

## HIGHLY EFFICIENT ORGANIC DEVICES

Karl Leo, TU Dresden  
Mommstr, Dresden, 01219, Germany  
T: +49-351-463-34389, F: -7065, leo@iapp.de

Organic semiconductors with conjugated electron system are currently intensively investigated for optoelectronic applications. This interest is spurred by novel devices such as organic light-emitting diodes (OLED), and organic solar cells. For both devices, high efficiency is a key parameter for many applications. In this talk, I will discuss some of the recent progress on highly efficient OLED and solar cells, in particular results using doped transport layers /1/: Surprisingly, doping (for raising the conductivity) has been largely ignored till now in organic devices, in contrast to classical silicon technology where controlled n- and p-type doping has always been a standard technique needed for virtually all devices. The concept of molecular doping allowed to realize green OLED devices with the highest efficiencies reported so far /2/, well exceeding the efficiency of current inorganic GaN LED! The devices were pin-devices where the emitting layer is embedded between a p-doped hole transport layer and an n-doped electron transport layers. It has been shown that these pin-structures can also achieve extremely long lifetimes. White OLED have recently achieved very high efficiencies of 90lm/W /3/, significantly higher than fluorescent tubes, opening the path to a new form of high-efficiency area lighting devices. The doping concepts can be applied in organic solar cells as well. Here, the use of electrically doped transport layers is helpful for an optimized optical design since it yields large freedom in the choice of window layer thickness, this making it easy to put the absorber layers in the electric field maximum in the cavity /4/. Also, doped layers are a key point in efficient charge recombination junctions for tandem solar cells: It has been shown that a pn-junction is an excellent recombination contact causing very small voltage loss. Recently, we have achieved solar cells with certified efficiency exceeding 8% on larger area. /1/ K. Walzer, B. Maennig, M. Pfeiffer, M. K. Leo, Chem. Rev. 107, 1233 (2007) /2/ G. He, M. Pfeiffer, K. Leo, M. Hofmann, J. Birnstock, R. Pudzich, J. Salbeck, Appl. Phys. Lett. 85, 3911 (2004). /3/ S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lüssem, Nature 459, 234 (2009). /4/ R. Schueppel, R. Timmreck, N. Allinger, T. Mueller, M. Furno, C. Uhrich, K. Leo, and M. Riede, J. Appl. Phys. 107, 044503 (2010). \*: I would like thank Jan Blochwitz-Nimoth, Torsten Fritz, Kentaro Harada, Gufeng He, Qiang Huang, Björn Lüssem, Rico Meerheim, Martin Pfeiffer, Sebastian Reineke, Moritz Riede, Rico Schüppel, Gregor Schwartz, Karsten Walzer, Ansgar Werner, Xiang Zhou, and many others for their participation in this work.

## MECHANISM OF THE ENERGY LEVEL ALIGNMENT AND BAND BENDING IN ORGANIC DEVICES: WHY DOES THE FERMI LEVEL MOVE IN THE HOMO-LUMO GAP?

Nobuo UENO, Graduate School of Advanced Integration Science, Chiba University  
1-33, Yayoi-cho, Inage-ku, Chiba, Chiba, 263-8522, Japan  
T: +81-43-290-3447, F: +81-43-207-3896, uenon@faculty.chiba-u.jp

Organic semiconductor has an n- or a p-type charge-transport property that seems to be determined by the molecule itself. Related mysteries exist in regard to the energy level alignment (ELA) at organic/organic and organic/inorganic interfaces and the band bending. Many ultraviolet photoelectron spectroscopy (UPS) studies have shown that the vacuum level misalignment and drastic variation of the Fermi level (EF) in the organic band gap appear in various organic systems. Because thermal equilibrium concept strictly requires that the Fermi levels of the organic film and the electrode coincide at the interface after contact, our understanding of the ELA mechanism still lacks consistency with this requirement [1-3]. The mysteries on the ELA mechanism have been considered to originate from unknown electronic density of gap states (DOGS) due to unknown impurities that controls position of the EF in the HOMO-LUMO gap and thus band bending phenomena. However, the experiment has been impossible because of limitation of the sensitivity of UPS [4,5]. We will introduce direct measurements of the DOGS with ultrahigh sensitivity and ultralow background UPS and show experimental evidences that (i) there is a very low DOGS reaching the EF in organic-device related interfaces due to imperfect molecular packing [4-6] and (ii) the DOGS controls the EF position in the HOMO-LUMO gap to result in the band bending [6,7]. [1] S. Kera, Y. Yabuuchi, H. Yamane, H. Setoyama, K.K. Okudaira, A. Kahn, and N. Ueno, *Phys. Rev. B*, 70, 085304 (2004). [2] H. Fukagawa, S. Kera, T. Kataoka, S. Hosoumi, Y. Watanabe, K. Kudo, and N. Ueno, *Adv. Mater.* 19, 665 (2007). [3] S. Duhm, G. Heimel, I. Salzmann, H. Glowatzki, R. L. Johnson, A. Vollmer, J. P. Rabe, and N. Koch, *Nat. Mater.* 7, 326 (2008). [4] T. Sueyoshi, H. Fukagawa, M. Ono, S. Kera, and N. Ueno, *Appl. Phys. Lett.* 95, 183303 (2009). [5] T. Sueyoshi, H. Kakuta, M. Ono, K. Sakamoto, S. Kera, and N. Ueno, *Appl. Phys. Lett.* 96, 093303 (2010). [6] H. Y. Mao, F. Busiolotti, D.-C. Qi, R. Wang, S. Kera, N. Ueno, A. T. S. Wee, and W. Chen, *Org. Electronics* 12, 534 (2011). [7] T. Hosokai, H. Machida, S. Kera, A. Gerlach, F. Schreiber, and N. Ueno, submitted to *Phys. Rev. B*.

## **WHITE ORGANIC LIGHT-EMITTING DIODES FOR LIGHTING**

Ma Dongge, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences  
Changchun Renmin Street 5625, Changchun, Jilin, 130022, P.R. China  
T: 0086-431-85262357, F: 0086-431-85262873, mdg1014@ciac.jl.cn

White-light organic light-emitting diodes (WOLEDs) have drawn an increasing attention for application in backlights in liquid crystal displays and next generation solid-state lighting due to the advantages of light weight, low operating voltage and high contrast. This talk will discuss the advances in WOLEDs and our recent progresses made in developing efficient WOLEDs at CIAC. WOLEDs with a power efficiency of over 50 lm/W and CIE of (0.44, 0.41) have been achieved through proper selection of the active materials and optimal design of the device structure.

## NOVEL CATEGORIES OF ORGANIC LUMINESCENT MATERIALS USEFUL FOR ELECTROLUMINESCENCE

Chihaya Adachi, Center for Organic Photonics and Electornics Research (OPERA), and Center for Future Chemistry, Kyushu University

744, Motoooka, Nishi,, Fukuoka, Fukuoka, 819-0395, Japan

T: +81928026920, F: +81928026921, adachi@cstf.kyushu-u.ac.jp

Kenichi Goushi, Center for Organic Photonics and Electornics Research (OPERA), and Center for Future Chemistry, Kyushu University

Kou Yoshida, Center for Organic Photonics and Electornics Research (OPERA), and Center for Future Chemistry, Kyushu University

Keigo Sato, Center for Organic Photonics and Electornics Research (OPERA), and Center for Future Chemistry, Kyushu University

We demonstrate novel two ways to realize very small energy gap between singlet and triplet exciton levels  $dE(\text{ST})$ , which lead to high efficiency for radiative-exciton production. Since  $dE(\text{ST})$  can be determined by the exchange energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO),  $dE(\text{ST})$  for donor-acceptor type molecules and exciplexes is expected to be very small, due to the separation of the positive and negative charges located mainly in donor and acceptor units, respectively. Our observations show that a high reverse intersystem crossing (ISC) efficiency can be realized using these unique molecular systems. By taking advantage of the highly efficient ISC, we demonstrate a pronounced enhancement of electroluminescence efficiency under electrical excitation.

## ORGANOMETALLICS FOR ENERGY CONVERSION IN SOLAR CELLS AND OLEDs

Wai-Yeung Wong, Hong Kong Baptist University  
Department of Chemistry, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong  
T: (852)34117074, F: (852)34117348, rwywong@hkbu.edu.hk

Organometallic molecules have become a field of intense activities in the optoelectronic research. They hold great promise as versatile functional materials for use in energy interconversions. These include systems where light is transformed into electricity and vice versa. This lecture highlights the recent progress in the development of some organometallic complexes and polyene polymers which exhibit tunable luminescent and electronic properties. Focus is placed on evaluating their suitability as emitters in light-emitting applications and semiconductors in photovoltaic cells for solar power generation. The approaches based on structural variation of the organic groups to tune the emission and photovoltaic properties of these materials will be presented.

References: 1. Wong, W.-Y.; Lam, C.-L. *Acc. Chem. Res.* 2010, 41, 1246-1256. 2. Wong, W.-Y.; Wang, X.-Z.; He, Z.; Djuricic, A. B.; Yip, C.-T.; Cheung, K.-Y.; Wang, H.; Mak, C. S. K.; Chan, W.-K. *Nat. Mater.* 2007, 6, 521-527. 3. Wong, W.-Y.; Ho, C.-L. *J. Mater. Chem.* (Feature article) 2009, 19, 4457-4482.

## CONSTRUCT THE FUNCTIONAL MOLECULAR CRYSTALS AND APPLIED IN LUMINESCENT AND LASER DEVICES

Yuguang Ma, State Key Lab for Supramolecular Structure and Materials, Jilin University  
Qianjin road 2699, Changchun, Jilin, 130012, P.R. China  
T: 0431-85168480, F: 0431-85193421, ygma@jlu.edu.cn

Generally, the optoelectronic performance (luminescence and carrier mobility) of organic crystals constructed by pi-conjugated molecules depended on the molecular stacking modes. We present here our investigations for the relationship of molecular stacking structure and optoelectronic properties in pi-conjugated molecule crystals, involving construct crossed dipole stacking (X-stacking) for high crystal luminescence efficiency, J-type dipole stacking and strong  $\pi$ - $\pi$  interactions in the crystals of distyrylbenzene derivatives, uniaxially oriented molecular crystal of cyano substituted oligo(p-phenylene vinylene), and doped organic crystals exhibiting high luminescent efficiency, color-tunable emission. Recently a high luminescence efficiency cyano substituent oligo(para-phenylene vinylene) (CN-DPDSB) crystal ( $\eta = 95\%$ ) grown by the physical vapor transport (PVT) method showed well-balanced bipolar carrier-transport characteristic ( $\mu_{\text{hole}} = 2.5\text{-}5.5 \times 10^{-2} \text{ cm}^2/\text{Vs}$ ;  $\mu_{\text{electron}} = 0.9\text{-}1.3 \times 10^{-2} \text{ cm}^2/\text{Vs}$ ) and excellent optically pumped laser properties that the threshold for ASE is about  $4.6 \mu\text{J}/\text{pulse}$  ( $23 \text{ KW}/\text{cm}^2$ ), and the gain coefficient at the peak wavelength of ASE and loss coefficient caused by scattering are  $\sim 35$  and  $\sim 1.7 \text{ cm}^{-1}$ , respectively. That indicates CN-DPDSB crystal to be as a promising candidate for organic laser diodes.

## **SOLUTION PROCESSED CONJUGATED MATERIALS FOR ORGANIC PHOTOVOLTAIC DEVICES**

V. A. L. Roy, City University of Hong Kong  
Tat Chee Avenue, Kowloon Tong, Hong Kong, Hong Kong, 0000, China  
T: 3442 2729, F: 3442 0538, val.roy@cityu.edu.hk  
Zong-Xiang Xu, City University of Hong Kong

Organic photovoltaic (OPV) devices with potential application in low cost solar energy conversion have attracted huge attention in recent years. A major challenge is to design materials that allows for broad solar spectral coverage to enhance the generation of excitons as well as better charge carrier transport properties. The optical and electronic conductivity properties of a given semiconductor depend on factors such as film morphology, molecular orbital energy alignment and molecular packing. Therefore one of the important aspects is molecular alignment that enhances the intermolecular charge transport of the active material. Here, we discuss various carbon based conjugated system and their self-assembly properties for the solution processed high efficiency photovoltaic devices.

[1] P. Peumans, A. Yakimov, S. R. Forrest, J. Appl. Phys. 2003, 93, 3693. [2] J. G. Xue, S. Uchida, B. P. Rand, S. R. Forrest, Appl. Phys. Lett. 2004, 85, 5757. [3] S. Uchida, J. G. Xue, B. P. Rand, S. R. Forrest, Appl. Phys. Lett. 2004, 84, 4218. [4] M. Y. Chan, S. L. Lai, M. K. Fung, C. S. Lee, S. T. Lee, Appl. Phys. Lett. 2007, 90, 023504.

## NOVEL ELECTRONIC AND OPTICAL PROPERTIES OF GRAPHENE AND GRAPHENE NANOSTRUCTURES

Steven G. Louie, University of California at Berkeley  
Department of Physics, Berkeley, California, 94720, U.S.A.  
T: 15106421709, F: 15106439473, sglouie@berkeley.edu

We report results from theoretical studies on the electronic, transport and optical properties of graphene and graphene-based nanostructures. A number of phenomena derived from the unique electronic structure of graphene are shown. The carrier dynamics in graphene exhibits anomalous anisotropy when subjected to an external periodic electrostatic potential of nanometer dimensions (called graphene superlattices). Under appropriate conditions, these graphene superlattices are shown to be electron supercollimators and new generation of massless Dirac fermions may be created. The nanoribbons are semiconductors with novel electronic, magnetic and optical properties. Our latest studies have further found the following: Magnetic edge states are predicted to persist on chiral graphene nanoribbons and have been seen in scanning tunneling spectroscopy (STS) measurements. The properties of graphene under a 1D inhomogeneous magnetic field may be mapped into those of one under an electric field and vice versa. Because of reduced dimensionality, electron-electron interaction effects are particularly important, leading to strong excitonic effects in the optical response of single- and multi-layer graphene. Quantum phases in graphene and bilayer graphene such as the Berry's phase and the sign of the hopping integrals are directly extractable from angle-resolved photoemission spectroscopy. Charge transport across grain boundaries in graphene is also highly unusual, exhibiting a sizable transport gap for a broad class of grain boundaries. This work was supported by NSF, DOE and ONR.



## SYNTHESIS OF GRAPHENE AND ITS APPLICATIONS IN ELECTRONICS

Yunqi Liu, Institute of Chemistry, Chinese Academy of Sciences  
Zhongguancun, Beijing, 100190, China  
T: +86-10-62613253, F: +86-10-62559373, liuyq@iccas.ac.cn

Graphene, a single layer of graphite, has many extraordinary electrical, mechanical, and thermal properties, such as high carrier mobility, ambipolar electrical field effect, tunable band gap, room temperature quantum hall effect, high elasticity, and superior thermal conductivity. In this presentation, 1-8 we will report the preparation of few-layer graphene by chemical vapor deposition, solution exfoliation of graphite into large flake graphene by oleyl amine, and graphene ribbons prepared by a template method. An n-type field-effect transistor (FET) made of N-doped graphene and a high performance FET with graphene-modified source/drain electrodes are described. A general route toward patterning of graphene oxide by a combination of wettability modulation and spin-coating is also involved.

