Wednesday Morning, November 2, 2011

Nanometer-scale Science and Technology Division
Room: 203 - Session NS-WeM

Carbon-Based Nanomaterials
Moderator: M.C. Hersam, Northwestern University

8:00am **NS-WeM1 Characterization of Large Area Graphene Crystallites Grown on Cu Foil Substrates**, *P. Tyagi, Z.R. Robinson, H. Geisler, C.A. Ventrice, Jr.,* University at Albany, *H. Yang, T. Valla,* Brookhaven National Laboratory, *Y. Hao, R.S. Ruoff,* University of Texas at Austin

Graphene growth on Cu foils by catalytic decomposition of methane forms predominately single layer graphene films due to the low solubility of carbon in Cu. One of the key issues for the use of CVD graphene in device applications is the influence of defects on the transport properties of the graphene. In particular, the presence of grain boundaries within the graphene film will increase the probability for scattering of carriers, resulting in reduced mobilities. Therefore, an important goal is to develop techniques for growing graphene films with crystallites that have lateral dimensions of a few millimeters or larger. There are several factors that influence the size and orientation of the graphene crystallites such as the size and orientation of the grains within the metal foil, temperature gradients during growth, the hydrocarbon source pressure, and the growth temperature. By growing the graphene films using methane source pressures less than 50 millitorr, preanneal times of approximately an hour, growth temperatures of 1035 °C, and a tented Cu substrate geometry within a conventional tube furnace, graphene crystallites larger than a millimeter in size have been achieved.

Measurements of the graphene growth morphology and surface topography of the Cu substrate have been performed using scanning electron microscopy (SEM). The graphene crystallites show a dendrite pattern, and the Cu substrate typically shows a somewhat faceted structure at this growth temperature. Low energy electron diffraction (LEED) measurements show sharp diffraction spots but with multiple zero-order reflections, which results from the faceted structure of the Cu substrate after growth. Electron backscatter diffraction (EBSD) measurements have been performed on the Cu substrates to determine the crystallographic orientation and size of the substrate grains. Before growth, the average grain size is ~10 μm with a random orientation. After growth, the Cu substrate grain size is on the order of centimeters with a typical orientation towards the {100} surface termination. Synchrotron-based angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) measurements have also been performed to probe the electronic band structure of the graphene. A linear dispersion has been measured in the K direction with the Dirac point located near the Fermi level.

8:20am **NS-WeM2 Gas Adsorption on Pt-Clusters Supported by Graphene**, *J. Knudsen,* Lund University, Sweden, *T. Gerber,* University of Cologne, Germany, *E. Graanäs,* Lund University, Sweden, *P.J. Feibelman,* Sandia National Laboratories, *K. Schulte,* Lund University, Sweden, *P. Stratman, C. Busse, T. Michely,* University of Cologne, Germany, *J.N. Andersen,* Lund University, Sweden

Model systems of real catalysts consisting of nanoparticles deposited on substrates often have a broad size distribution, making it difficult to link the adsorption properties to the atomic scale structure of the nanoparticles using averaging techniques. Metal nanoparticles grown on a graphene/Ir(111) moiré film, however, show exceptionally well ordered arrays of nanoparticles with an extremely narrow size distribution [1, 2]. Further, it is possible to control the cluster size precisely by adjusting the amount of deposited material, since each moiré unit cell contains one cluster. The narrow size distribution and the easy control of cluster size make metal particles supported by graphene an ideal model system for adsorption studies with averaging techniques.

In this contribution we report on our studies on CO adsorption on such an ideal model system consisting of Pt-clusters grown on a graphene/Ir(111) moiré film using photoemission X-ray spectroscopy (XPS), scanning tunnelling microscopy (STM), and density functional theory (DFT) [3].

For Pt/graphene without CO we observe pinning of the graphene film, as a shoulder at the high binding energy side of the C 1s peak observed for pristine graphene. DFT calculations reveal that this shoulder should be assigned to carbon atoms positioned below and in the vicinity of the Pt clusters, which all are displaced towards the Ir(111) surface.

Upon CO adsorption we observe C 1s and the O 1s peak positions consistent with preferential adsorption in atop sites at the cluster step edges.

We also observe that the pinning-induced shoulder in the C 1s spectrum diminish upon CO adsorption, and interpret this as unpinning of the graphene film when CO adsorbs on the clusters step edges. From real time STM movies taken during CO dosing we show that the unpinning of the graphene film leads to coalescences of the Pt clusters, when the clusters are smaller than approximately 10 atoms.

