

Monday Morning, November 9, 2009

Graphene Topical Conference

Room: C3 - Session GR-MoM

Graphene and 2D Carbon Nanostructures

Moderator: M.Y. Zhu, College of William and Mary

8:20am **GR-MoM1 Graphene-based Materials**, *R.S. Ruoff*, The University of Texas at Austin **INVITED**

Our top-down approaches [1] inspired physicists to study individual layers of graphite obtained by micromechanical exfoliation, but our current approaches include growth on metal substrates and judicious use of isotopic labeling (^{13}C vs ^{12}C) to study the kinetics and mechanisms of deposition of large-area graphene and few layer graphene on metal substrates.[3] This talk will focus on our suggested path for obtaining large area growth of high quality graphene in ways compatible with methods of the semiconductor industry. In addition, I will present highlights of published work on polymer matrix composites with graphene as filler[4], on ultracapacitors based on graphene[5], on paper-like materials based on graphene[6], on the use of ^{13}C -labeled graphite (and ^{12}C -pure graphite and graphene) in a variety of areas[7], and on use of graphene as transparent but electrically conductive thin films[7]. *Support of our work by SWAN-NRI, DARPA-CERA, DARPA-iMINT, and prior support by NASA, is appreciated.*

(See also papers on <http://bucky-central.me.utexas.edu/publications.htm>)

1. Lu XK, Yu MF, Huang H, and Ruoff RS, *Tailoring graphite with the goal of achieving single sheets*, *Nanotechnology*, **10**, 269-272 (1999).

3. Xuesong Li, Weiwei Cai, Jinho An, Seyoung Kim, Junghyo Nah, Dongxing Yang, Richard Piner, Aruna Velamakanni, Inhwa Jung, Emanuel Tutuc, Sanjay K. Banerjee, Luigi Colombo, Rodney S. Ruoff, *Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils*, published online in *Science* on Science Express (May 7, 2009), hardcopy to appear in *Science*.

4. Sasha Stankovich, Dmitriy A. Dikin, Geoffrey H. B. Dommett, Kevin M. Kohlhaas, Eric J. Zimney, Eric A. Stach, Richard D. Piner, SonBinh T. Nguyen and Rodney S. Ruoff, *Graphene-based composite materials*, *Nature* **442** (2006) 282-285.

5. Meryl D. Stoller; Sungjin Park; Yanwu Zhu; Jinho An; Rodney S. Ruoff. *Nano Letters* (2008), **8** (10), 3498-3502.

6. Dmitriy, A. Dikin, Sasha Stankovich, Eric J. Zimney, Richard D. Piner, Geoffrey H. B. Dommett, Guennadi Evmenenko, SonBinh T. Nguyen, Rodney S. Ruoff. *Nature*, **448**, (2007), 457-460.

7. Cai, Weiwei; Piner, Richard D.; Stadermann, Frank J.; Park, Sungjin; Shaibat, Medhat A.; Ishii, Yoshitaka; Yang, Dongxing; Velamakanni, Aruna; An, Sung Jin; Stoller, Meryl; An, Jinho; Chen, Dongmin; Ruoff, Rodney S., *Science* (2008), **321**(5897), 1815-1817.

8. Supinda Watcharotone, Dimitry A. Dikin, Sasha Stankovich, Richard Piner, Inhwa Jung, Geoffrey H. B. Dommett, Guennadi Evmenenko, Shang-En Wu, Shu-Fang Chen, Chuan-Pu Liu, SonBinh T. Nguyen, Rodney S. Ruoff. *Nano Letters*, **7**(7), (2007), 1888-1892.

