natural damping expressed by the typical tension-velocity Hill's relationship is not so easy to integrate in a simple way into the artificial muscle functioning. We discussed the use of a textile braided sheath, particularly in the case of the so-called McKibben structure, to obtain a Hill's model-like dynamic behaviour of the artificial muscle. Experiments are reported to compare "quick-release" experiments - as defined in muscular physiology - between artificial muscles prototypes whose braided weave is made of metallic strands and prototypes whose weave is made of rayon twisted textile strands. It is shown that only in the second case a typical hyperbolic tension-velocity curve is got with a curvature close to this of human skeletal muscle. It is also shown how laws of friction in textile can explain this analogical behaviour with the Hill's-model, interpreted as a force model including a typical non-linear viscous component. An original interpretation of Hill's model in terms of natural adaptation to load variations is given and the advantage for an artificial muscle to get this biomimetic character analyzed.

Session H-4

Biologically Inspired Systems and Robotics

H-4:IL01 Biomolecular Motor-powered Devices

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Biomolecular motors, such as the motor protein kinesin, can serve as biological components in engineered nanosystems. Initially, a nanoscale transport system termed molecular shuttle has been explored by others and us as a model system. The development of this system has revealed a number of challenges in engineering at the nanoscale, particularly in the guiding, activation, and loading of these shuttles. Overcoming these challenges requires the integration of a diverse set of technologies, and continues to illustrate the complexity of biophysical mechanisms. A proof-of-principle application of the developed technologies is a "smart dust" biosensor for the remote detection of biological and chemical agents, which is enabled by the integration of recognition, transport and detection into a submillimeter-sized microfabricated device. These efforts to engineer hybrid systems advance our understanding of the physical principles shaping the evolution of biological systems. Hybrid systems also provide a route towards achieving some of the application goals of synthetic biology without the undesired possibilities inherent in living systems capable of self-replication.

H-4:IL02 Photon-fuelled DNA Nanomachine Carrying Azobenzene as Molecular Engine

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DNA has begun to be regarded as a promising self-assembling nanomaterial for construction of delicate nanostructures and nanodevices. One merit of using DNA is that the molecular design of two- and three-dimensional nanostructures or nanodevices can be programmed through sequence-specific hybridization. As synthetic modification of DNA can be easily carried out using phosphoramidite chemistry, DNA can be functionalized with ligands, fluorophores, and intercalators. However, one of the problems limiting the application of DNA nanodevices is that fuels, such as short DNA oligonucleotides, added during each working cycle results in waste that gradually lowers the operating efficiency. Accordingly, new nanodevices that use "clean" fuels are highly desired. For this purpose, we created photoresponsive DNA carrying azobenzene as "molecular engine", and formation and dissociation of DNA hybridization has been reversibly photoregulated by irradiating with either UV (320-380 nm) or visible light (>400 nm). With this photoresponsive DNA, we can design various photon-fueled DNA nanomachines and drive them only by photo-irradiation. Since light is one of the clean energies that do not produce any waste, the nanomachines do not deteriorate after many cycles of operations.

H-4:IL03 Smart Materials and Systems in BioRobotics

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Biorobotics is the combination of Biomedical Engineering and Robotics and, as such, it clearly includes the applications of robotics in the biomedical fields, like in surgery and rehabilitation. Biorobotics, however, is also the science of studying living organisms by building physical models of them, i.e. biomimetic robots. Nature provides numerous examples of smartness to imitate and to translate in robotics, from animals and plants. One major principle that we find in the diversity of animals is embodied intelligence, or morphological computation: smart materials and structures contribute in a fundamental way to the control of movements. Several examples are given from the BioRobotics Institute of the Scuola Superiore Sant'Anna in Pisa, Italy. They show mining smartness from Nature, for building a variety of biomimetic robots, inspired to the octopus, to the lamprey and swimming animals, to hopping insects, to worms. Not least, the smartness of animal models used for a biomedical device, like the case of the warm-inspired robotic colonoscope.

H-4:IL04 A Low-temperature Approach to Spiking Neural Circuits

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Neuromorphic circuits seek to emulate biological neurons and synapses for use in applications that involve processing large quantities of imprecise information. Implementations of the soma (cell-body) using silicon CMOS have been proposed, but these cannot be fabricated over large areas on flexible substrates that are often indispensable. We have fabricated spiking soma circuits that operate at biological time scales and are compatible with flexible substrates using ambipolar nanocrystalline-silicon thin-film transistors with a maximum process temperature of 250 °C. These circuits can easily be scaled down to realize high circuit densities. Depending on the complexity of the soma circuit, increased biological functionality such as spike frequency adaptation, and setting specific refractory periods can be achieved. The frequency-current (discharge) curve of the circuit also resembles that of biological neurons. In addition, we have designed a simple synapse circuit that operates using rectangular voltage pulses to produce a Hebbian learning rule that depends on both spike frequency and timing. Finally, SPICE simulations show that these synapse designs can perform useful computation including associative learning, coincidence detection, and extraction of a fundamental frequency.

H-4:IL05 Bio-inspired Gecko-mimicking Robot: From Locomotion Behaviour and Dynamics to Robot Design

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Gecko possesses exceptional abilities to move freely on various inclined, even inverted, substrates, no matter smooth or rough. The abilities are highly desirable for modern mobile robots to search and rescue people in the collapsed buildings, to climb on vertical surface for cleaning, et. al. thus gecko becomes a ideal biological model for developing the gecko-mimicking (GM) robots. Gecko's outstanding locomotion ability is originated from many synergetic effects. Morphology studies characterize the hairs (or setae) on toe of a gecko foot as half million self-cleaned, keratin, hierarchical structures with spatula terminal 5 to 10 nm diameter and 100 to 200 µm long. Here we report our studies on the gecko's locomotion behaviour and dynamics, more exactly, reaction force measurement on freely moving gecko. The study answers the questions how do they modulate their muscle to adapt the needs to move on various directions-from climbing up and down or moving on horizontal direction on vertical surface? We use a newly developed force measuring array correspondent to measure the three-dimensional reaction forces and recorded the locomotion behaviours simultaneously. The results raise some general rules for developing gecko-mimicking robot and the rule was successfully introduced to the gecko-robot design. Videos show the newly developed gecko-mimicking robot, which can climb on vertical substrate.

H-4:IL06 A Soft Robot Inspired to the Octopus

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While robotics is traditionally based on the concept of rigid links connected by joints, in order to negotiate natural environments robots need more flexibility and adaptability, in analogy with biological systems. The octopus represents an ideal source of inspiration for robotics, for the infinite number of degrees of freedom and for its capability of controlling the stiffness of its limbs. Specifically, the octopus arms are totally soft structures with a special muscular structure (muscular hydrostat), which serves as modifiable skeleton, allowing the octopus to actively control the stiffness of its arms. Following a deep biological and biomechanical study of the *Octopus vulgaris*, the prototype of a soft robot arm has been built based on an artificial muscular hydrostat. The muscular, nervous and connective tissue arrangement and biomechanics have been replicated for the soft actuators, electrical cables and mechanical structure. Longitudinal cables and transverse shape memory alloy (SMA) imitate longitudinal and transverse muscles respectively. The robot arm can contract perform the basic movements of the octopus arm, like elongation, shortening, and bending.

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H-4:IL07 Biomechanics in Bio-flights and its Application to Bio-inspired Robots

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Insect flight is now an active and well-integrated research area, attracting participation from a wide range of talents. Aiming at developing an effective tool to unveil key mechanisms in bio-flight as well as to provide guidelines for bio-robotics design, we propose a comprehensive computational framework, which integrates aerodynamics, flight dynamics, vehicle stability and maneuverability. Here we present results based on hovering aerodynamics with rigid and flexible wings of hawkmoth and fruitfly. Based on these results and knowledges, we have developed a hummingbird-inspired, flapping flexible wing Micro Air Vehicle (MAV) with a weight of 2.6 g and a wingspan of 12 cm. We carry out an integrated study of the flexible wing aerodynamics by combining the insect dynamic flight simulator and wind tunnel experiments. Our results provide a quantitative prediction of unsteady aerodynamics of a four-winged MAV in terms of vortex and wake structures and their relationship with aerodynamic force generation and further confirm the effectiveness of the clap and fling mechanism employed in this bio-inspired MAV as well as the importance of the wing flexibility in designing small flapping-wing MAVs.

H-4:IL08 Emergent Functionality of Cellular Buildup Wet Robotics

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We have demonstrated an environmentally robust hybrid (biotic-abiotic) robotic system that uses living components, called "Cellular Build Up Wet Nano Robotics". Our group has already presented a bioactuator using rat heart muscle cells, but it is difficult to keep rat heart muscle cells contracting spontaneously without maintaining the culture conditions carefully. By contrast, insect cells are much robust over a range of culture conditions (temperature, osmotic pressure and pH) compared to mammalian cells. Therefore, insect cells are more practical use of a hybrid wet robotic system, and they can be driven without precise environmental control. From this point of view, to utilize robust biological components as a functional systems and self assembly process and their emergent functionality, and to build up such a soft and wet machines will lead us an innovative fundamental change and produce a new principle and design to future man-made systems. We demonstrate the example of a micro bioactuator and mechanical systems driven by biochemical energy. This novel muscle-powered bioactuator successfully show autonomous beating at room temperature for a long time without maintenance. Experimental results suggest the possibility of constructing an environmentally robust hybrid wet robotic system with living components and open up a new science and technology, biorobotic approach, medical, environmental monitoring, agriculture and industrial application.

H-4:IL09 Bio-inspired Strategies for Effective Navigation in Complex Chemical Plumes

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We lack tracking strategies for autonomous vehicles that can duplicate the performance of animals. Current approaches ignore how animals optimize their ability to navigate in noisy and unpredictable signal environments, particularly: 1) preprocessing methods to maximize input of useful signals; 2) strategies to reduce information complexity and; 3) parallel information processing to increase context-sensitive, adaptive responses. We implemented signal processing routines and motion control algorithms for chemical plume tracking in a turbulent flow environment using a strategy incorporating the above features 1-3. Upstream motion is induced by a binary response to supra-threshold odor spikes and cross-stream steering is controlled by contrast between bilaterally-separated sensors. The geometry of sensor placement acts to favorably shape the quality of incoming information necessary for these two tasks. Our algorithm is dynamic by using a Bayesian approach to recompute odorant spike thresholds to adapt to changing plume conditions. Also, the degree of upstream movement to above threshold spikes is weighted according to the bilateral signal contrast intensity. Our strategy performs similarly to animals in our test conditions, using measures of search success and path kinematics.

H-4:IL10 Energetically Autonomous Robots: EcoBot (Artificial Symbiosis for Self-sustainability)

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EcoBots are the world's 1st example of real robots powered from live bacteria feeding on natural organic matter. This is possible via the use of Microbial Fuel Cells (MFCs), which are bio-electrochemical transducers converting biochemical energy directly into electricity. EcoBot-I (2003), was powered by 8 MFCs running on E. coli fed with sugar plus artificial electron mediators in the anode; its task was phototaxis. EcoBot-II (2005) was powered from 8 MFCs containing a mixed culture microcosm and used no artificial electron mediators. The MFCs were fed with various types of organic matter (e.g. rotten fruits & dead flies). EcoBot-II could wirelessly report the ambient temperature in addition to following the light. EcoBot-III (2010) is powered by a collection of 48 small-scale MFCs and demonstrates -in primitive form- self-sustainability. It can collect food and water from its environment and maintain onboard fluid circulation as well as waste excretion and other tasks. This series of EcoBots is the world's 1st demonstration of artificial symbiosis - the integration between microbes and mechatronic units into one robotic entity. This presentation will cover the development of EcoBots and MFC technology, and address some of the main engineering and philosophical challenges.

H-4:IL11 Underwater Adhesive Systems for Robotic Applications

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We propose a new underwater adhesive by mimicking a principle found in the beetle foot. The new adhesive is designed by creating a specific microstructure on the silicone polymer surface and tested using a force transducer. The various test substrates were used for evaluating the effect of surface energy on the adhesion force. The experimental results showed that the adhesive force underwater was stronger on the hydrophobic surfaces than on the hydrophilic ones. We attempted to apply the new adhesive on a miniature toy (mass 7 g). The area of 150 square millimeters of the adhesive was sufficient to hold the toy underwater. We also successfully demonstrated that the adhesives could be used repeatedly in multiple adhesive cycles.

H-4:L12 Design and Application of Smart Soft-morphing Structure for Bio-mimetic Underwater Robot: Turtle-like Robot

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This paper presents the Smart Soft-morphing Structure which is appropriate actuator for the bio-mimetic swimming robot because of its higher degree of freedom than traditional motor based linkage structure and shows its application to the robot such as turtle-like robot. Smart Soft-morphing Structure is the composite consisted of active component, passive component and matrix. Active component is to provide actuating force to the actuator which is composed of smart material embedded in the eccentric position. Passive component which is for controlling actuating shape of actuator such as out-of-plane bending, twisting and in-plane shear deformation is consisted of designed rigid anisotropic material. In case of matrix, it is to combine active and passive components firmly and decide overall shape of actuator. With this new type of actuator, we could mimic marine and freshwater turtle's locomotion by optimal design of each component of Smart Soft-morphing Structure. With the wireless control unit, our turtle-like robot could move forward and change its direction in the water. Also, we have shown the possibilities that this new actuator can be used as universal actuator for biomimetic underwater robot based on the database of design actuator to make certain actuating motion.

Session H-5

Biomolecular Computing

H-5:IL01 Progress in Molecular Computing

M.N. STOJANOVIC, Department of Medicine, Columbia University, Fort Lee, NJ, USA

We will discuss our recent progress in the construction of molecular systems for analysis of molecular inputs, focusing on those that mimic game-playing automata and those that analyse cell surfaces. All systems will be based on nucleic acid catalysts.

H-5:IL02 Molecular Theory of Biointerfaces

I. SZLEIFER, Department of Biomedical Engineering, Northwestern University, Evanston, IL, USA

Biological environments are highly inhomogeneous in composition at the nanoscale. In this presentation we will show examples that demonstrate the importance of the coupling that exists between molecular organization, physical interactions and chemical equilibrium, e.g. acid-base or ligand-receptor. We will show the predictions from a quantitative molecular theory in two different scenarios. We predict that the pH inside a hydrogel can be very different from the buffer in contact with it and the variation occurs over an interface of nanometer thickness. As a proof of concept we will show how a protein penetrating into the gel can change its charge depending upon the position. A second example is related to the interactions of polymer coated micellar drug delivery systems. We will show how combining pH responsive polymers with specific ligand-receptor binding may lead to synergetic effects that result in binding constant that can be enhanced by order of magnitudes as compared to the product of the different components. We will close with a discussion of how new intuition needs to be developed in order to understand the highly non-linear coupling that exist between molecular organization, chemical equilibrium and physical interactions that are ubiquitous at biointerfaces.

H-5:IL03 Driving DNA Nanodevices with in Vitro Transcription Circuits

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Cell-free biochemical circuits with a limited number of components can help to gain insight into the design principles of more complex naturally occurring systems. Particularly simple in vitro circuits can be constructed on the basis of so-called "genelets" - these are synthetic in vitro DNA switches that can be regulated through their RNA transcripts. We recently demonstrated, how a synthetic biochemical clock constructed from such genelets can be used to control the motion of a simple DNA nanodevice - the DNA "tweezers". In order to study important aspects of synthetic circuit design such as "modularity" or "back-action", we

investigated how an increase in molecular "load" (i.e., amount of DNA tweezers) to the oscillator circuit affected the overall dynamics of the system. To improve the performance of the loaded circuit, we developed an "insulator genelet", which allowed us to drive large amounts of load without distorting the oscillations of the system too strongly.

Session H-6

Ongoing and Perspective Applications of Bio-inspired Technologies

H-6:IL01 Bioinspired Surfaces for Friction Control

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Nowadays, elastomers are widely used in various mechanical devices ranging from printing rolls to biodegradable scaffolds for tissue engineering. Among other functions, a vast array of elastomer-based units involves sliding or anti-slip elements, such as in tires, belts, wiper blades, syringe seals, etc, whose behavior is defined by frictional interaction between elastomer and its counterface. Highly deformable elastomer usually forms a large real area of contact with its mating surface, which often prevents sliding in the accepted sense. Instead, the displacement of contacting bodies is accommodated by stick-slip or detachment waves, which lead to uncontrollable and unstable surface behavior resulting in vibration, noise, diminished accuracy, energy loss and increased wear that affect the function and shorten the service life of machine components. These technical problems may, however, be overcome by employing surface textures originally evolved in the biological world. Here we report on a biomimetic surface pattern capable of eliminating stick-slip disturbances and adjusting elastomer friction from as low as about 50% to about 100% of that of unmodified surface, rendering this texture potentially attractive for many tribological applications based on rubber-like materials.

H-6:IL02 DNA Origami as a Calibration Standard for Super-resolution Microscopy

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In recent years, a number of approaches have emerged that enable far-field fluorescence imaging beyond the diffraction limit of light, namely super-resolution microscopy. These techniques are beginning to profoundly alter our abilities to look at biological structures and dynamics and are rapidly spreading into biological laboratories around the world. Here, I will summarize our efforts to advance super-resolution imaging and focus on the development of self-assembled nanoscopic rulers for calibration and evaluation of super-resolution microscopes. These nanoscale rulers are made of self-assembled DNA nanostructures and arrange a precisely defined number of fluorescent dyes with nanometer precision so that the resolving power of a microscope can be easily tested. We demonstrate the potential of the nanoscale rulers with different super-resolution techniques including stimulated emission depletion microscopy and super-resolution microscopy that is based on the successive localization of single molecules. The DNA based bottom-up approach to microscopy standards has the potential to be widely applied beyond super-resolution imaging.

H-6:IL03 An Antifouling Coating Having Low Surface Energy and a Bio-inspired Microstructure

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This paper reports a novel antifouling coating for combination of low surface energy and bio-inspired surface microstructure. Novel polymers with low surface energy were firstly synthesized by integration of the characteristics of silicone and fluoropolymers; its adhesion force and water resistance are improved greatly by an organic-inorganic hybrid preparation process. Then, a micro-nano binary structure was

constructed on the surface of the coating by doping silica nanoparticles in the polymer. Therefore, the coating combines the advantages of a low surface energy and a microstructure, which will assist in antifouling. The contact angle was used to characterise the surface energy of the composite coating, and its antifouling performance was determined by the seawater immersion test. The results showed that the contact angle of the new polymer was 103°, which is much higher than that normally displayed by both silicone and fluoropolymers. The composite coating possessed a still higher contact angle, up to 150°. The seawater immersion test results show the coating has excellent anti-fouling effects over short-time periods, but its application for long-term anti-fouling needs further investigation.

H-6:L04 Light Transmission in the Window Plant *Fenestraria aurantiaca* as Inspiration for Innovative Biomimetic Solutions

I. SCHÄFER, Carinthia University of Applied Sciences (AT), Radolfzell, Germany

Fenestraria aurantiaca (F.a.) is a succulent situated in the Namib desert. The extreme climate conditions there forced the plant to develop specialized adaptations to deal with heat, light and aridity. F.a. grows with most of its round shaped, four centimeters long and one centimeter thick body under the sand. Just the top, with a light transparent surface - the window - on it, protrudes from the surface. Experiments with light, infrared and detailed microscopy studies show the physical, biological and chemical capabilities of F.a.. It was found that the window works as a lens, light from a 90° angle is directed into the plant. Up to 90% of the visible light is blocked depending on the wavelength. The transparent tissue inside showed a transparency up to 90%. Generally F.a. has four principles: light handling, surface cleaning, heat avoidance and water storing. Innovative solutions based on them seem to be possible among others in photovoltaic systems. An example solution called "buried solar cells" is presented. Also the possibilities of the principles for the use on daylight systems to illuminate buildings passively are discussed. Another working field is the screen of mobile devices, where the clarity and readability suffers from direct sunlight.

SPECIAL SESSION H-7

Biomimetic Flow Control in Aquatic and Aerial Systems and its Application to Bioinspired Autonomous Vehicles

H-7:IL01 Influence of Flexibility on Flapping Wing Performance

B. BALACHANDRAN, Department of Mechanical Engineering, University of Maryland, College Park, MD, USA

Investigations conducted into the role of flexibility in flapping wing systems will be discussed in this presentation. Two different computational approaches are used to study the associated fluid-structure interactions. In one approach, the fluid model is based on the Navier-Stokes equations for viscous incompressible flow, where all spatio-temporal scales are directly resolved by means of Direct Numerical Simulations. In the other approach, the fluid model is an inviscid, potential flow model, based on the unsteady vortex lattice method. The results obtained are illustrative of the benefits of flexibility and provide clues to the possible role of nonlinear phenomena in the enhancement of aerodynamic performance.

H-7:IL02 Controlling Flow Structures by Wing Motion in a Flapping-flight Model

M. IIMA, Hiroshima University, Higashi-Hiroshima, Japan

In insects' flight, various flow (or vortex) structures are utilized, by which the flight mechanism has different properties from the conventional steady-wing aerodynamics. The flow structure not only enhances the lift by the particular mechanisms but also affects the stability. The control of vortex-using flight is not easy because the flow structure can not be operated directly by wing. Further, the whole system including the center-of-mass motion is strongly nonlinear. If we want to control the flight not in a quasi-steady manner but in a quick manner, the linear stability theory can not be applied. To overcome the problem, we focus on saddle solution, whose importance has been pointed out in the analysis of strong interaction between spatially-localized structures in nonlinear systems. The saddle is unstable but accessible via the stable manifold in phase space. The final state is sorted out through the unstable manifold, which can be used to control the system. To apply this idea to the flapping flight, we need to check whether it is possible to access to the stable manifold by the flapping motion alone. In this paper, the accessibility is shown in a two-dimensional flapping model. The final state is determined by detailed flapping controlled by one parameter.

H-7:IL03 Numerical Simulations of the Clap-fling-sweep of Hovering Insects

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The Lighthill-Weis-Fogh clap-fling-sweep mechanism is a movement used by some insects to improve their flight performance. As first suggested by Lighthill (1973), this mechanism allows large circulations around the wings to be established immediately as they start to move. Initially, the wings are clapped. Then they fling open like a book, and a non-zero circulation is established around each of them. Thus one wing can be considered as the starting vortex for the other. Then they sweep apart, carrying these bound vortices and generating lift. Since the insect wings have relatively low aspect ratio and rotate, 3d effects are important, such as spanwise flow and stabilization of the leading edge vortices (Maxworthy, 2007). To explore these effects, we perform direct numerical simulations of flapping wings, using a pseudo-spectral method with volume penalization. Comparing 2d and 3d simulations for the same setup clarifies the role of the three-dimensionality of the wake. Our results show that the 2d approximation describes very well the flow during fling, when the wings are near, but 3d effects become crucial when the wings move far apart. Possible extensions of the numerical method for modeling the interaction with thin elastic wings using FSI will also be presented.

H-7:IL05 Reversed Flapping Flight and Inverted Hydrodynamical Drafting

JUN ZHANG, L. MORET, L. RISTROP, T. SCHNIPPER, Applied Mathematics Laboratory, Courant Institute, New York University, New York, USA

Flying birds and swimming fish are familiar sights to everyone, but their remarkable locomoting abilities are often poorly understood. Inspired by these examples found in nature, we discuss two recent laboratory experiments on interactions between unsteady flows and dynamic boundaries (here flapping wings or fins). In the first experiment, we study the physical origin of flapping flight and investigate how wing flexibility determines the flight speed and even the flight direction. There, we found that the finite wing rigidity (which allows passive pitching when flapped) could lead to reversed flapping flight. In the second experiment, we investigate the group dynamics of multiple locomotors as they interact with each other through the passing flows. Unlike the well-known hydrodynamic drafting of rigid objects placed in tandem, flexible structures like flags show inverted drafting where the leading body enjoys a reduced drag while the follower suffers a drag increase.

H-7:IL06 Advantages of an Ornithopter against an Airplane with a Propeller

S. SUNADA, Osaka Prefecture University, Sakai, Osaka, Japan

Small and lightweight airplanes as MAVs (Micro Air Vehicles) have a serious problem: they are strongly affected by wind gusts. However, birds and insects seem to fly stably in wind, even though they are smaller and more lightweight than the airplanes. The big difference between them is that the former generate thrust by propellers and the latter by flapping their wings. How are their differences related to the variations of aerodynamic force and moment acting on them under

wind gusts? The present analysis, where blade element theory, momentum theory and quasi-steady assumption are applied, was made to obtain an answer to this question. The answer obtained by the present analysis is as follows: The variation of the aerodynamic force on an ornithopter by a side wind gust is much smaller than that of an airplane with one or two propellers, when a reciprocal of advance ratio of a propeller and a flapping amplitude of an ornithopter are small. Furthermore, it is well known that pitching and yawing moments act on an airplane with one propeller when it encounters side and vertical wind gusts, respectively. Such moments do not act on an ornithopter. These can be an advantage of an ornithopter against an airplane with a propeller(s).