References:

[1] A. T. N'Diaye, S. Bleikamp, P. J. Feibelman, et al., Phys. Rev. Lett. **97** (2006)

[2] A. T. N'Diaye, T. Gerber, C. Busse, et al., New Jour. Phys. **11** (2009)

[3] J. Knudsen, P. J. Feibelman, T. Gerber, E. Grånäs, K. Schulte, P. Stratman, C. Busse, J. N. Andersen, T. Michely (in manuscript)

8:40am **NS-WeM3 Seeding Atomic Layer Deposition of High-k Dielectrics on Epitaxial Graphene with Organic Self-Assembled Monolayers**, *J.M.P. Alaboson*, Q.H. Wang, J.D. Emery, A.L. Lipson, M.J. Bedzyk,* Northwestern University, *J.W. Elam, M.J. Pellin,* Argonne National Laboratory, *M.C. Hersam,* Northwestern University

The development of high-performance graphene-based nanoelectronics requires the integration of ultrathin and pinhole-free high-*k* dielectric films with graphene at the wafer scale. Here, we demonstrate that self-assembled monolayers of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) act as effective organic seeding layers for atomic layer deposition (ALD) of HfO_2 and Al_2O_3 on epitaxial graphene on SiC(0001). The PTCDA is deposited via sublimation in ultra-high vacuum and shown to be highly ordered with low defect density by molecular-resolution scanning tunneling microscopy. Whereas identical ALD conditions lead to incomplete and rough dielectric deposition on bare graphene, the chemical functionality provided by the PTCDA seeding layer yields highly uniform and conformal films. The morphology and chemistry of the dielectric films are characterized by atomic force microscopy, ellipsometry, cross-sectional scanning electron microscopy, and X-ray photoelectron spectroscopy, while high-resolution X-ray reflectivity measurements indicate that the underlying graphene remains intact following ALD. Using the PTCDA seeding layer, metal-oxide-graphene capacitors fabricated with a 3 nm Al_2O_3 and 10 nm HfO_2 dielectric stack show high capacitance values of ~700 nF/cm^2 and low leakage currents of ~5 x 10^{-9} A/cm^2 at 1 V applied bias. These results demonstrate the viability of sublimated organic self-assembled monolayers as seeding layers for high-*k* dielectric films in graphene-based nanoelectronics.

9:00am **NS-WeM4 Graphene-based Electronics and Optoelectronics**, *Ph. Avouris†,* IBM T.J. Watson Research Center **INVITED**
Graphene a two-dimensional, single atomic layer material with linear electron dispersion has rather unique electrical and properties[1]. There is currently strong interest in taking advantage of these properties for technological applications[2]. In my talk I will review some of the key properties of graphene, how these are affected by environmental interactions and how they can be utilized in electronics and optoelectronics.

Specifically, I will discuss high frequency (>100 GHz) graphene transistors[3,4], their fabrication and operation, as well as related device physics aspects, such as carrier transport mechanisms, electrical contacts, temperature effects, energy dissipation, etc. Simple integrated graphene circuits will also be presented. I will then discuss key optical properties of graphene and how they can be combined with its excellent electrical properties and used in optoelectronics applications. Specific examples involving ultrafast graphene photodetectors[5] and their applications in the detection of optical data streams[6] will be presented.

[1] Geim, A.K. *Science* 3, 1530 (2009)**.**

[2] Avouris, Ph., *Nano Letters* 10, 4285 (2010).

[3] Lin, Y.-M.; Dimitrakopoulos, C.; Jenkins, K.A.; Farmer, D.B., Chiu, H.-Y. ; Grill, A.; Avouris, Ph. *Science* 327, 662 (2010);

[4] Wu , Y.; Lin, Y.-M.; Bol, A.; Jenkins, K.; Xia, F.; Farmer, D.; Zhu. Y.; Avouris, Ph., *Nature*, on-line April 6 (2011).

[5] Xia, F.; Mueller, T.; Lin, Y.-M.; Valdes-Garcia, A.; Avouris, Ph. *Nature Nanotechnology* 4, 839 (2009)**.**

[6] Mueller, T.; Xia, F.; Avouris, Ph. *Nature Photonics* 4, 297 (2010).