9:00am **GR-MoM3 Investigation of Process Dependence of Graphene Growth on Nickel Thin Film**, *J. Mun*, KAIST, Republic of Korea, *C. Hwang*, Korea Research Institute of Standards and Science, Republic of Korea, *S. Lim*, National Nano Fab Center, Republic of Korea, *B.J. Cho*, KAIST, Republic of Korea

Recent study on graphene synthesis on metal thin film by chemical vapor deposition in a hydrocarbon ambient has shown promising results for the feasibility of formation of graphene layer over a large area.¹⁻⁴ However the graphene layer grown on metal thin film shows various kinds of defects on its surface such as islands of thick graphene layers, carbon dumps, and wrinkles from the different thermal expansion coefficient between metal and carbon, and so on.²⁻³ Control of such defects is critical for the technique to be useful, but the mechanism of the defect formation has not been well studied so far. In this work, the effect of various process conditions which affect the quality of graphene on nickel thin film is carefully investigated, including nickel thin film deposition process, ramping up ambient, annealing ambient, annealing temperature, thickness of nickel thin film, etc. During the high temperature annealing process, nickel thin film becomes highly agglomerated and thereby the surface becomes quite rough. Since the segregated carbon amount at nickel grain boundary is different from that segregated from crystalline nickel inside the grain, the agglomeration of nickel directly affects the thickness uniformity of graphene and roughness of graphene surface. It is found that the deposition process of nickel thin film affects the agglomeration and the e-beam evaporation of nickel has

shown less agglomeration upon annealing, compared to physical sputtering. It is also found that the annealing temperature in CH_4 is a critical factor to control the amount of thick graphite island on graphene. Furthermore, it is found that the gas ambient during ramping up affects the deformation of nickel thin film. All such detailed process conditions on graphene formation on nickel thin film are carefully investigated and will be presented.

¹Q. Yu et al., *Appl. Phys. Lett.* **93**, 113103 (2008).

²A. Reina et al., *Nano Lett.* **9**, 31 (2009)

³K. S. Kim et al., *Nature* **457**, 706 (2009)

⁴L. G. D. Arco et al., *IEEE Trans. Nanotech.* **8**, 135 (2009)

9:20am **GR-MoM4 Evolution of Electrical, Chemical, and Structural Properties of Transparent and Conducting Chemically Derived Graphene Thin Films**, *C. Mattevi*, *G. Eda*, Rutgers University, *S. Agnoli*, University of Padova, Italy, *S. Miller*, Rutgers University, *A. Mkhoyan*, University of Minnesota, *O. Celik*, *D. Mastrogiovanni*, Rutgers University, *G. Granozzi*, University of Padova, Italy, *E. Garfunkel*, *M. Chhowalla*, Rutgers University

An alternative path to graphene is represented by graphene oxide (GO) that can be readily exfoliated and then deposited from suspension on variety of substrates. GO is an insulator but controlled reduction provides tunability of the electronic properties leading the possibility of accessing zero-band gap graphene. However, the GO structure and opto-electronic properties at different stages of reduction are largely unknown. Here we focus on a detailed description of opto-electronic properties, chemical state [1] and structure [2] of single and few-layered GO at different stages of reduction. The residual oxygen forms sp^3 bonds with carbon atoms in the basal plane such that the carbon-carbon sp^2 bonding fraction in fully reduced GO is ~ 0.80 . The oxygen disrupts the transport of carriers delocalized in the sp^2 network, limiting the mobility and conductivity of reduced GO thin films. Our analysis reveals that removal of oxygen to achieve sp^2 carbon fraction of > 0.95 in GO should lead to properties that are comparable to graphene.

[1] C. Mattevi et al. "Evolution of electrical, chemical, and structural properties of transparent and conducting chemically derived graphene thin films" *Adv. Funct. Mater. In press*.

[2] K. A. Mkhoyan et al. "Atomic and electronic structure of graphene oxide" *Nano Lett.* vol.9, (2009), p 1058.

9:40am **GR-MoM5 Plasma-based Approach to Controlling the Oxygen Concentration in Graphene Oxide**, *S.G. Walton*, *M. Baraket*, *E.H. Lock*, Naval Research Laboratory

Graphene and graphene oxide have attracted widespread interest because of their unique structural and electronic properties, which lend themselves well to the production of nanoscale electronic and sensing devices. Indeed, graphene is a single monolayer thick carbon sheet with remarkably high electron mobility. The addition of oxygen increases the sheet thickness and decreases this mobility and, more interestingly, determines both the conducting and reactive properties of the material. One significant impediment to realizing the potential of graphene oxide is the development of an industrially viable approach to producing large area substrates of well-controlled oxygen concentration. In this respect, plasmas are an ideal candidate but problems associated with the large fluxes of energetic ions are a significant concern. The Naval Research Laboratory has developed a plasma processing system that is characterized by a uniquely low incident ion energy, in the range of a few eV, at or near the carbon-carbon and carbon-oxygen bond strength. We discuss the use of this system to reduce the oxygen concentration of graphene oxide. We examine the plasma processing conditions, plasma characteristics, and the resulting properties of the material in an effort to understand reduction mechanisms. This work was supported by the Office of Naval Research.