1. Chong-an Di, Dacheng Wei, Gui Yu, Yunqi Liu, Yunlong Guo, and Daoben Zhu, Patterned graphene as source/drain electrodes for bottom-contact organic field-effect transistors, *Adv. Mater.*, 2008, 20(17), 3289-3293. 2. Dacheng Wei, Yunqi Liu, Yu Wang, Hongliang Zhang, Liping Huang and Gui Yu, Synthesis of N-Doped Graphene by Chemical Vapor Deposition and Its Electrical Properties, *Nano Lett.*, 2009, 9(5), 1752-1758. 3. Dacheng Wei, Yunqi Liu, Hongliang Zhang, Liping Huang, Bin Wu, Jianyi Chen, and Gui Yu, Scalable Synthesis of Few-Layer Graphene Ribbons with Controlled Morphologies by a Template Method and Their Applications in Nanoelectromechanical Switches, *J. Am. Chem. Soc.*, 2009, 131(31), 11147-11154. 4. Jian Zheng, Chong-an Di, Yunqi Liu, Hongtao Liu, Yunlong Guo, Chunyan Du, Ti Wu, Gui Yu, and Daoben Zhu, High Quality Graphene with Large Flakes Exfoliated by Oleyl Amine, *ChemComm*, 2010, 46(31), 5728-5730. 5. Dacheng Wei, Yunqi Liu, Controllable Synthesis of Graphene and its Applications, *Adv. Mater.*, 2010, 22(30), 3225-3241. 6. Yunlong Guo, Chongan Di, Hongtao Liu, Jian Zheng, Lei Zhang, Gui Yu, and Yunqi Liu, General Route toward Patterning of Graphene Oxide by a Combination of Wettability Modulation and Spin-Coating, *ACS Nano*, 2010, 4(10), 5749-5754. 7. Liping Huang, Bin Wu, Gui Yu, and Yunqi Liu, Graphene: learning from carbon nanotubes, *J. Mater. Chem.*, 2011, 21(4), 919-929. 8. Hongtao Liu, Yunqi Liu, Daoben Zhu, Chemical doping of graphene, *J. Mater. Chem.*, 2011, 21(10), 3335-3345.

## SOLUTION-PROCESSED GRAPHENE MATERIALS FOR ALL-CARBON ELECTRONICS

Yongsheng Chen, Nankai University  
Weijin Rd 94, Tianjin, 300071, CHINA  
T: +86-22-2350-0693, F: +86-22-2349-9992, yschen99@nankai.edu.cn

Graphene has been thought as an outstanding choice for many organic and all-carbon device applications owing to its unique structure and many outstanding properties. In this presentation, the results of a series of investigation using solution-processed graphene (SPGraphene) as the active, transparent electrode and composite materials for organic, and flexible various devices such as OPV, OLED, FET, Supercapacitor, Memory Device, Organic Magnetic/Electrical Switch, Actuators and so on will be presented. The results demonstrate that it is highly possible that SPGraphene, produced at large scale, can be an excellent choice as both the transparent electrode and active material for the next generation organic electronics.

### References:

1. 'Toward All-Carbon Electronics: Fabrication of Graphene-Based Flexible Electronic Circuits and Memory Cards Using Maskless Laser Direct Writing', Jiajie Liang, Yongsheng Chen, Yanfei Xu, Zhibo Liu, Long Zhang, Xin Zhao, Xiaoliang Zhang, Jianguo Tian, Yi Huang, Yanfeng Ma, Feifei Li; ACS Appl. Mater. Interfaces, 2010, 2, 3310.
2. 'Graphene-based conducting ink for direct inkjet printing of flexible conductive patterns and their applications in electric circuit and chemical sensors', Lu Huang, Yi Huang, Jiajie Liang, Xiangjian Wan, Yongsheng Chen\* Nano Res., 2011, in press.
3. 'Towards Flexible All-Carbon Electronics: Flexible Organic Field-Effect Transistors and Inverter Circuits Using Solution-Processed All Graphene Source/Drain/Gate Electrodes', Yongsheng Chen, Yanfei Xu, Kai Zhao, Xiangjian Wan, Jiachun Deng, Weibo Yan Nano Res, 2010, 10, 714.
4. 'Flexible, Magnetic and Electrically Conductive Graphene/Fe<sub>3</sub>O<sub>4</sub> Paper and Its Application for Magnetic-Controlled Switches', Jiajie Liang, Yanfei Xu, Dong Sui, Long Zhang, Yi Huang, Yanfeng Ma, Feifei Li, Yongsheng Chen, J Phys Chem C, 2010, 114, 17465.
5. 'Polymer photovoltaic devices with transparent graphene electrodes produced by spin-casting', Yanfei Xu, Guankui Long, Lu Huang, Yi Huang, Xiangjian Wan, Yanfeng Ma, Yongsheng Chen, Carbon, 2010, 48, 3308.
6. 'Evaluation of Solution-Processed Reduced Graphene Oxide Films as Transparent Conductors', Hector A. Becerril, Jie Mao, Zunfeng Liu, Randall M. Stoltenberg, Zhenan Bao, and Yongsheng Chen, ACS Nano, 2008, 2, 463.
7. 'Organic solar cells with solution-processed graphene transparent electrodes', Junbo Wu, Hector A. Becerril, Zhenan Bao, Zunfeng Liu, Yongsheng Chen, and Peter Peumans, Appl Phys Lett, 2008, 92, 263302-1.
8. 'Organic Photovoltaic Devices Based on a Novel Acceptor Material: Graphene', Zunfeng Liu, Qian Liu, Xiaoyan Zhang, Yi Huang, Yanfeng Ma, Shougen Yin and Yongsheng Chen, Adv Mater. 2008. 20, 3924.

## **PROBING PHONON EMISSION VIA HOT CARRIER TRANSPORT IN SUSPENDED GRAPHITIC MULTILAYERS**

Haibing Peng, University of Houston  
Department of Physics and the Texas Center for Superconductivity, University of Houston, Houston,  
Texas, 77204, USA  
T: 713-743-8233, F: 713-743-3589, haibingpeng@uh.edu  
Carlos Diaz-Pinto, University of Houston  
Sungbae Lee, University of Houston  
Viktor G. Hadjiev, University of Houston

We study hot carrier transport under magnetic fields up to 15 T in suspended graphitic multilayers through differential conductance ( $dI/dV$ ) spectroscopy. Distinct high-energy  $dI/dV$  anomalies have been observed and shown to be related to intrinsic phonon-emission processes in graphite. The evolution of such  $dI/dV$  anomalies under magnetic fields is further understood as a consequence of inter-Landau level cyclotron-phonon resonance scattering. The observed magneto-phonon effects not only shed light on the physical mechanisms responsible for high-current transport in graphitic systems, but also offer new perspectives for optimizing performance in graphene-based nano-electronic devices.

## ASSEMBLY, MODIFICATION, HYBRIDIZATION AND FUNCTIONALIZATION OF GRAPHENE OXIDES

Shihe Yang, The Hong Kong University of Science and Technology  
Clear Water Bay, Kowloon, Hong Kong, Hong Kong SAR, -, China  
T: (852) 2358-7362, F: (852) 2358-1594, chsyang@ust.hk  
Yongcai Qiu, The Hong Kong University of Science and Technology  
Xinfeng Zhang, The Hong Kong University of Science and Technology

Graphene oxide (GO) is the graphene chemically modified with oxygen functional groups such as epoxides, alcohols, and carboxylic acids. Although the scalability for producing GOs portends their great potential in device applications, the development of physical and chemical methodologies to manipulate these atomically thin sheets is essential to putting them to use. We have developed simple and fast processes to obtain and control two-dimensional assembly of GOs. One of the methods we used was the bubble deposition. The surface coverage of the GO films could be finely tuned by changing the experimental conditions, e.g., deposition time, and concentrations of GO and surfactant, with the highest reaching above 90%. The control over the surface morphology and thickness of the GO films was readily achieved through successive layer-by-layer bubble deposition. The generality of this method has been revealed by direct GO deposition onto lithographically patterned silicon substrates with microelectrodes and flexible transparent PET substrates. Also demonstrated is the facile reduction of our GO films by thermal annealing, which results in conducting reduced-GO films. In another study, we have densely dispersed TiO<sub>2</sub> nanospindles onto GO sheets via a spontaneous self-assembly process. After annealing of the TiO<sub>2</sub>/GO hybrid nanocomposite in an NH<sub>3</sub> gas flow, the TiO<sub>2</sub> surface was effectively nitridated and the GO was reduced to graphene sheets (GS) in order to further fortify the electronic functionality of the nanocomposite. This anatase oxynitride/titanium nitride-GS (TiO<sub>2</sub> TiO<sub>x</sub>N<sub>y</sub>/TiN-GS) hybrid nanocomposite was studied as an anode material for lithium-ion batteries, showing excellent rate capability and cycling performance compared to the pure TiO<sub>2</sub> nanospindles. Our systematic studies have revealed that the TiO<sub>2</sub> TiO<sub>x</sub>N<sub>y</sub>/TiN-GS nanocomposite provide a promising solution to the problems of poor electron transport and severe aggregation of TiO<sub>2</sub> nanoparticles by enhancing both electron transport through the conductive matrix and Li-ion accessibility to the active material from the liquid electrolyte. Finally, by thermal nitridation of reduced graphene oxide sheets, we have obtained highly conductive (~1000-3000 S/m) N-doped graphene sheets as a result of the restoration of the graphene network by the formation of C-N bonded groups and N-doping. Even without carbon additives, the supercapacitors made of the N-doped graphene electrodes can deliver remarkable energy and power operated at higher voltage range of 4 V. Acknowledgments: This work is supported by RGC-UGC-HK and HKUST.

## THREE-DIMENSIONAL INTERCONNECTED GRAPHENE FOAMS AND THEIR COMPOSITES

Hui-Ming Cheng, Shenyang National Laboratory for Materials Science, Institute of Metal Research,  
Chinese Academy of Sciences

72 Wenhua Road, Shenyang, Liaoning, 110016, China

T: 86-24-2397 1611, F: 86-24-2390 3126, cheng@imr.ac.cn

Zongping Chen, Shenyang National Laboratory for Materials Science, Institute of Metal Research,  
Chinese Academy of Sciences

Wencai Ren, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese  
Academy of Sciences

Integration of individual two-dimensional graphene into macroscopic structures is essentially important for the application of graphene. A series of graphene-based composites have been recently fabricated using chemically-derived graphene sheets. However, these composites and structures suffer from poor electrical conductivity because of the low quality and/or high inter-sheet junction contact resistance of the chemically-derived graphene sheets. We report the direct synthesis of a three-dimensional porous graphene macrostructure by template-directed CVD, which we call graphene foam (GF). This porous graphene bulk material consists of an interconnected network of graphene, which is flexible and has fast transport channel of charge carriers for high electrical conductivity. Even with a GF loading as low as 0.5 weight percent, GF/poly (dimethyl siloxane) (PDMS) composites show a very high electrical conductivity of 10 S/cm, 6 orders of magnitude higher than chemically-derived graphene-based composites. Using this unique network structure and the outstanding electrical and mechanical properties of GFs, as an example, we demonstrate the possibility of GF/PDMS composites for flexible, foldable and stretchable conductors. 1. Z. P. Chen, W. C. Ren, L. B. Gao, B. L. Liu, S. F. Pei, H. M. Cheng\*, Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition, Nature Materials, DOI: 10.1038/NMAT3001, (2011).

## NOVEL SYNTHESIS OF SINGLE-LAYER GRAPHENE AND DISPERSIBLE GRAPHENE DECORATED WITH UNIFORM AU NANOPARTICLES

Mingsheng Xu, Zhejiang University  
Zheda Road #38, Hangzhou, Zhejiang, 310027, China  
T: 0086-571-87952557, F: 0086-571-87952337, msxu@zju.edu.cn  
Xi Yang, Zhejiang University  
Junjie Li, Zhejiang University  
Hongzheng Chen, Zhejiang University

Graphene has recently attracted a great deal of interest in both academia and industry because of its unique electronic [1] and optical properties [2]. The superb characteristics of graphene make this material one of the most promising candidates for various applications, such as ultrafast electronic circuits [1,3] and photodetectors [2], clean and renewable energy [4], and rapid single-molecule DNA sequencing [5]. The electronic properties of graphene systems heavily rely on the number of graphene layers [6], on their intrinsic defects [7], and on the coupling of the graphene sheet with the underlying substrate [1]. Fine control over the thickness and the crystalline structure of graphene layers is essential to realize the unique properties of graphene. We present our recent efforts on synthesizing single-layer graphene fully covering an entire substrate at low temperature [8] by surface segregation method and synthesizing uniform graphene-based composite composing of Au nanoparticles (Graphene-Au) by chemical route [9]. On the one hand, our surface segregation results demonstrate how to control the amount of carbon atoms for graphene formation to yield graphene films with a fine controlled thickness and crystal structure. On the other hand, our chemical route demonstrates how we can control the dispersibility of the Graphene-Au composite and the uniformity of Au nanoparticle decorated at the graphene basal plane, and thus show enhanced electrocatalytic activity. Our methods represent significant steps toward the scalable synthesis of high-quality graphene films with predefined thickness and toward realizing the unique properties of graphene films or graphene-based nanocomposites with high dispersibility in water.

[1] A. K. Geim, et al. Nat. Mater. 2007, 6, 183-191. [2] F. Xia, et al. Nat. Nanotechnol. 2009, 4, 839-843. [3] Y. M. Lin, et al. Science 2010, 327, 662. [4] V. Yong, et al. Small 2010, 6, 313-318. [5] M. S. Xu, et al. Small 2009, 5, 2638-2649. [6] B. Partoens, et al. Phys. Rev. B 2006, 74, 075404. [7] J. Lahiri, et al. Nat. Nanotechnol. 2010, 5, 326-329. [8] M. S. Xu, et al. ACS Nano 2011, 5, 1522. [9] X. Yang, et al. J. Mater. Chem. (in press)

## CONTROL OF WETTABILITY ON CARBON-NANOFIBER SURFACES: FROM HYDROPHILICITY TO SUPERHYDROPHOBICITY

Hrudya Nair, Catalytic Processes and Materials, Faculty of Science and Technology, MESA+ Institute for Nanotechnology, University of Twente

P.O.Box 217, Enschede, Overijssel, 7500 AE Enschede, The Netherlands

T: +31 (0) 53 489 3033/3529, F: +31 (0) 53 489 4683, H.Nair@tnw.utwente.nl

Roald M. Tiggelaar, Mesoscale Chemical Systems, Faculty of Science and Technology, University of Twente

Arie van Houselt, Catalytic Processes and Materials, Faculty of Science and Technology, University of Twente

Leon Lefferts, Catalytic Processes and Materials, Faculty of Science and Technology, University of Twente

Carbon nanofibers (CNFs) are cylindrical or conical structures with a diameter ranging from a few to hundreds of nanometers and a length of few nanometer to millimeters [1]. They are made of graphene sheets and are further classified as bamboo type, herringbone type, cup-shaped etc depending on the orientation of graphene sheets with respect to the fiber axis. CNFs have promising properties due to their inert nature and unique electrical and mechanical properties. They may for example be used as a catalyst support in three-phase reactions [2] or as a superhydrophobic (i.e. contact angle  $> 150^\circ$ ) layer in microfluidic devices [3].