H-7:LO8 Fabrication Methods for Artificial Butterfly Scales and Shark Ribs for Micro Aerial Vehicles

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Low Reynolds number aerodynamics is of great importance for the optimization of Micro Air Vehicles (MAV). A possibility to improve the flight performance of MAVs is to take inspiration from efficient flyers and swimmers in nature. Studies have shown that the scales on the wing of a butterfly as well as the ribs present on the dermal denticles of sharks can have a positive effect on the fluid dynamic performance, using different principles of flow boundary layer control which increase the lift to drag ratio. In this contribution we present different fabrication methods for mimicking the scales on the wings of butterflies as well as the ribs present on the skin of sharks. Six different manufacturing techniques are developed and compared for the fabrication of artificial scales with a size of between 10µm and 500µm using tension induced and bimetal based methods. The shark ribs are realized based on a flat carbon fiber wing with insertion of steel sheets of different geometries, which act as the ribs. These fabrication methods build the basis for a systematic exploration of the design parameter space and testing the wings in a wind tunnel. An initial set of results is presented.

H-7:IL09 Aerodynamics of Flying Fish

HAECHEON CHOI, HYUNGMIN PARK, DUHO JE, School of Mechanical and Aerospace Engineering, Seoul National University, Seoul, Korea

The flying fish is an exceptional marine flying vertebrate, moving in two different media, i.e. swimming in water and flying in air. The flying fish has the hypertrophied fins and cylindrical body with a ventrally flattened surface for proficient gliding flight. These morphological features of flying fish have attracted great interest for aerial locomotion and its control. Therefore, we discuss these features from the measurement data of aerodynamic force and moment and from the flow field data. We find that the lift to drag ratio is maximum at attack angles (angle between the longitudinal body axis and the flying direction) of around 0 degree. The lift coefficient is largest at attack angles around 30-35 degrees, at which the flying fish is observed to emerge from the sea surface. From glide polar, we find that the gliding performance of flying fish is comparable to those of mid-size bird wings such as the hawk, petrel and wood duck. We also find that the flying fish achieves the reduction of drag and increase of lift-to-drag ratio by flying close to the sea surface. Finally, we investigate the role of rays existing on the lower surface of pectoral fin on the aerodynamic performance. The details will be discussed in the full paper.

H-7:IL10 Dynamics and Control of Biomimetic Swimming via Localized Vortex Shedding

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Analytical models for biomimetic locomotion in fluids often fail to capture the subtle dynamics of vortex shedding and vortex-body interactions, while computational models often achieve high fidelity at the expense of accessibility to model-based methods for control design. This talk will present an intermediary modeling approach based on the idealized representation of vortex-body interactions as Hamiltonian systems, focusing on fish-like and jellyfish-like propulsion involving localized vortex shedding. Computational results will be presented alongside experimental data illustrating strategies for efficient solitary navigation and for energy harvesting within schools of biomimetic vehicles.

H-7:IL11 Robotics for Human Swimming Movement
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Swimming movement of human is quite peculiar compared to those of other aquatic animals. For the human swimming movement, the robotics is utilized mainly from two objectives. First one is to acquire the knowledge for the human swimming. Since the human swimming is also studied in the field of sports biomechanics, the robotic approach can be useful for the field. For example, it is very difficult to measure directly the fluid force acting on the human body. Therefore, an underwater robot arm was developed by the authors. This robot arm has five degrees-of-motion (three for shoulder and two for elbow) and can perform the swimming motions of the crawl, breast, back, and butterfly strokes as the upper limb as well as the lower limb by changing the hand part into the foot part. The resultant forces acting on the robot as well as the joint torque were measured by the experiment in a circulating water tank. The measured data were utilized for the modeling of the fluid force in the simulation. Recently, the authors developed a swimmer mannequin robot as well. Using this robot, the fluid force acting on the trunk on the swimmer was modeled. Finally ongoing project of developing swimming humanoid robot is also introduced.

H-7:L12 Biomimetic Wings
D. PIETROGIACOMI, G.P. ROMANO, Dept. Mechanical and Aerospace Engineering, University "La Sapienza", Roma, Italy

Among all cetacean, the humpback whale (megaptera novaeangliae) has the higher capability to perform underwater acrobatic trajectories. These short-range maneuvers are used to trap krill and other crustaceans. This outstanding skill is basically dependent on large flippers whose peculiarity is the presence of bumps along the leading edge, called tubercles. The question to be solved is if these tubercles are able to delay wing stall and to attain higher lift in comparison to a conventional wing (Miklosovic et al, 2004; Fish & Lauder, 2006). The present experimental investigations employ different measurement techniques in order to evaluate the amount of possible gain, the potential drawbacks and the physical reasoning for such a phenomenon. In particular, three wing models have been tested in wind tunnel: one without tubercles for comparison; one with tubercles with constant wavelength and amplitude; one with tubercles with wavelength and amplitude decreasing linearly from the root to the tip. By using a force balance, the drag and lift acting on the three wings were measured as a function of the angle of attack. Measurements of the velocity field on planes orthogonal and parallel to the wing plane are also performed in order to point out the specific phenomena involved.

H-7:IL14 Dynamics of Swimming in Larval Fish
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Larval zebrafish swim by undulatory body motions, and can reach 70 body lengths/s with a tail beat frequency of 100 Hz. We designed a combined modelling and experimental approach to understand the swimming mechanism. We measured the kinematics of swimming with high-speed video recordings and the generated flow with digital particle image velocimetry. We modelled the free-swimming behaviour of the fish larva using computational fluid dynamics (CFD). We used the measured body deformation as model input, and predicted the forward body motion and rotations. The predictions agree well with experimental observations (e.g. swimming speed and generated vortices in the wake). Second, a spatial forward dynamics model of the locomotion system of larval fish was constructed that includes the essential muscular dynamics and architecture, non-linear elasticity as well as simplified external forces on the body, representing skin friction and pressures. The model predicts shape deformations of the body and forward motion of the centre of mass during fast starts and subsequent cyclic swimming, and was tested against recorded motions. Turning angle during fast starts, body speed and travelling body wave were predicted well by the model.

H-7:L16 Bioinspired Parylene-coated Stress-driven Artificial Hair Cell for Flow Sensing in Air and Water
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Hair cells are bio-mechanoreceptors which translate motion into signals to provide flow velocity and pressure gradient information. We show the design and development of a novel biomimetic artificial hair cell sensor. A microelectromechanical system (MEMS) has been fabricated exploiting a stress-driven geometry: a nitride-based multilayered cantilever beam structure generates a stress gradient that bends the beam out of plane, reaching a tip height greater than 500 μm . The surface fluid flow will bend the cantilever while a Nichrome strain gauge along the beam will sense the deformation. A parylene conformal coating follows as an efficient method for water sealing: continuous water flow and pulsed air flow set-ups demonstrated the flow sensing capabilities. A signal variation with respect to the no-flow voltage signal is detected and an exponential decay with frequency is shown. This is the most suitable bio-mimetic approach to an artificial hair cell: an array of different cantilever beam lengths can set the dynamic range while a suitable parylene thickness can be effective in the post-fabrication for tuning the flexural stiffness maximizing the sensitivity closer to the natural hair cell. Possible applications are artificial lateral line systems in underwater vehicles.

Poster Presentations

H:P02 Bio-inspired Reinforcement Models from Nacre and Bamboo
AN YUANLIN, LIU ZHIMING, WU WENJIAN, Department of Chemistry and Biology, College of Science, National University of Defense Technology, Changsha, China

Nature has created lots of biomaterials possessing excellent mechanical properties which manmade materials still cannot achieve. Nacre of molluscan shells and bamboo are both reinforced materials with amazing toughness. Three-point bending behaviors were performed vertical and parallel to the aragonite platelets surfaces and across and along the bamboo fiber by a universal testing machine. The loading curves indicated that nacre fractured stepwisely and possessed similar three-point strength vertical and parallel to the aragonite platelets surfaces. However, the loading curves of bamboo exhibited very different fracture processes along and across the bamboo fibers and the three-point bending strength across the bamboo fibers was about 10 times as the one along. The SEM images showed the details of fracture surfaces and explained the behaviors. Nacre is a kind of platelets reinforced biomaterial while bamboo is a kind of fibers reinforced one. Two kinds of reinforcement models were brought out from the inspiration of nacre and bamboo. The platelets reinforcement model and fiber reinforcement model possess different mechanical behaviors and could be used depending on the conditions.

H:P03 Enhanced Mixing in the Asymmetric Bifurcation Tube Network Mimicking the Lung Airway
M.Y. KANG, J.E. HWANG, JIN W. LEE, Dept of Mech. Eng., POSTECH, Pohang, South Korea

Human bronchial tree is a complex network of short tubes. Key morphological parameters such as diameter, length and bifurcation angle have been analyzed from the view point of optimality, and it has been confirmed that the change of the generation-average parameters with generations conforms to the optimum structure corresponding to minimum energy loss or maximum space filling. This study found out an additional optimality characteristics of the lung morphology that the asymmetry of bifurcation results in an enhanced mixing between expired flows from different alveolar regions and/or between the inspired and the expired flows. Five-generation bronchial tree models with varying degrees of asymmetry were analyzed numerically. Mixing efficiency changed with the degree of asymmetry and showed a maximum at the asymmetric structure resembling the human bronchial tree. The numerical predictions were confirmed by experiments where five-generation experimental models were fabricated by rapid-prototyping and the degree of mixing was visualized by the change of color distribution in the tube network, using two colloidal solutions with different colors. This result can be used for the design of various mixers with enhanced mixing efficiency.

H:P04 Plant Surface with Anisotropic Frictional Properties

E.V. GORB, S.N. GORB, University of Kiel, Kiel, Germany

The upper part in trapping organs (pitchers) of the carnivorous plant *Nepenthes alata* is covered with prominent lunate cells and crystalline wax coverage. To examine the influence of the surface anisotropy, caused by the shape of lunate cells, on insect attachment, we measured traction forces of ladybird beetles *Coccinella septempunctata* on surface samples of (1) intact pitchers, (2) chemically de-waxed pitchers, and (3) their polymer replicas, placed horizontally. Forces were measured, when beetles walked on test surfaces in directions, corresponding to the upright or inverted positions of the pitchers. On all tested surfaces, beetles produced significantly higher forces in the direction towards the pitcher bottom. Experiments with intact beetles having both claws and adhesive pads versus claw-ablated beetles showed that claws were mainly responsible for attachment enhancement in the downward pitcher direction, since, in this direction, they could interlock with overhanging edges of lunate cells. The anisotropic properties of the plant surface and its polymer replicas make these surfaces suitable as possible prototype materials for technical implementations requiring frictional anisotropy.

H:P05 Self-assembly Driven Enzyme Motion

J.S. LECKIE, R.V. ULIJN, M.D. HAW, University of Strathclyde, Glasgow, UK

A controllable and efficient 'active colloidal engine' utilising enzyme-driven peptide self-assembly is explored, exploiting our previously reported self-assembling aromatic peptide system. In detail, the enzyme alkaline phosphatase is driven by the supramolecular assembly of the dipeptide derivative Fmoc-FY into fibre structures, similar to actin-polymerization driven motion used in biology. The phosphorylated peptide (Fmoc-FpY) forms 5nm in diameter spherical micelle structures in water, above a critical micelle concentration of 5mM. In the presence of alkaline phosphatase the phosphate group of the tyrosine side chain is cleaved resulting in β -sheet fibre networks of unphosphorylated dipeptide. This micelle to fibre transformation has been characterised using spectroscopic; light scattering and chromatographic techniques. Visualisation of enzyme motion is achieved by conjugation of the enzyme to a fluorescing quantum dot via a carbodiimide coupling reaction and observation is achieved by single particle tracking fluorescence microscopy. Without the peptide substrate present the enzyme is expected to exhibit Brownian motion and upon addition of the peptide, fibre formation is proposed to guide and direct the enzyme motion.

H:P06 Mimicking Bone Architecture in a Metallic Structure

T.S. GOIA, K.B. VIOLIN, J.C. BRESSIANI, A.H.A. BRESSIANI, Instituto de Pesquisas Energéticas e Nucleares, Sao Paulo, SP, Brazil

The porous metallic structure has been developed to mimic the natural bone architecture, having interconnected porosity, disposing enough space to cell migration, anchoring, vascularization, nourishing and proliferation of new bone tissue. The titanium is used as porous implants due its excellent mechanical properties and biological interaction. Research evolving porous titanium has been done with purpose to find ideal pore size, total porosity percentage and influence of those in the increasing of bone-implant bond strength interface. Samples of commercially pure titanium (cpTi) were prepared by powder metallurgy adding 16% natural polymer (gelatin). The hydrogenated metallic powder (TiH₂) and the polymer were mixed in aqueous solution, homogenized and frozen in molds near net shape. The water was removed in kiln and the polymer by thermal treatment (350 °C/1h) before sintering (1300 °C/1h). As a result, macropores and micropores were formed within the structure with mean diameter of 900 μ m and =30 μ m respectively, distributed homogeneously. The apparent porosity was near 50%. The processing technique allowed formation of open porosity, in which the macropores mimics the trabecular bone structure and micropores allows the bone implant anchorage.

H:P07 Novel Bionic Biomembrane Supported by Gold Nanoparticles /Cellulose Hybrid Films

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Most of life processes in the biology are realized by material transit across biomembranes. As one of the main methods to study biomembrane, the construction of highly active bionic biomembrane

system is very important. Herein, a systematic work is done to obtain a new bionic biomembrane system with both a long life stability as solid-supported BLMs and a dimensional functionality as free-standing BLMs. Based on the gold nanoparticles/cellulose hybrid films, a novel system of bionic biomembrane is demonstrated. The ratio effects of lecithin to cholesterol to the stability of bilayer lip membranes (BLMs) are studied systematically. Lipid solution with a good membrane stability under air condition and in some aqueous solutions are prepared. It is found that the BLMs could form bilayers and sustain a long period in aqueous solutions and bind well with the gold nanoparticles/cellulose hybrid films. The electrochemical properties of the BLMs and the bionic composite membrane were also studied.

H:P08 Creation of Biomimetic polymer thin films by Single Step Phase Separation Method

JIAN-JE CHEN, QUOC-PHONG HO, **MENG-JIY WANG**, Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan, R.O.C.

The incorporation of biological functionalities into synthetic polymers provides particular potential for advances in studying the interactions between biomolecules and materials. In this study, biomimetic thin films were prepared from polymethyl methacrylate (PMMA) and polystyrene-co-maleic anhydride (PSMAA). The thin films with concave patterns with the average diameter ranging from submicron to a few tenths of microns were prepared based on the single-step phase separation method. The biofunctionalization was facilitated by doping the microstructured thin films with biomolecules such as extracellular matrix proteins and adhesive molecules. In addition, the nitrogen plasma treatments were also applied to functionalize the surfaces. The creation of similar nano or micro structures on polymer thin films with different biofunctionalities provided a particular opportunity for the investigations focused on the surface chemistry of the patterned materials, which usually required sample preparations in multiple steps. The results indicated that the creation of topographical cues alone improved the biocompatibility of polymer thin films. Moreover, both the extracellular matrix protein and adhesive molecule promoted the growth of L-929 fibroblasts due to the incorporation of nitrogen composition and the increase of surface wettability. The overall results showed that the integration of nano- to micro- environments and chemical functionalities into the materials provide promising effects for promoting mammalian cell growth.

H:P10 Bio-inspired Active Electrolocation Sensors for Inspection of Tube Systems

M. GOTTWALD, G. VON DER EMDE, Universität Bonn, Institut für Zoologie, Bonn, Germany

At night, the weakly electric fish *Gnathonemus petersii* uses an active electrosensory system for orientation and foraging in turbid, streaming waters. During active electrolocation the fish continuously scans the environment with self-generated electrical fields. Each field originates from an electric current pulse (electric organ discharge; EOD) generated by an electric organ in the tail. The EOD signal is sensed by electroreceptor organs in the fish's skin, which are distributed over almost the entire body surface with the highest density at a foveal head region. Nearby objects are perceived because of the local EOD-modulations which they cause at the electroreceptive skin. This skin area is called the electric image of the object. By analysing the electric image *G. petersii* can sense an object's distance, dimensions and electrical properties. The principles and algorithms used in active electrolocation can be applied for technical sensor systems analysing objects and materials in conductive media under no-light conditions. We have designed and tested technical electrolocation sensors for wall inspections of fluid-filled biological and technical pipe systems. Our sensors can solve tasks such as identifying material faults of the inner tube wall, finding leakages, and detecting inclusions or objects blocking the tube.

H:P11 Design and Fabrication of Bio-inspired Artificial Cochlea

WAN DOO KIM, SHIN HUR, WON JOON SONG, YOUNG DO JEONG, SUNG JAE BAE, Korea Institute of Machinery and Materials, Daejeon, Rep.of Korea

The sound waves travel to the brain along the auditory nerve in the cochlea of the inner ear. The cochlea has two core mechanosensory components. One is the basilar membrane which is to separate the incoming sound waves by their frequencies and the other is the hair

cells which act as the sensory receptors generating bioelectric signals. Scaled-up polymer membranes designed by mimicking the human basilar membrane were used for investigation of the frequency-separation characteristic. The effects of the shape, and thickness and the material properties of the basilar membrane on the variation of the frequency separability were analyzed by the finite element analysis. The results of analysis were evaluated to the displacement field formed on the bio-inspired polymer membrane was acquired by Laser Doppler scanning vibrometer (LDV) and post-processed frequency-wise. Also, mems scaled artificial basilar membranes made of PVDF (polyvinylidene fluoride) are manufactured using microfabrication processes. The mechanical behavior of PVDF artificial basilar membrane was measured to evaluate its performance as a mechanical frequency analyzer using LDV. The experiment results showed that the microfabricated artificial basilar membrane has a property as a mechanical frequency analyzer.

H:P12 Gold Nanostructures on Flexible Substrates for Thrombin Detection

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We demonstrated a facile fabrication of gold nanostructures including gold nanothorns (Au NTs), gold nanocorals (Au NCs), gold nanoslices (Au NSs) and gold nanowires (Au NWs) on flexible plastic substrates via electrochemical growths. Simple and highly sensitive biosensors were fabricated from the Au nanostructures and a thrombin-binding aptamer. The aptamer was used as a molecular recognition element for the detection of thrombin. On the nanostructured gold substrates, the thrombin-binding aptamer was immobilized to facilitate the coupling of thrombin to the probe molecule. The binding of thrombin to the aptamer sequence was monitored by electrochemical impedance spectroscopy (EIS) in the presence of ferricyanide/ferrocyanide. Thrombin (1 - 50 pM) was detected linearly. Among the Au nanostructures, Au NWs exhibited excellent selectivity, stability and sensitivity for thrombin detection due to their high surface areas.

SYMPOSIUM I

Progress in Wearable/Wireless and Implantable Body Sensor Networks for Healthcare Applications

Oral Presentations

Session I-1 Sensor Technology

I-1:IL01 Techniques for Contact-free Monitoring - Current Applications and Challenges

S. LEONHARDT, Philips Chair for Medical Information Technology, Helmholtz-Institute, RWTH Aachen University, Aachen, Germany

Personal Health Care, Ambient Assisted Living, Body Sensor Networks and Wireless Health are synonyms for the ongoing attempt to bring diagnosis and therapy to the private home, mainly driven by demographic changes and economical reasons. Medical Devices carried by the patient at home may become wearable, textile or implantable and may be connected by means of wireless communication with each other or with central medical services. However, many of the techniques developed in this context will also influence the traditional ways we deliver care in hospitals. Diagnosis and therapy both require adequate information extracted from the patient. Hence, physiological measurement technologies, especially if non-obtrusive and contact-free, are a crucial ingredient to this scenario. The talk will present some suitable technologies and application examples, including capacitive ECG monitoring, ballistocardiography in bed, magnetic impedance monitoring, infrared thermography and reflective PPG imaging.

I-1:IL02 Continuous Monitoring of Functional Activities using Wearable, Wireless Gyroscope and Accelerometer Technology

R.C. WAGENAAR, I. SAPIR, Y. ZHANG, S. MARKOVIC, L.M. VAINA, T.D.C. LITTLE, Boston University, Boston, MA, USA

The development of functional activity monitors (FAMs) will allow rehabilitation researchers and clinicians to evaluate treatment efficacy,

to monitor compliance to exercise instructions, and to provide real time feedback in the treatment of movement disorders during the performance of daily activities. The purpose of the present study was to develop and test a small sized wearable FAM system comprised of three sensors positioned on the sternum and both thighs, wireless Bluetooth transmission capability to a smartphone, and computationally efficient activity detection algorithms for the accurate detection of functional activities. Each sensor was composed of a tri-axial accelerometer and a tri-axial gyroscope. Computationally efficient activity recognition algorithms were developed, using a sliding window of 1 second, the variability of the tilt angle time series and power spectral analysis. In addition, it includes a decision tree that identifies postures such as sitting, standing and lying, walking at comfortable, slow and fast speeds, transitions between these functional activities (e.g. sit-to-stand and stand-to-sit), activity duration and step frequency. In a research lab setting the output of the FAM system, video recordings and a 3D motion analysis system were compared in 10 healthy young adults. The results show that the agreement between the FAM system and the video recordings ranged from 98.10% to 100% for all postures, transfers and walking periods. There were no significant differences in activity durations and step frequency between measurement instruments.

I-1:IL03 Sensing Biological Signals under Ambient Assisted Living

KWANG SUK PARK, Seoul National University, Seoul, Korea

Smart and nonintrusive biological signal monitoring technologies have been developed which can realize ambient assisted healthcare. Sensors are installed in daily using ambient devices such as chairs, beds, toilet seats and etc. and biological signals are monitored nonintrusively without interrupting subjects' ordinary daily activities. ECG and EMG can be measured using capacitive coupling over insulating material like clothes. BCG can be measured using force sensing materials like PVDF, EMFi and loadcell sensors. PPG also can be monitored over clothes by optimally controlling input light. Blood pressure can be estimated using pulse arrive time from nonintrusively measured ECG and PPG. HRV can be calculated as accurately as done by conventional ECG. Sleep can be evaluated by classifying sleep stages based on these signals. This monitoring does not interrupt subject's ordinary daily activities and

can be applied subject transparently for quite long period of time. Also, progress of this technology will broaden the way of ambient assisted healthcare to increase the quality of life.

I-1:IL04 Smart Hydrogel-based Biochemical Microsensor Array for Medical Diagnostics

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With the rapid development of micro systems technology and microelectronics, smart implantable wireless electronic systems are emerging for the continuous surveillance of relevant parameters in the body and even for closed-loop systems with a sensor feed-back to drug release systems. With respect to diabetes management, there is a critical societal need for a fully integrated sensor array that can be used to continuously measure a patient's blood glucose concentration, pH, pCO₂ and colloid oncotic pressure twenty four hours a day on a long-term basis. In this work, thin films of metabolite-specific or "smart" hydrogels were combined with microfabricated piezoresistive pressure transducers to obtain "chemomechanical sensors" that can serve as selective and versatile wireless biomedical sensors and sensor arrays for continuous monitoring several metabolites. Sensor response time and accuracy with which sensors can track gradual changes in glucose, pH, CO₂ and ionic strength, respectively was estimated in vitro using simulated physiological solutions. The biocompatibility and hermeticity of the developed multilayer encapsulation for the microsensor array has been investigated concerning the long-term stability and enduring functionality that is desired for permanent implants.

I-1:IL05 Biocompatible Chip and System Packaging for Implantable Applications

M. OP DE BEECK, K. QIAN, J. O'CALLAGHAN, K. MALACHOWSKI, C. VAN HOOFF, Imec, Leuven, Belgium

A packaging process for implantable electronic systems is proposed, combining biocompatibility and hermeticity with extreme miniaturization. In a first phase of the total packaging sequence, chips are encapsulated to realize a bi-directional diffusion barrier preventing body fluids to leach into the package causing corrosion, and preventing IC materials such as Cu to diffuse into the body, causing various adverse effects. For cost effectiveness, this hermetic chip sealing is performed as post-processing at wafer level, using modifications of standard clean room fabrication techniques. In a second phase of the packaging process, all chips of the final device will be electrically connected in a so-called interposer, fabricated using implantable polyimide or alternative polymers and bi-metallization based on gold or platinum, and on IrOx for electrodes in direct contact with tissue. Cost aspects are considered when developing this metallization process, since precious metals as gold, platinum and IrOx are expensive. Device assembly is the final packaging step, during which all system components such as electronics, passives, a battery,... will be interconnected. To provide sufficient mechanical support, all these components are embedded using a biocompatible elastomer such as PDMS.

