Graphene Topical Conference
Room: 306 - Session GR+TF+NC-MoM

Graphene and 2-D Carbon Nanostructures
Moderator: B.C. Holloway, Luna Innovations Incorporated, M.Y. Zhu, College of William and Mary

8:20am GR+TF+NC-MoM1 Electrical Transport Properties of Two-Dimensional Carbon Nanostructures, *Y. Wu*, National University of Singapore, *H. Wang*, National University of Singapore and Data Storage Institute, Singapore, *S.S. Kushvaha*, National University of Singapore, *S.Y.H. Lua*, National University of Singapore and Data Storage Institute, Singapore **INVITED**
Recently 2D carbon nanostructures have attracted great interest due to their peculiar structural and electronic properties, especially after the successful mechanical exfoliation of single and few layer graphene from bulk graphite and epitaxial growth of graphene on SiC. We have reported previously the growth of well-aligned 2D carbon nanostructures – carbon nanowalls(CNWs), using MPECVD. Although the CNWs are structurally not as perfect as graphene sheets obtained by other techniques, its free-standing structure makes it an excellent candidate for studying electrical transport properties of 2D carbon nanostructures using end-point contacts of various types of materials including normal metal, semiconductor and superconductors. In this talk, we will present our results on (1) lateral electrical transport measurements using end-point Ti and Nb electrodes with a gap length in the range of 200 nm – 3000 nm (2) vertical transport measurements using nanoprobes in a UHV system. In (1) we focus on conductance fluctuation and proximity effect and in (2) we investigate the contact resistance between 2D carbon and different types of materials. In lateral transport measurements using Ti electrodes, excess conductance fluctuations with peculiar temperature-dependence from 1.4 to 250 K were observed with an electrode gap length of 300 and 450 nm, whereas the conductance fluctuation is greatly suppressed above 4.2 K when the electrode gap length increases to 800 and 1000 nm. The former is discussed in the context of the presence of both a small energy bandgap, while the latter is attributed to the crossover from mesoscopic to diffusive transport regime. On the other hand, in the case of Nb electrodes, we have observed proximity effect in samples with an electrode gap length of 200 – 500 nm and a reentrant behavior for samples with smaller gap length. Strong conductance oscillation was observed in samples using four-point probes which is attributed to the formation of SNS structures in CNW. In the vertical transport measurement using nanoprobes, it was found that the end-point contact resistance of carbon nanowalls on stainless steel is the lowest, followed by graphite, Si, Cu, Au (100 nm) / Ta (1 nm) / Si and Au wire. Both the contact resistance and I-V characteristics are in good agreement with the results of first principles calculations reported in the literature. The results may serve as the guides for selecting metal contacts in graphene-based devices.

9:00am GR+TF+NC-MoM3 Characterization of Functionalized Carbon Nanosheets as a Step Towards the Development of Advanced Graphene Devices, *R.A. Quinlan*, College of William and Mary, *E. Widenkvist*, Uppsala U., Sweden, *J. Groff*, College of William and Mary, *M. Rooth*, Uppsala U., Sweden, *M. Kelly*, Stanford U., *R.A. Outlaw*, College of William and Mary, *V. Coleman, O. Karis, B. Sanyal, O. Eriksson, H. Grennberg*, Uppsala U., Sweden, *B.C. Holloway*, Luna Innovations, Inc., *U. Jansson*, Uppsala U., Sweden
Carbon nanosheets (CNSs) are novel free-standing carbon nanostructures, composed of horizontal basal planes and vertical sheets which are made up of 1-7 graphene layers.[1] Previous work described the successful creation of defects in the graphene lattice via an acid-treatment and the characterization of these defects with x-ray absorption near-edge spectroscopy (XANES). The presence of a peak in the carbon K-edge spectra at 287eV was assigned to a C-O σ^* resonance. Theoretical modeling of a di-vacancy in a graphene bilayer system reproduced the spectra and predicts metallic conductivity of the states surrounding the defect.[2] Here we report the further characterization of functionalized carbon nanosheets (f-CNSs) via high resolution x-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS). Measurements were made at room temperature up to 700K with as-deposited, water- and acid-treated CNSs. XPS measurements indicate an increase in the oxygen content of the nanostructures from 1-2% in as-deposited up to 3-4% in the acid-treated samples. The decrease of sub-peak areas in the C1s and O1s spectra with heating correlates well with the decrease in atomic oxygen content. The partial pressures of H_2, O_2, CO_2, CO and H_2O measured desorbing from the f-CNSs support the model of oxygen and hydrogen decorated defects in the graphene system. The XPS and TDS results support XANES measurements of similar samples. These results support the use of a non-oxidizing acid-treatment for controlled defect formation in a graphene system, a first step towards the development of graphene based devices.