We will discuss the wetting properties of catalytically grown CNF layers. These layers are grown by chemical vapor decomposition of ethylene over a 25nm Ni thin film catalyst-layer, supported on an oxidized silicon wafer. The morphology (diameter, thickness) of the CNFs is examined using a high resolution scanning electron microscope. The wetting behavior is studied by evaluating the contact angles on the layers.

Typically superhydrophobicity on CNF substrates is obtained by chemical post – treatment of the surface [4]. Here we show that by varying the growth parameters one can really control the surface wettability from hydrophilic ( $\sim 40^\circ$ ) to superhydrophobic ( $\sim 159^\circ$ ), without further chemical post-treatments.

Moreover, as an example of the precise control we will show a case study of droplet evaporation on such a pristine superhydrophobic CNF sample. On these samples, the water droplet evaporates while the contact area with the CNF surface remains constant (no contact line dynamics) [5].

[1] De Jong, K.P. and Geus J.W., Catal. Rev.Sci. Eng. 42(4), (2000) 481-510.

[2] Kobayashi, J., Mori, Y., Okamoto, K., Akiyama, R., Ueno, M., Kitamori, T. and Kobayashi, S., Science 304 (2004) 1305.

[3] Joseph, P., Cottin-Bizone, C., Benoit, J.-M., Ybert, C., Journet, C., Tabeling, P., and Bocquet, L., PRL 97 (2006) 156104.

[4] Lau, K.K.S., Bico, J., Teo, B.K., Chhowalla, M., Amaratunga, G.A.J., Milne, W.I., McKinley, G.H. and Gleason K.K., Nanoletters 3 (12) (2003) 1701.

[5] Gelderblom, H., Marin, A. G., Nair, H., Houselt, A., Lefferts, L., Snoeijer, J., Lohse, D., Physical Review E 83, (2011) 026306.

## LOW-VOLTAGE ORGANIC THIN-FILM TRANSISTORS AND CIRCUITS FOR FLEXIBLE ELECTRONICS

Hagen Klauk, Max Planck Institute for Solid State Research  
Heisenbergstr. 1, Stuttgart, 70569, Germany  
T: +49 711 689-1401, F: +49 711 689-1472, H.Klauk@fkf.mpg.de

Organic thin-film transistors (TFTs) are of interest for applications that require electronic functionality with low or medium complexity distributed over large areas on unconventional substrates, such as flexible plastic film. Generally these are applications in which the use of silicon-based devices and circuits is technically or economically not feasible, such as flexible active-matrix displays and large-area sensor arrays. In organic TFTs, the semiconductor is a thin polycrystalline layer of conjugated organic molecules and is deposited either by vacuum sublimation or by a solution process. Especially for portable, battery-powered applications it is desirable that the TFTs can be operated with voltages in the range of about 2 to 3 V. A promising approach to organic TFTs that can be operated with such low voltages are gate dielectrics based on an ultra-thin organic self-assembled monolayer (SAM). These dielectrics have a thickness of about 5 nm, a capacitance close to  $1 \mu\text{F}/\text{cm}^2$ , and leakage current densities below  $10^{-5} \text{ A}/\text{cm}^2$  at 3 V, despite the fact that they are prepared at temperatures below  $100^\circ\text{C}$  and are thus fully compatible with plastic substrates. Depending on the choice of the organic semiconductor, the field-effect mobility in organic TFTs is usually close to  $1 \text{ cm}^2/\text{Vs}$ . The static and dynamic performance of organic p-channel TFTs with lateral dimensions of a few microns is already sufficient for active-matrix displays with VGA resolution where the TFTs operate with frequencies of a few tens of kilohertz. Increasing the performance of organic TFTs into the Megahertz regime is possible by scaling the lateral TFT dimensions down to about  $1 \mu\text{m}$  or slightly below, which requires innovative patterning techniques compatible with flexible large-area substrates. Substantial advances have also recently been made in the environmental stability of organic TFTs and in the development of high-mobility, air-stable organic n-channel TFTs that are necessary for the realization of organic complementary circuits, for example to implement the row and column driver circuits of flexible displays and sensor arrays.



## HIGH-PERFORMANCE PRINTED ORGANIC TRANSISTORS

Jun Takeya, ISIR, Osaka University  
8-1, Mihogaoka, Ibaraki, Osaka, 567-0047, Japan  
T: +81-6-6879-8400, F: +81-6-6879-8404, takeya@sanken.osaka-u.ac.jp

Development of high-performance printed semiconductor devices is highly desired with the expectation for the next-generation technologies of “printable electronics”. We report newly developed arrays of patterned crystalline OFETs formed from hot solution. Mobility of 5-10 cm<sup>2</sup>/Vs is achieved for the present OFETs, opening a practical way to realize printed and flexible electronics with sufficient switching speed.

**ORGANIC FIELD EFFECT TRANSISTORS WITH PENTACENE FILMS EMBEDDING METALLIC AND ORGANIC NANOCCLUSERS AS CHARGE TRAPPING SITES: STRUCTURE AND ELECTRIC BISTABILITY STUDY**

Yu-Tai Tao, Institute of Chemistry, Academia Sinica  
128, Section 2, Academia Road, Taipei, 115, TAIWAN  
T: +886-2-27898580, F: +886-2-26511488, ytt@chem.sinica.edu.tw

Electronic devices based on organic semiconductors are attracting much attention due to their potential in fabricating flexible electronics. Field effect transistors, memories are among the key components in these applications. Pentacene films deposited on a silica surface decorated with metallic nanoparticles or organic clusters constitute the three-terminal transistor/memory device, with the metal nanoparticles or organic clusters serve as charge trapping sites. The crystallinity and packing orientation of the pentacene film depend on the surface modification of the metallic nanoparticles or the structure of organic clusters. Electrical bistability can be observed with these composite films as conducting channel. The threshold voltage shifts(memory window), on/off ratio, response time and the retention characteristics depend on the surface modification of nanoparticles or the surface property of the organic clusters used. A detailed discussion of the morphology of the pentacene films as a function of the structure of pentacene/insulating dielectric interface and the I-V hysteresis of the transistor/memory device will be provided.

## MATERIALS ENGINEERING AND NANOSTRUCTURE CONTROL FOR HIGH EFFICIENCY POLYMER SOLAR CELLS

Ye Tao, National Research Council of Canada  
1200 Montreal Road, M-50, Ottawa, Ontario, K1A 0R6, Canada  
T: +001-613-998-2485, F: +001-613-998-1627, ye.tao@nrc-cnrc.gc.ca  
Ta-Ya Chu, National Research Council of Canada  
Jianping Lu, National Research Council of Canada  
Serge Beaupre, Departement de Chimie, Universite Laval  
Mario Leclerc, Departement de Chimie, Universite Laval

Using photovoltaic (PV) effect to generate electricity from solar energy represents a highly appealing solution to our need for clean, abundant, and renewable energy sources, and to our desire for protecting the environment. Organic semiconductor based PV cells are viewed as one of the most promising candidates for low cost solar cells due to the low material cost and the possibility of using wet processes, such as spin-coating, ink-jet, and roll-to-roll printing for fabrication on flexible plastic substrates. Since the introduction of the BHJ concept in mid-90's, much research effort in this field has been directed to the control of the BHJ nano-scale morphology, and to the development of new low band gap p-type polymers. As a result, significant improvement has been made in the past decade on the power conversion efficiency (PCE) of BHJ polymer solar cells. In this work, through controlling the processing conditions, we were able to control the nano-scale morphology of the bulk heterojunction active layer comprised of poly (N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7' -di-2-thienyl-2',1',3' -benzothiadiazole) (PCDTBT) and PC71BM, and improved power conversion efficiency from 6.0% to 7.1% for large area devices. We have also developed a new alternating copolymer of dithienosilole and thienopyrrole-4,6-dione (PDTSTPD), which possesses both a low optical bandgap (1.73 eV) and a deep HOMO energy level (5.57 eV). The introduction of branched alkyl chains to the dithienosilole unit was found to be critical for the improvement of the polymer solubility. By blending PDTSTPD with PC71BM, and proper control of the active layer morphology, we have achieved 7.3 % PCE under one sun of AM1.5G simulated irradiation on solar cells with an active area of 1 cm<sup>2</sup>.

## MAKING NANOGRAPHENE

Kian Ping Loh, National University of Singapore  
Department of Chemistry, 3 Science Drive 3, Singapore 117543, Singapore, Singapore, 117543,  
Singapore  
T: 98271029, F: 67791691, chmlhkp@nus.edu.sg  
Jiong Lu, National University of Singapore

In this talk, I will discuss new chemical strategies to synthesize graphene, from large area sheets to nanographene.

Majority of the solution-phase methods produce irregularly-sized and shaped graphene sheets due to the intrinsic randomness in the defect-mediated exfoliation or cutting process of the precursor graphitic flakes. To produce highly regular graphene nanostructures, a fabrication process that is driven by thermodynamics, as in crystal growth, should be more suitable than defect-mediated fragmentation processes. To this end, we will show how we apply templated-directed synthesis to fabricate regular-sized graphene quantum dots. The dynamics of carbon cluster diffusion and aggregation to form nanographene islands is recorded by dynamic Scanning Tunneling Microscopy. The charge transfer interactions between graphene and fullerene, as well as the Van der Waals epitaxy of graphene on self-assembled C60 will be discussed.

Graphene forms functional hybrids with organic molecules, quantum dots and polymers and these can exhibit non-linear optical limiting properties, saturable absorption properties, outstanding photovoltaic and biosensing properties. Some examples of these applications studied in our laboratory will be given in this talk.

Acknowledgement: This project is funded by the National Research Foundation Competitive Research Funding - Graphene and Related Materials R-143-000-360-281.

### References

1. Graphene oxide as a chemically tunable platform for optical applications Kian Ping Loh, Qiaoliang Bao, Goki Eda, Manish Chhowalla, Nature Chemistry, ASAP (Dec 2010)
2. Graphene-based SELDI probe with ultrahigh extraction and sensitivity for DNA oligomer Tang LAL, Wang JZ, Loh KP\*, Journal of the American Chemical Society, 132, 32, 10976-10977 (2010)
3. A graphene oxide organic dye ionic complex with DNA-sensing and optical-limiting properties Balapanuru, J., Yang, J.-X., Xiao, S., Bao, Q., Jahan, M., Polavarapu, L., Wei, J., Xu, Q.-H. and Loh, K.P., Angewandte Chemie International Edition, 49 (37), 2010, 6549-6553.
4. Room-temperature synthesis of soluble carbon nanotubes by the sonication of graphene oxide nanosheets, Wang SA, Tang LAL, Bao QL, Kian Ping LOH\* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 131,46, 16832 (2009)
5. Solution-gated epitaxial graphene as pH sensor, Ang PK, Chen W, Wee ATS, Kian Ping LOH\* et al. JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 130,44, 14392 (2008)

## STUDIES ON ELECTRONIC STRUCTURES OF ORIENTATED GRAPHENE NANORIBBONS

Lifeng Chi, Physikalisches Institut, WWU Muenster  
Wilhelm-Klemm-Str. 10, Muenster, 48149, Germany

T: +49-251-8333651, F: +49-251-8333602, chi@uni-muenster.de

Dingyong Zhong, Alexander Timmer, Stefan Linden, Haiming Zhang, Harald Fuchs, Helmut Zacharias,  
Physikalisches Institut, WWU Muenster, Germany

Xinliang Feng, Klaus Müllen, Max Planck Institute for Polymer Research, Mainz, Germany

On-surface covalent coupling under ultrahigh vacuum (UHV) conditions is new concept to create robust, ordered molecular surface structures that may also exhibit novel properties. Starting from designed small primer molecules, on-surface synthesis of graphene nanoribbons (GNRs) has been achieved [1]. To study the electronic structures of these novel GNRs with well defined width and shape, both local measurement by means of scanning tunneling spectroscopy (STS) and integral measurement in terms of angle-resolved photoemission spectroscopy (ARPES) have been conducted. Due to the elongated form of the GNRs, the ARPES experiments have to be carried out on well orientated GNRs achieved by using high index metal crystal surfaces. Information of both band gap and band structures was obtained which consistent with the theoretical calculations. [1] J. Cai et al., Nature 466, 470 (2010).

## SYNTHESIS OF CARBON NANOFIBER PAPER USING CHEMICAL VAPOR DEPOSITION METHOD

Eyassu Woldesenbet, Louisiana State University and Southern University  
2508 Patrick Taylor Hall, Baton Rouge, LA, 70810, USA  
T: 2255785900, F: 2255785924, woldesen@me.lsu.edu  
Ephraim Zegeye, Louisiana State University  
Yoongyoung Jin, Southern University

A novel method of fabricating carbon nanofiber (CNF) paper has been reported by growing nanofibers on the surface of self assembled hollow glass microballoons. A layer of hollow glass microballoons were first formed on a silicon wafer substrate by a unique method similar to dip coating. This unique method comprised of immersing the wafer in ethanol suspension of Ni coated microballoons and lowering the level of suspension by draining from the bottom. The hollow glass microspheres used for making the suspension were coated with Ni using electroless deposition technique. Random networks of carbon nanofibers were formed by directly depositing them on the surface of the self assembled microballoons using water assisted thermal chemical vapor deposition (CVD) of acetylene at 5700 C, at atmospheric pressure. The CNFs grown on one microballoon networked with CNFs on an adjacent microballoons. Thus the self assembled layer of microballoon was bonded together effectively with the help of CNF networks to form microsphere reinforced CNF paper structure in approximately 15minutes of growth time. The dimensions of the CNF paper was as big as the dimension of the wafer ( ~18 „e 60 mm ), and easily peeled off from the wafer. The paper could find potential application in thin film conductive syntactic foams, as a sensing element, and as a lithium ion anode.

## **SYNCHROTRON SPECTROSCOPY FOR THE ANALYSIS OF CARBON-BASED NANOMATERIALS**

T.K. Sham, Department of Chemistry, University of Western Ontario  
1151 Richmond Street, London, Ontario, N6G 3S8, Canada  
T: 1-519-661-2111x86341, F: 1-519-661-3022, tsham@uwo.ca

The advent of maturing third generation synchrotron technology has provided unprecedented research opportunities in probing the structure and electronic properties of matter, especially nanomaterials. Synchrotron is an accelerator based light source that is tuneable in energy (from IR to hard X-rays) and polarization (linear, circular and elliptical), highly collimated, and pulsed. This presentation will give an overview of synchrotron techniques including X-ray Absorption Fine Structures (XAFS), X-ray Emission Spectroscopy (XES), X-ray Excited Optical Luminescence (XEOL) and spectro-microscopy using STXM (Scanning Transmission X-ray Microscopy) and their applications in the studies of functional carbon based materials such as carbon nanotubes, carbon nanowires, carbon nanoparticles, nanodiamond, graphene and graphene oxide based materials among others.