I-1:IL06 Chip-level Electronic Noses for Breath Analysis

M. CREGO-CALAMA, S.H. BRONGERSMA, D. KARABACAK, Holst Centre/ imec the Netherlands, Eindhoven, The Netherlands

We have developed very sensitive integrated sensing elements for gas detection. The polymer-coated microbridges in high-density arrays can detect ppm-level concentrations of vapors using on-chip integrated read-out techniques. The demonstrated technology is very suitable for miniaturization of electronic nose devices thanks to the low power consumption (<1 μ W/bridge) and small form factor. An accurate e-nose requires small, integrated, low-power detectors with individually tuned chemical coatings. Current solutions, like chemi-resistors or quartz crystals are however not scalable or power-efficient enough to build low-power small form factor e-noses. Imec and Holst Centre have developed a new generation of microbridges with embedded individual piezoelectric "shakers" in a high-density array with very high fabrication yield. The novel design allows for rapid coating of a range of absorbents on individual microbridges using commercial inkjet printing technology. The suspended structures vibrate individually, and changes in their modes of vibration (resonances) are monitored as an indication of vapor

absorption in their coatings. Due to the high length-to-thickness ratio the gas sensor chip has a high sensitivity to low-concentration vapors.

I-1:LO8 Micro-fluidic Device for Colorimetric Analysis of Sweat

V.F. CURTO, C. FAY, S. COYLE, D. DIAMOND, F. BENITO-LOPEZ, Clarity: Centre for Sensor Web Technologies, National Centre for Sensor Research, Dublin City University, Dublin, Ireland

Micro-Total-Analysis (μ TAS) and Lab-on-a-Chip (LOC) are important concepts for the development of personalised health care and point of care diagnostic devices. A step further is the possibility of making those devices wearable, opening new routes to monitor physical and/or biochemical conditions of the wearer in real-time. In addition, the integration of chemical sensors in the microchannel of microfluidic devices, although challenging, has several technological advantages compared to bench based sensor devices, such as reduction of the volume that is needed to monitor certain analytes, minimisation of cross-contamination from the surrounding environment and continuous flow operation, among others. Recently, the synthesis and use of ionogels has shown an exponential growing in literature.¹ Ionogels are solid or gel-like polymeric materials that endow room temperature ionic liquids, molten salts, which are characterised by large electrochemical stability, high conductivity and low vapor pressure. Through the smart design of a microfluidic platform, an electronic-free device capable of performing colorimetric real-time analysis of pH has been fabricated, where ionogel sensing materials are integrated inside the microchannels.

1. J. LeBideau et al, *Chem. Soc. Rev.*, 40 (2011) 907-925.

Session I-2

Smart Fabrics and Wearables

I-2:IL01 Upperlimb Gesture Reconstruction through Textile and Inertial Sensory Fusion

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A novel method devoted to the reconstruction of the joint angles in a kinematic chain is described. The reconstruction algorithm is based on the fusion of the information deriving from inertial sensors (accelerometers) and conductive elastomer strain sensors. Accelerometers provide a reliable reconstruction when they are employed as inclinometers in quasi-static conditions. They suffer from artifacts when they are used to detect fast movements or when interactions with the environment occur. The knowledge of the frequency components of the movement to be detected permits removal of these artifacts. Conversely, conductive elastomer sensors have a complex dynamic response, but they can easily provide the frequency content of the movement to be detected. A filtering strategy of the inertial sensor signals based on the elastomer sensor response provides a reliable reconstruction of joint variables during the movement.

I-2:IL02 Adhesive Bonding Technology for Reliable Interconnections of Smart Embedded Electronic Modules and Various Textile Circuits

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Interconnection of electronics and textile circuits is still a main challenge for the fabrication of reliable smart textiles. This paper describes the enhancements of the adhesive bonding technology whereby electronic modules are bonded to textile substrates with a thermoplastic non-conductive adhesive (NCA) film. The modules are placed onto textile circuits with an NCA-film in between. After applying pressure and heat the adhesive melts and conductors of each member get in touch. Subsequently cooling solidifies the NCA resulting in an electrical-mechanical interconnection of the electronic module and the fabric. This paper shows the suitability of this technology for knitted, woven, non-woven and embroidered fabrics with metal coated yarns as well as with litz-wires as conductors. Besides, it shows that the interconnection

process works well with thermoplastically insulated conductors. In addition, the design of interposers has been improved in respect to contact generation and miniaturization. Therefore the pitch of the contact pads of each of the contact members is set to 1.27 mm. A textile display was realized with smart RGB-pixels which are controlled over the I²C-bus on a "QuadroPolTex"-Woven substrate. It demonstrates the applicability and the potential of this technology.

I-2:L03 A Wearable Remote Brain Machine Interface Using a Smartphone and the Mobile Network

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A Remote Brain Machine Interface (RBMI) can be defined as a means to control a machine that is in a different geographical location than the user. Thus far, simulations for such interfaces using multiple channels of non-invasive EEG signals acquired through tethered systems have been used for control of vehicles in military and exploratory applications, and for ongoing research on RBMI controlled robotic surgery. However, simple applications of RBMI in home automation for the elderly, home security etc can be built using fewer and more portable sensor systems. As a case study, we have implemented such an interface using a smartphone for the RBMI. The system consists of a wearable Bluetooth-enabled head band with dry electrodes for EEG and EOG signals, a smartphone to collect and relay the data, a laptop with internet connectivity at a remote location to retrieve the data and generate control commands. In this paper, we describe the information architecture, the design of the wearable nanosensors and algorithms for control command generation based on EEG and EOG. A selected demonstration will be shown.

I-2:L04 A Novel Wearable System for Elderly Monitoring

T. FAETTI, R. PARADISO, Smartex srl, Navacchio (PI), Italy

The average age of European population is growing year by year and the social impact of this trend will affect the future economy of developed countries, since elderly people suffer from many chronic diseases limiting their capabilities, the home assistance is one of the main emerging needs. One common aspect of the oldness is to make the individual prone to Hypothermia due to several age-related physiological factors such as lower metabolism, thinner skin, malnutrition, delayed perception of hot/cold. Hypothermia can lead to mortality during the night in elderly affected by diseases or disabilities. In this paper we present a pajama that aims to monitor elderly people while sleeping. Such a system, developed in the scope of EU funded project MOBISERV, is able to monitor 1 lead ECG signal, upper body movements and skin temperature in 2 different sites through a distributed Body Sensor network, communicating to a main data logger through ANT wireless protocol. Final goal of the system is to prevent the onset of hypothermia, unobtrusively monitoring physiological parameters of a subject and raising alarms if wrong patterns are detected.

I-2:IL05 Real-time Analysis of Sweat using Integrated Chemical Sensors

C. COYLE, F. BENITO-LOPEZ, V. CURTO, R. BYRNE, D. DIAMOND, Dublin City University, Dublin, Ireland

Sweat analysis is a non-invasive measure that can offer valuable physiological information. Sweat is easily accessible to wearable sensors integrated into our clothing. To perform sweat analysis fluid sampling and handling is needed to collect sweat and deliver it to a sensing device. The sensor must be robust, low-power and lightweight. For real-time measurements the device must have wireless capabilities to transmit data. The overall device must be comfortable to wear, ideally flexible. We have developed a micro-fluidic device to monitor sweat pH in real-time. The device uses optical components to perform colorimetric analysis of a pH sensitive dye. This work began as part of BIOTEX, an EU FP6 project, when a textile patch was developed. Since then the device has been miniaturised through the development of a flexible micro-fluidic chip and integration of surface mount components. This has resulted in an improvement of sensor performance and a smaller device more suitable for wearable applications.

I-2:IL06 MICROFLEX Project - Microtechnology in Smart Fabrics

S.P. BEEBY, M.J. TUDOR, R.N. TORAH, K. YANG, Y. WEI, University of Southampton, Southampton, UK

The EU funded FP7 project MICROFLEX is concerned with the functionalization of textiles by developing materials and process whereby active materials and miniature mechanical structures can be fabricated on the surface of the fabric using screen and inkjet printing. The project has successfully realised an array of active inks that can be processed at low temperatures compatible with fabrics. The miniature mechanical structures are achieved using a sacrificial fabrication approach where printed films are selectively removed leaving freestanding mechanical structures. By combining the sacrificial process with the active materials, printed MicroElectroMechanical Systems (MEMS) can be realised on the surface of the fabric. This capability offers a much wider range of sensing and actuating functions and performance compared with basic films. The Microflex project is currently developing demonstrators for the industrial partners Saati Group S.p.A., Bonfort, Elasta, Klopman International Srl and Paul Boye Technologies.

Session I-3

Wearable and Implantable Sensor Integration

I-3:KL CMOS Integration of Nano-Bio-Sensors

S. CARRARA, EPFL - École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

Integrated Nano-Bio-Sensing for diagnosis of patients is a key factor to provide better, more rationale, effective and ultimately low-cost health care also at home. The ultimate goal of improved health care on those subjects is the extension of the patients' autonomy, the possibility for auto-monitoring, the improvement of their comfort levels and their integration into everyday life. On-line monitoring is also required in sportsmen training, as well as in people involved in public utilities. For those, maintenance of the safety by through embedded systems to alert emergencies is a key issue. However, all the systems in the market do not measure the human metabolism at molecular level (metabolites). The only available systems for metabolic control are limited to glucose monitoring and used for diabetic patients. However, many other molecules are crucial in human metabolism. The aim of this talk is to present an innovative concept for multi-panel, highly-integrated monitoring systems at molecular level. The considered metabolites are glucose, lactate, glutamate, ATP, and injected drugs. Carbon nanotubes are considered to improve the sensors performance. Innovative VLSI solutions are discussed including the system remote powering.

I-3:IL01 Nanosensors, e-bra, Printable Electronics and Smart Devices for Point-of-Healthcare

V.K. VARADAN, College of Medicine, University of Arkansas, Fayetteville, AR, USA & Pennsylvania State University, Hershey Medical Center, Hershey, PA, USA

In medicine and healthcare, the growing need and market demand for Point of Care (POC) systems to improve patient's quality of life, are driving the development of wireless nanotechnology based smart systems for diagnosis and treatment of various chronic and life threatening diseases. This talk addresses the recent development of nanodiagnostic sensors and nanotherapeutic devices with functionalized nanowires and nanotubes on a flexible polymer or textile based thin film electronics to monitor and control of major life threatening diseases including 1) neurodegenerative diseases, 2) cardiovascular diseases, and 3) diabetes and metabolic diseases. We have developed an e-bra which is used as a platform on which the various textile based nanosensors for cardiac health monitoring are integrated into the fabric via smart phone. Selected movies illustrating the applications of both invasive and non-invasive wireless nanosensor systems to patients and surgical procedures will be shown at the talk. Movies on heart rate variability sensors will illustrate the use of the flexible nanosensors on both women and men, and the optimum workout needed for persons jogging, running on treadmill, etc.

I-3:IL02 A Smart Biological Signal-responsive Focal Drug Delivery System for Treatment of Refractory Epilepsy

M.T. SALAM¹, A.H. HAMIE¹, D.K. NGUYEN², **M. SAWAN¹**, ¹Polystim Neurotechnologies Laboratory, École Polytechnique de Montréal, Québec, Canada; ²Neurology Service, Department of Medicine, Notre-Dame Hospital, Centre Hospitalier de l'Université de Montréal (CHUM), Québec, Canada

In this paper, we propose new biological signal-responsive implantable device that triggers direct seizure suppression drug into the epileptogenic zone at electrographic seizure onset. We describe the high performance seizure onset detection algorithm, low-power circuit techniques and focal pharmacological treatment for seizure suppression. The implantable device is composed of a preamplifier, a signal processor, a seizure detector and a micropump. The device records high quality intracerebral electroencephalographic (icEEG) recording using high conductive electrodes and low noise preamplifier. The recorded signal is processed continuously using low-power technique and subsequently detect seizure onset accurately. The low-power miniaturized micropump is able to deliver sufficient amount of anticonvulsive drug Diazepam to block a seizure activity within the epileptogenic zone. The detection algorithm was validated with Matlab tools and a prototype device was assembled with discrete components in a circular (\varnothing 40 mm) printed circuit board. The device was validated using the icEEG recordings obtained from 3 drug-resistant epilepsy patients during 3-week invasive study. The average seizures detection delay is 10 sec from electrographic seizure onset, well before seizure progression.

I-3:IL03 Implantable Wireless System for Stimulation of the Retina

W. MOKWA, Institute of Materials in Electrical Engineering I, RWTH Aachen University, Aachen, Germany

The mostly cause of blindness in the developed countries is a degeneration of the retina. For restoring this loss of vision besides pure biological approaches the substitution of the lost functions by means of an electronic implant seems to be possible. It has been shown that electrical stimulation of retinal ganglion cells yields visual sensations. Therefore a retina implant especially for blind humans suffering from Retinitis Pigmentosa based on this concept seems to be feasible. There are two main approaches for stimulating retinal ganglion cells. In the epiretinal approach visual images are recorded by a camera. The image information is transformed by a neural network into corresponding signals appropriate for stimulation of retinal ganglion cells. These signals are transmitted to an implanted receiver unit by magnetic coupling. Here the signals are decoded and transferred to a stimulation circuitry that selects stimulation electrodes located inside the eye on top of the retina and generates current pulses to the electrodes. By this, action potentials in retinal ganglion cells are evoked causing visual sensation. In the subretinal approach the space between sclera and the retinal nerve cells is used by replacing the degenerated photoreceptors by a stimulation electrode array. Meanwhile successful experiments have been performed on a variety of patients. This paper wants to give an overview about technical aspects of these activities.

I-3:IL04 Use of Machine Learning Algorithms for Interpreting Wearable Physical Activity Monitor Data

P. FREEDSON, University of Massachusetts, Amherst, Department of Kinesiology, Amherst, MA, USA

Wearable monitors to evaluate habitual physical activity has become the method of choice over the last decade. This assessment method is an important advance to enhance our understanding of the dose-response relationships between physical activity exposure and numerous health-related outcomes. The most widely used sensor to evaluate habitual physical activity is the accelerometer which is typically secured to the waist, wrist, ankle, or thigh to provide researchers data that can be collected continuously over several days. This presentation will first provide an overview of the history of the use of wearable accelerometers which capture both the quantity and quality of human movement. The presentation will then describe novel methods for data processing of the accelerometer using machine learning algorithms such as artificial neural networks and support vector machines. We use respiratory gas exchange measures and direct observation collected while participants perform numerous physical activities to obtain criterion measures of physical activity energy expenditure and activity type. A discussion of how we train and apply the neural network and support vector machine algorithms using these criterion measures will also be presented.

Session I-4

Energy Harvesting, Sensor Networks, Signal Processing, Data Transmission

I-4:IL01 Energy Harvesting from Motion for Body Sensor Networks

E.M. YEATMAN, P. MITCHESON, Department of Electrical & Electronic Engineering, Imperial College London, London, UK

Energy harvesting - the collection of otherwise unexploited energy in the local environment - is attracting increasing attention for the powering of electronic devices. Wireless sensor networks are a particularly important application: they can have low power requirements, but need to avoid the maintenance burden of battery recharging and replacement. Wireless sensors powered by motion such as machine vibration are beginning to be exploited commercially, but body mounted or implanted applications remain challenging, because of the size constraints and the low frequency and variable nature of body motion. This talk will review the principles and state-of-art in miniature motion energy harvesters. It will focus on approaches suitable for body sensor applications, and present a number of device types developed for this application. It will also consider the challenges in power conversion circuits for body motion harvesters, and introduce some possible solutions. Finally, a wireless node architecture will be presented in which the energy harvesting is integral to the capture and transmission of data.

I-4:IL02 Signal Processing for Capsule Endoscope Video

T.A. RAMSTAD, Dept. of Electronics and Telecommunications, The Norwegian University of Science and Technology (NTNU), Trondheim, Norway

Capsule endoscopes communicating video information over radio channels are important for inspection of the digestive system, especially the small intestine which cannot be reached by wired endoscopes. Due to the endoscopes' small size, and correspondingly limited battery capacity, it is challenging to provide continuous operation for up till 10 hours, which is the goal of this study. High attenuation through human tissue necessitates low bit rate and efficient modulation. Furthermore, limiting the processing power implies simple algorithms. We therefore suggest frame-by-frame compression using differential coding (DPCM), resulting in a bit-rate reduction by a factor of 10-20. For further bit-rate reduction the transmitted frame rate is reduced, and increased again in the receiver by frame interpolation based on bi-directional block matching techniques. The transmission method suggested is pulse position modulation (PPM) combined with bit interleaving and channel coding. High constellations of PPM provides at least 4-fold power reduction compared to binary transmission. Multiple cooperating receiving antennas are used for further power reduction, and for endoscope position tracking. The presentation will show simulated video material based on the developed configuration.

I-4:IL03 Algorithms for Strongly Increased Robustness and Reliability of Wearable Sensor Nodes

J. PENDERS, I. ROMERO, T. BERSET, C. VAN HOOFF, imec / Holst Centre, Eindhoven, The Netherlands

Wearable and miniaturized sensors are instrumental in revolutionizing healthcare. An example is a wearable ECG patch, allowing comfortable cardiac health monitoring over several days from the home environment. Achieving reliable and high integrity recording however remains a challenge in ambulatory conditions due to the high level of noise introduced by motion artifacts. In this lecture, we present an algorithm framework for motion artifact reduction in ambulatory ECG recordings. Two algorithmic approaches are presented. The first uses redundancy from multi-lead ECG recordings, and applies a statistical method, Independent Component Analysis, for de-noising the ECG recordings. The second method is an adaptive filter that uses Electrode-Tissue impedance as the measurement of noise. These methods can be combined to allow artifact filtering in a wide range of daily life situations. Results show that these algorithms significantly improve the reliability of heart rhythm analysis, and extend its applicability to situations in which the individual is walking, running and exercising. The implementation of these algorithms in ultra-low-power circuits leads to development of a platform for reliable ECG monitoring on-the-move.

I-4:IL04 Analysis and Biomedical Signal Processing in Wearable Devices for Cardiovascular Diseases Prevention

A.M. BIANCHI, Dipartimento di Bioingegneria, Politecnico di Milano, Milano, Italy

In this presentation, we discuss the possibility of sleep evaluation from signals, which are not usually used for this purpose. In particular, we take into consideration the heart rate variability (HRV) and respiratory signals for automatic sleep staging, arousals detection, and apnea recognition. This is particularly useful for wearable or textile devices that could be employed for home monitoring of sleep for subjects at risk, such as cardiological patients. The HRV and the respiration are analyzed in the frequency domain, and the statistics on the spectral and cross-spectral parameters put into evidence the possibility of a sleep evaluation on their basis. Comparison with traditional polysomnography (PSG) revealed a classification accuracy of 89.9% in rapid eye movement (REM) non-REM sleep separation and an accuracy of 88% for sleep apnea detection. Additional information can be achieved from the number of microarousals or arrhythmia detection. The obtained results support the idea of automatic sleep evaluation and monitoring through signals that are not traditionally used in clinical PSG, but can be easily recorded at home through wearable devices (for example, a sensorized T-shirt) or systems integrated into the environment (a sensorized bed).

I-4:LO6 Wearable Hybrid Sensor Array for Motor Cortex Monitoring

R.A. SHOURESHI, New York Institute of Technology, New York City, NY, USA; **C.M. AASTED**, University of Denver, Denver, CO, USA

As part of the goal of developing wearable sensor technologies, we have designed and built a hybrid sensor headset for monitoring brain activity. Through the use of electroencephalography and near-infrared spectroscopy, the sensor array is capable of monitoring neural activity across the primary motor cortex and wirelessly transmitting data to a computer for real-time processing to generate control signals, which are transmitted to wireless devices for various applications. This paper focuses on current results using this technology for artificial limb control and discusses the development of the headset as well as the neural networks employed for processing motor cortex activity and determining the user's intentions. Initial results relevant to artificial limb control are presented and discussed, including the performance of the system when actuating an artificial limb with four degrees of freedom. Our headset provides a more natural control mechanism than traditional solutions, through the use of direct brain control. The technology resulting from this research is currently also being investigated for application in areas including phantom limb pain treatment, robotic arm control, general brain-computer interfaces, lie detection, and even a video game interface.

I-4:LO7 BSN-based Activity Classification: A Low Complexity Windowing-&-Classification Approach

M. GIUBERTI, G. FERRARI, University of Parma, Parma, Italy

Wireless sensor networks (WSNs) are becoming more and more attractive because of their flexibility. In particular, WSNs are being applied to a user body in order to monitor and detect some activities of daily living (ADL) performed by the user (e.g., for medical purposes). This class of WSNs are typically denoted as body sensor networks (BSNs). In this paper, we discuss BSN-based human activity classification. In particular, the goal of our approach is to detect a sequence of activities, chosen from a limited set of fixed known activities, by observing the outputs generated by accelerometers (and, sometimes, gyroscopes and magnetometers) at the sensors placed over the body. In general, our framework is based on low-complexity windowing-&-classification. First, we consider the case of (time-wise) disjoint activities; then, we extend our approach to encompass a scenario with consecutive non-disjoint activities. While in the first case windowing is separate from classification, in the second case windowing and classification need to be carried out jointly. The obtained results show a significant detection accuracy of the proposed method, making it suitable for healthcare monitoring applications.

I-4:IL09 Ultra Low Power Signal Processing for Wearable Computers

R. JAFARI, The University of Texas at Dallas, Richardson, TX, USA

Continuous and real-time monitoring of human activities has numerous applications in health-care and wellness domains. Light-weight wearable

computers utilizing inertial sensors are ideal for real-time monitoring. However, power requirement is a major obstacle for miniaturization of wearable systems, due to the need for sizable batteries. We propose an ultra low power hierarchical decision making architecture which can be viewed as a tiered wakeup circuitry. The significant power saving is achieved by performing a preliminary ultra low-power signal processing and hence, keeping the microcontroller off when the incoming signal is not of interest. The preliminary signal processing is performed by a set of special purpose functional units, also called screening blocks. This hierarchical architecture attempts to reject the signals that are of not interest as early as possible, keeping the remaining screening blocks inactive. We consider a set of tunable parameters, namely bit resolution and number of samples, to introduce power vs. accuracy trade-offs for screening blocks. We propose a methodology for finding the optimum set of screening blocks, minimizing the power while an accuracy constraint is maintained. Our experimental results illustrate the efficacy of the proposed approach.

Session I-5

Healthcare Applications

I-5:IL01 Capturing Surrogate Signs - The Role of BSN for Disease and Rehabilitation Management

GUANG-ZHONG YANG, The Hamlyn Centre, Imperial College London, UK

One of the key motivations for Body Sensor Network (BSN) research is to provide "ubiquitous" and "pervasive" monitoring of physiological and biochemical parameters in any environment without activity restriction. The purpose of this talk is to address the use of surrogate signs for pervasive monitoring and discuss how BSN can contribute towards this new paradigm of patient care. We will use the monitoring of post-operative recovery of patients undergone minimally invasive surgery as the exemplar to demonstrate the sensing, data analysis, and behaviour profiling involved. The talk will also present our clinical experiences in using surrogate signs for assessing the efficacy of rehabilitation programmes and associated technical challenges in sensor design and embodiment. Technically, the talk will cover the use of bio-inspired design for providing distributed inferencing and ultra-low power on-node processing, demonstrating how this alternate paradigm based on the strategies used by biological systems can be used to deal with the challenges of scale, complexity, heterogeneity, and uncertainty involved in pervasive sensing and long-term behaviour profiling as required for capturing surrogate signs for pervasive sensing.

I-5:IL02 Remote Monitoring for Chronic Disease Management

M. SARFAZADEH, UCLA, Computer Science Department, Los Angeles, CA, USA

Many of the largest information technology industry leaders today have turned their attention to Wireless Health with wireless services, new personal hardware products, search technologies that focus on health and wellness with data and guidance. The impact on individuals is also unprecedented with individualized, lifetime, health promotion, services that join consumer fitness and entertainment, disease management, and a major advance in geriatric care with individualized guidance and monitoring for individuals in their homes and institutions. Research in wireless health is radically different from research in other areas of Computer Science and Engineering. In this talk we will review key ingredients of a successful research paradigm in Wireless Health. We use Remote Health Monitoring Systems as a case study. We will concentrate on Congestive heart failure, a chronic condition that is a leading cause of hospitalization in the world and a major part of the rising health care costs.

I-5:IL03 Brain Computer Interfaces for Spinal Injured Patients

H. LAKANY, University of Strathclyde, Department of Bioengineering, Glasgow, UK

Brain machine interfaces attempts to establish a direct channel for communication between brain and a machine that overrides normal

nervous system pathways. The concept of operation of Brain machine interfaces potentially offer people with severe motor disabilities means to translate specific brain activity to control assistive devices contributing to restoration of their independence and improving their quality of life. In this talk, we review current research in the field of Brain computer interfaces for spinal cord injured patients and discuss the main challenges to implementation of real-time systems that suitable for this particular patient group. We introduce our Strathclyde Brain Computer Interface (S-BCI) which uses a virtual electric wheelchair platform to develop and test the BCI technology. We shall then compare its performance to other BCI systems. A discussion on how BCIs could be used as assistive devices and in rehabilitation to augment brain plasticity and what is required to improve performance of BCI systems. The talk concludes with a set of recommendations for the design and implementation of BCI for spinal injured patients.