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* NSTD Student Award Finalist
† NSTD Recognition Award

9:40am NS-WeM6 Plasma-based Approach to Controlling the Properties of Graphene, *S.C. Hernández, M. Baraket, S.G. Walton, W.K. Lee, C.R. Tamanaha, P.E. Sheehan, J.T. Robinson, V.D. Wheeler, R.L. Myers-Ward, L.O. Nyakiti, Eddy, D.K. Gaskill*, Naval Research Laboratory (NRL)

Graphene has attracted a widespread of interest because of its unique structural and electronic properties however, manipulation of these properties is necessary before realizing its full potential as the next generation material in a broad range of electronic and sensing applications. Specifically, tailoring the surface chemistry of graphene by the addition of functional groups is an attractive way to simultaneously manage the conductivity and reactivity of this material. This work discusses the use of electron-beam generated plasmas to controllably functionalize graphene synthesized from different methods. Electron-beam generated plasmas, produced in a variety of background gases (e.g. N_2, O_2, SF_6, NH_3) were used to introduce functional groups in a range of atomic densities at the graphene surface, without damage to the underlying graphene structure. Plasma processing conditions and characteristics, as well as the resulting chemical, structural, and electrical properties of the functionalized graphene were examined. This work is supported by the Office of Naval Research.

10:40am NS-WeM9 Solution Plasma-Assisted Surface Functionalization of Chemically Converted Graphene Sheet toward an Enhancement of Solubility in Solution, *N. Tsuda, T. Ueno, N. Zettsu, S. Cho, O. Takai, N. Saito*, Nagoya University, Japan

Graphene, a one-atom layer of graphite, possesses a unique two-dimensional structure and excellent mechanical, thermal, and electrical properties. Thus, it has been regarded as an important component for making various functional composite materials. Graphene can be prepared through micromechanical exfoliation, epitaxial growth, and chemical vapor deposition and electrochemical approaches. Different from these approaches, chemical synthesis of graphene using graphite, graphite oxide (GO) or other graphite derivatives as starting materials were tested to be effective for producing chemically converted graphene (CCG) from various precursors, such as graphite, carbon nanotubes, and polymers, in large scale and at low costs. Therefore, CCG is more suitable for synthesizing high-performance graphene based composites.

Graphene oxide can be chemically reduced to CCG. Hydrazine monohydrate was most widely used, mainly due to its strong reduction activity and the stability in aqueous media. Upon reduction with hydrazine, most oxygen-containing functional groups of graphene oxide are eliminated and the π-electron conjugation within the aromatic system of graphite is partially restored. As a result, the reduced graphene oxide (or CCG) is usually precipitated from the reaction medium because of the recovered graphite domains of CCG sheets increased their hydrophobic property and π-stacking interaction. The use of hydrazine as reducing agent also has several disadvantages. The trace residual may strongly decrease the performance of CCG in devices.

In this work, we demonstrate solution plasma-assisted surface functionalization of chemically converted graphene sheet in order to enhancement of solubility in both aqueous and organic solvent. Solution plasma (SPP) is a plasma discharge in solution, which is expected a higher reaction rate under low-temperature conditions, and the greater chemical reaction variability since the molecular density of liquid is much higher than that of gas phase.

A colloidal grapheme oxide sheets was treated with SP in ammonium containing aqueous solution in order to make reduced CCG and functionalize CCG surface with primary amine group.. A glow discharge was produced at bipolar-pulsed voltages with pulse width and frequency of 2 ms and 15 kHz, respectively. The all products were characterized by IR, Raman, spectroscopy, AFM, XRD, and TEM. Furthermore, we also demonstrate an introduction of organic and polymeric molecule as a second component onto the aminated CCG surface to insulate hydrophobic property and π-stacking interaction of neighboring CCG sheets in aqueous solution, and to be organic solvent solubilization.

11:00am NS-WeM10 Horizontally Aligned Carbon Nanotubes on Quartz Substrate for Electrolyte-Gated Chemical and Biological Sensing, *S. Okuda, Y. Ohno, K. Maehashi, K. Inoue, K. Matsumoto*, Osaka University, Japan

Electrolyte-gated carbon nanotube field-effect transistors (CNTFETs) based highly sensitive chemical and biological sensors were demonstrated. Dense, well-aligned CNTs grown on quartz substrates were utilized as channels of CNTFETs. Using the large number of CNTs is a simple strategy to realize excellent performance of CNTFETs. First, the pH dependence of CNTFETs was measured in buffer solution ranging from pH 4.0 to 8.3 by monitoring the drain current (I_D) in the CNTFET. Clearly and stepwise increases in I_D were observed against the change in pH in the solution. The detection limit for changes in pH was estimated to be 0.015, which is a superior

characteristic to that of conventional CNTFETs. The result indicates that CNTFETs on quartz substrates can be used as highly sensitive pH sensors. Moreover, label-free biomolecule sensing was demonstrated. The target protein was a class of antibody, immunoglobulin E (IgE). To achieve the electric detection of IgE, we used aptamer-modified CNTFETs with multichannel. Then, binding event of target IgE onto the aptamers was detected. IgE-concentration dependence measurements revealed that we succeeded in detection of nM quantities of IgE. In conclusion, electrolyte-gated multichannel CNTFETs will be useful for highly sensitive chemical and biological sensors.