## INTERFACE SCIENCE IN NANOSTRUCTURED CARBON-BASED MATERIALS: AN ELECTRONIC STRUCTURE VIEW OF SOFT X-RAY SPECTROSCOPY

Jinghua Guo, Lawrence Berkeley National Laboratory  
MS 6R2100, 1 Cyclotron Road, Berkeley, CA, 94720, USA  
T: +1 510-495-2230, F: +1 510-495-2067, [jguo@lbl.gov](mailto:jguo@lbl.gov)

The ability to control the particle size and morphology of nanostructured carbon-based materials is of crucial importance nowadays both from a fundamental and industrial point of view considering the applications of solar photovoltaic, energy storage such as hydrogen storage and Li-ion batteries, chemical and biosensors etc. The properties of matter at nanoscale dimensions can be dramatically different from the bulk or the constituent molecules. The differences arise through quantum confinement, altered thermodynamics or changed chemical reactivity. In general, electronic structure ultimately determines the properties of matter, thus a complete understanding of the electronic structure of nanoscale systems and tailoring their properties will lead to progress in renewable energy science.

The applications of soft x-ray absorption (XAS) and emission spectroscopy (XES) on a variety of carbon systems have yielded characteristic fingerprints. In the soft x-ray region, the question tends to be, what are the electrons doing as they migrated between the atoms? XAS and XES have basic features that are important to interface science. With high-resolution synchrotron radiation excitation, resonant inelastic x-ray scattering (RIXS) has emerged as a new source of information about electronic structure and excitation dynamics. The experimental findings regarding x-ray spectroscopic studies of various carbon-based materials including diamond, graphite, graphene layer, B-doped diamond and Li-intercalation in graphite, contacting polymers, fullerenes ( $C_{60}$ ,  $C_{70}$ ,  $C_{84}$ ), fullerites ( $C_{59}N$ ,  $La_2 C_{80}$ ,  $Gd C_{82}$ ) and single walled carbon nanotubes will be presented. We will show the bandgap measurements in diamond and carbon nanotubes, charge-transfer in Ti-doped  $C_{60}$  and  $Gd C_{82}$ , in-situ characterization of SWNTs in hydrogen atmosphere to reveal the  $H_2$ -adsorption induced changes in structure and electronic structure of the carbon based materials, and recent progress on in-situ study of carbon-based anode and electrolyte materials in Li-ion batteries.



## ELECTRONIC STRUCTURES OF ORGANIC SEMICONDUCTORS STUDIED BY PHOTOELECTRON YIELD SPECTROSCOPY: FROM SINGLE CRYSTAL TO LIQUID DEVICE

Hisao Ishii, Chiba University  
1-33 Yayoi-cho, Inage-ku, Chiba-shi, Chiba, 263-8522, Japan  
T: +81-(0)43-290-3524, F: +81-(0)43-290-3524, ishii130@faculty.chiba-u.jp  
Yasuo Nakayama, Chiba University

The information of the electronic structures of organic electronic materials is indispensable for understanding and improving organic electronics. So far, photoelectron spectroscopy (PES) has been widely applied for that purpose. But when we want to investigate practical electronic structure, PES has some problems. Firstly, PES needs at least high vacuum environment to perform measurement. Organic devices usually work under influence of air, and their electronic structures not only in vacuum but also in air should be investigated. The necessity of vacuum environment also disturbs the measurement of liquid sample with high vapor pressure. Secondly, most organic samples have very low conductivity, and PES measurements often encounter difficulty due to sample charging: holes which are created by photoemission tends to stay in surface region to disturb further photoemission. So, thin film preparation is necessary for PES, and it is not easy to apply PES to organic single crystals.

To overcome the above demerits of PES, we have focused on photoelectron yield spectroscopy (PYS). In this technique, the total number of photoelectrons is recorded as a function of incident photon energy. By using current-mode-detection of photoelectron, PYS can be performed both in vacuum and atmospheric conditions. By applying an electric field to sample surface, we can measure PYS of even extremely insulating material. In this paper, we will report on recent efforts of PYS investigation of electronic structures of various materials in practical situation which cannot be studied by conventional PES. The main topics are as follows.

(i) The electronic structure of organic single crystals: observation roughness-induced gap state  
It has been widely believed that structural disorder induces broadening of intrinsic energy level and the formation of gap-state. But the direct observation of such a gap-state is still limited, and the origin and formation mechanism are not well understood. In order to investigate such effects, the direct comparison in electronic structure between well-ordered and disordered systems should be desired. By comparing very flat and rough surfaces of anthracene single crystals, we have succeeded to directly observe the roughness-induced effect to the electronic structure.

(ii) The electronic structures of liquid organic semiconductors  
Very recently, an organic light emitting diode using liquid organic semiconductor, 9-(2-ethylhexyl)carbazole (EHCz) doped with rubrene, has been reported. In order to understand the operation mechanism, the electronic structure of this host-guest system was investigated by PYS. The relative energy location of HOMO states between the host and guest molecules was successfully determined. We focused on the difference in polarization energy between solid and liquid phase, which is very important to search good liquid materials for organic electronics.

## QUANTIZED CONDUCTANCE OF A SUSPENDED GRAPHENE NANOCONSTRUCTION

Alina Veligura, University of Groningen  
Nijenborgh 4, Groningen, Groningen, 9747 AG, The Netherlands  
T: +310503634919, F: +31 50 363 4879, a.veligura@rug.nl  
Nikolaos Tombros, University of Groningen  
Juliane Junesch, Marcos H. D. Guimarães, University of Groningen  
Ivan J. Vera Marun, Harry T. Jonkman, University of Groningen  
Bart J. van Wees, University of Groningen

A yet unexplored area in graphene electronics is the field of quantum ballistic transport through graphene nanostructures. Recent developments in the preparation of high mobility graphene are expected to lead to the experimental verification and/or discovery of many new quantum mechanical effects in this field. Examples are effects due to specific graphene edges, such as spin polarization at zigzag edges of a graphene nanoribbon and the use of the valley degree of freedom in the field of graphene valleytronics. As a first step in this direction we present the observation of quantized conductance at integer multiples of  $2e^2/h$  at zero magnetic field and 4.2 K temperature in a high mobility suspended graphene ballistic nanoconstriction. This quantization evolves into the typical quantum Hall effect for graphene at magnetic fields above 60mT. Voltage bias spectroscopy reveals an energy spacing of 8 meV between the first two subbands. A pronounced feature at  $0.6 2e^2/h$  present at a magnetic field as low as  $\sim 0.2T$  resembles the '0.7 anomaly' observed in quantum point contacts in a GaAs-AlGaAs two dimensional electron gas, having a possible origin in electron-electron interactions [1].

The produced graphene devices were suspended over the trenches in LOR-A, a polydimethylglutarimide based organic resist. The resist has a high glass transition temperature of 190°C and therefore is very resistant to chemical and thermal treatments. This polymer property allows the fabrication of large (suspended over area of 35  $\mu m^2$ ) high quality suspended graphene devices with almost no limitations on contact material [2].

1. Nikolaos Tombros, Alina Veligura, Juliane Junesch, Marcos H. D. Guimarães, Ivan J. Vera Marun, Harry T. Jonkman, Bart J. van Wees, Quantized conductance of a suspended graphene nanoconstriction, Nature Physics, submitted
2. N. Tombros, A. Veligura, J. Junesch, J. J. van den Berg, P. J. Zomer, M. Wojtaszek, I. J. Vera Marun, H. T. Jonkman, and B. J. van Wees, Large yield production of high mobility freely suspended graphene electronic devices on a PMGI based organic polymer, Journal of Applied Phys. accepted.

## CHEMICAL AND STRUCTURAL ROLES OF GRAPHENE IN STEM CELL GROWTH AND DIFFERENTIATION

Chwee Teck Lim, National University of Singapore  
Division of Bioengineering, Faculty of Engineering, 9 Engineering Drive 1, Singapore, 117576, Singapore  
T: (65) 65167801, F: (65) 67791459, [ctlim@nus.edu.sg](mailto:ctlim@nus.edu.sg)  
Wong Cheng Lee, National University of Singapore  
Candy Haley Yi Xuan Lim, National University of Singapore  
Lena Ai Ling Tang, National University of Singapore  
Hui Shi, Kian Ping Loh, National University of Singapore

Over the last two decades, while there have been significant advances in stem cell therapy and tissue engineering, the search for an ideal substrate for stem cell culture and differentiation continues. Human bone marrow derived mesenchymal stem cells (hMSCs) have been widely recognized to have significant biological and clinical importance due to their ability to differentiate into multiple cell types. While stem cell differentiation depends largely on the various soluble factors and biomolecules, lineage commitment of stem cells can also be governed by their interaction with nanoscale features of the extracellular matrix (ECM). Nanotechnology has emerged as a promising tool to design and create materials with nano-sized features and architectures which are capable of biomimicking the native ECM environment for stem cell culture and differentiation. In particular, graphene has generated great interest because of its unique chemical, mechanical and electrical properties. The synergy of the properties of graphene and differentiation potential of stem cells could provide exciting opportunities for new and novel therapeutic applications. However, little is known about the effect of graphene on stem cell fate. Here, we report the interaction between stem cells and graphene in terms of stem cell growth and differentiation. Our preliminary results show that graphene promoted differentiation of MSCs towards the osteogenic lineage under the influence of soluble factors while differentiation towards the adipogenic lineage is greatly suppressed. We attribute the unique differentiation profile of MSCs on graphene to the pi-pi interactions between graphene and the soluble biomolecules involved during the differentiation process.

## CARBON NANOTUBES AND GRAPHENE FOR DRUG DELIVERY AND CANCER THERAPIES

Zhuang Liu, Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University  
199 Ren-Ai Road, Bldg 910, Rm 405, Suzhou, Jiangsu, 215123, China, Peoples Republic  
T: 8651265882036, F: 8651265882846, zliu@suda.edu.cn

Typical sp<sup>2</sup> carbon nanomaterials include bulky balls, carbon nanotubes (CNTs), and graphene. In the past few years, the in vivo biodistribution and toxicity of functionalized single-walled carbon nanotubes (SWNTs) have been studied in animals. Owing to their interesting chemical and physical properties, SWNTs are useful for biomedical imaging and cancer treatment, in vitro and in vivo. Graphene is a star in material sciences. Utilizing the strong optical absorbance of nano-graphene in the near-infrared (NIR) region, we have achieved highly effective in vivo photothermal ablation of tumors in animal experiments by intravenous administration of functionalized nano-graphene and the followed low-power NIR laser irradiation on the tumor. No obvious toxicity effect of functionalized nano-graphene is noted in our detailed toxicology study. Taken together, sp<sup>2</sup> carbon nanomaterials are promising for future multimodality cancer therapy and imaging.

Reference [1] Liangzhu Feng, Zhuang Liu\* "Graphene in Biomedicine: Opportunities and Challenges" *Nanomedicine*, DOI: 10.2217/NNM.10.158 (2011) (Invited Review) [2] Kai Yang, Jianmei Wan, Shuai Zhang, Youjiu Zhang, Shuit-Tong Lee, Zhuang Liu\* "In vivo Pharmacokinetics, Long-Term Biodistribution, and Toxicology of PEGylated Graphene in Mice" *ACS Nano*, 5, 516-522 (2011) [3] Zhuang Liu\*, Kai Yang, Shuit-Tong Lee "Single-walled Carbon Nanotubes in Biomedical Imaging" *J. Mater. Chem.* 21, 586-598 (2011) (Invited Review) [4] Xiaowen Liu, Huiquan Tao, Kai Yang, Shuit-Tong Lee and Zhuang Liu,\* "Optimization of Surface Chemistry on Single-Walled Carbon Nanotubes for in vivo Photothermal Ablation of Tumors" *Biomaterials*. 32, 144-151 (2011) [5] Kai Yang, Shuai Zhang, Guoxin Zhang, Xiaoming Sun, Shuit-Tong Lee and Zhuang Liu\* "Graphene in Mice <sup>13</sup>C Ultra-high in vivo Tumor Uptake and Highly Efficient Photothermal Therapy" *Nano Lett.* 10, 3318-3323 (2010) (Highlighted by Nature)

## RECENT ADVANCES IN THE APPLICATIONS OF CARBON BASED NANOMATERIALS

Jignasa Solanki, S. V. National Institute of Technology, India  
S. V. National Institute of Technology, Ichhanath, Surat, Gujarat, 395 007, India  
T: 0091 0261 2201642, F: 0091 261 2227334, [sjn@ched.svnit.ac.in](mailto:sjn@ched.svnit.ac.in)  
Z. V. P. Murthy, S. V. National Institute of Technology, India

The distinctive and tunable properties of carbon-based nanomaterials enable new technologies for identifying and addressing many technical challenges. The objective of this review is to critically assess a broad overview of the methodology, advantages and limitations of carbon-based nanomaterials with respect to applications in chemical fields including energy conversion, catalysis, hydrogen storage, and air pollution treatment etc.. Aiming to demonstrate the impact of nanomaterials on the development of novel energy conversion applications, recently reported developments have been included. Special emphasis is given to the applications of carbon nanotubes as it has great potential in chemical applications among all carbon-based nanomaterials. Even though discussed only in brief, incorporated is a segment highlighting nanomaterials synthesis technique called chemical vapor deposition, as well as catalytic applications of nanomaterials that can be used in the design of future chemical production.

## GRAPHENE-BASED MICROFLUIDIC DEVICE FOR SINGLE CELL DETECTION

Priscilla Kailian Ang, Department of Chemistry, National University of Singapore, Singapore  
3 Science Drive 3, Singapore, Singapore, 117543, Singapore

T: +6596555996, F: 67791691, priscilla\_ang@nus.edu.sg

Ang Li, Singapore-MIT Alliance for Research & Technology (SMART), Singapore  
Chwee Teck Lim, Division of Bioengineering and Department of Mechanical Engineering, National  
University of Singapore, Singapore

Kian Ping Loh, Department of Chemistry, National University of Singapore, Singapore

Due to the unique combination of optical transparency and highly sensitive surface conducting channel, graphene grown by chemical vapour deposition affords the possibility of dual-mode sensing based on optical and field-effect properties. This opens up new possibilities for making integrated cellular semiconductor nanodevices where the binding of cells can be followed using optical microscopy whilst the associated changes in cell surface charge can be tracked using the space charge effect in the graphene semiconductor. As a proof-of-concept, the stage-dependent alteration of negative charges on erythrocytes by *Plasmodium falciparum* is studied at the single-cell level. Such a synergistic approach provides a powerful methodology for the study of cell surface charge density which influences cytoadherence of *Plasmodium falciparum* infected red blood cells (IRBCs) to endothelium.

