

# 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 ( $^{13}\text{C}$  vs  $^{12}\text{C}$ ) 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  $^{13}\text{C}$ -labeled graphite (and  $^{12}\text{C}$ -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.

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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.<sup>1-4</sup> 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.<sup>2-3</sup> 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  $\text{CH}_4$  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.

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

<sup>2</sup>A. Reina et al., *Nano Lett.* **9**, 31 (2009)

<sup>3</sup>K. S. Kim et al., *Nature* **457**, 706 (2009)

<sup>4</sup>L. 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. Mastrogianni*, 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  $\text{sp}^3$  bonds with carbon atoms in the basal plane such that the carbon-carbon  $\text{sp}^2$  bonding fraction in fully reduced GO is  $\sim 0.80$ . The oxygen disrupts the transport of carriers delocalized in the  $\text{sp}^2$  network, limiting the mobility and conductivity of reduced GO thin films. Our analysis reveals that removal of oxygen to achieve  $\text{sp}^2$  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 SiO<sub>2</sub> 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 (C<sub>60</sub>)-graphite intercalation compounds (C<sub>60</sub>-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 C<sub>60</sub>-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 C<sub>60</sub> 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 C<sub>60</sub> 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 cm<sup>2</sup>. 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 ~10<sup>8</sup> to ~10<sup>2</sup> kΩ/sq and mechanical stiffening from ~10 to 50 GPa. Hence, nanosheets represent two-dimensional materials with tunable conductivity and stiffness. When transferred onto SiO<sub>2</sub>/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 H<sub>2</sub>-D<sub>2</sub> 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<sub>z</sub>-orbitals, where the p<sub>z</sub>-orbital of beta-carbon would be hybridized with a d-orbital of the Pt atom and the other p<sub>z</sub>-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.

# Monday Afternoon, November 9, 2009

## Graphene Topical Conference

Room: C3 - Session GR+SS-MoA

### Epitaxial Graphene on SiC

Moderator: P.N. First, Georgia Institute of Technology

2:00pm **GR+SS-MoA1 Observing the Quantization of Zero Mass Carriers in Epitaxial Graphene, J.A. Stroscio**, National Institute of Standards and Technology **INVITED**

The cyclotron motion of electrons in a magnetic field has historically been a powerful probe of the Fermi surface properties of metals and two-dimensional electron systems. Oscillations in many measurable properties such as magnetization, thermal conductivity, and resistance, all reflect the quantization of closed orbits and the resulting discrete density of states due to the formation of Landau levels. Here, we show a new ability to observe magneto-oscillations in scanning tunneling spectroscopy of epitaxial graphene as a function of both magnetic field and electron energy [1]. These oscillations arise from Landau quantization of the 2-dimensional Dirac electron and hole quasiparticles in the topmost layer of multilayer epitaxial graphene grown on SiC. In normal metals and two dimensional electron gases the Landau levels are equally spaced. In graphene however, the charge carrier velocity is independent of their energy. Consequently, the Landau level energies are not equally spaced and include a new characteristic zero energy state (the  $n=0$  Landau level). Using scanning tunneling spectroscopy of graphene grown on silicon carbide, we directly observe non-equally spaced energy level spectrum of Landau levels, including the hallmark zero-energy state of graphene. We measure the local variation in the electrostatic potential of graphene by spatially mapping the  $n=0$  Landau level. As the magnetic field is varied at fixed tunneling energy, oscillations are detected in the tunneling conductance, which are shown to be a method to measure low energy electronic band structure. These tunneling magneto-conductance oscillations are used to determine the linear energy-momentum dispersion of graphene through the Dirac point with extremely high energy and momentum resolution.

[1] David L. Miller, Kevin D. Kubista, Gregory M. Rutter, Ming Ruan, Walt A. de Heer, Phillip N. First, Joseph A. Stroscio, Science (in press).

2:40pm **GR+SS-MoA3 Graphene Materials Development, G.G. Jernigan, J.L. Tedesco, J.G. Tischler, E. Glaser, J. Caldwell, P.M. Campbell, D.K. Gaskill**, US Naval Research Laboratory, **J.A. Robinson, M.A. Fanton**, Electro-Optics Center Penn State

Development of graphene is a materials issue. Exfoliated graphene has shown the promise of high carrier mobilities, but for graphene to become technologically viable, epitaxial graphene formed over large areas must be developed. Reported carrier mobilities for epitaxial graphene grown on SiC range from  $> 250,000$  to  $< 1,000$   $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ . Mobility results can vary with measurement method, measurement temperature, and sample size. We will present our results, which encompass the aforementioned range of mobilities, for graphene formed on Si-face and C-face SiC.