I-5:LO4 Smart Healthcare Textile Sensor System for Pervasive Realtime Health Monitoring

P. RAI, P. SHYAMKUMAR, S. OH, H. KWON, G.N. MATHURA, V.K. VARADAN, M.P. AGARWAL, Dept. of Electrical Engineering, University of Arkansas, Fayetteville, Arkansas, USA; Biomedical Engineering, University of Arkansas, Fayetteville, Arkansas, USA; Global Institute of Nanotechnology, Fayetteville, Arkansas, USA

Physiological parameters- multi-lead Electrocardiograph (ECG), Heart rate variability, blood pressure, pulmonary function and core temperature are essential for medical treatments. A portable and wearable system, which can record them simultaneously, and transmit them for diagnosis and archiving, can make pervasive health monitoring possible. Design and testing of such a smart healthcare textile system is presented here. A wearable textile based solution with Flexible dry electrode technology was implemented for ECG. Additionally, an innovative plethysmographic blood pressure monitoring system was designed and tested as an alternative to a sphygmomanometer. The system has been evaluated with conventional health monitoring equipment. Long term testing of the system is also presented to evaluate its performance and consistency. The sensor systems were tested and conditioned for daily activities of patients such as walking and running, and to accommodate basic textile features like washability for reuse. The flexible wireless protocol was shown to enable the textile system to transmit the data to a remote server for observation and post processing. It can facilitate point of care medicine and streamline ambulatory medicine.

I-5:IL05 Wearable Inertia Sensor Application in the Rehabilitation Field

T. TAMURA, M. SEKINE, H. MIYOSHI, Y. KUWAE, T. FUJIMOTO, Chiba University, Graduate School of Engineering, Chiba, Japan

For the aged society, the physical activity of daily living is important to improve the quality of life. The simple quantitative evaluation of physical activity as well as rehabilitation is required. We have developed wearable inertia sensors as well as evaluating system. We evaluated parameters such as RMS and autocorrelation function of stride and step for common neuro-physiological test in rehabilitation. The normal and fall-risk subjects were performed the 10 m trial. Furthermore obtained data from the wearable motion sensor were compared to the general estimation parameters such as performing time and Activities of Daily Living (ADL) score. In 10 meter trial, the result indicated that the ADL score is weakly correlated to the RMS of acceleration signal. However, the relationship between walking speed and RMS was highly correlated. The ADL score is general daily living activities and the walking is one of daily activities. The walking speed, RMS and auto-correlation function of step and stride were significantly different between normal and fall-risk subjects. In conclusion, the obtained acceleration and angular velocity signals may help us the evaluation of daily activities and rehabilitation training quantitatively.

Poster Presentations

I:P01 Towards ZnO-based Implantable Biosensing Devices

S. ELZWAWI, H-K, KIM, R. HEINHOLD, M.W. ALLEN, Department of Electrical and Computer Engineering, University of Canterbury, Christchurch, New Zealand, and The MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand

ZnO is a non-toxic, biocompatible semiconductor with many attractive properties for the fabrication of biosensing devices. These include a wide direct band gap (3.37 eV), adsorbate sensitive surface electron layers, large spontaneous and piezoelectric polarizations, and a high isoelectric point. Combined with the availability of low cost techniques for the growth of thin films and a wide range of nanostructures, these properties can be harnessed to fabricate the main components necessary for self-powered implantable biosensing devices on a single ZnO substrate. These components include (i) high quality biosensing Schottky contacts, (ii) thin film MESFET transistors with selective biosensing Schottky gates, (iii) miniature surface acoustic wave structures for wireless communication, and (iv) Schottky contact rectified piezoelectric nanopower generators¹⁻³. In this paper, we present a methodology for the reliable fabrication of high performance Schottky contacts to ZnO thin films and nanostructures which provide the key building block for many of the above device components, and discuss the biosensing potential of ZnO MESFET transistors.

1. Allen et al, *Appl. Phys. Lett.* 91, 053512 (2009); 2. Yeh et al, *Adv. Mater.* 21, 4975 (2009); 3. Wang et al, *Science* 316, 102 (2007).

I:P03 Implantable Measurement System for Dairy-cattle Monitoring with Long Recording Time

A. BJARNASON, T. VUORELA, J. VERHO, J. RIISTAMA, J. VAISANEN, J. VANHALA, J. LEKKALA, J. HYTTINEN, Tampere University of Technology, Tampere, Finland

The paper describes a new implantable measurement system, further developed from an implantable measurement device implemented earlier at Tampere University of Technology, to assess the psychophysiological well-being state of Dairy-Cattle. By measuring single-channel Electrocardiogram (ECG), body temperature and activity of the cattle we provide veterinarians and animal scientists with a tool to assess cattle stress and well-being. This information can be linked e.g. to the cattle milk production. The new device has a real-time signal processing on-board to derive the heart rate from the ECG signal as well as a wireless radio frequency transmission of the data from implant to a receiver device attached on the collar of the cattle. By collecting the data through a wireless link we are able to extend the recording period from three weeks of the earlier version of the device up to 3 months. The algorithm for the ECG peak detection is a modified version of the Pan-Tompkins algorithm optimized for cattle application with ECG recordings based on approximately 2500 hours of data collected from previous experiments and recordings.

I:P04 Basic Characteristics of RFID Antenna for Urination Detection

H. NAKAJIMA, M. TAKAHASHI, K. SAITO, K. ITO, Chiba University, Chiba, Japan

RFID (Radio Frequency IDentification) system has been expected to be expanded in new fields. Therefore, this report shows a sensing system for urination by attaching an RFID tag to a paper diaper. If the paper diaper is dry, the RFID tag embedded in it can communicate with Reader installed at the end of a bed. In contrast, if it is wet, being prevented by urination, the tag cannot communicate. Thus urination could be checked by change of the characteristics. As the result, it could be possible to reduce physical and mental strain of both patients and their care personnel. Hence, the tag antenna was designed and the characteristics of the antenna were calculated. In addition, it was measured by use of a phantom. When the paper diaper was dry, the reflection coefficient of the antenna (S11) was enough for impedance matching at 950 MHz. On the other hand, when it was wet, S11 got worse. Moreover the gain of foot direction is important because Reader is installed in this direction. Although the antenna gain exceeded the target in the case of the dry diaper, it fell below the target in the case of the wet diaper in this direction. The results show that urination considerably changes the antenna characteristics and that this system can be used to detect the urination.

Biomedical Applications of “Smart” Technologies

Oral Presentations

Session J-1

Active and Stimuli Responsive Biomaterials

J-1:IL01 Design and Development of Light Sensitive Chitosan Based Nanocarriers for Gene Delivery

N. DUCEPPE, **M. TABRIZIAN**, Biomedical Engineering Department, McGill University, Montreal, Quebec, Canada

A multifunctional, and photo-inducible nanoplex made of chitosan (Ch) and hyaluronic acid (HA) is developed for delivery of nucleic acid. Self-assembled Ch/HA nanoparticles was attached to ortho-nitrobenzyl (o-NB) photo-labile molecules (PL)-gold nanoparticles via thiol groups and to QDs-conjugate ssDNA through amide bond linkage to form nanoplexes. The composition of DNA nanocarriers was validated by transmission electronic microscopy, energy dispersive x-ray spectroscopy, gel electrophoresis and spectrophotometry. Both the change in zeta potential (34 ± 11 to -29 ± 6 mV) and the loss of the o-NB characteristic peaks in nuclear magnetic resonance spectra, after the exposure of the PL molecule to ultraviolet-A light, confirmed the photo-labile properties of the system. The potential of the nanoplexes to induce transfection was assessed by flow cytometry and fluorescent microscopy imaging. Over 30% transfection of HEK-293 was obtained with the nanoplex after a one-minute exposure of cells to UV light. This corresponds to a 15 % increase in the transfection efficiency compared to unexposed Ch:HA:AuPL nanocarriers. This high transfection efficiency was associated with the unique design of the carrier system and its photo-responsiveness feature for facilitating the DNA release.

J-1:IL02 Movable Polyrotaxanes for Enhancing Multivalent Interaction with Receptor Proteins

N. YUI, Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University, Tokyo, Japan

Modulating cellular response to foreign surfaces is crucial on designing biomaterials for a variety of medical devices. In order to propose the importance of controlling molecular mobility at biomaterials, we have extensively studied a variety of polyrotaxanes, in which many cyclic compounds are freely mobile along a linear polymeric chain. In this paper, a series of polyrotaxane surfaces were prepared from an inclusion complex consisting of alpha-cyclodextrin and poly(ethylene glycol), and their surface properties were characterized in terms of dynamic contact angle, QCM-D, fibrinogen adsorption, ELISA assay of adsorbed fibrinogen, and platelet adhesion. Also, mannose-immobilized polyrotaxanes were prepared from azidated polyrotaxanes, and their interaction with a receptor protein, Concanavalin A, was analyzed by SPR and FRET measurements. The results strongly emphasize the effectiveness of polyrotaxane structures on preventing unwilling body reactions and enhancing multivalent interaction with the receptor protein. It is considered that the molecular movability, including the sliding and rotation of cyclic compounds threaded onto a linear chain, in the polyrotaxanes plays a dominant role on these events.

J-1:IL03 Smart Nano-bio Materials within Cellular Machinery

E.A. ROZHKOVA, Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL, USA

Interfacing of Nanotechnology with Life Sciences is cross-cutting field of research that is expected to overcome emerging challenges of

civilization, including sustainable energy supply, information storage and advancing of health technologies. Bionanotechnology is a multidisciplinary challenge directed to developing of smart materials capable of guiding, controlling and altering important biological pathways. Nanoscale materials that possess specific physical or chemical functionalities can implement energy transduction or transformation in vivo under external stimulus application. Once these materials are integrated with biomolecules they synergistically combine physical properties of inorganic material and the biorecognition function of bioorganic moieties. Such engineered nano-bio hybrids can be interfaced with living cells, the elementary functional units of life for bio-actuation via altering intracellular biochemical pathways. I will focus on our efforts to develop smart nanobio hybrid materials, and to study their performance within cellular machinery under application of external stimuli, such as light or magnetic fields.

1. EA Rozhkova, *Adv Materials* 2011; 2. Kim, Rozhkova, Novosad et al, *Nature Materials* 2010; 3. EA Rozhkova, I Ulasov, T Rajh et al, *NanoLetters* 2009.

J-1:IL04 Design of Biodegradable Injectable Polymers Exhibiting Temperature-responsive Sol-gel Transition

Y. OHYA, Department of Chemistry and Materials Engineering, Kansai University, Suita, Osaka, Japan

Biodegradable polymers exhibiting sol-gel transition between room temperature and body temperature are expected to be useful as injectable polymers in biomedical applications. Such polymer solution would be in a sol state in a syringe at room temperature but would then become a hydrogel in situ after injection into the body without any cross-linkers, which may be toxic. Such systems would easily entrap pharmaceutical agents, cells or growth factors and form a depot by a simple syringe injection at a desired site, where the depot acts as a sustained drug delivery system or a cell-growing scaffold for tissue regeneration. To exhibit a temperature-responsive sol-gel transition in water, such polymers should possess amphiphilicity with a delicate balance of hydrophilicity and hydrophobicity. Moreover, mechanical strength of the gel formed is also important to be applied as biomaterials. In this presentation, our recent results are reported on the syntheses and biomedical applications of branched amphiphilic copolymers consisting of biodegradable polylactide (PLA) and biocompatible poly(ethylene glycol) (PEG) exhibiting temperature-responsive sol-gel transition, high mechanical strength in gel state, and good biocompatibility.

J-1:IL05 Ureido-polymers Exhibiting UCST-type Phase Transition Behavior under Physiologically Relevant Conditions

N. SHIMADA, M. NAKAYAMA, A. KANO, **A. MARUYAMA**, Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka, Japan

There are few examples of polymers that exhibit upper critical solution temperature (UCST) behavior under physiological conditions of temperature, pH and ionic strength. In this study, we demonstrated that polymers with ureido groups undergo UCST-type phase transitions under physiologically relevant conditions. Poly(allylurea) copolymers showed UCST behavior at pH 7.5 in 150 mM NaCl even at the low polymer concentration of 0.13 mg/ml. Their phase separation temperatures (T_p) could be controlled up to 65 °C. Similar thermosensitivity was observed with copolypeptides consisting of L-citrulline having an ureido group. This is the first demonstration of a non-vinyl polymer that shows UCST behavior under physiologically relevant conditions. We suggest that the ureido modification will be useful for production of polymer materials with UCST behavior in aqueous media.

J-1:IL06 Engineering Synthetic Hydrogels as Functional Stem Cell Microenvironments

M.P. LUTOLF, Institute of Bioengineering, EPF Lausanne, Switzerland

Proper tissue maintenance and regeneration relies on intricate spatial and temporal control of biochemical and biophysical microenvironmental cues that instruct stem cells to acquire particular fates. Despite progress in our understanding of key signaling pathways regulating stem cell fate, to date, many stem cell populations cannot be efficiently cultured in vitro without rapidly changing their properties. To address this challenge, we have been developing biomaterial-based approaches to display and deliver stem cell regulatory signals in a precise and near-physiological fashion, serving as powerful artificial microenvironments ('niches') to manipulate stem cell fate both in culture and in vivo. In this talk I will highlight recent efforts in my laboratory to develop microarrayed artificial niches based on a combination of biomolecular hydrogel and microfabrication technologies. These platforms allow key biochemical characteristics of stem cell niches to be mimicked and the physiological complexity deconstructed into a smaller, experimentally amenable number of distinct signaling interactions.

J-1:L07 Responsive Janus Hydrogels

SUNAE HWANG, SONA LEE, JONGHWI LEE, Chung-Ang University, Seoul, South Korea

Anisometric structures of materials have attracted intense research interests since they are considered to open up novel capabilities and related applications. In here, Janus particles of biocompatible polymers were prepared and their unique properties were explored. Chitosan-alginate Janus particles were prepared by ionic gelation for the development of biocompatible embolic particles. They showed self-aggregation behavior through their own surface charges, which was dependent on various external stimuli such as pH, and salt concentrations. Apparently, the disc-like shape of these particles promoted the formation of complete self-aggregated hydrogel clusters. Anisometric hydrogels showed a slower swelling rate and a lower equilibrium swelling ratio than their control symmetric hydrogels. Overall, by controlling the morphology and structure of Janus hydrogels, a wide range of mechanical and swelling properties are available from novel applications. These particles could provide intelligent functionality to the current embolization technology and other particle applications.

J-1:IL09 Nanomaterials Improve Cellular Interactions for Medical Implants

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Nanomaterials provide unique biomimetic characteristics and special physicochemical, biological, surface, and mechanical properties in controlling cell functions. Managing adhesion and differentiation of specific type of cells is critical for tissue regeneration and the success of medical implants. This talk will present examples of nanomaterials that have been developed to improve cellular interactions and tissue growth. The first study investigated the effects of nanophase ceramics, nano-ceramic/polymer composites and a bone morphogenetic protein derived short peptide on the functions of human mesenchymal stem cells (hMSCs). The results showed that the nanocomposites promoted the hMSC adhesion and osteogenic differentiation. Next, nanostructured hydroxyapatite coatings were developed to address the critical challenges in controlling biodegradation and tissue integration of novel magnesium-based implants. The degradation results suggest the nanocoatings positively mediated magnesium degradation; thus allowing implants to maintain mechanical strength throughout the healing process, and then to degrade when new tissue grows. In summary, nanomaterials are promising for use in medical implants and should be further studied for clinical translation.

Session J-2 Enabling Tools

J-2:IL01 FluidFM: A Force-controlled Nanosyringe for Single-cell Studies and More

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Glass micropipettes are the typical instrument for intracellular injection, patch clamping or extracellular deposition of liquids into viable cells. The micro pipette is thereby slowly approached to the cell by using micro manipulators and visual control through an optical microscope. During this process, however, the cell is often mechanically injured which leads to cell death and failure of the experiment. To overcome these challenges and limitations of this conventional method we developed the FluidFM technology, an evolution of standard AFM microscopy combining nanofluidics via cantilevers with integrated microfluidic channel.¹ The channel ends at a well defined aperture at the apex of the AFM tip while the other extremity is connected to a reservoir. The instrument can therefore be regarded as a multifunctional micropipette with force feedback working in liquid environment. We are focussing on three applications for single-cell biology: i) displacement² and adhesion of microorganisms, ii) force-controlled formation of gigaseal, and iii) single virus deposition on cell surfaces. Yet, the FluidFM is suited for local surface-chemistry experiments too.

1. Meister et al, *Nano Lett.* 9 (2009) 2501; 2. Dörig et al, *Appl. Phys. Lett.* 97 (2010) 023701.

J-2:IL02 Microfluidic Devices for Cancer Cell Capturing

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Isolating Circulating Tumor Cells (CTCs), which are present at ratios as low as 1 to 10 per billion blood cells is however extremely challenging. Recently, microfluidic CTCs capture devices have come to the fore, providing enrichment levels up to 2 orders of magnitude higher than previous methodologies (e.g. magnetic cell sorting using magnetic beads covalently conjugated with anti-epithelial-cell adhesion-molecule [EpCAM] antibodies). Building on these recent developments, new devices are being designed that may help identify advanced breast cancer patients who are candidates for trastuzumab- (herceptin) based therapy. Plasma-based polymerization processes were used to make the device readily amenable to conjugation with monoclonal antibodies which bind with high affinity to the target cancer cells. Using the breast cancer cell line SK-BR-3 as a model for cells overexpressing HER2, a ~80% immuno-capture efficacy of HER positive cells from full blood for the herceptin functionalized PDMS in model and validation studies.

J-2:IL03 New Methods of Bioanalysis using Functionalised Nanoparticles and SERS

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Functionalized nanoparticles have been used in a number of different studies including detection of DNA at ultra low levels, immuno histochemistry and more recently as substrates for surface enhanced resonance Raman scattering (SERRS) based imaging approaches. The advantages of using metallic nanoparticles are that they are very bright in terms of their optical characteristics and also if functionalized in a particular manner to provide a SERRS response give a unique vibrational fingerprint. Here we present the functionalization of gold and silver nanoparticles in such a way that the enhancement effect can be greatly increased through biological recognition and as such effectively turns on the SERRS effect. This process can give rise to exquisite selectivity in terms of the interaction of the nanoparticles, especially when DNA hybridizations are used and single base mismatches can be analyzed at room temperature. Dye oligonucleotide silver nanoparticles (DOSN) have also been used to detect double stranded DNA through triplex formation to switch on the SERRS and a distance relationship between nanoparticles and SERRS response established for the first time. In an advancement of this approach functionalized nanoparticles have also been used as imaging agents for single cells and when functionalized with an appropriate antibody can give back information on the expression of specific receptors on cell surfaces as well as sub-cellular compartmentalization information. Finally in moving away from the in vitro applications the functionalized nanoparticles can be modified

in such a way that they are active in vivo and preliminary data relating to in vivo studies of imaging and therapeutic uses of functionalized SERRS active nanoparticles will also be presented.

J-2:IL04 Metallic and Composite Functionalized Plasmonic Nanoparticles for Biomedical Applications

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Fabrication of plasmon-resonant metallic and composite nanoparticles and their applications to engineering, biosensors, and biomedicine present a new rapidly growing field of nanobiotechnology and biophotonics. Here, we give a short review of our recent work on fabrication, optical properties, functionalization, and biomedical applications of plasmon-resonant metallic and composite nanoparticles. Our experimental examples include gold nanospheres, gold and gold/silver nanorods, gold nanoshells with silica cores, silver nanocubes and gold/silver alloy nanocages. Several methods for spectral tuning of plasmon resonances through variations in size, shape, and structure of particles are discussed. We also describe novel composite nanoparticles consisting of a gold/silver nanocage or gold nanorod core and a mesoporous silica shell doped with the photodynamic sensitizers. These nanocomposites seem an attractive theranostic platform for simultaneous diagnostic and photodynamic therapy owing to photosensitizer and for plasmonic photothermal therapy owing to plasmonic core. Finally, we consider applications of functionalized nanoparticle bioconjugates to dot immunoassays, dark-field light microscopy imaging, and laser photodynamic and photothermal therapies.

J-2:IL06 Investigation of Cell-nanostructure Interactions with Force Microscopy

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For a systematic investigation of adhesion between living cells and smart materials, techniques must be available that allow studying cellular interactions at the cellular and sub-cellular level. We are using a method that is based on atomic force microscopy for characterizing the adhesion forces of cells with Piconewton resolution at timescales from a few seconds up to several days. In the experiments, a cell is attached to a functionalized cantilever. Then, the cantilever is retracted and the detachment force is recorded. We have recently applied this method to quantify the adhesion strength of fibroblast cells to nanostructured surfaces. These nanostructured surfaces are produced using a self-assembly process (diblock-copolymer micelle nanolithography) and provide anchorage points for single cellular adhesion receptors (integrins) in a quasi-hexagonal lattice with nanometre resolution. By analysing cell adhesion forces at different timescales, we found that the nanoscale spacing between individual integrins in the cell membrane cooperatively controls the strength of cell adhesion, the stability of adhesion clusters and cell elasticity. We are currently extending our work towards studying the effects of external stimuli on cell adhesion forces.

J-2:IL07 Self-folding Polymers Enable Microfluidics with a Twist

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We describe the reversible self-folding of polymeric films into intricate 3D microfluidic networks and investigate their utility as bio-inspired synthetic vasculature for in vitro tissue culture models. We first characterize the self-folding mechanism, whereby initially planar films self-fold into curved geometries due to stress gradients that arise from differential ultraviolet (UV)-crosslinking and solvent conditioning; films reversibly curve/flatten upon film desolvation/resolvation. We controlled film curvature by varying film thickness and UV exposures and we achieved wafer-scale assembly of micropatterned geometries including

helices, polyhedra and corrugated sheets. We then describe self-folding microfluidic networks. We demonstrate localized 3D chemical delivery of biochemicals to discrete regions of cells (1) cultured on the curved self-assembled surfaces and (2) cultured in a thick, surrounding hydrogel. Our methodology is compatible with planar microfabrication techniques and effectively harnesses the many strengths of self-assembly and microfluidics to enable chemical delivery in 3D. Judicious layering of pores, serving as sources and sinks, may enable spatiotemporal control over the 3D microchemical environment.

M. Jamal et al, Nature Communications (2011; in press)

Session J-3

Medical Diagnostics and Imaging

J-3:IL01 Single Molecule Tracking in Live Cells

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Tracking individual nano-objets in live cells during arbitrary long times is a ubiquitous need in modern biology. We present methods for the detection and tracking of small absorbing nanoparticles on live cells. One of the most promising relies on the photothermal effect and the detection of the Laser Induced Scattering around a NanoAbsorber. We show that this technique provides a unique potential to record arbitrary long trajectories of proteins labelled with a tiny non-fluorescent nanoparticle. Applications of single molecule methods in neurobiology will be presented.

J-3:IL02 MRI Tracking of Transplanted Stem Cells

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Noninvasive in vivo imaging of transplanted stem cells is an effective method to clarify the mechanisms involved in stem cell transplantation therapy. Conventionally, SPIO particles were used for MRI tracking of the stem cells due to its high sensitivity. However, it was recently pointed out that the SPIO particles are exocytized as time and the free SPIO may be taken up by macrophage, resulting in the misunderstanding of the fate of the transplanted stem cells. We then developed water-soluble polymeric MRI contrast agent composed of gadolinium (Gd) and bio-inert water soluble polymers, which was designed to be excreted into the urine when it comes out of the cells. This property results in a very powerful MRI tracking system only for the living cells. We labeled rat mesenchymal stem cells or endothelial progenitor cells with the contrast agent, and the stem cell differentiation plasticity, in vivo survival, and migration in ischemic limbs were investigated. Interestingly, survival and migration of the transplanted stem cells were greatly affected not only by the kind of stem cells but also the ischemic/non-ischemic situation. These phenomena were first quantitatively observed by using our novel cell tracking system.

J-3:IL03 Immuno-pillar Chip: New Platform as a Diagnostic Tool for Diseases

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Recently, a concept of "protein profiling of human plasma", where a lot of plasma proteins are measured at the same time, has paid much attention for clinical diagnostics. By measuring several proteins which are correlated strongly with disease, we are expecting that a highly accurate diagnosis becomes possible. We are advancing the research aiming at the development of a plasma profiling device for clinical diagnostics. Recently, we developed a new device called an "immuno-pillar chip", which has the desired features for a plasma profiling device. It has hydrogel pillars (diameter: 200 µm, height: 50 µm) fabricated inside a microchannel, with many antibody molecules immobilized onto 1 µm diameter polystyrene beads. For detection of disease markers, we confirmed that the chip provides rapid analysis (total assay time: 4-12 min) with high sensitivity, it is easy-to-use (no special skills are needed), and it uses small volumes of the sample and reagent (0.25 µL each for plasma or 2 µL each for whole blood). Moreover, multiplex assay for

three biomarkers was also possible. We are working on the development of a multi-biomarker detection chip for the diagnosis of diabetic nephropathy by using this device in cooperation with the Department of Medicine at Nagoya University now.