[1] Wang et al., Free-standing subnanometer graphite sheets. Applied Physics Letters, 2004. 85(7): p. 1265-1267
[2] Coleman et al., Defect formation in graphene nanosheets by acid treatment: an x-ray absorption spectroscopy and density functional theory study. Journal of Physics D: Applied Physics, 2008(6): p. 062001.

9:20am GR+TF+NC-MoM4 Application of Carbon Nanowalls to Negative Electrode in Lithium-Ion Battery for High-Rate Use, *N. Kitada*, *H. Yoshimura*, Yokohama City University, Japan, *O. Tanaike*, Advanced Industrial Science and Technology, Japan, *K. Kojima*, *M. Tachibana*, Yokohama City University, Japan
Recent design and fabrication of electrode in Lithium-ion battery have been focused for the high rate use since rapid charge and discharge of the battery with high power density are usually required for quick start and stop of electric vehicle or hybrid electric vehicle in next generation. One of the ways to develop the electrode for high rate use is to use nano-sized active materials since the diffusion distance of lithium ions in the solid during charge and discharge is decreased by using them. Here, we reports a new nano-sized and graphitized carbon material, two-dimensional carbon nanostructures called carbon nanowalls (CNWs) [1-5], as a promising one for negative electrode material of lithium ion battery in high rate use. CNWs were synthesized at very low temperature of 973K by a dc plasma-enhanced chemical vapor deposition. They were mixed with binder Polyvinylidenefluoride in N-methylpyrrolidone, pressed and then dried to produce carbon sample electrodes. Conventional three electrodes test cells were constructed for electrochemical measurements by carbon sample as a working electrode and two lithium foils as counter and reference ones. Lithium insertion properties were studied using these test cells by cyclicvoltammetry (CV) and charge/discharge measurements. CNWs is found to be an interesting graphitic active material for negative electrode of lithium ion battery having reversible capacity of more than 200 mAh/g with relatively stable charge/discharge potential which is very similar to the properties of graphite, even though CNWs are synthesized at very low temperature of 973K without any graphitization process at high temperature. These CNWs are well layered particles in nano scale having large exposure surface of graphene edge, which is expected to be suitable for lithium insertion at high rate charge/discharge, and present results of CVs and charge/discharge tests support it. [1] Y. Wu et al., Adv. Matter. 14, 64(2002). [2] M. Zhu et al., Carbon. 42, 2867(2004). [1] S. Kurita et al., J. Appl. Phys. 97, 104320 (2005). [2] K. Kobayashi et al., J. Appl. Phys. 101, 094306 (2007). [3] I. Kinoshita et al., Chemi. Phys. Lett. 450, 360 (2008).

9:40am GR+TF+NC-MoM5 Carbon Nanosheets: Novel Two-Dimensional Materials, *A. Beyer, C.T. Nottbohm, X. Zhang, A. Turchanin*, Universität Bielefeld, Germany, *A. Sologubenko, J. Mayer*, RWTH Aachen, Germany, *A. Gölzhäuser*, Universität Bielefeld, Germany
1 nm thick, mechanically and thermally stable carbon nanosheets are fabricated by combining molecular self-assembly with lithography. Self-assembled monolayers of aromatic molecules are cross-linked via electron or EUV irradiation. The cross-linked monolayers are released from the substrate, resulting in "free-standing carbon nanosheets" with the thickness of a single molecule.[1] We show that the nanosheets can be transferred onto arbitrary surfaces and we determine their elastic constants by AFM. We have found that nanosheets posses an extraordinarily high mechanical and thermal stability.[2] Carbon nanosheets can be used as ultrathin sample supports for transmission electron microscopy (TEM). Free-standing nanosheets were transferred onto TEM grids and nanoparticles were deposited onto them. When imaged by high-resolution TEM, the nanoparticles show a much higher contrast than those made with a conventional carbon film.[3]

[1] W. Eck, A. Küller, M. Grunze, B. Völkel, A. Gölzhäuser: Free-standing nanosheets from cross-linked biphenyl self-assembled monolayers, Adv. Mat., 17, 2583-2587, (2005)
[2] A. Turchanin, M. El-Desawy, A. Gölzhäuser: High thermal stability of cross-linked aromatic self-assembled monolayers: Nanopatterning via selective thermal desorption. Appl. Phys. Lett., 90, 053102 (2007)
[3] C. T. Nottbohm, A. Beyer, A. S. Sologubenko, I. Ennen, A. Hütten, H. Rösner, W. Eck, J. Mayer, A. Gölzhäuser: Novel carbon nanosheets as support for ultrahigh resolution structural analysis of nanoparticles. Ultramicroscopy, in press.