## GRAPHENE PHOTONICS: LIGHT CREATION, MODULATION AND DETECTION

Qiaoliang BAO, Department of Chemistry, National University of Singapore  
3 Science Drive 3, Singapore, 117543, Singapore

T: 65-65164778, F: 65-67791691, [chmbq@nus.edu.sg](mailto:chmbq@nus.edu.sg)

Kian Ping LOH, Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore  
117543 Singapore

Graphene has attracted enormous research interests due to its exceptional electronic transport properties and potential applications in nanoelectronics. The photonic properties of graphene are equally remarkable. Its universal optical conductance is defined by the fine structure constant and is independent of frequency over a wide range.[1] Its zero-gap nature affords benefits the high bandwidth detection of light.[2] The easy saturation of its absorption due to Pauli blocking enables graphene to be used as saturable absorbers in broadband, ultrafast mode-locked lasers for telecommunication.[3,4] The two dimensional (2D) nature of graphene enables the design of photonic circuits with ultrathin channels, where graphene can assume different functions of light creation, routing or modulation and detection. Here we will review our recent progress to develop graphene photonic devices, which include mode-locked laser, light modulator and photodetector. Firstly we would like to review our initiative works on graphene mode-locked lasers. Due to wavelength independent saturable absorption in visible-to-near-infrared range, wide-band tuneable lasers were invented to generate ultra-short pulses in telecommunication C band (around 1550 nm)[3,4] as well as even short near-infrared wavelength at 1050 nm[5]. Stable mode locked pulses with single pulse energy up to 7.3 nJ and pulse width of 415 fs have been directly generated from the laser.[6] Secondly, we experimentally and theoretically investigated the interaction between graphene and transverse electromagnetic wave. By tuning the chemical potential of graphene, the sign of complex dynamics conductivity can be varied sensitively at infrared frequencies, which allow varying amount of contribution from intraband and interband conductivities, leading to certain modulation of light during propagation.[7] Last, we report our recent work in graphene-based photodetector. The use of graphene nanoribbons with a transport bandgap enables us to significantly suppress the dark current in phototransistor, which affords much larger signal-to-noise ratio and improved responsivity. We also highlight our progress in fabricating a printable graphene-TiO<sub>2</sub> hybrid film for high-gain photodetection.[8]

References: [1] Nair, R. R., Blake, P., et al. *Science* 2008 320, 1308-1308. [2] Mueller, T., Xia, F. N. A. & Avouris, P. *Nature Photonics* 2010 4, 297-301. [3] Bao, Q., Zhang, H., Loh, K. P., et al. *Adv. Funct. Mater.* 2009 19, 3077-3083. [4] Bao, Q., Zhang, H., Yang, Loh, K. P, et al. *Adv. Funct. Mater.* 2010 20, 782-791. [5] Zhao, L., Bao, Q., Loh, K. P, et al. *Opt. Lett.* 2010, 35, 3622. [6] Zhang, H., Bao, Q., Loh, K. P., et al. *Opt. Express* 2009 17, 17630-17635. [7] Bao, Q., Loh, K. P., et al. Submitted 2011. [8] Manga, K. K., Bao, Q., Loh, K. P. et al. *Adv. Mater.* 2010, 22: 5265-5270.

## FIELD EMISSION FROM CARBON NANOTUBES

Cheol JinLee, Korea University  
Anam-Dong, Seongbuk-Gu, Seoul, Seoul, 136-713, Korea  
T: +82-2-3290-3216, F: +82-2-921-4722, cjlee@korea.ac.kr

Carbon nanotubes (CNTs) have attracted much attention for field emission applications due to their excellent properties and unique morphology. There are many reports on CNT based field emission applications such as field emission displays, flat lamps, x-ray sources, high-resolution electron-beam instruments, microwave amplifiers and terahertz wave amplifiers. Field emission properties of CNTs are deeply dependent on not only diameter, crystallinity, density and morphology of CNTs but also post treatment of CNTs. Thus, it is desirable to control of CNT materials for optimized field emitters for various applications. Up to now, various techniques have been developed for fabricating CNT field emitters using as-grown, spraying, electrophoresis, screen-printing, and attaching methods, etc. By the way, the above techniques suffer from weak mechanical adhesion between CNT emitters and the cathode, or severe degradation of CNT emitters due to the residual organic materials used in the process. Therefore, a robust CNT emitter fabricated by the organic binder-free process with strong adhesion is still a great challenge. Here we investigate field emission properties of CNTs according to various parameters and we also demonstrate an advanced technique to fabricate CNT emitters with an organic binder-free process. This method can promise strong mechanical adhesion, good electrical contact and damage-free CNT tips, resulting in enhanced field emission properties and excellent emission stability.



## **CONTACT RESISTANCES STUDY OF CARBON NANOTUBE VIA INTERCONNECTS GROWN UNDER VARIOUS CONDITIONS**

Xuhui Sun, Soochow University  
199 Ren-Ai Road, Suzhou, Jiangsu, 215123, China  
T: +86-512-65880943, F: +86-512-65882846, xhsun@suda.edu.cn

This paper presents an in-depth electrical characterization of contact resistance in carbon nanotube (CNT) via interconnects grown under various conditions. Following the bottom-up approach of interconnect fabrication processes in the nanoelectronics industry, a via test structure to extract the contact resistance is designed and fabricated to obtain the contact resistances via a two-terminal extraction method. Si process-compatible metals, Ti, Cr, and Al, are used as underlayer metals to study the growth behaviors and contact resistances of vertically aligned CNTs, together with the two most effective catalysts, Ni and Fe. Relationships between contact resistances and various combinations of catalysts and underlayer metals are investigated. Further, the interface between CNT and underlayer metal is investigated using X-ray photoemission spectroscopy (XPS) to elucidate the relationship between local electronic structure and contact resistance.

## A CNT BASED DEVICE FOR ELECTROCHEMILUMINESCENCE SENSING

Danilo Demarchi, Politecnico di Torino  
Corso Duca degli Abruzzi, 24, Torino, TO, 10129, Italy  
T: +39 011 090 4122, F: +39 011 090 4099, danilo.demarchi@polito.it  
Alberto Tagliaferro, alberto.tagliaferro@polito.it

The system presented is based on the production and use of bundles of Carbon NanoTubes (CNTs) as electrodes for building ElectroChemiLuminescence (ECL) device sensors.

For this purpose we have grown self standing cylinder-shaped bundles of Multi-Walled Carbon NanoTubes (MWCNTs) by means of a catalytic Chemical Vapour Deposition (CVD) system, fed by camphor and ferrocene gases. Ferrocene has been selected as the catalyst source because it is a good precursor for the production of iron nanoparticles, which play the role of catalyst in the formation of nanotubes. Camphor has been chosen as carbon precursor due to the fact that it is non-toxic, commercially available and inexpensive. Moreover, the structure of camphor molecule makes it an ideal carbon precursor to produce fullerenes and nanotubes. Finally, camphor and ferrocene have similar melting and boiling points and this favors the co-evaporation process of the reagents mix (ferrocene: melting point 174°C, boiling point 249°C; camphor: melting point 180°C, boiling point 204°C).

The bundles were subsequently back-contacted and encapsulated into epoxy resin as electrical insulator and sealant, for their use as voltammetric electrodes. A ruthenium-complex solution ( $\text{Ru}(\text{bpy})_3^{2+}$  in phosphate buffer) has been used as ECL label. A custom potentiostat and software have been developed to perform all electrochemical experiments. The system is a three electrode electrochemical cell where the Reference is in silver, the Counter in gold and the Working is the produced bundle of CNTs. 500  $\mu\text{l}$  of solution are spotted into a small glass container placed on the top of a Photo Multiplier Tube (PMT) then, the three electrodes are dipped in, and a suitable voltage sweep is applied to induce ECL reaction. At its emitting voltage, the chemical solution starts to produce light that is collected and amplified by the underneath PMT, which transfers to the control system a voltage proportional to the intensity of the collected light.

CNT bundles have shown a singular and very interesting behavior, in fact it has been observed a periodical light emission that lasts for hundreds of stimulus cycles, likely due to the structure of CNTs. Thanks to a data-processing algorithm, which exploits this behavior, the experiments show that it is possible to obtain a great increase in detection limit as compared to the commonly used metal working electrodes, allowing the detection of a ruthenium concentration of 40  $\text{pg}/\mu\text{l}$  (i.e. a  $10^{-7}\text{M}$  molar detection level).

## STABILITY AND ELECTRONIC PROPERTIES OF FUNCTIONALIZED CARBON NANOTUBES AND GRAPHENE LAYERS

Magdalena Birowska, Institute of Theoretical Physics, Faculty of Physics, University of Warsaw  
Hoza 69, Warsaw, 00-681, Poland

T: +48 22 55 32 384, F: +4822 5532 333, magda.birowska@gmail.com

Karolina Milowska, Institute of Theoretical Physics, Faculty of Physics, University of Warsaw

Jacek A. Majewski, Institute of Theoretical Physics, Faculty of Physics, University of Warsaw

We present results of extensive theoretical studies of functionalized carbon nanotubes (CNTs) and graphene layers (GLs). Our studies are based on the *ab initio* calculations in the framework of the density functional theory (DFT). We have performed calculations for various metallic and semiconductor single- and multi-wall CNTs and epitaxial graphene, functionalized with simple organic molecules such as OH, COOH, NH<sub>n</sub>, CH<sub>n</sub> and metals, such as Al, Fe, Ni, Cu, Zn, and Pd. We determine the stability of the functionalized systems and resulting changes in the electronic structure. These studies provide valuable quantitative predictions that are of importance for design of novel composite materials and functional devices such as electric sensors of chemical and biological substances.

The functionalization of CNTs and GLs is an important problem of nanotechnology, which has recently attracted a lot of research activities, mostly because of the huge potential of CNT applications for new materials and functional devices. The functionalization is a prerequisite for effective dispersion and binding of the systems in polymer or epoxy matrices. It is also necessary to facilitate attachment of biological substances to channels made out of CNTs and/or GLs in electrical devices.

We discuss the dependence of the cohesive properties of functionalized carbon systems on the density of the adsorbed molecules. We calculate binding energies, heat of formation, resulting deformations of CNTs and GLs, and changes in the electronic structure induced by functionalization. We determine the critical density of molecules and metallic atoms that could be adsorbed on the surface of CNTs and GLs. All these factors influence the electrical and mechanical properties of the functionalized systems and are important for reliable description of the sensor electrical characteristics and also for modeling composite materials. Our studies shed light on physical mechanisms governing the binding of the adsorbed molecules and allow for comparison of the role played by two hosts.

Just to mention few specific results, we find that the stability of the functionalized CNTs is weakly dependent on the diameter of the CNTs and its metallic or semiconducting character, whereas the stability strongly decreases with the density of the adsorbed groups. It turns out that the functionalization of the single graphene layer can open its electronic gap; which could be utilized in graphene devices.

The very interesting and intriguing physical picture emerges from studies of CNTs and GLs covered with metallic atoms, particularly in the context of spintronic applications.

## CARBON NANOTUBE BASED CHEMICAL AND BIOSENSORS

M. Meyyappan (Xuhui Sun representing), NASA Ames Research Center  
MS 229-3, Moffett Field, CA, 94035, USA  
T: 650 604 2616, F: N/A, m.meyyappan@nasa.gov

Carbon nanotubes(CNTs) have shown interesting electronic, mechanical, optical, thermal, and other properties and therefore have been pursued for a variety of applications by the nanotechnology community ranging from electronics to nanocomposites. We have been pursuing development of chemical and biosensors using carbon nanotubes for the last ten years and this talk will present our progress to date. In the case of chemsensors, we use an interdigitated electrode as a chemresistor where purified single-walled carbon nanotubes(SWCNTs) serve as the conducting medium. When the chemresistor is exposed to a gas or vapor, the change in resistance is recorded; if SWCNTs do not respond to a particular gas or vapor, then doping or functionalization strategies are used. A sensor array is constructed with 32-96 sensor elements with chemical variations across the sensor array. In the sensor training mode, a pattern of resistance changes is generated from the sensor array for a particular analyte and later in the identification mode, a pattern recognition algorithm is used to identify that analyte from the background. This talk will present examples from our work to demonstrate the functioning of the sensor. In the case of the biosensor, a 'lock and key' approach is used wherein a preselected probe for a given target is attached to the tip of a carbon nanofiber(CNF). Numerous CNFs are grown using plasma chemical vapor deposition on a silicon wafer which serve as individual, freestanding, vertical electrodes. This nanoelectrode array(NEA) can use DNA, aptamer and antibody probes and electrochemical impedance spectroscopy is used upon probe-target binding for signal analysis. Results will be presented for identification of e-coli and ricin using this NEA. The author thanks all past and present NASA Ames colleagues for their contributions to the application development efforts, especially Jing Li, Yijiang Lu, and Jessica Koehne.

## FLOATING CATALYST SYNTHESIS AND DRY DEPOSITION OF CARBON NANOTUBES FOR THIN FILM FLEXIBLE ELECTRONICS APPLICATIONS

Esko I. Kauppinen, Aalto University  
Puumiehenkuja 2, P.O. Box 16100, Espoo, FI-00076 Aalto, FINLAND  
T: +358 40 509 8064, F: +358 9 470 23517, esko.kauppinen@tkk.fi

We present the floating catalyst synthesis of the high quality single walled carbon nanotubes and nanobuds (SWCNT and CNB; Anisimov et al., 2010; Nasibulin et al., 2007). We discuss their formation mechanisms during floating catalyst CVD synthesis from CO at ambient pressure and at temperature range 700-1000 oC using iron nanoparticle catalyst. We discuss the effect of reactor operating temperature on the individual tube as well as bundle length and their diameter distributions, being determined both by electron microscopic as well as optical methods (Ying et al., 2010). Especially, we discuss the control of tube chirality distributions via introducing trace amounts of CO<sub>2</sub> and NH<sub>3</sub> into the reactor. Methods for SWCNT direct dry deposition from the reactor at ambient temperature and pressure to form thin films and to manufacture transparent electron emitters, sensors, thin film conductors and field effect transistors (TFT) are presented. Flexible SWCNT-PET conducting films show transparency-sheet resistance surpassing that of ITO-PET films (Kaskela et al., 2010). SWCNT network TFTs on both silicon as well as polymeric substrates show mobilities of 35 cm<sup>2</sup>/Vs and on/off ratio of 5\*10<sup>6</sup>. We also fabricate logic circuits on flexible substrates (Sun et al., 2010). Anisimov, A.S., A. G. Nasibulin, H. Jiang, P. Launois, J. Cambedouzou, S. D. Shandakov, E. I. Kauppinen (2010) Mechanistic investigations of single-walled carbon nanotube synthesis by ferrocene vapor decomposition in carbon monoxide. Carbon 48, 380-388. Sun, D.-M., M. Timmermans, Y. Tain, A. G. Nasibulin, E. I. Kauppinen, S. Kishimoto, T. Mizutani and Y. Ohno (2011) Flexible high-performance carbon nanotube integrated circuits. Nature Nanotechnology. DOI: 10.1038/NNANO.2011.1. Kaskela, A., A.G. Nasibulin, M. Zavodchikova, B. Aitchison, A. Papadimitratos, Y. Tian, Z. Zhu, H. Jiang, D.P. Brown, A. Zakhidov and E.I. Kauppinen (2010) Aerosol synthesized SWCNT networks with tunable conductivity and transparency by dry transfer technique. Nano Lett. 10, 4349–4355. A. G. Nasibulin, P. V. Pikhitsa, H. Jiang, D. P. Brown, A. V. Krashennnikov, A. S. Anisimov, P. Queipo, A. Moisala, D. Gonzalez, G. Lientschnig, A. Hassanien, S. D. Shandakov, G. Lolli, D. E. Resasco, M. Choi, D. Tománek, and E. I. Kauppinen, (2007) A Novel Hybrid Nanomaterial, Nature Nanotechnology 2, 156-161. Tian, Y., H. Jiang, J. v. Pfaler, Z. Zhu, A. G. Nasibulin, T. Nikitin, B. Aitchison, L. Khriachtchev, D. P. Brown, and E. I. Kauppinen (2010) Analysis of the Size Distribution of Single-Walled Carbon Nanotubes Using Optical Absorption Spectroscopy. J. Phys. Chem. Letters 1, 1143-1148.