J-3:IL04 In Situ Orthopaedic Sensors

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Although improvements have been made in implant design to increase bone formation and promote successful osseointegration using nanotechnology, the clinical diagnosis of early bone growth surrounding implants remains problematic. The development of a device allowing doctors to monitor the healing cascade and to diagnose potential infection or inflammation is necessary. Biological detection can be examined by the electrochemical analysis of electron transfer (or redox) reactions of extracellular matrix proteins involved in bone deposition and resorption. The use of nanomaterials as signal amplifiers in electrochemical sensors has greatly improved the sensitivity of detection. Nanotechnology-enabled electrochemical sensors that can be placed on the implant surface itself show promise as self-diagnosing devices in situ, possibly to detect new bone growth surrounding the implant and other cellular events to ensure implant success. This talk will address the significance of developing a bone-growth sensing device, which converts the cellular process into a readable electrical signal, and could revolutionize current methods of medical diagnosis. Also discussed will be supporting technologies and recent advances in other sensing devices for orthopaedic applications.

J-3:IL07 DNA-functionalized Nanoparticles for Biosensing

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DNA-modified nanoparticles disperse in an aqueous medium due to electrostatic repulsion between anionic phosphate groups in the DNA backbone. Interestingly, when complementary single-stranded DNA, whose base number is identical to that of the DNA on the surface, is added to the dispersion of DNA nanoparticles to form the fully matched double helix on the surface, the DNA nanoparticles become unstable and spontaneously form aggregates in a non-crosslinking manner. Furthermore, we have found that the double-stranded DNA-carrying nanoparticles acquire high colloidal stability to disperse in an aqueous medium when a terminal single-base mismatch exists at the interface between the DNA corona and the disperse medium. Exploiting the unique colloidal behavior of the DNA nanoparticles, we have devised a facile single-nucleotide polymorphism genotyping method. We applied the SPR imaging technique on our original, power-free microfluidic devices to the detection of the nanoparticles aggregation. Through a combination of non-crosslinking aggregation of DNA nanoparticles and molecular recognition by aptamers or aptazymes, we have also developed analytical systems for detecting cGMP, ATP, FMN, theophyllin, and Hg(II).

J-3:IL08 Single Gold Nanorod Detection Using Confocal Light Absorption and Scattering Spectroscopy

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There is a significant clinical need for novel molecular imaging approaches that can be used in clinical environments in humans for early detection of disease. In recent years, a number of groups have demonstrated that optical fluorescence-based spectroscopic and imaging approaches could potentially address this need. However, despite significant advances in developing highly specific fluorescence probes, optical molecular imaging approaches are not used to their full potential in humans, either in research or clinical environments. There are two main reasons for that: (1) optical technologies are limited by fluorescent label optical signals, which are inherently weak and incapable of penetrating several centimeters of tissue, and (2) the brightest fluorescent labels are usually highly toxic and cannot be used in humans. Recently significant attention has been directed toward applications of metal nanoparticles to medical problems. Gold nanorod-based labels have the potential to overcome both problems mentioned above. However, samples containing a large number of gold nanorods usually exhibit wide spectral lines. This linewidth limits the use of nanorods as effective molecular labels, since it would be difficult to simultaneously image several types of nanorod markers uncontrolled for aspect ratio. We measured native scattering spectra of single gold nanorods with the confocal light absorption and scattering spectroscopy (CLASS) system

we recently developed, and found that single gold nanorods have a narrow spectrum as predicted by the theory. That suggests that nanorod-based optical molecular markers with controlled narrow aspect ratios should provide spectral lines sufficiently narrow for effective biomedical imaging.

J-3:L09 Nanoparticles for Detection of a Deadly Virus Using a Co-localization Strategy

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Hendra virus is a new and deadly emerging pathogen, which was first detected after an outbreak in 1994 in Australia resulting in the death of horses and humans. Since 1994, there have been more than 30 outbreaks with annual occurrence since 2006. The serious damage to livestock and the public health threat to the human population have attracted the attention of the Australian government and the general public. Early detection of Hendra virus will be essential for any successful countermeasure strategies, but a Hendra virus biosensor is not commercially available at the moment. This work shows the possibility to detect Hendra virus in a biological sample through the use of functional particles conjugated with Hendra virus-specific antibodies. The virus is revealed by the simultaneous presence of two different types of functional particles; this strategy is called "co-localization". The developed method has been compared to the state-of-the-art of the Hendra virus detection. The possibilities offered by this strategy represent a proof-of-concept for the development of a fast and portable Hendra virus biosensor. The same principle and device should be applicable to other emerging viruses in the future.

J-3:L11 Random, Aligned and Patterned Coaxially Electrospun Fibres as Biomimetic Materials in Medical Imaging

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Random, aligned and patterned hollow core-shell structured fibres were prepared by the coaxial electrospinning of polycaprolactone (PCL) and polyethylene oxide (PEO), using a multi-axis translational stage. The effects of various process parameters including applied voltage, working distance and shell/core flow rate on the size and morphology of the resultant fibre deposition were investigated. It has been found that the flow rate ratio of core and shell solutions plays a much more important role in determining the structure of the resulting fibres than the other parameters. A shorter separation distance between the spinneret and the translational stage allows the whipping instability to be suppressed, a straight jet to be formed and the fibres to be aligned and patterned. Complex patterned hollow PCL fibres, such as bent, latticed, crossed obliquely and concentrically circular can be produced, with diameters in the 1-100 micron range. These patterned hollow fibres may have application as biomimetic materials in a range of medical imaging applications, providing ground truth as controllable physical phantoms which mimic both the micro- and macroscopic geometry of neuronal and muscle tissue. An application in diffusion Magnetic Resonance Imaging will be presented.

Session J-4

Tissue Engineering and Regenerative Medicine

J-4:IL01 From Bone to Cartilage to Cardiac Tissue: Nanotechnology-derived Supramolecular Nanotubes for Tissue Engineering Applications

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In this study, two types of DNA supramolecules, helical rosette nanotubes (HRNs) and twin base linker nanotubes (TBLs), with unique surface chemistry and tailorable cytocompatibility properties, were formulated and tested for bone, cartilage, and cardiac tissue applications. Mimicking DNA self-assembling mechanisms, HRNs and TBLs formed by guanine and cytosine motifs organize spontaneously into nanotubes in aqueous solutions without the need for further chemicals, UV light, etc. At several nanometers in diameter and several millimeters in length, HRN and TBL nanotubes have similar dimensions and properties as natural tissues. Using a porcine animal model, HRNs have been used to enhance in vivo bone and cartilage formation, while at the same time suppressing fibroblast and bacteria functions. HRNs have even been used to deliver bone growth factors to further enhance bone growth. HRNs have also been used to deliver difficult to deliver drugs such as anti-cancer Tamoxifen. Moreover, composites composed of poly(2-hydroxyethyl methacrylate) (PHEMA), carbon nanofibers (CNFs) and HRNs have been shown that cardiomyocyte functions were enhanced with increasing amounts of CNFs and HRNs in the composites. In summary, as novel self-assembled chemistries, HRNs and TBLs have demonstrated significant in vitro and in vivo promise for bone, cartilage, and cardiac tissue engineering and, thus, should be further explored as simple injectable materials which can solidify at body temperature alone.

J-4:IL02 Cellular Multilayers as an Engineered Tissue Model Fabricated by Layer-by-Layer Assembly of Cell and Proteins

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Development of artificial three-dimensional (3D) tissues possessing a similar structure and function as natural tissue is a key challenge in tissue engineering and pharmaceutical fields. We developed a simple and unique bottom-up approach, hierarchical cell manipulation technique, using nanometer-sized Layer-by-Layer films consisting of fibronectin and gelatin (FN-G) as a nano-extracellular matrix. The FN-G nanofilms prepared directly on the cell surface acted as a stable adhesive surface for adhesion of the second cell layer. Various 3D-layered constructs consisting of single or multiple types of cells were successfully fabricated, and the multilayered constructs like a blood vessel wall were useful as an in vitro blood vessel model to analyze drug responses. Recently, we also developed a rapid bottom-up approach by a single cell coating using FN-G nanofilms, because fabrication of two-layers is limited through the above technique. This rapid approach easily provided approximately 10~20 layered tissues after only one day of incubation, and fully vascularized tissues with over 1 cm width were obtained by a sandwich culture of the endothelial cells. These hierarchical cell manipulations will be a promising technology to achieve artificial 3D-human tissues.

J-4:L03 Biomimetic Apatite-based Biomaterials: on the Underestimated Impact of Synthesis and Post-synthesis Parameters

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Nanocrystalline apatites are major constituents of hard tissues and attempts are made worldwide to prepare synthetic analogs. However the impact of synthesis/post-synthesis parameters is often underestimated, although their control is essential for precisely identifying

the phases in presence and unveiling potential evolutions. We followed here, by XRD, FTIR/Raman spectroscopies, thermal and compositional analyses, the effects of temperature, pH, maturation time, the presence of foreign ions, drying and sterilization conditions on the physicochemical features of precipitated apatites. Samples prepared with increasing temperature, pH or maturation time are closer to stoichiometry. The presence of foreign ions strongly influences the nonstoichiometry. Evolutions of cell parameters and crystallite dimensions were evidenced from XRD data, depending on synthesis parameters. Freeze-drying allowed to limit alterations and preserve the reactivity of the samples, yet prone to further evolve after re-immersion in solution. Some modifications were detected after autoclave sterilization. This work underlines the need for a good control of synthesis/post-synthesis parameters when dealing with the preparation/production of biomimetic apatites, as well as a complete characterization scheme.

J-4:L04 Surface Cell Growth Engineering Assisted by Novel Protein Nanomaterial and the Impact of Genetic Tailoring on their Properties

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Bacterial inclusion bodies (IBs) are highly pure protein deposits of a few hundred nanometers produced by recombinant bacteria supporting the biological activities of the embedded polypeptides arising a wide spectrum of uses as functional and biocompatible materials upon convenient engineering. The biophysical features of these proteinaceous nanoparticles, such as activity and size, have been never engineered and very few was known about their physicochemical properties. In this study, we have characterized the relevant nanoscale properties of IBs as particulate materials using SEM, DLS, AFM and CM. Moreover, we have also explored how the produced particles can be tailored by simple approaches. Moreover, IBs-grafted patterned surfaces dramatically stimulate mammalian cell proliferation exclusively on the IBs patterned areas, proving the potential of IBs in tissue engineering and regenerative medicine among other promising biomedical applications.

1. E. Vazquez, et al, *Nanomedicine*, 5 (2) (2010) 259-268; 2. E. García-Fruitós, et al, *TIBEC*, 936, (2011) 1-6, in press; 3. C. Díez-Gil, et al, *Biomaterials*, 31 (2010) 5805-5812; 4. (a) Patent ES- P200900045 (b) E. García-Fruitós, et al, *Adv. Mater.*, 21 (2009) 4249-4253; 5. J. Seras-Franzoso, *Nanomedicine*, (2011) in press.

J-4:L05 Engineered Nanostructured Coatings for Enhanced Biointegration of Orthopaedic Implants

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By applying ion beam assisted deposition, we have fabricated pure cubic ZrO₂ coatings with 2-25 nm grain size. Adhesion and proliferation experiments with a bona fide mesenchymal stromal cell line indicated ZrO₂ coatings to be superior in supporting adhesion and growth, as compared to CoCr, Ti and HA. Absorption experiments with fibronectin (FN) from human plasma using ELISA experiments resulted in higher FN adsorption on nanoengineered surfaces as compared to orthopaedic materials. These experiments indicated a clear correlation between cell adhesion and FN adhesion. We examined possible mechanisms of enhanced FN absorption using quantum mechanical calculations to build an atomic model of a designed ZrO₂ nano-pyramidal surface and CHARMM force field parameterization to simulate the 13FN3-14FN3 fragment absorption on the surface. We have found that the immobilization of the FN fragment on the model atomic smooth surface has a lower absolute value of adsorption energy in comparison with the model nano-pyramid surface. Attractive electrostatic interactions

between negatively charged ZrO₂ nano-pyramids and positively charged amino acid residues of the FN fragment results in the FN matrix assembly needed to achieve focal adhesion.

J-4:IL06 Enzyme-mediated Injectable Biodegradable Hydrogel for Biomedical Applications

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Injectable hydrogel systems are widely used in tissue engineering and drug delivery. Hydrogels are formed from polymers through either physical and/or chemical crosslinkages; the latter is non-reversible and thus comparably more stable. Recently, enzymes such as transglutaminase and horseradish peroxidase (HRP) have been utilized to form chemically-crosslinked hydrogels. We have developed hydrogels based on the oxidative coupling of phenols using HRP. Typically, HRP-mediated crosslinking reaction requires the addition of exogenous hydrogen peroxide as the oxidant, the concentration of which controls the extent of phenol crosslinks of the hydrogel. This system does not involve toxic chemicals or reactions in the hydrogel formation process, thus allowing therapeutic proteins, growth factors and cells to be incorporated without damaging these biological molecules. This system also allows us to control the mechanical strength of the hydrogel, while achieving a rapid gelation rate. This feature offers several advantages for controlling the degradation, drug release and cell proliferation or differentiation, while preventing uncontrolled leakage of the bioactive agents during the gelation process *in vivo*.

J-4:LO8 Responsive Biomaterials for Dynamic Cell Culture and Regenerative Medicine

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Physical and chemical cell microenvironment properties have become increasingly recognized as regulators of cellular functions, such as migration and differentiation. While advances have been made in the fabrication of materials for cell culture, the properties of these material systems typically are fixed upon formation. *In situ* control of material properties is needed to study their effect on dynamic cellular processes such as differentiation. Here, we will discuss synthetic approaches for stimuli triggered control of material properties, specifically hydrogel modulus and epitope presentation, via the incorporation of photolytically or enzymatically cleavable sequences within the gel-forming macromers and resulting hydrogels. Utilizing these materials, we will examine the influence of microenvironment structure on cell function, specifically fibroblast and epithelial cell phenotype, toward understanding the role of extracellular matrix signals in disease progression and tissue development. Incorporation of photolytically or enzymatically degradable sequences within monomers and hydrogels enables the design of unique, dynamic cell culture platforms for exploring how real-time changes in properties influence cell fate for regenerative medicine.

J-4:LO9 Morphological Optimization of Silk Fibroin Electrospun Nanofibers for Wound Healing Enhancement

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Due to excellent biocompatibility, silk fibroin (SF), *Bombyx mori*, makes itself an excellent candidate biomaterial to use for tissue engineering. The unique properties of SF provide a wide range of opportunities to create advance scaffold designs which have benefits for cellular response in tissue formation. As the contribution with electrospinning process, this study explored optimal preparation for ultra-fine electrospun SF with high porosity, surface area and ease of production for various purposes. The concentration effect of low molecular weight poly(ethylene-oxide) (PEO 600 kDa) and relative humidity were investigated to fabricate a biomimetic nanostructured matrices by scanning electron microscope (SEM). The average diameter of the individual segment of SF nanofiber was decreased to 290±46 nm after PEO extraction. Furthermore, the potential for use as wound healing material was assessed by *in vitro* evaluation in terms of cellular activities with normal human dermal fibroblast (NHDF) which have been recognized as a representation for damaged tissues in application of wound therapy. Results obtained regarding cell viability, cellular adhesion and proliferation of NHDF on the silk fibroin matrix which could be a potential candidate for bioactive wound healing material.

Session J-5

Targeted Delivery and Release Systems

J-5:LO2 Molecular Chaperon Inspired Biomaterials for Protein Delivery

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The molecular chaperone function is an important concept that is expected to lead to breakthroughs in drug delivery systems, especially for protein delivery. We have reported that amphiphilic polysaccharide nanogels act as artificial molecular chaperone. The nanogels with cancer antigen proteins can trigger an unprecedented immune response, enabling their use in cancer immunotherapy (clinical trials from 2004). The hydrophobic antigen proteins were effectively complexed with the nanogel without aggregation. The complexes (<50 nm) obtained were colloidal stable and effectively internalized antigen-presenting cells. Cationic amphiphilic polysaccharide nanogels have been found to be effective for antigenic protein delivery for adjuvant-free intranasal vaccines. The cationic nanogels were efficiently delivered to myeloma cells and primary T lymphocytes, although these cells were resistant to protein transduction domain-mediated protein delivery. The anti-apoptotic protein Bcl-xL delivered by the nanogels efficiently blocked apoptosis of these cells, establishing functional regulation of cells by proteins delivered by the nanogels. Cationic amphiphilic nanogels is a useful tool to deliver proteins for development of new cancer therapy and immune regulation.

J-5:LO3 Synthesis, Stability, and Release Processes of Submicron Vaterite Containers in Biological Media

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Calcium carbonate as inorganic biomaterial has attracted much attention in recent years owing to its advantages such as chemical stability, bioactivity, biocompatibility for potential applications in drug delivery. Here we report on the synthesis and characterization of porous monodisperse vaterite containers with controllable average sizes from 400nm to 10µm. An elegant release mechanism for enclosed substances via recrystallization is presented. As a model experiment, a fluorescent marker was encapsulated and imaged during the release process by two-photon microscopy. A strong influence of particles size, concentration, and immersion medium on the recrystallization and release was observed. To inhibit recrystallization, containers can be immersed in pure ethanol. To understand the release process in living systems, recrystallization in physiological solution, PBS buffer, and cell culture medium was investigated. Immersion in sodium chloride accelerated the recrystallization with respect to water. In PBS buffer and culture medium, specific ions (such as PO₄-3) stimulated exchange-reactions between particles and the immersion solution, creating an additional recrystallization process and forming new crystal structures (hydroxyapatite), which further accelerated the dye release.

J-5:IL04 Nanoparticle-mediated Drug Delivery: Biophysical Interactions to Therapeutic Applications

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Transport of drugs or drug delivery systems across the cell membrane is a biologically complex process, often difficult to understand because of its dynamic nature. In this regard, lipid model membranes, which mimic many aspects of cell membrane lipids, have been very useful in determining the role of lipids in cellular interaction process. In our studies, we explore model membranes to better understand the interaction of drugs and nanoparticles (NPs) and their significance in improving drug delivery. Interfacial properties of NPs - such as their surface charge, the presence of surface functional groups, and surface hydrophilicity/hydrophobicity - are known to influence the efficiency of NPs in transporting biotherapeutic agents to target tissue. In this regard, studies of the biophysical interactions of NPs with model membranes could provide a simple yet effective approach to understanding the role of

membrane lipids in the uptake and transport of NPs across biological barriers and rational approach for developing efficient nanocarrier systems for various biomedical applications. In our studies, we explored applications of NPs for delivery of therapeutics in conditions such as cancer, stroke, and vascular disorders. The results of these studies will be presented.

J-5:IL05 Stimuli-sensitive Liposomes for Drug Delivery

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We developed highly temperature-sensitive liposomes by surface modification of stable liposomes with thermosensitive polymers, which change their property from hydrophilic to hydrophobic around 40 °C. These liposomes retained drugs at physiological temperature, but released them above the transition temperature of the polymers. When the polymer-modified liposomes encapsulating doxorubicin were administered intravenously to tumor-bearing mice and subsequently mild heating at 43-45 °C was applied to the tumor site, tumor growth was strongly suppressed. We also attempted to prepare multifunctional liposomes with temperature-responsive and imaging functions by the incorporation of dendron-based lipid having Gd-chelates into the temperature-sensitive liposomes. We could follow accumulation of the Gd-lipid-containing liposomes in the tumor with MRI. In addition, we prepared pH-sensitive liposomes, which are destabilized at weakly acidic pH, by surface modification with pH-sensitive polymers having carboxyl groups. These liposomes introduced contents into cytosol of dendritic cells. We found that these pH-sensitive liposomes can be used as an antigen delivery system which induces cellular immunity.

J-5:L07 Hepatocyte-specific Gene Delivery with Galactose-bearing Cationic Polymers with Different Molecular Structures

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The promising virus vector therapeutic results are often limited by the effect of the virus vector itself, thus synthesize an efficient non-viral vector is of prime importance. For this reason, several synthetic materials including cationic polymers have been molecularly designed. Therefore, it is well known that the capability of the polymers of some cationic vinyl monomers to buffer the endosomal pH results in enhanced transfection efficiency, but also in a relatively high toxicity. However, in the last decades, the capacities of polymers bearing pendant carbohydrates (glycopolymers) to reduce the toxicity of the complex and to interact with specific receptors on the cellular membrane have been proved. Thus, since the glycopolymers may not only decrease the toxicity of the cationic chain but also serve as targeting agent, we have rationally designed a new glycopolymer-based gene delivery carrier. The *in vitro* interaction and intracellular trafficking of the carrier/gene polyplexes in hepatocytes and *in vivo* liver targeting was investigated. The specific gene expression and the gene silencing efficiency of these carriers were remarkably enhanced by the introduced pendant carbohydrates.

J-5:IL09 Supramolecular Nanodevices from Functionalized Block Copolymers for Molecular Therapy

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Nanotechnology-based medicine (Nanomedicine) has received progressive interest for the treatment of intractable diseases, such as cancer. Engineered polymeric nanodevices with smart functions play a key role in Nanomedicine, including drug carriers, gene vectors, and imaging probes. This presentation focuses present status and future trend of the development of polymeric nanodevices particularly for drug and gene delivery. Polymeric nanodevices with 10 to 100 nm in size can be prepared by programmed self-assembly of block copolymers in aqueous entity. Most typical example is polymeric micelles with distinctive core-shell architecture. Several micellar formulations of antitumor drugs have been intensively studied in preclinical and clinical trials, and their utility has been demonstrated. Critical features of the polymeric micelles as drug carriers, including particle size, stability, and loading capacity and release kinetics of drugs, can be modulated by

the structures and physicochemical properties of the constituent block copolymers. The development of smart polymeric micelles that dynamically change their properties due to sensitivity to chemical or physical stimuli is the most promising trend, directing to the targeting therapy with high efficacy and ensured safety.

J-5:IL10 Nanostructure Processing of Advanced Biomaterials and Biosystems

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Nanostructured materials are of interest for a variety of applications. Through controlled synthesis in reverse microemulsions, my laboratory has achieved polymeric nanoparticles for the glucose-sensitive delivery of insulin. These stimuli-responsive materials allow for the appropriate insulin delivery to diabetic patients only when their blood sugar levels are high, without the need for external blood sugar monitoring. We have also developed apatite-polymer nanocomposite particles for the sustained, zero-order delivery of protein therapeutics. In addition, nanostructure processing has been employed in artificial implant and tissue engineering applications. For example, we have obtained orthopedic implants and bone scaffolds with superior mechanical strength and bioactivity. By combining microfabrication and nanotechnology, we have also created various microstructures in kidney-specific dimensions and shapes for bioartificial device applications.

J-5:L11 Development of Novel Polyion Complex Vesicles, "PICsomes", and their Biomedical Applications

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Self-assembled fabrication of monodispersed vesicles have recently received much attention from both fundamental and applied standpoints in biomedical field. Previous examples of vesicles usually involves several bothersome processes, including film formation, sonication, thermal treatment, and extrusion, to obtain monodispersed particles with well-controlled sizes. In this study, we report the first example of spontaneously formed unilamellar polyion complex vesicles (Nano-PICsomes) through simple self-assembly of a pair of oppositely charged PEG-block-anioner and homo-cationer in aqueous medium. Vesicle sizes are tunable in the range of 100-400 nm with a narrow size distribution, simply by changing the total polymer concentration. Nano-PICsomes were able to encapsulate various kinds of water-soluble materials in the inner water phase, and the PIC vesicle wall showed semipermeability. Moreover, cross-linking of the vesicle membrane allows tuning of permeability, and enhancement in stability under the physiological condition. Finally, we demonstrated an excellent blood-circulation property of Nano-PICsomes in the bloodstream of mice. Thus, Nano-PICsomes has a great potential for nano-DDS carriers and *in vivo* nanoreactors.

J-5:L12 Enhanced Nanoparticle Delivery Using Fractional Laser Microablation of Skin

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We are proposing a new method of nanoparticle delivery into the skin to the depth up to 400 μm using combined fractional laser microablation of the skin surface and the ultrasonic treatment. Fractional laser microablation was used to overcome the protective skin barrier. The Palomar Lux2940 erbium laser (Palomar Medical Products Ltd., USA) was used as a light source. Its parameters were the following: the wavelength 2940 nm, the pulse energy from 0.5 to 3.0 J. The pulses possessed a spike structure (from one to three spikes per pulse depending on the energy) with the spike duration of 200 μs. The microchannels were produced by means of a probe that allowed micro-ablation of skin areas as multiple dots or lines. In *in vitro* and *in vivo* experiments typically five horizontal cuts were made in the skin on the area with the dimensions 5 x 5 mm. The separation between the cuts was nearly 1.2 mm, the depth varied depending on the treatment regime. In regime I the depth of cuts was 150 μm, in regime II it was nearly 300 μm. *In vitro* and *in vivo* studies have shown that laser fractional ablation provides the penetration

of titanium dioxide nanoparticles with the diameter ~ 100 nm from the skin surface to the depth, varying from 150 to 400 μm . The ultrasound was also used to enhance the penetration of the particles into the skin. It was generated by the Dinatron 125 ultrasonic transmitter (Dinatronics, USA) with the frequency 1 MHz and the power density 1.5 Wcm^{-2} in the continuous wave regime. The visualization of microchannels, filled with the suspension of nanoparticles, was implemented using the Spectral Radar OCT System OCP930SR 022 (Thorlabs Inc., USA) at a wavelength of 930 nm. The diffuse reflectance spectra were measured using the USB4000 multichannel spectrometer (Ocean Optics Inc., USA) in the spectral region from 400 to 900 nm. The QR400-7-VIZ/NIR fiber optic probe (Ocean Optics Inc.) consisting of seven fibers with the internal diameter 400 μm and the numerical aperture 0.2 was used in the measurements. Histological testing of the skin areas, subjected to the treatment, shows that the particles stay in the dermis at the depth up to 400 μm no less than for three weeks.