11:20am NS-WeM11 Gas-phase Studies and Growth of Well-Defined Carbon Nanotubes, *A. Kumar, P. Lin, R.M. Sankaran*, Case Western Reserve University

Carbon nanotubes (CNTs) have attracted interest for a wide-range of technological applications including nanoelectronic, energy storage, and energy conversion devices. In many of these applications, the nanotube structure must be sufficiently controlled at the growth stage; however, current growth methods typically produce mixtures of tubes, including multi-walled, single-walled, and a range of different chiralities, that must be purified and separated to facilitate applications.

We are interested in controlling the properties of CNTs at the growth stage. We have recently developed a two-step process [1-3] to study and grow CNTs consisting of a microplasma reactor that controls the size- and composition of the nanoparticle catalysts and a flow furnace that nucleates and grows the nanotubes. In addition, the nanotubes are monitored *in situ* by aerosol measurements to provide real-time feedback and allow the reactor conditions to be rapidly optimized. By tuning the size of our catalyst, we have found that the fraction of single-walled CNTs in the as-grown product can be varied. Similarly, by tuning the composition of the catalyst, we have found that the chirality distribution of the as-grown nanotubes is changed. Here, we will present results for Ni-based bimetallic catalysts and the influence of the catalyst size and composition, as well as other growth parameters such as carbon feedstock and growth temperature, on nanotube growth. In addition to aerosol measurements, the nanotubes are collected and characterized by micro Raman spectroscopy and UV-Vis-NIR absorbance spectroscopy. The structure and properties of the nanotubes and their relationship to the catalyst and other growth parameters will be discussed in detail.

1. W-H. Chiang et al., Appl. Phys. Lett. 91, 121503 (2007).
2. W-H. Chiang et al., J. Phys. Chem. C 112, 17920 (2008).
3. W-H. Chiang et al., Nat. Mater. 8, 882 (2009).

11:40am NS-WeM12 Visualizing Defect Distributions in Carbon Nanotubes using Linear Dichroism Signals in Scanning Transmission X-ray Microscopy (STXM) and TEM-EELS, *E. Najafi, A.P. Hitchcock, D. Rossouw, G. Botton*, McMaster University, Canada

The X-ray Linear Dichroism (XLD) signal in spatially resolved X-ray absorption spectromicroscopy of individual carbon nanotubes (CNT) [1] has been shown to be sensitive to the local density of sp^2 defects along the nanotube. This dichroic signal is as strong for single-walled [2] as for multi-walled CNT, which is rather surprising given the much higher curvature in SWCNT than MWCNT. The link between the strength of the XLD of the C 1s -> π* peak at 285.2 eV and defect density within the sampled area has been verified by intentionally inducing sp^2 defects by ion bombardment [3]. This XLD signal is potentially useful for guiding optimization of CNT synthesis and preservation of the quality of nanotubes through various processing steps used to make functional devices where defect distribution and character play an important role. However STXM has limited spatial resolution; 10 nm, state-of-art while this work was performed at ~25 nm. Recently we have demonstrated that Electron Linear Dichroic (ELD) signals similar to XLD can be measured in q-dependent C 1s electron energy loss spectroscopy carried out in an aberration compensated, monochromated transmission electron microscope. The signals are detected by operating in STEM mode, carefully arranging the conditions such that the spectrometer accepts a narrow range of off-axis scattered electrons (with a specific location, identified in diffraction mode), and using a tilt stage to change the orientation of the CNT relative to the incident and outgoing electron directions. STEM-EELS maps measured with 2 nm sampling over a portion of a MWCNT, and over a range of tilt angles provide quantitative maps of the ELD signal. The experimental conditions will be described and the defect mapping capability of this method will be demonstrated.

STXM measurements were carried out at the SM beamline at the Canadian Light Source, which is supported by the Canada Foundation for Innovation (CFI), NSERC, Canadian Institutes of Health Research (CIHR), National Research Council (NRC) and the University of Saskatchewan. We thank

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[2] E. Najafi, J. Wang, A.P. Hitchcock, J. Guan, S. Denommee and B. Simard, J. Am. Chem. Soc. 2010, 132, 9020-9029.

[3] A. Felten, X. Gillon, M. Gulas, J.-J. Pireaux, X. Ke, G. Van Tendeloo, C. Bittencourt, E. Najafi and A.P. Hitchcock, , ACSNano 2010, 4, 431–4436

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