## AB INITIO STUDIES OF ELASTIC PROPERTIES OF FUNCTIONALIZED CARBON NANOTUBES AND GRAPHENE LAYERS

Karolina Milowska, Institute of Theoretical Physics, Faculty of Physics, University of Warsaw  
ul. Hoża 69, Warsaw, 00-681, Poland

T: +48 22 5532 244, F: +48 22 5532 333, karolina.milowska@gmail.com

Magdalena Birowska, Institute of Theoretical Physics, Faculty of Physics, University of Warsaw

Jacek A. Majewski, Institute of Theoretical Physics, Faculty of Physics, University of Warsaw

We present results of extensive studies of elastic properties of carbon nanotubes (CNTs) and graphene layers (GLs) functionalized with simple molecules, radical and fragments. These studies are based on the *ab initio* calculations in the framework of the density functional theory. This work provides novel predictions for the Young modulus of the functionalized CNTs and GLs, crucial for design of new composite materials. The calculations reveal that the functionalization of CNTs and GLs diminishes their Young modulus, but not to the extent that could hamper strong enforcement of the composite materials. New composite materials made by adding CNTs or graphene nanoribbons (GNRs) to various materials such as alloys, polymers, and metals are expected to enhance their properties, such as mechanical strength, electrical and thermal conductivity, and chemical stability. However, pristine CNTs and graphene flakes or ribbons are not soluble in water or in organic solvents and have tendencies to create bundles. This drastically limits its use in industrial applications like nano-composites. The chemical functionalization of CNTs allows for improved bonding of CNTs into the composite matrix, however, may weaken the strong stiffness of CNTs. Since the magnitude of this effect is generally unknown, we have undertaken theoretical studies of this issue.

We study the effects of functionalization of single wall CNTs (SWNTs) and GLs with simple organic molecules  $\text{CH}_n$ ,  $\text{NH}_n$ ,  $\text{OH}$ , and  $\text{COOH}$ , focusing on their Young modulus and Poisson ratio. We determine Young modulus by comparing the total energy of unstressed and stressed systems, e.g., applying the tensile stress along the symmetry axis of CNTs. The total energies are obtained from the *ab initio* calculations in the framework of the density functional theory. The geometry has been optimized just allowing for deduction of the Poisson ratio.

Specifically, the calculated Young modulus of the (9,0) pure CNT equals 1.39 TPa and compares excellently to experimental finding (1.25 TPa) and previous theoretical works (0.8 – 1.5 TPa). Also Poisson ratio is in excellent agreement with experimental values (0.21 in both cases). The functionalization of the CNTs does reduce their Young modulus, roughly proportionally to the density of the attached molecules. For example, Young modulus of (9,0) CNT functionalized with OH is 0.78 TPa. However, the functionalized CNTs remain strong enough to be implemented as an enforcement of the new composite materials. We discuss also the differences between elastic properties of the functionalized CNTs and graphene layers.

## SCIENCE AND TECHNOLOGY OF ULTRANANOCRYSTALLINE DIAMOND FILMS FOR APPLICATION TO MULTIFUNCTIONAL SYSTEM COMPONENTS AND DEVICES

Orlando Auciello, Argonne National Laboratory  
9700 South Cass Av, Lemont, Illinois, 60439, USA  
T: 630-252-1685, F: 630-252-4798, [auciello@anl.gov](mailto:auciello@anl.gov)

A review will be presented on the status of the revolutionary UNCD film technology developed and patented at Argonne National Laboratory.

UNCD thin films are grown by microwave plasma or hot filament chemical vapor deposition, using a novel patented Ar/CH<sub>4</sub> plasma chemistry. UNCD films exhibit 2-5 nm grain size (thus the trade name UNCD). UNCD films, can be integrated with other materials, such as metal oxide piezoelectric thin films, which enables a new generation of hybrid low-voltage/energy saving, piezoactuated, high-performance MEMS/NEMS devices.

UNCD films exhibit exceptional mechanical, tribological, chemical, electrical, electron emission, and biocompatible properties, which enable application to a broad range of system components and multifunctional devices from the macro to the nanoscale, namely: 1) low friction/energy saving coating for mechanical pump seals for the petrochemical and car industries, 2) RF MEMS/NEMS resonators and switches for wireless communications and radar systems, 3) NEMS devices; 4) low threshold electric field electron emission for field emission displays and other cold cathode devices; 5) Biomedical devices (e.g., bioinert coating for encapsulation of a microchip implantable in the retina to restore sight to people blinded by retina degeneration, coating for other implantable devices for treatment of vision problems (glaucoma and retina detachment), UNCD tribological coating with low friction and negligible wear for prosthesis – knees, hips, heart valves).

The UNCD film technology is commercialized by Advanced Diamond Technologies, a Company co-founded by O. Auciello and colleagues and spun-off from Argonne in 2004.

This work was supported by US Department of Energy, Office of Science, Office of Basic Energy Sciences-Materials Science, under contract DE-AC02-06CH11357 and DARPA under contracts MIPR 06-W238. Use of the Center for Nanoscale Materials was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357

## NANOCRYSTALLINE DIAMOND GROWTH IN A SURFACE-WAVE PLASMA

Masataka Hasegawa, AISTNanotube Research Center  
Tsukuba Central 5, Tsukuba, Ibaraki, 305-8565, Japan  
T: +81-29-861-5686, F: +81-29-861-4522, hasegawa.masataka@aist.go.jp  
Kazuo Tsugawa, AISTNanotube Research Center  
Masatou Ishihara, AISTNanotube Research Center  
Jaeho Kim, AISTNanotube Research Center  
Yoshinori Koga, AISTNanotube Research Center

Nanocrystalline diamond (NCD) films have been synthesized in a wide substrate temperature range using a surface-wave plasma in a microwave plasma chemical vapor deposition (MWPCVD) growth process. The temperature range of the diamond growth in the surface-wave plasma varies from below 100 °C to over 700 °C, and NCD films are grown on plastic substrate below 100 °C. This work reveals marked distinctions in growth characteristics from other CVD diamonds. On the basis of them, the NCD growth mechanism in the surface-wave plasma is discussed. We have deposited NCD films at substrate temperatures from 80 °C to 700 °C in a hydrogen-rich surface-plasma of a H<sub>2</sub>/CH<sub>4</sub>/CO<sub>2</sub> (CH<sub>4</sub> = CO<sub>2</sub> = 5 vol. %) gas mixture in a MWPCVD reaction chamber. In the growth experiments, the temperature dependence of growth rates has been investigated. We have found less temperature sensitive, activation energy of growth rates of the NCD in this work than those in the others such as microcrystalline diamond (MCD), ultrananocrystalline diamond (UNCD) by MWPCVD, and UNCD by hot-filament CVD (HFCVD). In the surface-wave plasma, diamond crystals continuously re-nucleate through the CVD growth process even in a hydrogen-rich plasma, which leads to the NCD growth, while UNCD grows in a hydrogen-poor plasma. This result implies that the growth mechanism of NCD in the surface-wave plasma is different from that of CVD diamonds grown in other type plasmas. The temperature insensitive growth rate can be explained by gas-phase nucleation with substrate temperature. In addition, the continuous nucleation in the plasma with a constant rate gives an account of the crystal size distribution in the NCD film grown in the surface-wave plasma. Low temperature NCD growth even below 100 °C is also considered to be brought by it. The electron density and the electron temperature of the plasma are determined by using double-probe measurements. The plasma diagnosis reveals low electron temperatures of 2 - 3 eV in the process region, which is a distinctive characteristic of the surface-wave plasma. The low electron temperature is essential for the continuous renucleation of diamond in a hydrogen-rich plasma during the nanocrystalline diamond growth for a wide range of substrate temperature from under 100 to over 700 °C.



## DIAMOND IN NITRIDE ELECTRONICS

Erhard Kohn, ulm university  
Albert-Einstein-Allee 45, Ulm, 89081, Germany  
T: +49 731 50-26179, F: +49 731 5026155, erhard.kohn@uni-ulm.de  
Sylvain Delage, Alcatel-Thales, Marcoussis, France  
Mohammed Alomari, ulm university, Germany  
David Maier, Patrick Herfurth, Carsten Pietzka, ulm university, Germany  
Ziyao Gao, Stefano Rossi, ulm university, Germany

Diamond and the III-Nitride materials are two highly stable wide bandgap semiconductors with many extreme properties for operation under extreme conditions. GaN devices are usually based on heterostructures, enabling bandgap engineering, a feature not available in the case of diamond yet. Nevertheless diamond possesses intriguing thermal, mechanical, optical and electrochemical properties and may be able to complement Nitride devices in many ways. Examples already discussed extensively in the past are thermal management of power devices and electrochemical sensing in harsh environment.

To the diamond community the most interesting question may be: Where is the frontier in III-Nitride technologies and how can diamond fit in. The talk will therefore try at first to illustrate the capabilities of III-Nitride electronic devices under extreme conditions, especially at high temperature and in corrosive environment. High temperature large signal 1 MHz operation of GaN-based HEMTs has been possible for 50 hrs at 900 °C (in vacuum), demonstrating an extreme temperature stability of the system. GaN (and its ternaries AlGaIn and InAlN) in direct contact with the environment is considered to be highly corrosion resistant. Nevertheless native oxides can be formed at high temperature or under anodic polarization in the liquid. In addition, in the presence of H-radicals, GaN and Ga-oxide can be reduced. Thus, their surface is still reactive.

Combining both materials in a common device structure means to grow either GaN on diamond or vice versa, where GaN is wurzite and diamond cubic. Thus, both use generally nucleation layers like AlN in the case of GaN growth and nanodiamond particle seeding or BEN on Si interlayers in the case of diamond growth. Especially critical is the high temperature diamond growth regime with high H-radical density in connection with the GaN surface reactivity.

Nevertheless, results are now available for both cases. GaN HEMT structures have been realized by direct growth on diamond. On the other hand, GaN HEMT structures have also been overgrown by nanodiamond films. Microwave HEMT performance has been demonstrated for both cases. Another interesting substrate is transparent sapphire for biochemical analytics. Here GaN and diamond structures can be grown side by side, enabling highly corrosion resistant ISFETs or electrochemical sensor arrays of high spacial resolution compatible with optical fluorescence analysis.

Following the overview, the talk will conclude discussing latest advancements in these fields.

## NITROGEN VACANCY CENTERS IN NANO-SCALE DIAMONDS

James Rabeau, Macquarie University  
North Ryde, Sydney, New South Wales, 2109, Australia  
T: +61298504161, F: +61298504161, james.rabeau@mq.edu.au

Diamond has been central to a number of new and exciting breakthroughs in quantum and biological science for the past several years. The underpinning feature of diamond that makes this possible is the ability to host bright and optically stable colour centres at room-temperature. Of the hundred or so optical defects in diamond, the nitrogen-vacancy (NV) centre has attracted the most attention primarily for its photo-stability, spin polarised optical transition and long spin coherence time. By combining and exploiting each of these in different ways, landmark demonstrations have been made including single photon emission, spin qubits, magnetometry and bright fluorescent biolabels. Recent experiments show that the properties of NV centers in extremely small host diamond crystals are not the same as what is observed in larger or bulk crystals [1]. Here we report on methods for exploring this behaviour in more detail and understanding what gives rise to the changes in optical behaviour.

1. C. Bradac, T. Gaebel, N. Naidoo, MJ Sellars, J. Twamley, LJ Brown, AS Barnard, T. Plakhotnik, AV Zvyagin, JR Rabeau, *Nature Nanotechnology* (2010) 5, 345-348, "Observation and control of blinking nitrogen vacancy centres in discrete nanodiamonds"

## **NOVEL BIOMOLECULAR DETECTION PRINCIPLES IN LIQUID ENVIRONMENT USING NANODIAMOND PARTICLES FOR CHEMICALLY-INDUCED LUMINESCENCE SWITCHING**

Milos Nesladek, IMOMEC division IMEC, Hasselt University  
Wetenschapspark 1, Diepenbeek, Limburg, 3500, Belgium

T: +32-11268833, F: +32-11268899, milos.nesladek@uhasselt.be

Vladka Rezacova, Faculty of Biomedical Engineering, Czech Technical University Prague, Czech Republic

Jan Šturza, Institute of Nuclear Physics, Academy of Sciences of the Czech Republic, v.v.i., Prague

Petr Cígler, Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i., Prague

Miroslav Ledvina, Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i., Prague

High biocompatibility, size ranging from ~ 5 nm, stable luminescence from its color centers and simple carbon chemistry for biomolecule grafting make nanodiamond (ND) particles attractive alternative to molecular dyes for drug-delivery. Here we present a novel method for remote monitoring of chemical processes in biological environments based on color changes from photoluminescence of NV centers in ND by driving the NV luminescence chemically. This method is based on alternation of the ND surface electric field developed by interacting molecules with the diamond surface. Our technique has advantages over FRET (Foerster Resonance Energy Transfer) for which the sensitivity to size scales as  $1/r^6$ , allowing working with particles of molecules of size  $< 5$  nm. In our method, due to  $1/r^2$  scaling, luminescence effects are observed up to ~ 20 nm of depth. This allows construction of optical chemo-biosensors operating in cells visible in classical confocal microscopes. We demonstrate this phenomenon on oxidized and hydrogenated ND as well as single crystal diamond implanted in nm-depth by N and containing engineered NV centers. The hydrogenation of NDs leads to quenching of luminescence related to negatively charged (NV<sup>-</sup>) centers and this way produces changes in the intensity ratio between NV<sup>-</sup> (636 nm) to neutral NV<sup>0</sup> (575nm) centers. The working function of ND probe in biological environment is demonstrated by attaching charged polymers and other molecules on variously terminated ND surface including fluorinated diamond. Finally we discuss the ND size-effect enhancing the luminescence switching.

## DEEP-DOPANT EFFECT FOR DIAMOND ULTRAVIOLET SENSOR

Yasuo Koide, National Institute for Materials Science (NIMS)  
Namiki 1-1,, Tsukuba, Ibaraki, 305-0044, Japan  
T: +81-29-860-4311, F: +81-29-860-4005, koide.yasuo@nims.go.jp

Diamond is an attractive semiconductor for applying to high-power electronic devices operated at a breakdown voltage larger than 10kV and a frequency higher than a few GHz. However, since ionization energies of the p and n-types dopants were as large as 0.37 and 0.57 eV, respectively, it was difficult to activate thermally hole and electron in diamond, which led to small carrier concentration at room temperature (RT). Such the large ionization energy of dopants originates from a relatively small permittivity of diamond and limits the operation of diamond electron devices at RT. Thus, realization of high activation efficiency of both the B and P dopants at RT is a big challenge for manufacturing the diamond electron devices. Here, we named various phenomena caused by the large dopant energy by a deep-dopant effect. In the present paper, we will show the electrical properties which were produced by the deep-dopant effect in the diamond. One is the electrical properties of the diamond pn-junction, and the other is the photoconductivity gain property of diamond ultraviolet (UV) detectors. The ionized dopant and carrier profiles in the pn-junction of diamond with the P donor and the B acceptor are theoretically analyzed by simply solving a one-dimensional Poisson equation. The width of the depletion layer is around two times larger than that of the space-charge layer since there exists a transition region at the depletion layer edge. It is predicted that the static saturation property of a bipolar pnp-junction transistor is affected by the large width of the depletion layer. However, the deep-dopant effect is found to be weakened with increasing temperature. Photoconductivity gain (PG) and persistent photoconductivity (PPC) properties observed in the diamond UV detector are theoretically explained by solving rate equations which describe generation and recombination processes through the deep-dopant effect. Formation of one-sided pn-junction between the epilayer and substrate and slow hole capture rate of acceptor and hole trap levels provide accumulation of photo-generated hole in the epilayer, which produces the photocurrent larger than the ideal current value. The PPC current after turning off the deep ultraviolet light is interpreted as due to the slow hole capture rate of the acceptor and trap levels. Thus, the deep-dopant effect is concluded to be the characteristic feature of diamond devices, which significantly affects the electronic and photonic properties of diamond devices.