J-5:L13 **Specific Targeting of Cell Organelles**

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Next-generation drug-delivery systems should be able to target individual organelles inside cells. The combination of targeted delivery of drug-loaded nanocarriers to target cells and their subsequent delivery inside cells might significantly improve the efficiency of therapy. Intracellular drug delivery with subsequent organelle targeting opens new opportunities in overcoming problems associated with multiple pathologies, including lysosomal storage diseases and multidrug resistance (MDR) tumors. Delivery of deficient enzymes for the treatment of lysosomal diseases requires specific targeting of lysosomes, while facilitating apoptotic cell death in MDR tumors would require targeting of mitochondria or lysosomes. Clearly, this challenge calls for some novel approaches in engineering multifunctional nanomedicines capable of accumulating in the target tissue, penetrating inside cells, bypassing lysosomes, and bringing pharmaceuticals to individual organelles. The use of certain Rhodamine derivatives, such as RhB or Rh123, as targeting ligands results in the specific association of Rh-modified pharmaceutical nanocarriers (liposomes or lipid-core polymeric micelles) with lysosomes or mitochondria. This allows for the targeted delivery of model or real drug molecules inside these organelles with subsequent biological effects in vitro and in vivo. Examples of specific targeting of lysosomes and mitochondria in cell and animal models as well as analytical methods developed to follow the intracellular fate of nanomedicines illustrate the benefits of this new approach.

Session J-6

Biomedical Applications of Shape Memory Materials and Smart Textiles

J-6:IL01 **Progress in Interactive Textiles for Health Monitoring**

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Interactive textiles have the capability to interact with the user, which means they embed sensors, local intelligence and actuators to achieve this goal. This interactivity requires to dispose of smart textiles, made of smart materials, completing the often used wording "Smart fabrics and interactive textiles" or SFIT. The term smart is used to refer to materials that sense and respond in a pre-defined way to environmental stimuli. Health monitoring is an important field of application for smart textiles. Results and sometimes products such as shirts measuring electrocardiogram, respiration or body temperature have been achieved and are examples of state-of-the-art from the monitoring point-of-view. Making use and combining these signals to derive higher-level information and to provide feed-back in a comprehensive way to the user or to a caregiver are the starting point to interactivity. Sometimes, the textile provides itself interactivity, but it is usually combined with discrete electronics and sometimes organic electronics. The convergence between textiles, smart materials and information technology will be explored in the case of health monitoring. Several projects and their results will be presented as illustration.

J-6:IL02 **Shape Memory Polyurethanes for Minimally Invasive Surgical Procedures**

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Due to their peculiar properties, Shape Memory Polymers (SMPs) can be considered ideal materials for the repair of tissue defects using minimally-invasive procedures since the body temperature can be used as a driving force to activate the shape memory behavior. In our work, SMPs scaffolds were optimized to exhibit adequate properties, without affecting (or with minor effects on) thermal and shape memory properties, and to fulfill the needs of minimally invasive surgery (e.g. repair of bone defects, cerebral aneurism occlusion). The scaffolds were prepared by solvent casting/ particulate leaching from a polyurethane (PU) with shape memory properties (MM4520, Mitsubishi H.I.). For comparison, two SMPU foams (CHEM 3520 and 5520) were selected. By SEM and microCT analyses, MM4520 scaffolds showed a regular pore morphology, with pores of controlled dimensions and spherical shape, smaller than those of CHEM foams. MM4520 scaffolds and CHEM foams showed similar thermo-mechanical properties. Shape recovery of MM4520 scaffolds was similar to that of CHEM foams, the shape recovery behavior being lower for scaffolds with smaller pores. In vitro cell interaction tests with the L929 fibroblast cell line showed a good cells proliferation up to 7 days of culture.

J-6:L03 **Application of a Shape-memory Polymer in a Soft-tissue Fixation Device for Anterior Cruciate Ligament Reconstruction**

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Shape-memory polymers (SMPs) have been proposed for a variety of biomedical applications where it is advantageous to insert a device in a minimally invasive manner and then deploy it into its functional shape in the body. An expandable soft-tissue fixation device, developed for anterior cruciate ligament reconstruction, is presented here as an example to illustrate how shape-memory can be used in orthopedic applications to improve mechanical performance of a device. The device consists of a poly(ether ether ketone) (PEEK) sheath that is compressed into a temporary low profile shape. The PEEK sheath is activated by a mechanical stimulus (i.e. insert) that allows the sheath to expand and compress a soft-tissue graft against bone. The objective was to investigate the in vitro biomechanical performance of this shape-memory fixation device in comparison to static fixation devices. We demonstrate that the shape-memory fixation device is able to generate better graft compression and higher fixation strength compared with static fixation devices, without compromising the ease-of-insertion and integrity of the graft. This work highlights the advantages of using shape-memory to develop expandable fixation devices for a multitude of orthopedic applications.

J-6:L04 **Understanding in-vivo Abrasion Fatigue of Common Suture Materials Used in Arthroscopic and Open Shoulder Surgery**

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In orthopaedic surgery the reattachment of tendon to bone requires suture materials that have stable and durable properties to allow healing at the tendon-bone interface. Failure rates of this type of surgery can be as high as 25%. Large proportions of these failures are caused by in-vivo abrasion of the suture with bone and suture anchor materials because the suture is not rigidly restrained within the eyelet. Suture movement occurs through the eyelet by the surgeon during surgery, or with limb movement after surgery. During movement the suture is subjected to bending and frictional forces that can lead to fatigue induced failure. This paper investigates the mechanism of bending abrasion fatigue induced failure of common number two grade suture materials. Sutures were oscillated over a stainless steel wire at low frequency under load in both dry and lubricated states. Video microscopy of the suture during abrasion combined with optical microscopy analysis of partially and fully abraded sutures was used to determine failure mechanism.

Poster Presentations

J-1:P01 Development of Nanosystems to Release Atenolol
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The structure of aluminum monohydroxide resulting from synthesis by ammonium hydroxide with aluminum chloride (or aluminum nitrate, for example) by a sol-gel process, gives a purified and chemically inert material with many applications possibilities due its great specific surface area. A pseudoboehmite is the choice in this project for adsorption/desorption of atenolol. The molecular interaction with the pseudoboehmite substrate were studied by FTIR (Infrared Spectroscopy), DSC (Scanning electron /TG Thermogravimetry), UV-vis (Ultraviolet-visible spectroscopy) and SEM (Scanning Electron Microscopy). The SEM characterization has been used to quantify the local structural surface for the correlations with the synthesis process; and the Spectroscopies and Thermogravimetric techniques were used for measurements of the adsorption/desorption concentrations of the drug in physiological solution. This procedure gives information to the chemistry and surface of these fine ceramics material that would be applied like excipient in medications to control the drug delivery and plasmatic concentrations in optimal conditions.

J-1:P02 Development of Biocompatible Y-stabilized ZrO₂ Fabricated by Spark Plasma Sintering

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Due to the merits of zirconia ceramics such as high strength, toughness, abrasion resistance, and chemical stability in vivo, yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) are currently used in the femoral head of hip prostheses. However, this material has a limited applications range because it is a bioinert material that does not interact with bone tissue and thus does not easily integrate directly in the bone. Therefore, we need to add different material's layer which enables the in vivo formation of a bone-like apatite layer that exhibits bioactivity, composite bioactive ceramics, and facilitates interactions and integration in bone tissue. In addition, by developing a surface structure that enhances mechanical bonding, this material can be expected to be used as an alternative aggregate under load bearing conditions. In the present study, various method were carried out with the objective of controlling interactions between zirconia ceramics and the body such as structural design of the material surface, addition of bioactivity using reagents treatment, confirmation of formation of the apatite layer using immersion in simulated body fluid, wettability testing and develop structure with mechanical properties equal to bone strength.

J-1:P04 The Effect of Reaction Temperature and Surface Modification on Magnetite Nanoparticles

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Magnetite nanoparticles were synthesized via the chemical co-precipitation method. The size of the magnetite nanoparticles was carefully controlled by varying the reaction temperature and through surface modification. Herein, the hexanoic acid and oleic acid were introduced as coating agents during the initial crystallization phase of the magnetite. Both of the bare magnetite and the coated magnetite were of cubic spinel structure and spherical-shaped morphology. The reaction temperature and the surface modification critically affected particle size, electrical conductivity, and magnetic properties of these particles. In this study, the particle size of the magnetite nanoparticles was successfully controlled to be in the range of 10 - 40 nm, suitable for various biomedical applications. The electrical conductivity of the smallest particle size was 1.3×10^{-3} S/cm, which was higher than that of the largest particle by about 5 times. All of the magnetite nanoparticles showed the superparamagnetic behavior with high saturation magnetization. Furthermore, the highest magnetization was obtained from the hexanoic acid coated magnetite nanoparticles of 58.72 emu/g.

J-2:P05 Apatite Coating on Titanium Samples by Powder Metallurgy

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Titanium and its alloys are widely used as orthopedic and dental implant materials. However, they do not bond to living bone. It is desirable to provide a bone-bonding ability to Ti metal and its alloys. This ability can be achieved by surface modification such as chemical treatments. The aim of this study was to evaluate in SBF the apatite-forming ability of Ti subjected to different pre-treatments. Titanium dense and rough were compared. The rough titanium samples were obtained by powder metallurgy. The groups studied were the alkali-treated; alkali and heat-treated; acid and alkali-treated; alkali-CaCl₂-heat and hot water treatment. The groups were soaked in SBF for 1, 3, 6 and 9 days. The obtained coatings were analyzed by diffuse reflectance FTIR spectroscopy (DRIFT), scanning electron microscopy (SEM) and the surface phases were analyzed by X-ray diffractometry. The apatite formation was present in all groups, however, the apatite-coating was more effective in samples obtained by powder metallurgy.

J-3:P08 High-sensitivity Detection for Biomarkers of a Pancreatic Cancer Using M13 Phage and Quantum-dot Nanocomplexes

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The monodispersity and long rod shape of the phage enable the organization of various nanomaterials into periodically ordered hierarchical structures that could be useful for biomedical applications. We constructed quantitative detection system of pancreatic cancer biomarkers using M13 phage and quantum-dot nanocomplexes. CEACAM1 and Ca19-9 were selected from biomarkers for pancreatic cancer. A microporous nickel foam was used as a template to align M13 phage. Two different coat proteins on a M13 phage were used for collection and quantification of biomarkers. The minor coat proteins (Protein-3 domain) of a M13 phage were engineered to incorporate peptides which have a high affinity to a porous nickel. The main coat proteins (Protein-8 domain) were designed to express proteins on the surface of P8 which bind to Fc region of biomarker-detecting antibodies. Quantum dots conjugated with antibodies operated as a quantification agent for biomarkers collected by M13 phages. We demonstrated pancreatic cancer biomarkers can be quantitatively assayed with high-sensitivity at a resolution of ng/mL using our novel complexes.

J-4:P11 Effect of Surface Topography on Attachment and Growth Behaviors of Bone Cells Cultured on Novel Nanofibrous Replica Substrates

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Cellular cultures with micro- and nano-sized topographical features of rough-surfaced substrates prepared by electrospinning and various methods have been widely studied in literatures regarding promotion of attachment and differentiation of cell growth. However, there is no report on in vitro responses of bone cell behaviors on a novel cast film surface that replicates electrospun nanofiber topography. The purpose of this study is to understand the mouse-calvaria-derived preosteoblastic (MC3T3-E1) cellular behaviors on the nanofibrous-textured substrates compared to TCPS, smooth-surfaced film and non-woven electrospun nanofiber (fiber diameter 814 ± 131 nm) made of biomaterial poly(lactic acid). The substrate roughness (Ra) and topographical profiles were characterized by atomic force microscopy. The surface and cellular morphology were observed by scanning electron microscopy. The wettability of substrates were estimated on water contact angle test. MCT3T3-E1 cellular attachment and proliferation were quantified by MTT assay. The results demonstrated that we successfully prepared a novel film surface, which better promotes proliferation and differentiation of bone cells cultured.

J-4:P13 Application of α -TCP/HAP Functionally Graded Porous Beads for Bone Regenerative Scaffold

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α -TCP/HAP functionally graded porous beads were fabricated for use as a scaffold for bone regeneration. In this research, compositionally graded layer porous beads, from TCP of inner area to HAP of surface area, were fabricated. It is known that the dissolution rate of TCP is fast compared with that of HAP in living body, thus the inner area would be expected to dissolve prior to the surface area. These beads allow the penetration of cells and blood vessel into the inner area of beads favouring new bone formation. At present, conditions to fabricate the functionally graded porous beads were established, and experiments using cells[MC3T3-E1] are in process.

J-4:P14 Development of Rotating-disk Electrospinning for High Throughput Production of PCL, PLA and PVA Nano-fibrous Scaffolds for Tissue Engineering Application

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Poly(epsilon-caprolactone) (PCL), poly(lactic acid)(PLA) and poly(vinyl alcohol) (PVA) polymeric nano-fibrous scaffolds have been studied immensely and proven to be promising candidates in tissue engineering as reported in literatures. Nano-fibrous scaffolds used in tissue engineering researches were commonly produced by electrospinning technique due to high repeatability and good control on fiber dimension. Although it is a simple technique, the low productivity of conventional electrospinning is limiting the industrialization of this method and its applications. A needle-less electrospinning setup consisting of a rotating thin-disk is proposed that can have up to 60 times the productivity of a conventional electrospinning setup. A feasibility study was done by comparing results from conventional single nozzle electrospinning setup and rotating-disk electrospinning with PCL, PLA and PVA polymeric solutions. The threshold voltages, productivity, average fiber size, fiber-size distribution and morphologies of rotating-disk electrospun fibrous scaffolds were compared to those obtained by conventional electrospinning method along with its tissue engineering applications.

J-4:P15 Loading of Polylactide Electrospun Microfibers with Antioxidant Agents: Evaluation of the Effect on Cells under Oxidative Stress Conditions and Applications for DNA Purification

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The main problem in tissue engineering is the rejection of biomaterial scaffolds introduced in human body. It is well known that the generation and harmful effects of reactive oxygen radicals (ROS) in transplanted organs play a fundamental role in the rejection process and destruction of the foreign material by the immune system. Biological systems can protect themselves against harmful effects of ROS and free radicals by designing and formation of antioxidants. The present work is focused on the preparation of scaffolds constituted by electrospun microfibers of a biodegradable polymer (PLA) loaded with different polyphenols as antioxidant agents. Special attention is paid to the study of fiber morphology, crystallinity and the release kinetics of the different selected agents. Biocompatibility of all drug-PLA mixtures has been demonstrated by in vitro analyses. Furthermore, suppression of oxidative stress has been evaluated and showed good prospects when p-coumaric acid was employed. Finally, antioxidant loaded scaffolds were revealed also interesting for DNA purification. Hence, damage caused by environmental high-oxidative conditions (as expected from cellular disruption) can be avoided and consequently high quality DNA can be employed for applications such as PCR and cloning.

J-4:P16 Fabrication of Scaffold for Bone Regeneration by Taylor Made Stereolithography

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Recently, regenerative medicine attracts very wide attention.

Regenerative medicine is a method of medical care for the purpose of recovery of the lost human organic function, resulted by an accident or diseases. It is considered that there are three important factors in the regenerative medicine; cell, scaffold and cell growth factor. In this research, the taylor made stereolithography method was used to fabricate a highly precise biodegradable scaffold which is suited for individual bone defect part. The stereolithography, one of rapid prototyping methods, is a method of modeling by using optical hardening resin irradiated by ultraviolet laser. We have used the optical hardening resin by mixing biodegradable β -tcp as the bone formation material. At present, confirmation of detailed fabrication conditions of stereolithography are in proceeding. Experiments by using osteoblasts cells are intended.

J-5:P17 Using Multifunctional Iron Oxide/Alumina Core/Shell Magnetic Nanoparticles as Affinity Probes and Photothermal Agents for Pathogenic Bacteria

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Bacterial infections may cause serious outcome without providing timely medical-treatment. Effective medical treatment relies on prompt characterization of infected bacterial strains. In this work, we initially discovered that Fe₃O₄ MNPs have the capability to absorb near infrared (NIR) light. The temperature of the MNP suspension under illumination with NIR light increased significantly. The results implied that Fe₃O₄ MNPs could be potentially used as photothermal agents in hyperthermia-based therapeutics. We further demonstrated that functionalization of the surface of iron oxide magnetic nanoparticles with a layer of alumina coating (Fe₃O₄@Al₂O₃ MNPs) allows them to have targeting capability toward pathogenic bacteria. Thus, the as-prepared Fe₃O₄/alumina core/shell MNPs possess several desirable features, including magnetic properties, absorption capability in the NIR region, and the ability to target pathogenic bacteria. We then combined these two features of the Fe₃O₄@Al₂O₃ MNPs for the development of new hyperthermia therapeutics for pathogenic bacteria. The Fe₃O₄@Al₂O₃ MNPs were used to probe target bacteria. The magnetic properties of the Fe₃O₄@Al₂O₃ MNPs allow conjugated target species to aggregate at a specific location under a magnetic field. Then, an NIR laser can be used to irradiate the aggregated spot and therefore inhibit the cell growth of the target bacteria because of the photothermal effects. The cell growth of nosocomial pathogenic bacteria can be effectively inhibited by over 95% within 10 min of light irradiation when targeted by the Fe₃O₄@Al₂O₃ MNPs. This approach provides a potential therapeutic approach for the treatment of infected diseases caused by pathogenic bacteria.

J-5:P18 Development of Cationic Poly(amino acid)s for Efficient Nucleic Acid Delivery

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For therapeutic applications, nucleic acids need delivery vehicles to reach the cytoplasm/nucleus, as they are susceptible to enzymatic digestion and also are inefficiently taken up by cells. Polyion complexes (PICs) of nucleic acids with polycations have been widely developed for enhanced stability of nucleic acids and their facilitated cellular uptake. Nevertheless, translocation of uptaken PICs from the endosome to the cytoplasm (endosomal escape) still remains to be a major challenge in nucleic acid delivery. To improve endosomal escape of PICs, this study aimed at fine-tuning polycationic structures. By focusing on the pH drop from the extracellular milieu (pH7.4) to the endosome (pH5.5), polycations were designed to show larger portions of amine protonation with the pH drop. Indeed, a series of polyaspartamide derivatives with varying numbers of repeating aminoethylene units in the side chain were prepared by aminolysis of poly(beta-benzyl L-aspartate), as low molecular weight aminoethylene compounds are known to undergo considerable amine protonation with the pH drop. Eventually, the polyaspartamide derivatives bearing two/four repeating aminoethylene units achieved efficient endosomal escape of their PICs, leading to high transfection efficiency with low cytotoxicity.

J-5:P19 Sol-gel Synthesis and Characterization of Lanthanide-substituted Nanostructured Calcium Hydroxyapatite

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Synthetic calcium hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is known to be one of most important implantable material and is used as substitute material for human hard tissues (bones and teeth). The general importance of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ has led to extensive research in numerous areas. Lanthanide-substituted $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ show interesting luminescent properties and could be a good candidates for biocompatible drug carriers. In this study, nanostructured Ce- and Sm-substituted $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ samples have been synthesized using an aqueous sol-gel chemistry route. For the characterization of obtained specimens, the XRD, SEM, UV-visible reflection and IR spectroscopy and luminescence measurements were recorded. It was shown that phase purity of the end products highly depends on the amount of lanthanide element. The reflectance of lanthanide-substituted calcium hydroxyapatite samples is wavelength independent in the wavelength range of 450-800 nm and equal almost 100%. The cerium-substituted samples show a significant decrease of transmission at ~ 300 nm. The characteristic samarium absorption line (~ 430 nm) is evident in the UV-vis reflection spectra of samarium-substituted hydroxyapatites. The luminescent properties of these samples are also investigated.

J-5:P20 Characterization of Hydrogels Based on PVP / Sodium Alginate Containing Pseudoboehmites Nanoparticles Treated with Octadecylamine for Pharmaco Applications

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Hydrogels based on poly (N-vinyl-2-pyrrolidone) (PVP) obtained by ionizing radiation are sterile, biocompatible can be used as topics dressings. Due to the high degree of hydration of the gel, it has a low

mechanical strength, which is one of the biggest problems in its application. The objective of this work was to study the properties of the hydrogel based on PVP / sodium alginate containing pseudoboehmites nanoparticles treated with octadecylamine for pharmaco applications, order drug release when immobilized on a matrix of PVP / alginate / pseudoboehmite. Pseudoboehmite nanoparticles were obtained by sol-gel route, from aluminum nitrate and ammonia as precursors, and subsequently were treated with octadecylamine. The hydrogels based on PVP / alginate / pseudoboehmite treated were prepared by ionizing radiation with doses of 30 and 35kGy. The characterization of hydrogels obtained was made by means of thermomechanical (tensile tests, DTA and TG) and physicochemical (swelling) tests. The results obtained showed that the hydrogel based only on PVP and sodium alginate showed highest tensile strength. The presence of pseudoboehmite in the hydrogels decreases the formation of crosslinks, while the presence of PEG in the agar and causes a decrease in Tg of the polymer matrix.

J-5:P21 Calcium-alginate Hydrogel for Electrically Controlled Drug Release

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The Electrically Controlled Drug Delivery System is a system which is capable of adjusting the drug release rate in response to electric field. The aim of this work was to study the drug release behavior from calcium-alginate hydrogels, (Ca-Alg), based on the effect of crosslinking ratio, drug characteristics, with and without electric field. The drug-loaded Ca-Alg hydrogels were prepared by solution-casting using CaCl_2 as the crosslinking agent and benzoic acid, folic acid, and tannic acid as the model drugs. The average molecular weight between crosslinks, the crosslinking density, and the mesh size of the Ca-Alg hydrogels were determined via the Equilibrium Swelling Theory as modified by Bray and Merrill then using scanning electron microscopy (SEM) to study the morphology. The release mechanism and the diffusion coefficient of Ca-Alg hydrogels were investigated using a modified Franz-Diffusion cell in MES buffer solution at pH 5.5 and 37 °C for 48 h. The amount of drug release was analyzed by UV-Visible spectrophotometry. The diffusion coefficient of drug in Ca-Alg hydrogels decreased with increasing crosslinking ratio. Moreover, the diffusion coefficient of drug in Ca-Alg hydrogels depend on the size of drug, the charge drug, and the electric field stimuli.

HOT POSTERS

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A:HP88 Microencapsulated Systems for Self-healing Coatings and Adhesives

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The main approach to self-healing polymeric materials is based on microencapsulation of reactive chemicals and subsequent embedding in a polymer matrix. Upon mechanical injury or corrosion, the mending agents are released from the capsules and react forming a polymer network, which heals the damage and restores structural integrity. The overall aim of our research is to identify a robust method for the preparation of stable microcapsules with an industrially relevant core material for future use in self-repairing coatings and adhesives. A series of microcapsules were synthesized with different polymeric shells. Changing the encapsulation process by adding more shell wall monomers and pre-polymers allows the modulation of physical and mechanical properties of microcapsules. The size of the microcapsules and the thickness of their shell walls can be tuned for various coating thicknesses and chemical environments. A range of healing agents were microencapsulated to maximize compatibility with different host polymers. The characteristics of the microcapsules, their impact on the matrix mechanical properties and the self-healing performances in various conditions were explored.

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A:HP89 Poly(Para-Phenylene Vinylene)/Zeolite Y Composites and Electrical Conductivity Response towards Ketone Vapors

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The work is an attempt to improve the selectivity and sensitivity of a Y Zeolite to detect 3 different ketone vapors (acetone, methyl ethyl ketone (MEK) and methyl iso buthyl ketone (MIBK)), the vapors which are flammable and toxic components. Three different types of cation in the Y Zeolite Y; Y Zeolite (Si/Al=5.1, Na⁺), Y Zeolite (Si/Al=5.1, NH₄⁺), Y Zeolite (Si/Al=5.1, H⁺) has been blended with poly(paraphenylene vinylene) doped with H₂SO₄ or dPPV. All composites show definite positive responses towards the ketone vapors: acetone, MEK, and MIBK. The electrical conductivity sensitivities of the composites increase linearly with increasing surface area of the Y Zeolite. The highest electrical conductivity sensitivity is obtained with the dPPV/Y Zeolite (Si/Al = 5.1, NH₄⁺), higher than those of dPPV_Y Zeolite (Si/Al = 5.1, Na⁺) and dPPV_Y Zeolite (Si/Al = 5.1, H⁺) when exposed to acetone. Amongst the Ketone vapors, acetone induces the highest electrical conductivity sensitivity, whereas MIBK induces the lowest electrical conductivity sensitivity.