10:00am **GR-MoM6 Graphene Growth on Transition-Metal Thin Films**, *P.M. Albrecht*, *E.A. Sutter*, *P.W. Sutter*, Brookhaven National Laboratory

Epitaxy on transition metal substrates is a promising approach for the large-scale synthesis of graphene for potential applications in microelectronics and sensing. In particular, the controlled layer-by-layer growth of graphene on Ru(0001) has been shown to result in macroscopic monocrystalline graphene domains with lateral sizes greater than 200 microns, perfect thickness uniformity, and very low defect density [1]. Whereas the first graphene layer interacts strongly with the Ru(0001) template, the second layer is essentially decoupled from the metallic support, thus preserving the

atomic structure and exotic electronic properties of isolated single-layer graphene [2]. A viable route towards large-area, free-standing graphene would be to grow on polycrystalline transition-metal thin films rather than single crystals, followed by the dissolution of the metal template to detach the graphene and transfer it to another support. Two groups have recently demonstrated the growth of few-layer graphene on polycrystalline Ni films using this method [3, 4].

Here, we report a study of graphene growth on Ru thin films. The polycrystalline Ru template layers were deposited on SiO₂ by magnetron sputtering in ultrahigh vacuum. We used in-situ annealing and scanning tunneling microscopy (STM) to study the recrystallization and grain growth of the Ru template, crucial to forming a starting surface suitable for the growth of macroscopic graphene domains. STM also provided a detailed understanding of the interaction of the growing graphene layer with Ru grains with different surface orientations, grain boundaries, as well as highly vicinal surfaces. Cross-sectional transmission electron microscopy (TEM) was used to directly image the graphene-metal interface for the first time. Our results provide a basis for the scalable synthesis of graphene on transition metal thin films.

- [1] P. W. Sutter, J.-I. Flege, and E. A. Sutter, *Nature Mater.* 7, 406 (2008).
- [2] E. Sutter, D. P. Acharya, J. T. Sadowski, and P. Sutter, *Appl. Phys. Lett.* 94, 133101 (2009).
- [3] A. Reina et al., *Nano Lett.* 9, 30 (2009).
- [4] K. S. Kim et al., *Nature* 457, 706 (2009).

10:40am **GR-MoM8 Is Fullerene-Intercalation in Graphite a Vehicle to Graphene Surface Layer Doping?**, P. Reinke, S. O'Donnell, University of Virginia

In order to exploit the extraordinary properties of graphene several materials-based challenges have to be addressed to reach full device functionality. The challenges include opening and control of a bandgap, n- and p type doping while preserving the ambipolarity at the K-point, and sustaining the high mobility of charge carriers. We introduce here a novel and highly versatile method for the modulation of the electronic properties of graphene, which is based on fullerene (C₆₀)-graphite intercalation compounds (C₆₀-GIC). The goal is to electronically decouple the top graphene sheet from its substrate through the introduction of an intercalated layer of fullerene molecules, which are a wide bandgap material and thus do not significantly perturb the bandstructure around the Dirac point of graphene. The fullerene layer can subsequently be doped and thus the charge transfer to the graphene is controlled via the modulation of the intercalated fullerene layer. The synthesis of the C₆₀-GICs is achieved by an annealing process, where the supersaturation of the gasphase with fullerenes is used to drive the molecule into the graphite lattice. The parameter space for successful intercalation is controlled by the substrate temperature, fullerene concentration and the defect structure of the graphite. The intercalation process is observed with scanning tunneling microscopy and spectroscopy which probes the geometric and electronic structure of the top layer. The presence of sub-surface fullerenes is detected through the appearance of a Moire pattern and a weak distortion of the topography, usually presented in a well-defined area around step edges. The spatial distribution of intercalated regions is used to describe the kinetics of the intercalation process and to elucidate the mechanistic aspects of the material synthesis. The graphene doping through the incorporation of a second dopant (e.g. K) in the C₆₀ layer is investigated with STM. The electronic structure of the top graphene layer is measured with STS, and the spatial distribution of charge-puddles and their relation to the sub-surface C₆₀ lattice will be discussed.