## SURFACE MODIFICATIONS OF NANODIAMONDS: TOWARDS ENHANCED CHEMICAL REACTIVITY

J.C. Arnault, CEA LIST, Diamond Sensors Laboratory  
bâtiment 451, point courrier 45, Gif sur Yvette, 91191, FRANCE  
T: (33) 1 69 08 71 02, F: (33) 1 69 08 78 19, jean-charles.arnault@cea.fr

Nanodiamonds (NDs) constitute excellent candidates for biomarkers, combining the ability to covalently graft biomolecules on their surface with the presence of stable coloured N-V centers in the diamond core. However, their surface chemistry presents a wide variety of oxidized groups as well as amorphous and / or graphitic carbon. An initial surface treatment is thus required to ensure high grafting yield and reproducibility. Different strategies were previously reported in the literature such as chemical treatments [1], annealing under controlled atmosphere [2-4] or RF-plasma exposures [5].

Two different ways to homogenize NDs surface terminations will be here presented:

(i) Surface hydrogenation of NDs using Microwave Plasma Chemical Vapour Deposition (MPCVD) will be first described [6]. The MPCVD reactor is connected to a UHV system equipped with XPS and AES. Kinetics of oxygen removal were followed by surface analysis of hydrogen treated NDs (H-NDs). Their enhanced surface reactivity was then confirmed using photochemical reaction with alkenes and a spontaneous coupling of aryldiazonium salts. These results strongly suggest similar electronic surface properties between bulk and nanodiamond materials.

(ii) Surface graphitisation of NDs is also a promising way for chemistry. Prato reaction was recently reported on such modified surfaces [7]. Our in situ study of the graphitisation of NDs using UHV annealing will be presented. The effects of the annealing parameters on the graphitization kinetics will be discussed. The best conditions were then reported using an ex situ furnace allowing the preparation of stable colloid suspension of graphitised NDs. These suspensions were characterised using DLS and Zeta potential measurements.

Our original approach combines in situ and ex situ experiments. First, surface modifications of NDs are monitored by electron spectroscopies (XPS, AES) to better understand the involved mechanisms. Samples are transferred without air exposure after the hydrogen plasma or the UHV annealing. Second, suitable conditions are used for ex situ treatment to modify larger quantities of NDs, usable for chemistry.

References [1] A. Krueger et al., *Langmuir*, 2008, 24, 4200. [2] S. Osswald et al., *J. of the American Chem. Soc.*, 2006, 128, 11635. [3] K. B. Holt et al., *Phys. Chem. Chem. Phys*, 2008, 10, 303. [4] Y. Liu et al., *Chemistry of Materials*, 2004, 16, 3924. [5] Q. S. Yu et al., *Appl. Phys. Lett.*, 2006, 88, 231503. [6] H. A. Girard et al., *Diam. and Relat. Mater.* 2011, 19, 1117. [7] D. Lang et al., *Diam. Relat. Mater.* 2011, 20, 101.

## BIOMIMETIC DIAMOND INTERFACES FOR PROTEIN IMMOBILIZATION

Christoph E Nebel, Fraunhofer-Institute for Applied Solid State Physics  
Tullastrasse 72, Freiburg, BW, 79108, Germany

T: +497615159291, F: +49761515971291, christoph.nebel@iaf.fraunhofer.de

René Hoffmann, Fraunhofer-Institute for Applied Solid State Physics (IAF), Freiburg 79108, Germany

W. Smirnov, Fraunhofer-Institute for Applied Solid State Physics (IAF), Freiburg 79108, Germany

Nianjun Yang, Fraunhofer-Institute for Applied Solid State Physics (IAF), Freiburg 79108, Germany

Oliver Ambacher, Fraunhofer-Institute for Applied Solid State Physics (IAF), Freiburg 79108, Germany

Protein-immobilization on solid electrodes is up-to-now very hard to realize without generation of unintended structural variations. The characterization of protein properties suffers severely from this fact as little variations of the folded protein structure causes dramatic variations of the electronic properties. In this presentation we introduce "diamond" with adjusted surface properties to interact with the redox protein "cytochrom c" without causing structural modifications of cyt c. The "adjustment" of the surface of boron-doped diamond for optimized protein interaction can be achieved by realizing electrochemically a mixed surface of hydrogen (H) and OH termination. We demonstrate that the mixed H/OH termination of the diamond surface mimics perfectly a "protein-like" surface. We have applied variously characterization methods to investigate the detailed properties of the diamond/protein interaction. We applied a combination of electrochemical techniques and atomic force microscopy (AFM) with single molecule resolution, XPS and phenyl-grafting to identify H-bonding on the surface of diamond. These experiments reveal that moderately OH-terminated diamond shows stable immobilization of Cytochrome c with high electron transfer activity, driven by a combination of electrostatic and hydrophobic interaction. This surface mimics natural binding partners, where coarse orientation is governed by electrostatic interaction of the protein's dipole and hydrophobic interactions are involved in formation of the electron transfer complex. The results will be introduced and discussed in detail in this presentation.

## SELF-ASSEMBLED NANODIAMONDS LAYERS FOR INNOVATIVE DIAMOND-BASED DEVICES

H.A. GIRARD, CEA LIST

CEA Saclay, Diamond Sensors Laboratory, Bat.451, PC 45, Gif sur Yvette, 91191, France

T: +33 1 69 08 47 60, F: +33 1 69 08 78 19, hugues.girard@cea.fr

P. Benayoun, C. Gesset, E. Scorsone, J.C. Arnault, P. Bergonzo, CEA LIST

Diamond is an outstanding material due to the combination of its mechanical, electrical, thermal, and optical properties. For scientific and technological applications, its high chemical and mechanical resilience, high surface stability, high thermal conductivity, and wide bandgap make diamond a versatile material in the fields of electrochemistry, heat spreaders, biological platform, sensor devices. However, its 3D-structuration, at the micro- or nanoscale, can be required to achieve MEMS or NEMS devices [1], optical systems [2-3] but also biomedical devices [4]. This structuration is currently achieved by top-down approaches, mostly based on mask etching. While these methods lead to well defined structures, the growth of a thick diamond layer and its post-processing, such as lithographic steps, are time and cost consuming. A bottom-up approach appears as more rational and flexible, by the use of nanodiamonds acting as growth seeds from which diamond layer can be grown. Technological challenge is thus to control the deposition and the organization of these nanodiamonds onto pre-structured substrates. Playing on chemical and electrostatic interactions between the substrate and the nanodiamonds, we developed in our lab versatile approaches to realize self-assembled diamond nanoparticles layers [5] [6]. By this mean, structured diamond coatings are achieved on 3D surfaces even when exhibiting high conformation, as well as on vertical wells and vias, and this has even become achievable on nanometric patterns. Furthermore, adding nanodiamonds to polymeric systems, 2D-organized nanodiamonds layers are obtained, allowing structuration at the nucleation stage, without any lithographic processing. In this study, we will show how nanodiamonds surface chemistry can be a powerful tool to achieve innovative structures for biomedical, sensing or optical systems.

[1] A. Kromka et al., *Diamond Relat. Mater.*, 2009, 18, 734.

[2] L. Ondic et al., *ACS Nano*, 2011, 5, 346.

[3] T. M. Babinec et al., *Nat Nano*, 2010, 5, 195.

[4] P. Bergonzo et al., *Irbm*, 2011, 32, 91.

[5] E. Scorsone et al., *J. Appl. Phys.*, 2009, 106, 014908.

[6] H. A. Girard et al., *ACS Appl. Mater. Inter.*, 2009, 1, 2738.

## FUNCTIONAL B-DOPED NANOCRYSTALLINE CVD DIAMOND FILMS

Ken Haenen, Hasselt University & IMEC vzw  
Institute for Materials Research (IMO) & IMOMECE, Wetenschapspark 1, Diepenbeek, Limburg, 3590,  
Belgium  
T: +32-11-268875, F: +32-11-268899, ken.haenen@uhasselt.be

Chemical Vapour Deposition (CVD) diamond is a versatile material with extreme mechanical, thermal, electronic and optical properties. The synthesis of ~ 100 nm to 200 nm thin nanocrystalline diamond (NCD) films by the microwave plasma enhanced CVD (MW PE CVD) technique has proved an enormous step forward for this material to show its potential in action [1]. The use of state-of-the-art seeding procedures based on water-based colloidal solutions of ultradispersed nanodiamond powder [2], allow the deposition of closed films of less than 100 nm on 2D as well as 3D structures, minimizing deposition times while retaining an acceptable surface roughness.

First, more light will be shed on the crucial influence of grain size and grain boundaries by studying the magnetotransport and (electro-)optical properties of heavily B-doped films on the metallic side of the metal-insulator transition. These films, 150 nm thick and grown with identical deposition conditions except for small variations in the methane-to-hydrogen ratio (1...5 %), show a very rich transport behaviour. Based on Matthiessen's rule, it is possible to construct a 2-phase model, separating the intra- and intergrain contributions for the resistivity and the mobility [3]. As all layers have a carrier concentration exceeding  $10^{21} \text{ cm}^{-3}$ , even superconducting properties can be detected when sufficiently cooled down [4]. The differentiation in the granular nature of the material, induced by the variation in the used methane-to-hydrogen ratio, is also reflected in the critical temperature describing the transition towards the superconducting state of zero resistance, an effect that is not fully understood to date.

From an application driven point of view, these layers are ideal candidates to be functionalized with high extinction coefficient dye molecules, to serve as new, high-quality absorbers for electrochemical solar cells [5]. To conclude, an introduction will be given to possible synthetic methods to attach Ru-based complexes to its surface via linker molecules. While the bonding mechanism of the attached molecules is investigated with XPS, the charge transfer characteristics of these NCD-based heterojunctions are assessed using highly sensitive, photocurrent-based spectroscopic techniques.

[1] O.A. Williams, M Nesládek, M Daenen, S. Michaelson, A. Hoffman, E. Osawa, K. Haenen, R.B. Jackman, *Diamond Relat. Mater.* **17/7-10**, 1080-1088 (2008).

[2] O.A. Williams, O. Douhéret, M. Daenen, K. Haenen, E. Osawa, M. Takahashi, *Chem. Phys. Lett.*, **445/4-6**, 255-258 (2007).

[3] S.D. Janssens, P. Pobedinskas, J. Vacik, V. Petráková, B. Ruttens, J. D'Haen, M. Nesládek, K. Haenen, P. Wagner, submitted to *New J. Phys.* (2011).

[4] B.L. Willems, G. Zhang, J. Vanacken, V.V. Moshchalkov, S.D. Janssens, K. Haenen, P. Wagner, *J. Phys. D-Appl. Phys.*, **43/37**, 374019 (2010).

[5] Y.L. Zhong, A. Midya, Z. Ng, Z.K. Chen, M. Daenen, M. Nesládek, K.P. Loh, *J. Am. Chem. Soc.*, **130/51**, 17218 (2008).



## **ULTRANANOCRYSTALLINE DIAMOND (UNCD) FILMS AND THEIR APPLICATION TO MEMS, BIOSENSORS, AND NANOMANUFACTURING**

Dr. John A. Carlisle, Advanced Diamond Technologies, Inc.  
429 B Weber Road, #286, Romeoville, Illinois, 60446, USA  
T: 8152723969, F: 9284373507, [carlisle@thindiamond.com](mailto:carlisle@thindiamond.com)

Hongjun Zeng, Nicolaie Moldovan, Prabhu Arumugam, Advanced Diamond Technologies, Inc.

Due to advances in reaction design and deposition chemistry, a variety of diamond materials can now be deposited onto wafers up to 300 mm in size, with excellent thickness and property uniformity, enabling high-yield production of microdevices. In this presentation advances made over the past several years to enable thin, smooth diamond films for MEMS will be reviewed with emphasis on materials and microfabrication strategies needed to integrate diamond with other materials for MEMS devices. UNCD (ultrananocrystalline diamond) spans a family of thin smooth diamond materials. UNCD wafers serve to demonstrate the availability of the technology and to allow designers to integrate diamond into new process flows. NaDiaProbes, which are all-diamond AFM probes used for metrology and nanomanufacturing, are the first example of a commercially available diamond MEMS device that leverages wafer-scale processing of UNCD wafers using established microfabrication techniques. How ADT looks at wafer-scale production of UNCD-based MEMS devices going forward as well as our technology roadmap for UNCD-enabled products under development will be presented. Particular emphasis will be placed on the development of UNCD coatings and MEMS devices for RF devices, nanomanufacturing, and chem/bio-sensing related applications.

## DIAMOND-BASED ELECTRONIC DEVICE TECHNOLOGIES (INVITED)

Makoto Kasu, NTT Basic Research Laboratories  
3-1 Morinosato-Wakamiya, Atsugi, Kanagawa, 243-0198, Japan  
T: +81-46-240-3451, F: +81-46-240-4729, kasu.makoto@lab.ntt.co.jp  
Kazuyuki Hirama, NTT Basic Research Laboratories

Diamond is a semiconductor with a wide band gap of 5.47 eV and possesses the highest thermal conductivity and the highest breakdown electric field among semiconductors. Therefore, diamond transistors are expected to exhibit the highest RF power capability. [H-terminated diamond FET] Hydrogen (H)-terminated diamond in air possesses holes on the surface at a concentration of  $\sim 1 \times 10^{13}$  cm<sup>-2</sup>. FET with a 0.1  $\mu$ m-gate length exhibited a drain current of 0.67 A/mm, cut-off frequencies for current gain (f<sub>T</sub>) and for power gain (f<sub>MAX</sub>) of 45, 120 GHz, respectively [1], and output power densities of 2.1 W/mm at 1 GHz [2]. Recently we clarified that NO<sub>2</sub> adsorption on H-terminated surface leads to hole generation, and therefore, by using 300-ppm NO<sub>2</sub> we obtained a hole concentration of  $\sim 9.5 \times 10^{13}$  cm<sup>-2</sup>. Further, by NO<sub>2</sub>-adsorption, we observed a  $\sim 1.5$  fold increase in drain current and cut-off frequency of H-terminated FET [3]. [Ion implantation] So far, doping efficiency for ion-implanted diamond was quite low. However, by using high-pressure high-temperature (HPHT) annealing at conditions inside diamond stable phase, we demonstrated one-order improvement in the doping efficiency. With this technology, we fabricated B-implanted diamond FET, which showed a breakdown field of  $>1$  MV/cm and an operation at  $\sim 500$  °C [4]. [Arsenic-doped n-type diamond] Impurity doping is still challenge for diamond. For p-type, boron becomes an acceptor with an ionization energy of 0.37 eV. For n-type, phosphor (P) is a donor with 0.58 eV. We grew arsenic-doped diamond using tertiarybutylarsine by microwave plasma CVD, and observed n-type conduction [5]. Its ionization energy was  $\sim 1.0$  eV. [AlGaIn/GaN HEMT on diamond] In nitride power transistors, the maximum output power is limited by thermal dissipation through their substrates (normally SiC). Diamond which possesses the highest thermal conductivity is the best material. The most difficult problem was that nitride has the wurtzite lattice and diamond has the diamond lattice. However, by using (111) diamond surface, we achieved single-domain (0001) AlN heteroepitaxy on (111) diamond. The AlGaIn/GaN high-electron mobility transistor (HEMT) on diamond exhibited the lowest thermal resistance [6]. A part of this work was supported by the SCOPE Project. [1] K. Ueda, et al.: IEEE Electron Dev. Lett. 27 (2006) 570. [2] M. Kasu, et al.: IEE Electronics Lett. 41 (2005) 1249. [3] M. Kubovic, et al.: Appl. Phys. Express 2 (2009) 086502. [4] K. Ueda, et al.: Jpn. J. Appl. Phys. 49 (2010) 04DF16. [5] M. Kasu, et al.: Jpn. J. Appl. Phys. 49 (2010) 110209. [6] K. Hirama, et al.: Appl. Phys. Lett. 98 (2011) in press.