A:HP90 Fabrication of Polydiphenylamine and Zeolite Y Composites as a Sensing Material

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Volatile organic compounds especially halogenated hydrocarbons are widely used as solvents in many industries. Nevertheless, the toxicity of these compounds can have an adverse effect on the breathing and

when coming in contact with skin. So, the effective vapor sensing systems are required to identify these hydrocarbons. This work is focused on the fabrication of polydiphenylamine (PDPA) and Y_H+ zeolite composites to determine the electrical conductivity sensitivity responses towards the halogenated hydrocarbons: dichloromethane, 1,2-dichloroethane, and chloroform by using a custom built two point probe connected with a conductivity meter (KEITHLEY 6517A). The effects of the Si/Al ratios and zeolite content were investigated. The results show that the sensitivity of zeolite Y_H+ increases with increasing Si/Al ratios. The zeolite with a Si/Al ratio of 80 is chosen to form a part of the composites with the doped-PDPA (D-PDPA). The sensitivity of the composites towards dichloromethane, 1, 2-dichloroethane, and chloroform are -3.81×10^{-2} , -2.33×10^{-2} , -6.08×10^{-3} S/cm, respectively. The sensitivity of the composites increases with increasing zeolite content due to a greater interaction between the micro-porous structure and the those halogenated hydrocarbons. From the result, the PDPA/zeolite Y_H+ composites are potential sensing materials for detecting the halogenated hydrocarbon.

A:HP91 Modeling of Shape-memory Recovery in Crosslinked Semicrystalline Polymers

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Up to now there is no physically well-grounded mathematical model of the processes involved in shape-memory (SM) effect of crosslinked semicrystalline polymers, which could be able to describe and predict the behavior of corresponding SM polymeric materials. In present work a new theoretical approach based on the modified three-element Eyring-Halsey mechanical model was used for the derivation of an equation, which describes the thermally-induced recovery of preloaded covalently crosslinked polymer. This approach takes into account the influence of crystallizable polymer network as well as of entangled slipped molecular chains. Modeling of the temperature dependences of SM recovery strain and SM recovery rate detected at constant heating rate has been performed for three types of polyethylene with sufficiently different crystallinity and crosslink density at programming strain of 100%. The results of modeling agree well with the experimental data. The values of material parameters determined by fitting correspond satisfactorily to the estimations existing in literature. The influence of the entangled slipped molecules on SM recovery behavior as well as the dependences of important fitting parameters on the degree of branching and crosslink density are discussed.

A:HP92 Ceramics PMN-PT-PFN for Multilayered Capacitors

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We present the technology of obtaining and the main properties of PMN-PT-PFN ceramic samples. PMN-PT-PFN is the abbreviation of the solid solution with general formula $(1-y)[(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3]_1 - y\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ where $x=0.25$, $y=0.1$ i.e. 0.9(0.75PMN-0.25PT)-0.1PFN. The addition of PFN decreases the temperature of final sintering and as a result such composition is an interesting material for multilayer ceramic capacitors (MLCC). The powder of 0.9(0.75PMN-0.25PT)-0.1PFN has been obtained in three steps. In first step we obtained MgNb_2O_6 . In second step FeNbO_4 was obtained. In final third step the 0.9(0.75PMN-0.25PT)-0.1PFN was obtained from mixed powders MgNb_2O_6 , FeNbO_4 and PbO and TiO_2 . For obtained ceramics the following investigations have been made: XRD patterns, microstructure, EDS and main dielectric properties v.s. temperature. It has been stated that such ceramic powder is a good dielectric material for MLCC.

A:HP93 Nitridation of Thick Si Compacts to Produce SiAlON Ceramics

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Nitridation of relatively thicker (about 15mm) Si compacts to produce SiAlON ceramics was studied. 2 and 7 μm Si powder with two different additive systems, namely Ce/Ca and Y/Sm/Ca were used. Relatively fast heating rate (10 $^{\circ}\text{C}/\text{min}$) was applied and temperature and time was changed as a way to find out the shortest possible nitridation time. It was observed that all the dopant systems enhanced nitridation of Si and this enhancement depended on the type of dopants. Ce/Ca dopant system enhances the nitridation most but this enhancement caused melting of Si in the interior of the compacts, depending on the nitridation temperature, due to the exothermic nature of nitridation. It was found that by applying two step nitridation temperature, it was possible to nitride fully 15 mm thick compacts within maximum 4 h, irrespective of the dopant type.

A:HP94 Foreign Bodies - The Creation of Symbiotic Jewellery through the Development and Application of Stimulus-responsive Smart Materials and Microelectromechanical Systems

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With the increased prevalence of digital technologies in our everyday lives, the questions posed to the contemporary craft practitioner regarding creation of an emotionally resonant interaction between the digitally enhanced object and its wearer have become progressively more prominent in the applied arts. Through examining the notion that human biology is a part of material culture, where the body can be shaped, customised or altered through surgical intervention and scientific innovation, the need arises to explore how recent developments in material science and nanotechnologies can be viewed as contiguous rather than oppositional to the organic processes of the human body and how to bridge the gap between the craft practitioner and scientific discovery. More immediately however, this research project could alter the perception of smart materials and their application within the field of jewellery in both an artistic and scientific context. Potential practical applications of stimulus reactive jewellery exist in the areas of human computer interaction, transplant technology, identity management and artificial body modification including prosthetics, where such symbiotic jewellery organisms could be used to develop visually engaging yet multi-functional enhancements of the body.

A:HP95 Design of Hierarchically Structured Macro-mesoporous Alumina via the Sol-gel Process

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Significant interest has been directed toward the synthesis of hierarchical structured porous ceramics, which are defined as materials that contain a multilevel structure consisting of interconnected pores on different length scales. Hierarchical aluminas with pore sizes ranging from a few nanometers to micrometers were obtained using an one-pot sol-gel synthesis accompanied by phase separation. This strategy is a spontaneous route obtained from the aqueous and ethanolic solution of aluminum isopropoxide in the presence of propylene oxide and poly(ethylene oxide) (PEO). Propylene oxide controls the gelation, whereas the addition of PEO induces the phase separation. Mercury intrusion porosimetry and nitrogen physisorption isotherms provided evidences of porous structure at different hierarchical levels. By controlling the miscibility between alkoxy-derived condensates and solvent we produced various morphologies with micrometer-range heterogeneity. A series of aluminas with high surface area and pore volume were readily obtained, and the resulting materials might have potential application in fields such catalysis and separation media. This simple and reproducible strategy can be readily applicable to the fabrication of other hierarchical macro-mesoporous porous metal oxides.

A:HP96 Control of Hierarchical Porosity and Acidity of Alumina Supports Designed for Catalytic Conversion of Ethanol

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The targets for reducing greenhouse gas emissions have a significant increase in the consumption of biofuels in coming years, especially ethanol. Ethanol is highlighted, because, besides being used as a direct fuel source in automotive, may be used to produce H_2 , ethyl acetate, n-butanol and other chemical products by dehydrogenation reactions. In this investigation, the relationship between the structural, catalytic and surface properties of copper catalysts supported on different Al_2O_3 samples was studied in the ethanol dehydrogenation reaction. The copper catalysts (5-20 wt. %) were impregnated on Al_2O_3 with a hierarchical porous structure, obtained by sol-gel method, and characterized by different techniques. The characterization results showed that isolated copper species in the 5Cu/ Al_2O_3 sample promote the formation of acetaldehyde and H_2 from the dehydrogenation reaction. Moreover, larger Cu clusters obtained on catalysts with higher copper content favors the formation of ethyl acetate and acetaldehyde. Furthermore, a higher coverage of the Al_2O_3 surface by presence of greater amounts of Cu cluster promotes a decrease in the amount of Brønsted/Lewis acid sites, increasing the selectivity for the dehydrogenation reaction products in contrast to dehydration reaction products.

A:HP97 Interface Engineering of P3HT/TiO₂ Heterjunction in Hybrid Solar Cells

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The interface of TiO_2 /P3HT heterojunction in hybrid solar cells was modified by four different conjugated cyanoacrylic acids with various LUMO levels. The thiophene end-group in these interface modifiers (IMs) apparently improves the mutual compatibility of P3HT and TiO_2 . Incorporating a strongly electron-withdrawing -CN moiety adjacent to the -COOH anchoring group in the IMs induces a molecular dipole directing away from the titania surface and enhances the electron affinity of the molecules, simultaneously increasing the J_{sc} and V_{oc} of the device. EQE spectra clearly indicate that excitons that are generated in both IMs and P3HT make contribution to J_{sc} . Importantly, the LUMO of IMs plays an important role in determining the efficiency of the injection of electrons from P3HT to TiO_2 . The order of EQE at 570 nm, which represents the degree of contribution of P3HT, coincides perfectly with the order of the LUMO offset of IMs and P3HT, revealing that an energy-offset of greater than 0.3 eV between the LUMOs of P3HT and IMs promotes the smooth electron injection from P3HT through IM to TiO_2 . This study provides valuable guidelines for further designing novel IMs for developing high-efficiency polymer/inorganic hybrid solar cells and solid-state dye-sensitized solar cells.

A:HP98 Superhard TiB₂-based Composites with Different Matrix Fabricated from Elemental Powders by SHS-p-HIP

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TiB₂ is a superhard, high-temperature and high corrosion resistant material and it is under consideration for tungsten-free cutting tools and high temperature structural applications. Although such a covalent compound requires significantly elevated temperature for the consolidation, great exothermicity of TiB₂ synthesis by means of SHS (Self-propagating High-temperature Synthesis) can be "in situ" utilized. In this study, TiB₂-based composites are fabricated from titanium, boron and binder metal. In order to optimize consolidation process and improve fracture toughness of the products, three types of binder, based on cobalt, nickel or copper were investigated. In respect to hardness, limited amount of binder, 5, 10 or 15 vol.% respectively, were applied; each time 5 vol.% of Ti addition for reaction with boron completeness was used. The TiB₂ based composites were fabricated from elements in one process by means of the SHS process combined with p-HIP (pseudo-hot isostatic pressing) method. The raw elemental powders were homogenized by wet mixing using ball milling technique. Dried mixtures were pressed into a compact, coiled by heating element and then exposed to the SHS-p-HIP process. After SHS initiation, the compact was pressed pseudo-isostatically under pressure of 190MPa for 5 min. The sintering additives and their concentrations significantly affected the consolidation process as well as the properties of composites. The highest hardness was obtained for samples sintered with cobalt, containing intermetallic binder. However, elemental metal binder was detected as a main component for samples sintered with copper. The relative density, SEM microstructure, phase composition and hardness are compared in this study.

A:HP99 Graphene-based Nanocomposites for Supercapacitor Applications

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Electrochemical double layer capacitor (EDLC) is the most typical of supercapacitors and its charge storage mechanism is based on the charge separation at the interface between carbon and electrolyte. Graphene is an one-atom-thick layered sheet of SP² bonded-carbon atom packed in a honeycomb crystal lattice. Owing to its unique properties such as chemical stability, large surface area, and high electric conductivity, graphene or reduced graphene oxide (RGO) is extensively investigated as electrode materials for electrochemical capacitor applications. It was reported that high quality graphene nanosheets could be fabricated by the thermal exfoliation of graphite oxide (GO) using a rapid heating process in a preheated conventional furnace or arc discharge. Rapid heating is the most important for the effective thermal exfoliation of GO. Preparation of RGO using solid-state microwave irradiation under a hydrogen atmosphere is reported to produce high quality RGO. Electric Double layer capacitance of RGO depends on effective surface area, surface functional groups, hydrophilic nature and 3D porous structure. Herein, we report on preparation of RGO using microwave irradiation and its surface modification for EDLC electrode materials. More details will be discussed at the meeting.

A:HP100 Nb and Y Doping in BaTiO₃: Compensation Mechanisms and Ferroelectric Properties

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When Yttrium and Niobium are dissolved into BaTiO₃, both Nb⁵⁺ and Y³⁺ ions occupy the Ti⁴⁺ site in the BaTiO₃ lattice. Due to the difference in valence among ions, compensation mechanisms will take place. In the present work, samples of BaTiO₃ with different concentrations of Nb and Y were fabricated from powders. The mixtures of powders were pressed and sintered at 1500 °C. The structure becomes more cubic and paraelectric as the Nb concentration increases while the structure is more tetragonal as the Y concentration increases. Conductivity curves as a function of dopant concentration suggest that the compensation by free electrons and cation vacancies occur in the case of Nb doping. In the case of Y, the compensation seems to be holes and oxygen vacancies. Due to the presence of charge carriers high values of dielectric constant and dielectric loss were observed. Ferroelectric hysteresis and impedance spectroscopy curves are presented.

A:HP101 Structural Design Optimization of Multiferroic Composites for Maximized Energy Conversion

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Recently, multiferroic or magneto-electro-elastic composites, made of piezoelectric and magnetostrictive materials, have received a significant research interest for potential applications in novel multifunctional devices. These multiferroic composites possess the characteristics of their parent properties and also exhibit an additional functionality: the extrinsic magnetoelectric effect via elastic mediation. In such composite materials, the performance is critically dependent on the composition of constituent materials and their structural configuration. In this investigation, the systematic simulation approach to find optimal multiferroic heterostructure using the design optimization will be presented. The multiferroic BaTiO₃-CoFe₂O₄ composite is analyzed by a two-dimensional finite element formulation and the magnetoelectric coupling factor by some stored energy expressions is considered as an objective function to evaluate the magnetoelectric effect. For more practical exploitation of the design method, layout design optimization of 2-2 type laminate composites for maximizing the extrinsic magnetoelectric effect will be also presented.

A:HP102 Preparation and Properties of Thermal Camouflage Materials from PET Fiber Having ATO

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Five kinds of three-layer thermal camouflage materials were prepared by laminating base fabric containing antimony tin oxide (ATO) and PET mesh and color pigment coated nylon. First, 100d/24f PET fiber having 2 wt% ATO was extruded through the conjugated spinning process with 10 wt% ATO/PET master chip in sheath part and semi dull PET chip in core region. Inner layers, whose role were to absorb thermal energy of the target, were prepared using PET having ATO and Al metallic yarn with different ratios. Middle layers were 3~5 mm thick meshes made of 75d/24f PET and 15d monofilament PET to minimize the release of heat by providing sufficient amount of air. Outer layers were manufactured using 75d PET as a warp and 150d nylon as a weft, and followed by color pigment coating. Thermal image and emissivity of five samples were obtained from black body whose temperature was set at 70° and thermal camera located at 1m away from samples. Thermal transmission was also measured on UV/Vis/NIR spectrophotometer. It was found that emissivity of short wavelength (3-5um) was in the range of 0.67~0.76, and that emissivity of long wavelength (8~14um) was in the range of 0.54~0.63. Thermal images of samples were correlated well with their emissivity.

A:HP103 Electrical Conductivity and Response of PEDOT-PSS/Ion-Exchanged Zeolite Y Composites toward SO₂

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In our work, we propose to combine a conductive polymer, Poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonic acid) (PEDOT-PSS), with FAU zeolites to investigate the potential of the composites for use as SO₂ sensing materials. Electrical conductivity responses and the interaction mechanism of conductive polymer/zeolite composites sensor with sulphur dioxide were investigated. Poly(3,4-ethylenedioxythiophene)(PEDOT)/poly(styrene sulfonic acid) (PSS) complexes were prepared at 1:1 molar ratio of EDOT/PSS. The adsorption properties of the faujasite zeolite type (sodium form) with a Si/Al mole ratio of 5.1 were modified by changing the existing cation with monovalent cations. Composites with the PEDOT-PSS matrix containing the faujasite zeolites of type Y were fabricated to examine the effects of zeolite content (10-50 v/v%) and cation type (monovalent cation: H⁺, Li⁺, Na⁺ and K⁺) of faujasite zeolite type Y on the electrical conductivity response when exposed to SO₂. The preparation of the composite at 20% (v/v) of zeolite content gives the highest sensitivity to SO₂. The addition of the Y zeolite is thus shown to enhance the interaction between PEDOT-PSS and SO₂ molecules; the zeolite improves the sensitivity of the pristine PEDOT-PSS, but at the expense of a longer response time. The highest electrical conductivity response and sensitivity belong to the PEDOT-PSS/KY composite. The type of cations present in zeolite Y micropores is shown to critically affect the adsorption-desorption properties of the Y zeolite, which in turn influences the electrical sensitivity of the composite. The composite was tested through repeated sensing and recovery processes to investigate the reversibility and reproducibility. All composites show nearly reversible responses towards SO₂.

A:HP104 Novel Sulfonated Poly(arylene ether ketone sulfone) Proton Exchange Membrane for Using in DMFC

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Poly(ether ketone ether sulfone) (PEKES) was synthesized by the nucleophilic aromatic substitution poly-condensation between bisphenol S and 4,4'-difluorobenzophenone (system A), and between bisphenol S and 4,4'-dichlorobenzophenone (system B). Properties of both post-sulfonated polymers are compared with a commercial PEEK 150XF from Victrex®. Advantages of the synthesized PEKES is the better solubility of PEKES in H₂SO₄ relative to PEEK 150XF which results in higher attainable sulfonation degrees. The S-PEKES backbones contain the aromatic rings, the carbonyl groups (C=O) and the sulfone groups (-SO₂-), which promote the chain stiffness and thermal stability. The sulfonated polymer membranes were characterized by a LCR meter, the gas chromatography (GC), and the thermogravimetric analysis (TGA). Properties of both post-sulfonated polymers are compared with

those of a commercial PEEK 150XF from Victrex® and Nafion® 117. The proton conductivity values of S-PEKES of the highest DS are comparable to those of Nafion® 117 and S-PEEK. The methanol permeabilities of S-PEKES and S-PEEK 150XF membranes are relatively lower than Nafion® 117 by at least an order of magnitude. The thermal stabilities of S-PEKES and S-PEEK are higher than that of the commercial Nafion® 117.

A:HP105 Linear Direct Magnetoelectric Response in CoFe₂O₄/PVDF 0-3 Nanocomposites

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Free-standing flexible magnetoelectric 0-3 composite films comprising ferromagnetic CoFe₂O₄ nanoparticles (35-55 nm) in Poly(vinylidene fluoride) (PVDF) matrix have been prepared at low temperatures by solvent casting and melt crystallization. We will present the variation of the ferroelectric, piezoelectric, magnetic and magnetoelectric properties of corona-poled nanocomposites with nanoparticle content. Magnetoelectric voltage coefficients increase linearly with applied dc magnetic-bias fields up to 5 kOe. At this field, a maximum magnetoelectric voltage coefficient of 10 mV cm⁻¹ Oe⁻¹ was obtained for samples with 10 wt. % ferrite using a 50 kHz resonant signal. The observed linear magnetoelectric response is attributed to magnetic-field induced strain arising from rotation of the ferromagnetic nanoparticles in the polymer matrix.

This work was supported by FEDER "Programa Operacional Factores de Competitividade - COMPETE" (NANO/INMed-SD/0156/2007) and Fundação para a Ciência e a Tecnologia FCT (PTDC/CTM/69316/2006). P. M. acknowledges support from FCT (SFRH/BD/45265/2008). X. M. acknowledges support from the Herchel Smith Fund.

A:HP106 Broadband Vibration Energy Harvester with Variable Proof Mass using Single Crystal Piezoelectric Material

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In recent years a power sources such as batteries have limitations in wireless remote sensor systems owing to their limited lifetime, large size, and need frequent replacement and can be expensive to replace. As a quasi-perpetual and compact energy source, energy harvesting from the environment is being examined by many researchers throughout the world. Single crystal piezoelectric materials are potential candidates for vibration energy harvester for a wireless sensor node (WSN) and remote applications without any additional power source. An important issue is the resonant frequency of an energy-harvesting device. Because the maximum output power density is obtained when the resonant frequency of the piezoelectric resonator matches the frequency of the mechanical vibration. The band width of resonant frequency increased with increasing the probability of energy harvesting. Therefore, the broadband resonant frequency in cantilever energy harvester was required. We designed and fabricated a bimorph cantilever array with a variable Cu proof mass to obtain broadband frequency and sustainable power. The resonant frequency range of energy harvester was 60.2 to 63.7 Hz. The average power was 0.28 mW.

A:HP107 Nitrogen-doped Highly Conductive Carbon Film for Electronics

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We developed new type of nitrogen-doped highly conductive carbon film from solid carbon source with controlled thickness. Thin film was deposited on substrates by dip coating of a self-polymerizable nitrogen-containing molecule. After thermolysing of the film in an oven at elevated temperature, conductivity as high as 2000 S/cm had been obtained. XPS showed the film contained about 2% nitrogen and UPS indicated that the work function was about 4.7 eV, which is higher than that of few-layer CVD graphene. We suspected that the nitrogen doping together with the graphene domain in the film contributed to the high conductivity. Thin film transistors using the as-prepared thin film as bottom electrodes exhibited a ten-fold increase of mobility compared to devices based on gold electrode. Current work is focused on the structure of such film to find the origin of the high conductivity.

A:HP108 Field Emission Properties of Ti Nanowires Grown by Chemical Vapor Deposition

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Ti thin films were grown on graphite substrates by atmosphere pressure chemical vapor deposition (APCVD) at high temperatures employing titanium subchlorides TiCl_x(g), generated by reacting TiCl₄(g) and Ti(s), as the Ti source. On the thin films, Ti nanowires (NWs, diameters 50 - 80 nm, lengths several μm) were grown. Growth direction of the FCC-structured single-crystalline NWs was determined to be along the [200] axis. Field emission properties, turn-on field E_o and field enhancement factor β, of the vertically grown Ti NWs were determined to be 3.00 Vμm⁻¹ and 1173.2, respectively.

A:HP109 Study of the Interaction and Assembly of 1-pyrenesulfonic Acid Sodium Salt on Graphene in Aqueous Solutions

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Chemical exfoliation of graphite is the ideal technique for large-scale production of graphene and its processing in solution, which is desirable for several advanced applications. Ideally, the solvent should be cheap, not toxic and environmentally friendly. Here we report a method to exfoliate graphite in water using supramolecular interactions between graphene and 1-pyrenesulfonic acid sodium salt (1-PSA). This molecule is selected due to its ability to interact with graphene via p-p stacking, and because it is soluble in water, allowing stabilization of the graphene flakes in this solvent. In particular, we investigate the interaction and assembly of the molecules on graphene by using a combination of several techniques, such as UV-Vis spectroscopy, Raman spectroscopy, Atomic Force Microscopy, Transmission Electron Microscopy and X-ray Photoelectron Spectroscopy. We show that the exfoliation is quick, non-destructive and rather efficient: we achieved ~68% few graphene layers (~10% single-layers). We also observed that the interaction and assembly of the molecules with graphene is strongly affected by the amphiphilic nature of 1-PSA.

A:HP110 Optimization of a Pyrolysis Procedure for Obtaining CMC by PIP for Thermostructural Applications

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Polymer Impregnation Pyrolysis (PIP) is a cost effective technique for obtaining Ceramic Matrix Composites (CMC) modified with nanoparticles. Commercial UBE polymeric precursor (Tyranno polymer VL-100, diluted in xylene) of a SiC ceramic matrix (with 11 wt% O and 2 wt% Ti) was used to infiltrate 100x85x2 mm³ SiC felts (Tyranno ZM fibers, diameter 14 microns, 800 filament/yarn, 270 g/m², with 9 wt% O and 1 wt% Zr), applying different pyrolysis procedures. In particular, pyrolysis was performed in two conditions: 1) at 1000 °C for 60 min; 2) at 900 °C for 120 min. A pyrolysis at 900 °C could be more convenient since it can be easily performed in a steel furnace, without a refractory lining. The SiC felts were pretreated by CVD (Chemical Vapour Deposition) in order to deposit a pyrolytic carbon interphase (about 0.1 microns). Impregnation was performed under vacuum, and drying was carried out in an explosion-proof heating oven. Pyrolysis was performed in a AISI 310S austenitic steel furnace, under nitrogen flow. Geometric density was monitored during densification. Mechanical characterisation (bending tests at room temperature, following UNI EN 658-3:2002) was performed after 8-10 PIP cycles. The results were used to compare the influence of pyrolysis temperature on densification.