11:00am **GR-MoM9 1 nm Thin Carbon Nanosheets: Two-Dimensional Functional Materials**, A. Götzhäuser, University of Bielefeld, Germany
INVITED

A route for the fabrication of 1 nm thin and free-standing carbon films and membranes, whose electrical and mechanical behavior as well as surface functionalization can be tuned, is presented. Self-assembled monolayers (SAMs) of aromatic biphenyls are cross-linked by electron irradiation and then detached from the surface. This results in mechanically stable carbon nanosheets with the thickness of a single molecule and sizes up to several cm². Upon annealing at ~1000K, the cross-linked monolayers transform into a graphitic phase that consists of nanosize patches of graphene [1]. This transition is accompanied by a drop of the sheet resistivity from ~10⁸ to ~10² kΩ/sq and mechanical stiffening from ~10 to 50 GPa. Hence, nanosheets represent two-dimensional materials with tunable conductivity and stiffness. When transferred onto SiO₂/Si substrates, nanosheets can be visualized by Raleigh interference contrast. By using SAMs of appropriate biphenyls, a chemical surface functionalization of the nanosheets can be achieved, which allows their tailoring for technical applications. Nanosheet devices are presented and applications in microscopy as well as in polymer- and biophysics are discussed.

[1] A. Turchanin, A. Beyer, Ch. T. Nottbohm, X. Zhang, R. Stosch, A. Sologubenko, J. Mayer, P. Hinze, T. Weimann, A. Götzhäuser, *Adv. Mater.* 21, 1233 (2009)

11:40am **GR-MoM11 Catalytic Property and Morphology of Pt Clusters on Graphite Surface**, J. Nakamura, T. Kondo, K. Watahiki, Y. Iwasaki, J. Oh, T. Suzuki, Y. Honma, D. Hatake, University of Tsukuba, Japan

Understanding the interface interaction between platinum nano-cluster and carbon supports composed of graphitic materials is one of the most important need in development of electrocatalysts for fuel cell. We have studied the effects of the interface interaction on the catalytic properties using model catalysts of Pt-deposited highly oriented pyrolytic graphite (HOPG) by IETS-STs-STM, TPD, and molecular/atomic beam technique. The deposited Pt clusters show unique morphology and catalytic properties. That is, the shape of Pt clusters (1-5 nm) is a raft-like structure with one or few atomic heights. The Pt clusters show quite high catalytic activity for H₂-D₂ exchange reaction at 24 Torr. Desorption peak of CO from the Pt was observed at a low temperature of 300 K. The significant modification is ascribed to the interface interaction between Pt atoms and graphite surface. In the STM observation, it was found that Pt atoms are located on beta-carbon, indicating the shrinkage of Pt-Pt distance about 13% compared to that of the bulk Pt. The modification in the catalytic properties and the electronic structure of the flat Pt clusters is thus ascribed to the reduction in the lattice constant of Pt. It is explained that the d-band center of Pt shifts away from the Fermi level due to the reduction in the lattice constant. We show evidence of the interface interaction between Pt and graphite here. Distinct electronic states of the graphite near the Fermi level, "non-bonding π electronic states", were observed at the carbon atoms in the vicinity of the Pt clusters by STS measurements, which is interpreted by our newly proposed model: the conjugated bond of graphite between alpha- and beta-carbon atoms are re-hybridized into two p_z-orbitals, where the p_z-orbital of beta-carbon would be hybridized with a d-orbital of the Pt atom and the other p_z-orbital of alpha-carbon becomes a non-bonding p-orbital. Consequently non-bonding p electronic states forms at the alpha-carbon atoms of graphite in the vicinity of the Pt cluster. The proposed model is consistent with our experimental result of scanning tunneling microscopy and inelastic electron tunneling spectroscopy (IETS) measurements as well as STS results and our first-principles density functional calculations of the graphene sheet with a Pt cluster.

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