10:20am GR+TF+NC-MoM7 Enhanced Field Emission of Vertical Aligned Carbon Nanosheets, *M.Y. Zhu*, *R.A. Outlaw, H. Chen, M. Bagge-Hansen, D.M. Manos*, College of William and Mary
Field emissions from two-dimensional free-standing carbon nanosheets with ultra-thin edges synthesized in radio frequency (RF) plasma enhanced

chemical vapor deposition from CH_4/H_2 gas mixture have been previously reported. When C_2H_2/H_2 gas mixture was used, the growth temperature was lowered by 100-150 °C and well aligned vertical sheets with uniform height distribution were obtained. Typical C_2H_2 nanosheets were deposited on Si substrates using 80% C_2H_2 diluted in H_2 gas (5 sccm total gas flow rate) at 600 ºC substrate temperature and 35 mTorr total pressure with 1000 W RF power for 10 min. The growth rate of the nanosheets measured from cross-sectional scanning electron microscopic images was 10.8 µm/hr. In this report, field emission measurements were taken from nanosheet samples 1.8 µm in height. Custom LabView software controlled automatic diode I-V measurements of C_2H_2 nanosheets yielded a threshold field, for an emission current density of 10 µA/cm^2, of ~3 V/µm, which was ~2 V/µm lower than CH_4 nanosheets. At an applied field of 5.3 V/µm, the current density was 1.1 mA/cm^2 compared to the CH_4 nanosheets of ~0.007 mA/cm^2. Calculations from the Fowler-Nordheim plots and their linear fits indicated that the effective emission area of C_2H_2 nanosheets was ~15 times that of CH_4 nanosheets and the β factor of C_2H_2 nanosheets was ~26% higher than CH_4 nanosheets. The results are consistent with the morphology differences between the two kinds of nanosheets. The lifetime tests of C_2H_2 nanosheets conducted in a DC mode with a base pressure lower than 5×10^{-9} Torr showed a conditioning from an emission current of ~1.1 mA to a current level of 0.65 mA after 200 hour operation without any drop-outs or arcing failure. These tests were conducted with minimal anode cooling, which may account for the decay of the current on this timescale. The vacuum pressure of the testing system was recorded along with the emission current, and found to be closely correlated to the emission current.

10:40am GR+TF+NC-MoM8 Control of Structures and Electrical Properties of Carbon Nanowalls Using Plasma Enhanced CVD Employing N_2/O_2 Addition to C_2F_6/H_2 Gases, *W. Takeuchi,* Nagoya University, Japan*, M. Hiramatsu,* Meji University, Japan*, Y. Tokuda,* Aichi Institute of Technology, Japan*, H. Kano,* NU Eco-Engineering Co., Ltd., Japan*, M. Hori,* Nagoya University, Japan

Carbon nanowalls (CNWs), that is two-dimensional carbon nanostructure of freestanding vertically oriented graphitic sheets, attract great attentions because of several applications such as electrical devices. Recently, it was reported that the 2-D multilayer graphene sheet devices offer the high mobility and the huge sustainable currents. Therefore, CNW films would have high performances of electric devices, since the CNWs basically consist of graphene sheets. In order to realize the CNW devices, it is necessary to control structures and properties. In this study, we have successfully controlled structures and electric properties of CNWs. CNWs were fabricated on the quartz substrate by plasma enhanced CVD (PECVD) employing C_2F_6 gas with H radical injection. The influences of N_2 and N_2/O_2 addition to C_2F_6/H_2 gas mixtures on structures and electric properties of CNWs were investigated. The cross-sectional scanning electron microscopy (SEM), Hall measurement and secondary ion mass spectrometry (SIMS) were used to evaluate structures, electric properties and atomic compositions of CNWs, respectively. The SEM image of the CNWs film synthesizes by N_2/O_2 mixture gas addition indicated that the size of the individual graphene of CNWs increased with less branching. The Hall coefficient indicated the positive value for the CNW film synthesized without N_2 addition. In the case of N_2 addition, it displayed the negative one. The positive or negative value means p- or n-type conduction, respectively. CNW films doped with N atoms were characterized by SIMS to investigate the effect of the N_2 addition on the atomic composition of CNWs. The carrier and N concentration in the CNW films formed by N_2/O_2 mixture gas addition were almost the same as those in the CNW film by N_2 addition. It is considered that the N atom in the CNWs act as a donor and the electrical property of N-doped CNWs can be controlled by N atom concentration. These results will be crucial to fabricate the electrical devices of CNWs without deteriorating crystallinity.