## EFFECT OF DOPANTS ON DIAMOND (111), (110) AND (100) GROWTH RATES

Karin Larsson, Department of Materials Chemistry  
Lägerhyddsvägen 1, Uppsala, 751 21, Sweden  
T: +46 18 4713750, F: +46 18 513548, karin.larsson@mkem.uu.se  
Zou Yiming, Department of Materials Chemistry

The growth of diamond films requires a perfect recognition of the parameters affecting the growth process. It is crucial to understand how these parameters will affect the growth on an atomic level. It has been observed that the growth rate will be enhanced for a small N/C or B/C ratio. One of the purposes with the here presented work was to theoretically (by using DFT) outline the thermodynamic effect of the B dopant on a rate limiting steps (i.e. surface H abstraction by gaseous H) in the CVD growth mechanism of diamond (100), (111) and (110), and to compare with earlier observations for N. As was the situation with substitutional N within the upper part of the diamond lattice, substitutional B was found to have an improved effect on the H abstraction energy. It changed from a slightly endothermic value to a strongly exothermic one. This was not the case with BH<sub>x</sub> (or NH<sub>x</sub>) co-adsorbed on the surface. To outline the effect of B (or N) on the growth rate, one has to consider the barriers of energies. Hence, we have also carefully calculated the barriers for the H abstraction process. The energy barriers of abstraction were shown to substantially decrease with B (or N) positioned in the second C layer, leading to an improvement of the abstraction reaction rate by approximately a factor of 3 vs 5. However, co-adsorbed BH<sub>x</sub> (or NH<sub>x</sub>) species did not result in any decrease in energy barrier. Hence, the dopants B and N is here shown to have a positive effect on the diamond growth rate when substitutionally positioned within the lattice, and not just adsorbed to it. (These observations were explained by electron transfer from the dopant to the surface bonds (N), or from the surface bonds to the dopant (B)).

## EPITAXIAL GRAPHENE: GROWTH AND DOPING

Andrew T. S. Wee, National University of Singapore  
Dept of Physics, 2 Science Drive 3, Singapore, 117542, Singapore  
T: 65-65163333, F: 65-67774279, phyweets@nus.edu.sg

Wei Chen, Dept of Chemistry, National University of Singapore  
Yuli Huang, Chiba University, Japan

Han Huang, Jiatao Sun, Xingyu Gao, Siew-Wai Poon, Eng-Soon Tok, Dept of Physics, National University of Singapore

The growth of high quality epitaxial graphene will facilitate the development and commercialization of graphene nanoelectronics devices, and the main substrate-based approaches are chemical vapour deposition (CVD) on metal catalytic thin films and thermal decomposition of silicon carbide (SiC). We have performed detailed studies using in situ scanning tunnelling microscopy (STM), synchrotron photoemission (PES) and density functional theory (DFT) calculations to investigate the structure of the various reconstructions of 6H-SiC (0001) prior to its thermal decomposition to form epitaxial graphene (EG) [1-3]. We show that the transition from monolayer EG to trilayer EG adopts a bottom-up growth mechanism [4], and x-ray absorption fine structure studies indicate an increase in disorder of Si atoms in the SiC substrate beneath the surface and the formation of Si clusters [5,6].

A major challenge in graphene-based devices is opening the energy band gap and doping. Molecular functionalization of graphene is one approach to modifying its electronic properties. Surface transfer doping by surface modification with appropriate molecular acceptors represents a simple and effective method to non-destructively dope graphene [7-9]. Surface transfer doping relies on charge separation at interfaces, and represents a valuable tool for the controlled and non-destructive doping of semiconductors and nanostructures at relatively low cost, thereby facilitating the development of hybrid organic-graphene nanoelectronics. Molecular self-assembly of bimolecular systems on epitaxial graphene and HOPG is demonstrated [10,11]. Surface transfer hole doping of epitaxial graphene using oxide thin films is also discussed [12].

- [1] W. Chen, et al., Surf. Sci. 596 (2005) 176.
- [2] S. W. Poon, W. Chen, E. S. Tok, A. T. S. Wee, Appl. Phys. Lett. 92 (2008) 104102.
- [3] S. W. Poon, W. Chen, E. S. Tok, A. T. S. Wee, Phys. Chem. Chem. Phys. 12 (2010) 13522.
- [4] H. Huang, W. Chen, S. Chen, A. T. S. Wee, ACS Nano 2 (2008) 25.
- [5] X. Y. Gao, et al., Phys. Rev. B 78 (2008) 201404.
- [6] X. Y. Gao, et al., Appl. Phys. Lett. 95 (2009) 144102.
- [7] W. Chen, S. Chen, D. C. Qi, X. Y. Gao, A. T. S. Wee, J. Am. Chem. Soc. 129 (2007) 10418.
- [8] J. T. Sun, Y. H. Lu, W. Chen, Y. P. Feng, and A. T. S. Wee, Phys. Rev. B 81 (2010) 155403.
- [9] W. Chen, D. C. Qi, X. Y. Gao, A. T. S. Wee, Prog. Surf. Sci. 84 (2009) 279-321.
- [10] H. Huang, S. Chen, X. Y. Gao, W. Chen, A. T. S. Wee, ACS NANO 3 (2009) 3431-3436.
- [11] Y.L. Huang, W. Chen, H. Li, J. Ma, J. Pflaum, A. T. S. Wee, Small 6 (2010) 70-75.
- [12] Z.Y. Chen, et al., W. Chen, Appl. Phys. Lett. 96 (2010) 213104.

## DEVELOPMENT OF FUNCTIONAL GRAPHENE TRANSISTORS FOR BIOSENSOR APPLICATIONS

Ian D. Sharp, Walter Schottky Institut  
Am Coulombwall 4, Garching, 85748, Germany  
T: +49 89 289 12889, F: +49 89 289 12737, sharp@wsi.tum.de  
Lucas H. Hess, Walter Schottky Institut  
Max Seifert, Walter Schottky Institut  
Martin Stutzmann, Walter Schottky Institut  
Jose A. Garrido, Walter Schottky Institut

Given its large carrier mobilities, high chemical stability, and two-dimensional structure, graphene holds significant potential for sensor applications in aqueous environments. In this work, we demonstrate the operation of arrays of micron-scale graphene solution-gated field effect transistors (G-SGFETs) fabricated from large-scale material. The performance of graphene produced by epitaxial growth on silicon carbide is compared directly to that of material fabricated by chemical vapor deposition on copper. For both cases, the high ambipolar mobilities and large interfacial capacitances in electrolyte environments lead to transconductive sensitivities which are far superior to state-of-the-art devices based on silicon or group III-nitride materials. However, the low frequency noise of these devices is strongly affected by specific processing methods and must be carefully considered. Furthermore, biosensing applications require the development of methods to impart specific chemical functionality without adversely affecting the carrier mobility. Here, we show that direct photografting and photopolymerization can be used to graft stable organic layers onto the active regions of the transistors. Scanning Raman spectroscopy is used to show that photopolymerization does not disrupt the basal plane conjugation of graphene and that the polymerization reaction propagates from existing defect sites. This technique thus offers the possibility of providing tailored chemical functionality without adversely affecting the electronic properties of graphene. Together, these results provide a strong indication that graphene will have the ability to far outperform existing technologies for highly sensitive and selective biosensing.

## **SPIN CURRENT GENERATION BY ADIABATIC QUANTUM PUMPING IN GRAPHENE**

K S Chan, Department of Physics and Materials Science, City University of Hong Kong  
Tat Chee Avenue, Hong Kong SAR, China

T: 34427814, F: 34420538, apkschan@cityu.edu.hk

Qingtian Zhang, Zijing Lin, Department of Physics, University of Science and Technology of China

Junfeng Liu, Department of Physics and Materials Science, City University of Hong Kong

Graphene has become a major research focus since its discovery not only for its special electronic properties, but also for its potentials in spintronic applications. Owing to small spin-orbit interaction, electron spin in graphene has a long relaxation time. This special characteristic is very useful for using electron spin in graphene as information encoder. Nevertheless, the small spin-orbit interaction has the drawback that spin is difficult to control in graphene and this could be the main factor that hinders the development of graphene spintronics. In semiconductors, we have learnt through various studies in the past decade that spin-orbit interaction is a very useful tool for manipulating and generating spin polarization using electrical signals. So, for the development of graphene spintronics, there is an urgent need to look for alternative methods to manipulate and generate spin polarization. In this presentation, I will discuss the generation of spin polarized current in graphene using adiabatic quantum pumping. In adiabatic pumping a charge current can be generated without an external voltage bias by applying two a.c. electrical potentials. I will describe how we can use adiabatic pumping and ferromagnetic proximity effect to generate either pure spin current or completely spin polarized currents. Our estimation shows the charge current generated is in the nano-Ampere range. Our proposed method is useful for the development of graphene spintronic devices.

## THE FORMATION AND STABILITY OF VACANCY, DISLOCATION, AND GRAIN BOUNDARY IN GRAPHENE

Gun-Do Lee, Dept. of Materials Science and Engineering, Seoul National University  
Kwan-Ak Gu Kwan-Ak Ro, Seoul, 151-742, Republic of Korea  
T: 82-16-207-1058, F: 82-2-872-1058, gdlee@snu.ac.kr

Euijoon Yoon, Nong-Moon Hwang, Dept of Materials Science and Engineering, Seoul National University  
Young-Kuk Kim, Jisoon Ihm, Dept. of Physics, Seoul National University  
Cai-Zhuang Wang, Kai-Ming Ho, Dept. of Physics, Iowa State University

In the previous study, we found that a double vacancy in graphene is reconstructed into a 555-777 composed of triple pentagons and triple heptagons [1]. The structural change from pentagon-octagon-pentagon (5-8-5) to 555-777 has been confirmed by recent experiments [2, 3] and the detail of the reconstruction process in TEM images is carefully studied by the first principles (FP) calculation. It is found that a 5-7-7-5 defect is an intermediate structure in the structural changes between two 555-777 defects and between two 5-8-5 defects. Pentagon-heptagon (5-7) pairs are also found to play an important role in the reconstruction of vacancy in graphene and single wall carbon nanotube [4,5]. We also present the recent results on the formation and development of dislocation in graphene by using tight-binding molecular dynamics simulation (TBMD) and FP methods. It is found that the coalescence of 5-7 pairs with vacancy defects develops dislocation in graphene and induces the separation of two 5-7 pairs. Our TBMD simulations also show that adatoms are ejected and evaporated from graphene surface due to large strain around 5-7 pairs. It is observed that an adatom wanders on the graphene surface and helps non-hexagonal rings change into stable hexagonal rings before its evaporation. We also present recent TBMD and FP results on grain boundary in graphene

[1] G. -D. Lee Phys. Rev. Lett. 95, 205501 (2005) [2] C. O. Girit et al. Science 323, 1705 (2009) [3] J. Kotakoski et al. Phys. Rev. Lett. 106, 105505 (2011) [4] G. -D. Lee Appl. Phys. Lett. 97, 093106 (2010) [5] G. -D. Lee Phys. Rev. B 81, 195419 (2010)

## **GATE-INDUCED SEMICONDUCTIVE PROPERTY AND DEVICE-OPERATION IN BILAYER GRAPHENE**

Kazuhito Tsukagoshi, MANA, NIMS  
Namiki 1-1, Tsukuba, Ibaraki, 305-0044, Japan  
T: +81-29-860-4894, F: +81-29-860-4706, TSUKAGOSHI.Kazuhito@nims.go.jp  
Songlin Li, MANA, NIMS  
Hisao Miyazaki, MANA, NIMS

We present a review of our experiments on graphene transistors in its potential use as atomic film switching devices. We found that large transport energy gaps ( $>100$  meV) can be fulfilled in dualgated bilayer graphene underneath a simple alumina passivation top gate stack, which directly contacts the graphene channels without an inserted buffer layer. With the presence of energy gaps, the electrical properties of the graphene transistors are significantly enhanced, as manifested by enhanced on/off current ratio, subthreshold slope, and current saturation. For the first time, complementary-like semiconducting logic graphene inverters are demonstrated that show a large improvement over their metallic counterparts. This result may open the way for logic applications of gap-engineered graphene.



## **WELL-DEFINED GRAPHENE BASED NANOMATERIALS AND THEIR ENERGY-RELATED APPLICATIONS**

Linjie Zhi, National Center for Nanoscience and Technology  
Beiyitiao 11, Zhongguancun, Beijing, 100190, China  
T: 0086-10-82545578, F: 0086-10-82545578, zhilj@nanoctr.cn

Graphene based nanomaterials have attracted great attention recently. Understanding the structure-property relationship of graphene based nanomaterials is of importance for their practical applications. Chemical approach starting from carbon-rich precursors with well-defined structures is an effective strategy towards well-defined graphene based nanomaterials. Unique carbonaceous structures can thus be obtained through this approach. Besides their unconventional structures, the as-prepared carbonaceous nanomaterials perform interesting properties in various applications, especially in the energy-related areas. Their applications in lithium ion secondary batteries, solar cells, supercapacitors, and catalysis, will be discussed in the presentation.

## **ASSEMBLY OF GRAPHENE SHEETS INTO HIERARCHICAL STRUCTURES FOR HIGH-PERFORMANCE ENERGY**

Xiaodong Chen, School of Materials Science and Engineering, Nanyang Technological University  
50 Nanyang Avenue, Singapore, 639798, Singapore  
T: +65-6513-7350, F: +65-6790-9081, chenxd@ntu.edu.sg

The electrodes with the hierarchical nanoarchitectures could offer a huge increase in energy storage capacity. However, the ability to achieve such hierarchical architectures on a multiple scale still has remained a great challenge. herein, we report a scalable self-assembly strategy to create bio-inspired hierarchical structures composed of functionalized graphene sheets to work as anodes of lithium-ion batteries. The resulting electrodes with novel multilevel architectures simultaneously optimize ion transport and capacity, leading to a high performance of reversible capacity of up to 1600 mAh/g, and 1150 mAh/g after 50 cycles. Importantly, the process to fabricate such hierarchical structures is facile, low-cost, green and scalable, providing a universal approach for the rational design and engineering of electrode materials with enhanced performance, and it may have utility in various applications, including biological scaffold, catalysis, and sensors.