A:HP111 Chemical Production and Microelectronic Applications of Graphene and Nano-graphene Derivatives

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Graphene and graphenic derivatives have rapidly emerged as an extremely promising system for electronic, optical, thermal, and electromechanical applications. Several approaches have been developed to produce these materials (i.e. scotch tape, CVD, chemical and solvent exfoliation). In this work we report a chemical approach to produce graphene by reducing graphene oxide (GO) via thermal or electrical methods. A morphological and electrical characterization of these systems has been performed using different techniques such as SPM, SEM, TEM, Raman and XPS. Moreover, we studied the interaction between graphene derivatives and organic molecules focusing on the following aspects: - improvement of optical contrast of graphene on different substrates for rapid monolayer identification¹; - supramolecular interaction with organic molecules (i.e. thiophene, pyrene etc.)⁴; - covalent functionalization with optically active molecules²; - preparation and characterization of organic/graphene Field Effect Transistors³⁻⁵. Graphene chemistry can potentially allow seamless integration of graphene technology in organic electronics devices to improve device performance and develop new applications for graphene-based materials.

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A:HP112 The Interaction of Pyrene Derivatives with Graphene Nanoplatelets

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Graphene has raised intensive research interest as a promising material for future carbon-base nanoelectronics. At the moment, chemical exfoliation of graphene is the most promising technique to obtain large quantities at low cost and easily processable. A wide amount of research works demonstrated, in the last years, that several different classes of molecules can exfoliate graphite flakes into soluble graphene sheets with different efficiencies in achieving soluble aggregates and obtaining mono- and multi-layer sheets. A class of molecules which seems very effective in exfoliation and stabilizing graphene sheets are small poly-aromatic hydrocarbons (pyrenes, perylenes, anthracenes, etc.) functionalized with flexible or possibly polar sidechains. While graphene exfoliation is widely performed, a clear understanding of the exfoliation mechanism at molecular level is still missing. To better reveal the complex interaction between graphene and organic molecules in water, we performed a comparative study using pyrene derivatives with sulfonic and hydroxyl functionalizations. We studied those compounds' affinity towards different carbon substrates with atomic force microscopy (AFM) and UV/VIS spectroscopy, and tested their eligibility for exfoliation and solubilization of graphene.

B:HP16 Martensitic Transformation in Ti-Ni-Sn Alloy Ribbons

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Crystallization behavior of rapidly solidified Ti-Ni-Sn alloys amorphous ribbons and martensitic transformation behavior after crystallization were examined by means of differential scanning calorimetry (DSC), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Glass forming ability of Ti-Ni-Sn alloys increased with increasing Sn content and activation energy for crystallization increased from 151.2 ± 7.0 kJ/mol to 165.1 ± 9.0 kJ/mol with increasing Sn content from 5 at% to 7 at%, above which it almost kept constant. Crystallization occurs in the sequence of amorphous \rightarrow (Ti,Sn)2Ni and B2 \rightarrow B2 and Ti3Sn when Sn content is ≤ 5 at%, amorphous \rightarrow (Ti,Sn)2Ni \rightarrow B2 \rightarrow B2 and Ti3Sn when Sn content is in the range of 5 at% and 10 at%, amorphous \rightarrow (Ti,Sn)2Ni \rightarrow Ti3Sn \rightarrow B2 and Ti3Sn when Sn content is ≥ 10 at%. The

crystallized Ti-Ni-Sn alloys showed the B2-R-B19' martensitic transformation behavior. Rapid solidification was effective to separate the B2-R transformation from the R-B19' transformation in Ti-Ni-Sn alloys.

B:HP17 Fabrication of Work Operation Assistance Tool Applying Ti-Ni Superelastic Alloy

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Ti-Ni alloy had excellent shape memory and superelastic effect. Especially, superelastic effect showed unique mechanical properties. We have developed the work operation assistance tools applying Ti-Ni superelastic alloy. The superelastic wire was made from Ti-Ni wires of 1.5mm or 1.8mm in diameter and 70mm in length. The composition of this wire was Ti-50.8at%Ni. The transformation temperatures were measured by differential scanning calorimetry (DSC). From DSC measurement, this alloy showed the superelastic behavior at room temperature. The bending force test was investigated by tensile tester.

B:HP18 Shape Memory Characteristics of Porous 50Ti-30Ni-20Cu Alloy

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50Ti-30Ni-20Cu powders were prepared by gas atomization and porous specimens were fabricated by spark plasma sintering (SPS). XRD analysis showed that one-step martensitic transformation of B2-B19 occurred in all alloy powders and SPS specimens. DSC measurements of as-atomized powder, sintered bulk specimens and as-cast ingots were performed in order to study the effect of rapid solidification on martensitic transformation behaviors. The martensitic transformation starting temperature (Ms) of 50Ti-30Ni-20Cu powders ranging between 25 and 150 μ m is 32.1 $^{\circ}$ C and the austenite transformation finishing temperatures (Af) is 38.3 $^{\circ}$ C, respectively. The Ms and Af of the as-atomized powders is much smaller than those of SPS specimens and as-cast ingots for 50Ti-30Ni-20Cu alloy systems. The temperature hysteresis of the powders was only 7 $^{\circ}$ C. The porous specimen has been produced by SPS using rapidly solidified powders. A small uniaxial pressure of 5MPa was used during the SPS process. It was then found that the powders never deformed during the SPS consolidation because of the very low pressure and the spaces between powders became pores after SPS. This porous specimen has 20% porosity and 4.8g/cm³ mass density. The Ms of porous 50Ti-30Ni-20Cu specimen is 36.1 $^{\circ}$ C. The values of the transformation temperatures (Ms and Af) of porous specimens is just between those of rapidly solidified powders and those of as-cast ingots.

B:HP19 The Effect of Al Substitution on Microstructure and Martensitic Transition of Ni₄₈Mn_{39.5}Sn_{12.5-x}Al_x Heusler Alloy Ribbons

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In this work studies of microstructure of Al substituted ferromagnetic Heusler – based alloys are presented. The alloys had the following starting composition: Ni₄₈Mn_{39.5}Sn_{12.5-x}Al_x (x = 0, 1, 2 and 3). They were first produced by means of classical metallurgy, annealed and subsequently melt spun to form ribbons. The alloys were observed to undergo martensitic transformation from L2₁ Heusler type austenitic phase into martensite phase, what was proved by differential scanning calorimetry measurements. The amount of martensite increased with the amount of aluminum in the alloys. The presence of martensite at room temperature indicates that Al increases the M_s temperature. Transmission electron microscopy studies together with X-ray diffraction examination allowed to identify the dominating martensitic phase as a 10 M martensite. The resulting average chemical composition of the studied ribbons changed with respect to master alloys, which was demonstrated by EDAX microanalysis.

C:HP12 Nanowire Polypyrrole and Gelatin Hydrogels Blend for Electroactive Application

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Electromechanical properties of Nanowire Polypyrrole/Gelatin hydrogels blend were investigated in the oscillatory shear mode under electric field varying from 0 to 800 V/mm. Nanowire Polypyrrole was synthesized via an oxidation polymerization and doped with dodecylbenzenesulfonic acid. The dynamic moduli (G'), of Nanowire Polypyrrole/Gelatin hydrogels can be enhanced with increasing electric field. The storage modulus sensitivity ($\Delta G'/G_0$) increases with electric field strength. For the gelatin blends with nanowire polypyrrole concentration of 0.01, 0.1, 0.5, 1vol% and the pure gelatin hydrogel possess the storage modulus sensitivity values of 0.75, 1.04, 0.88, 0.99 and 0.46, respectively at the electric field strength of 800 V/mm. The results can be interpreted in terms of the polarizability between the conductive polymer and the matrix and the conductive polymer agglomeration at various electric field strength.

D:HP08 MWCNT Reinforced Polymer Fibres for a New Generation of Electric Conductive Textiles

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We report here a new family of non-metallic electrical conductive materials that can be extruded into fibers. The resulting thermoplastic-MWCNT (multi wall nanotube) fibers present conductivities within the Electro Magnetic Dissipation (EMI) region. We have developed new conductive fibers based on thermoplastic-MWCNT composites. Using an improved mixing method to produce the composite master-batches (assisted by ultrasonication) has led to better dispersion levels of CNT compared to the other composites tested (obtained by traditional melt-mixing methods). In good agreement with the high dispersion levels observed, the conductivity and spinability of the material into fibers are better, too. Through the modification of different variables during the mixing process of the master-batches, and different formulations, we have produced polypropylene composites (5% MWCNT) with low surface resistance ($10 \Omega/\text{square}$) that can be extruded into fibers. In fact, due to the good dispersion and high electrical conductivity achieved in the composites, the CNT network of the composites can be observed by SEM.

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D:HP09 Research through Design: A Way to Drive Innovative Solutions in the Field of Smart Textiles

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Research through design allows creating a dialogue with the material. It uses making and reflection on action as a generator of knowledge. Our aim is to explore the opportunities and challenges of smart textiles in the field of Product Service Systems. The Fablab is our set up, a place that allows us to combine the hacking-, scientific-, and design community. It stimulates collaboration and the knowledge exchange needed for the development of smart textile systems. A collaborative prototyping workshop for medical products combined two worlds; textiles in Saxion (focused on implementing conductives into textile structures and functional- / 3D printing to create systems for applications such as flexible heating systems and wearable technology) and Industrial Design at TU/e (focused on the design of intelligent products, systems and services by the research through design approach). TU/e students were able to foresee how to approach the project from a system level. This helped Saxion students to integrate temperature sensors, while Saxion students could support in choosing the right yarn resistance. Most of the results came from trial and error. The collaboration between disciplines speeded up the process by reducing the resistance to the new and skipped the frustration on failure.

E:HP09 Toward Low-cost Micro-reactors with High Temperature Uniformity

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Uniformity of temperature in micro-hot-plates (MHPs) may be critical in gas sensors, infrared emitters and micro-reactors (e.g. for CVD). However, available models for temperature distribution in MHPs are not sufficiently accurate; consequently, unless heat spreading plates may be integrated (which is often impossible due to both cost and complexity) conventional MHPs typically have rather large temperature differences within the active area. Here, by considering a perfectly circular geometry and small membrane thickness (as in typical MHPs), we show that the temperature distribution can be accurately expressed by a proper combination of modified Bessel functions. Afterwards, for a two-heaters MHP design, we compare two different boundary conditions for the outer heater, namely no heat flow from outer heater to the inner heater (as previously proposed in literature) and identical temperatures at the inner and outer heaters, and demonstrate that keeping the temperatures at the inner and outer heaters at the same value results in substantially improved temperature uniformity. Our results are consistently confirmed by FEM simulations and provide guidelines for the design of low-cost micro-reactors with high temperature uniformity without the need for heat-spreading plates.

E:HP10 Quartz Crystal Microbalances for Monitoring the Growth of ZnO Nanowires and Nanosheets

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The accurate control of nanostructures during low-temperature, low-cost wet-chemistry processes may be crucial for integrating nanostructures in MEMS. Quartz Crystal Microbalances (QCM) are widely used for monitoring vacuum deposition techniques. Our intent is to take advantage of QCM-substrates for on-line monitoring nanostructures grown by wet chemistry. Therefore, after recording QCM-admittance spectra during hydrothermal growth of nanostructures, we determined the components of the equivalent electrical circuit by curve fitting so that, by analyzing the time evolution of these components, we separately identified the effects of liquid loading and of nanostructures growth. As a proof-of-concept, we successfully monitored the growth of different ZnO nanostructures (quasi-1D nanowires and quasi-2D nanosheets) by immersing a QCM in equimolar solutions of zinc nitrate and HMTA at 90°C. In both cases, we found an initial stage with almost constant growth rate followed by a gradual reduction of the growth rate; moreover, not only the Q-factor was greatly reduced by the nanostructures, but this reduction was substantially faster for nanowires than for nanosheets, thus confirming that this Q-factor reduction is most likely due to the increase in surface roughness.

E:HP11 Fabrication of Sub-micron Metal-oxide-metal (MOM) Diodes Using Two Novel Techniques

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This work presents details of metal-oxide-metal (MOM) tunnel diodes fabricated with the aim of achieving sub-micron areal dimensions and a sub 5 nm thickness oxide, i.e. one which is sufficiently thin to allow direct electron tunnelling. These diodes have the potential to rectify THz radiation collected by micron-scale antennas from waste heat and successfully convert this into a DC current. The antennas are made with dimensions in the micron range: the diode must be much smaller than this, which presents challenges to lithography and material uniformity. A functional diode is achieved by using one metal which oxidises readily (in our case, titanium) and another which is inert (platinum); the choice of metals also ensures a maximum work function difference, essential for optimised diode performance. Here we have studied two main titanium oxidation techniques, and examined the structures physically (TEM, AFM, ToF-SIMS) and noted their influence on diode performance. Furnace oxidation produced 7 nm oxides. An alternative method of reactive ion etching was used to etch and regrow in situ a much thinner, controllable oxide via plasma oxidation. For device fabrication, phase shift lithography with a PDMS based mask has been used to produce 200 nm features in these structures.

E:HP13 Comparison of ZnO-based Piezoelectric Nanogenerators on Flexible Substrates

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In this work, we present and compare three different methods for fabricating piezoelectric nanogenerators onto flexible substrates which have become the most promising candidates for energetically autonomous wearable and medical/implantable devices. All devices are employing either high-density vertical-ZnO nanorod arrays or nanotextured ZnO films grown via a facile, low-cost hydrothermal method on Kapton and Polyethylene terephthalate (PET) substrates. The first method exploits ZnO seeding layers formed by sputtering, and the other two purely chemically developed seeding layers by spin-coating of HMTA-based sol-gel and zinc-acetate ethanol solution. Typical output voltages achieved under instantaneous and sinusoidal external excitation reached up to 4V for devices that did not exceed a few cm². The three alternative fabrication techniques are compared in order to assess their performance in terms of output power versus cost and ease-of-fabrication and to optimize a rapid and cost-efficient method for driving small and low-power devices.

The research activities that led to these results, were co-financed by Hellenic Funds and by the European Regional Development Fund (ERDF) under the Hellenic National Strategic Reference Framework (NSRF) 2007-2013, according to Contract no. MICRO2-45 of the Project "Development of Innovative sensor systems offering distributed intelligence – MEMSENSE" within the Programme "Hellenic Technology Clusters in Microelectronics – Phase-2 Aid Measure".

G:HP04 Harsh Environment SMART Sensor Systems

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Sensor systems can provide highly valuable information regarding the ambient conditions that occur in various extreme environments. On the surface of Venus, down-hole in oil wells and around steam pipes, temperature, pressure, chemical, acoustic and seismic sensors can help people to better understand such environments and in certain cases avoid catastrophic damage. Electronics, such as amplifiers and transmitters, greatly improve the efficacy of sensors by increasing the signal strength compared with background noise and minimizing the need for physical wiring, yielding a more autonomous system. Unfortunately, these harsh conditions require robust enclosures as well as high temperature survivable electronics and packaging. This can be extremely challenging for the target temperatures which range from 200 to 500°C for the aforementioned applications. To that end, this paper will discuss the evaluation and development of electronics and packaging for harsh environment smart sensor systems. Electronics evaluated include commercially available solid state electronics as well as advanced vacuum devices. Passive components, which pose a particularly challenging problem, were also evaluated, as were high temperature material systems to integrate all of these discrete devices.

G:HP05 Safety Assessment of Bridge Structures using Ambient Vibration

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It is a current practice to conduct load testing to evaluate the load-carrying capacity of bridge structures for the safety assessment. However, it is cumbersome for the field load test to be carried out in the case of bridges with large traffic volume since the test requires traffic interruption for a certain time of period. Therefore, a system or an algorithm is needed that enables the load-carrying capacity of bridge structures to be estimated without suspension of traffic. Recently, in order to meet such needs, research works on the algorithm capable of assessing the load-carrying capacity of bridge structures without incurring traffic dislocation using the ambient vibration due to the traffic loads are actively under way. In this study, relative load-carrying capacity (RLC) evaluation algorithm in which the change of load-carrying capacity of a bridge structure can be estimated by using the variation of natural frequency induced by the stiffness change due to the deterioration of the bridge

was proposed. Indoor test using a truss-typed model structure and field measurement were performed to verify the suggested algorithm and it was shown that the RLC estimation algorithm is suitable for the safety assessment of bridge structures in simple and efficient manner.

G:HP06 A Roadmap for In Situ Structural Health Monitoring of ADF Aircraft

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As a military air fleet ages an increasing number of safety-by-inspection (SBI) programs are generally required to manage the fleet's structural integrity. Currently, SBI programs rely on the periodic application of conventional non-destructive inspection (NDI), which can be a time-consuming and expensive process, particularly if the area of interest is in a location that requires disassembly for inspection. SBI programs also have implications for aircraft availability. These factors can contribute significantly to the decision to retire an aircraft. Structural Health Monitoring (SHM) provides, in principle, a far more cost efficient and rapid basis for an SBI program. In contrast to conventional NDI practice, a diagnostic inspection through SHM is done by means of a network of embedded or surface-mounted in situ sensors and actuators. Once the network is installed, inspections can be done without the need for component disassembly, and diagnostic information can be obtained at will and with minimal expense thus significantly reducing through life support costs and improving aircraft availability whilst maintaining safety. For these reasons, SHM promises to be an attractive option for the aircraft structural integrity manager when implementing SBI programs. The Australian Defence Science and Technology Organisation (DSTO) has a program of work aimed at developing SHM systems for retrofitment to existing Australian Defence Force (ADF) aircraft. As a first step the approach is to develop SHM systems that will fit seamlessly (i.e. minimising ADF procedure development requirements and the logistic footprint) into existing or new SBI programs. Initially, inspections will be undertaken at fixed intervals, e.g. using classic or continually adjusted SBI approaches. Once confidence is gained in the SHM system a continuous approach may be implemented where the maintainer does not have a predetermined inspection interval but relies on the system informing the maintainer about requirements for future maintenance actions.

The paper gives an overview of the DSTO roadmap for SHM system development, validation, certification and implementation, in the context of technologies and systems that meet ADF future requirements.

H:HP15 From Super-hydrophobic to Super-hydrophilic. Self-cleaning and Anti-fog Transparent Materials with Plasma Nanotechnology

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Examples of extreme wetting are present in a huge variety of living organisms. In particular in case of plant leaves, the adaptation to different environments led to the existence of super-hydrophobic and super-hydrophilic surfaces, but also hydrophobic and hydrophilic, at variable extents. This is the result of different combinations of outer chemistry (waxes) and micro/nano texture (cuticle folding, waxes structuring). In this contribution we report on a combination of cold plasma techniques aimed to reproduce extreme wetting states (and the full range between) on artificial materials, like transparent plastics, where self-cleaning (super-hydrophobic or super-hydrophilic) and/or anti-fog (super-hydrophilic) modifications are required for construction, automotive, optical applications. In particular, we have tailored the consecutive processes: 1. etching for producing a nano-scale maskless texturing of the plastic surface; 2. plasma deposition onto textured surfaces of differently wettable coatings. The characterization of extreme wetting states has been accomplished also with relation to their applicative performances (water adhesion, fogging). We show that a continuous tuning in the full wetting scale is achieved with stability in time of the modifications.

H:HP16 A Single Step Lymphocyte Sorting Based on Molecular Computing on Cell Surface

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The existing preparative isolation of narrow subpopulations of cells is primarily done with multi-step procedures. We develop, optimize, and then benchmark against standard procedures, our high-yielding, easy-

to-scale up, and generally applicable single-step separation procedures to isolate arbitrarily narrow subpopulations of lymphocytes uniquely characterized through presence and absence of multiple cell surface markers. Our method relies on an autonomous molecular computing cascade in which sets of molecules behave as molecular automata "answering" locally a series of "if.then" questions related to the composition of cell surfaces. We use a series of inter-reactive reagents that self-(re)organize on cell surfaces in order to reveal an affinity tag only on target cells that satisfy a precisely defined set of conditions. In contrast, on non-target cells, self-organization will be incomplete, resulting in the failure to tag. In our presentation, multiple cell-surface markers will be translated to the presence of fluorescein on the cell-surface as a tag; the dye can be captured by antibody and tagging can be monitored by flow cytometry. The resulting tag can be used to isolate in a single step the targeted cells in the presence of other subpopulations.

J:HP23 Development of Nanopatterned Surfaces to Control Bacterial Growth

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Bacterial adhesion on medical devices represents a pending problem causing a large part of hospital-acquired infections. Strategies based on the immobilization of biocidal substances were extensively explored to limit bacterial colonization. However, they suffer from their potential cytotoxicity or their role in the emergence of multi-resisting pathogens. Recent studies have reported that surface nanostructures impact significantly the bacterial functions. Therefore, we explored the development of chemically nanopatterned surfaces to control the bacterial behavior. By means of nanoimprinting technique and surface chemistry, we designed surfaces composed of nanometric adhesive features geometrically distributed in a non adhesive background. These nanopatterned surfaces were tested towards *E. coli* bacteria at different steps of the cell proliferation. Our results revealed that the nanopattern strongly influences the growth and the spatial arrangement of bacteria. By probing the individual cell by AFM and SEM techniques, we showed that the nanopattern influences also the cell morphology and the arrangement of appendices involved in the proliferation mechanism. Proteomic analysis are currently in progress to investigate how the nanopattern affects the composition of the cell membrane.

J:HP24 Hybrid Materials Containing Mn or Co-doped ZnO Nanoparticles for Controlled Drug Release

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Polyether-siloxane hybrids matrices show single properties as high mechanical resistance, transparency and flexibility being a potential material for several scientific and technological areas including the use in drug delivery devices. ZnO semiconductor nanoparticles has strongly attracted attention of the researchers due to their electronic, luminescent, catalytic and optoelectronics varying significantly with particle size. Other relevant factor is the possibility of ZnO nanoparticles doped with magnetic elements to create new class of materials known

as diluted magnetic semiconductors (DMS), a multifunctional material with magneto-optical properties. The aim of this work is to prepare a controlled drug release device combining the individual properties of each component in the same material, using the magnetic property of the DMS to drive the delivery device on the sick organ and the luminescent property of the ZnO to monitor the device position inside the human body.

J:HP25 Influence of Crystallinity and Fiber Orientation on Hydrophobicity and Biological Response of Poly(L-lactide) Electrospun Mats

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Poly(L-lactide) electrospun mates have been produced with random and aligned fiber orientation and degrees of crystallinity from 0 up to nearly 50%. These two factors, fiber alignment and degree of crystallinity strongly affect the hydrophobicity of the samples, being this larger for the aligned fiber mats and for the fibers with higher degree of crystallinity. Whereas the first effect can be associated to a decrease in the degree of porosity the second should be related to an increase in fiber stiffness as the observed fiber roughness variations does not show strong differences between the samples. Proliferation of human chondrocytes cultured in monolayer on these substrates is similar in both aligned and non-aligned amorphous mats. Crystallization of the aligned mats, on the other hand, nearly suppresses proliferation and the cells produce higher amounts of aggrecan, characteristic of the extracellular matrix of hyaline cartilage.

J:HP26 Reversible Peptide Binding to Temperature Responsive Hydrogel Particles

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The goal of this project is to synthesize temperature responsive hydrogel particles that can selectively bind and release peptides or proteins through metal affinity interactions. Particles of poly(N-isopropyl acrylamide-co-vinylbenzyl iminodiacetic acid) (PNIPAM-co-VBIDA) were synthesized by a two step dispersion polymerization using poly(N-vinyl pyrrolidone) as a steric stabilizer. The synthesis result in particles of controlled and uniform size that are colloiddally stable over a wide range of pH and ionic strength. The particles were shown to uptake nickel ions through chelation to the iminodiacetic acid groups. Peptides containing His6-tag (six consecutive histidine residues) were shown to selectively attach to the PNIPAM-co-VBIDA particles containing chelated nickel. No peptide binding was observed in control experiments using particles that lacked either nickel ions or the iminodiacetic acid ligand. The specifically attached peptides were successfully removed from the particles by imidazole. The imidazole acts as a competitive ligand that is more strongly attached than the peptides are to the chelated nickel. The novel particles with surface bound peptides or proteins have potential applications in sensors, biocatalysis, and in controlled delivery.





CIMTEC 2012

		<i>Flowsheet</i>		JUNE 10		JUNE 11		JUNE 12		JUNE 13		JUNE 14	
				A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.	A.M.	P.M.
4 th International Conference	SMART MATERIALS STRUCTURES & SYSTEMS	REGISTRATION											
		SYMPOSIUM A				A		A		A		A	
		Special Session A-10						A-10		A-10			
		Focused Session A-11								A-11	A-11	A-11	A-11
		Focused Session A-12				A-12		A-12		A-12		A-12	A-12
		Focused Session A-13				A-13		A-13		A-13		A-13	
		Special Session A-14				A-14		A-14					
		Focused Session A-15				A-15		A-15		A-15		A-15	A-15
		SYMPOSIUM B				B		B		B		B	B
		SYMPOSIUM C				C		C		C			C
		SYMPOSIUM D				D		D		D		D	
		SYMPOSIUM E				E		E		E		E	
		SYMPOSIUM F				F		F		F		F	F
		SYMPOSIUM G				G		G		G		G	
		Special Session G-6								G-6		G-6	
		SYMPOSIUM H				H		H		H		H	H
		Special Session H-7						H-7	H-7	H-7			
		SYMPOSIUM I				I		I		I		I	
		SYMPOSIUM J				J		J		J		J	J
		POSTER MOUNTING											
		POSTER DISCUSSION											
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