11:00am GR+TF+NC-MoM9 Wafer-Scale Synthesis and Electrochemical Property of Graphene Formed by Microwave Plasma Enhanced Chemical Vapor Deposition, *L.C. Chen*, National Taiwan University **INVITED**

The recent experimental breakthroughs on graphene-based nanoelectronics have triggered enormous academic activities. Among the production methods of graphene, mechanical exfoliation of graphite and surface evaporation of SiC are widely used. Despite the successful fabrication in surface evaporation of SiC, process integration of graphene into the well-established Si-based technology remains a challenging task. In view of this, it is also desirable to develop a reliable and large-scale (or wafer-based) production of graphene for practical applications. In this presentation, we will demonstrate a novel synthetic route for graphene growth on silicon substrate by microwave plasma enhanced chemical vapor deposition (MPECVD). The resultant nanoarchitecture exhibits a wall-like morphology with a high density of sharp edges. Structure wise, each nanowall is composed of SiC decorated by a few layer of graphene (i.e. concrete paint on concrete wall). Moreover, direct deposition of Pt nanostructures onto these graphene samples is also performed to explore their potentials for electrochemical energy applications. Preliminary cyclic voltammetry studies for electro-oxidation of methanol show a high ratio of forward anodic peak current to reverse peak current, suggesting an efficient oxidation of methanol to CO2 on the Pt/graphene electrode. The effective suppression in the reverse cathodic peak current probably suggests a selective growth of Pt on graphene. Other electrochemical properties (such as electron-transfer kinetics and chemical reactivity) of MPECVD-grown graphene will also be addressed in this presentation. Our synthetic approach offers an alternative route toward wafer-scale fabrication of graphene for fundamental research and opens up various potential applications in nanoelectronics, sensing, catalysis, and energy production.

11:40am GR+TF+NC-MoM11 Growth and Structures of Carbon Nanowalls during Plasma-Enhanced Chemical Vapor Deposition, *H. Yoshimura, N. Kitada, K. Kojima, M. Tachibana*, Yokohama City University, Japan

Recently two-dimensional carbon nanostructures called carbon nanowalls (CNWs) have been fabricated by plasma-enhanced chemical vapor deposition.[1] The CNWs are vertically grown on the substrate. According to our previous studies of Raman spectroscopy[2] and transmission electric microscopy (TEM),[3] and Ultraviolet photoelectron spectroscopy,[4] CNWs are composed of small crystallites with a high degree of graphitization. And these small crystallites so-called "nano-graphite domains" were slightly rotated each other. Such shapes and structures of CNWs may provide us with various applications, such as gas storage, membranes for electrochemical energy storage, and field emitters. The understanding of growth process and structures in CNWs is required for the practical applications. In this paper, we report the detail of growth process and structures of CNWs. CNWs were grown by using a dc plasma-enhanced chemical vapor deposition method with a gas mixture of CH_4, H_2, Ar. Typical flow rate of CH_4, H_2 and Ar were 10, 10, and 80 sccm (standard cubic centimeters per minutes at standard temperature and pressure). To investigate the growth process, specimens were prepared for plasma reaction times of 1, 2, 3, 4, 5, 7 and 15 minutes. The shapes and structures of the specimens were investigated by means of atomic force microscopy (AFM), grazing incidence X-ray diffraction (GIXD), and Raman spectroscopy. In addition, the change in the size and quality of crystallites was observed. As reported previously,[5] it was observed that CNWs changes from parallel to perpendicular to the substrate with deposition time. In addition, the transition structure from parallel to perpendicular was clearly observed. From these results, the growth process of CNWs will be discussed.

[1]Y. Wu, et al., Adv. Matter. 14, 64 (2002)
[2]S. Kurita, et al., J. Appl. Phys. 97, 104320 (2005)
[3]K. Kobayashi, et al., J. Appl. Phys. 101, 094306 (2007)
[4]I. Kinoshita, et al., Chem. Phys. Lett. 450, 360 (2007)
[5]B. L. French, et al., Thin Solid. Film, 494, 105, (2006).

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