Utilizing semi-insulating substrates, we have been able to correlate electrical characteristics with materials properties, which are dependent on the surface termination of SiC. Si-face graphene consistently shows lower mobilities than graphene grown on the C-face. XPS shows the differences between growth on the Si-face and the C-face are 1) the presence of an interfacial layer between the graphene and the SiC for Si-face films and 2) electronic differences between the C 1s peak for graphene on the C-face and the C 1s peak for graphene on the Si-face. The electronic differences may result from more graphene layers form on the C-face than on the Si-face. In particular, graphene forms only 1 to 3 layers on the Si-face even for long growth times at high temperature (e.g. 60 min at 1600 °C). STM images of graphene on the Si-face show an islanding mode of growth, which leads to the development of grain boundaries within the film, and  $\mu$ -Raman measurements show that the mobility increases as the domain size increases. Graphene formed on the C-face of SiC grows very rapidly, leading to films which are 10 to 30 nm thick and decorated with striped surface features (referred to as "giraffe stripes"). Independent of the presence of giraffe stripes, we observe that surface roughness does affect mobility, with smoother surfaces having higher mobilities. We have also performed far infrared magneto-transmission measurements (FIR-MT) on the graphene films. The C-face graphene shows a  $0(-1) \rightarrow 1(0)$  Landau level transition with a  $\sqrt{B}$  dependence and linewidths consistent with layers having carriers described as Dirac fermions with mobilities  $> 250,000$   $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  at 4.2K. The Si-face graphene showed much broader linewidths resulting from lower carrier mobility. One trend that holds for graphene on both faces of SiC is that fabrication of small area devices can result in

higher carrier mobilities and that carrier mobility increases as the carrier density decreases. Continued improvements in the electrical characteristics of epitaxial graphene can be realized through improvements in material quality.

3:00pm **GR+SS-MoA4 Defects Scattering in Graphene, J.-H. Chen, W. Cullen, C. Jang, M. Fuhrer, E. Williams**, University of Maryland, College Park

We have measured the effect of low energy charged particle irradiation on the electronic transport properties of clean graphene devices. Irradiation of graphene by 500 eV Ne and He ions creates defects that cause intervalley scattering as evident from a significant Raman  $D$  band intensity. The defect scattering gives a conductivity proportional to charge carrier density, with mobility decreasing as the inverse of the ion dose. The mobility decrease is four times larger than for a similar concentration of singly charged impurities. The minimum conductivity decreases proportional to the mobility to values lower than  $4e^2/\pi h$ , the minimum theoretical value for graphene free of intervalley scattering. Defected graphene shows a diverging resistivity at low temperature, indicating insulating behavior. The results are best explained by ion-induced formation of lattice defects that result in mid-gap states.

3:40pm **GR+SS-MoA6 Formation of Epitaxial Graphene on SiC(0001): Comparison of Si-face and C-face, P. Fisher, IBM, L. Luxmi, N. Srivastava, R. Feenstra**, Carnegie Mellon University, **Y. Sun**, Argonne National Laboratory, **J. Kedzierski**, MIT Lincoln Laboratory

The formation of epitaxial graphene on the SiC(0001) surface is described, comparing results for (0001) and (000 $\bar{1}$ ) surfaces (the so-called *Si-face* and *C-face*, respectively). The graphene is formed by heating the SiC to 1100 – 1400°C for 20 min in vacuum, during which time the Si preferentially sublimates, leaving behind the C which self-assembles into graphene. Development of the graphene layer(s) is observed by atomic force microscopy (AFM), low-energy electron diffraction and Raman spectroscopy, with the graphene thickness measured using both Auger electron spectroscopy and low-energy electron microscopy. High quality films are formed, with field-effect mobilities at room temperature exceeding 4000  $\text{cm}^2/\text{Vs}$ . It is found that graphene forms as 3-dimensional islands on the C-face, whereas it forms in a 2-dimensional manner on the Si-face. We believe that this difference occurs because of differing interface structures between the graphene and the SiC in the two cases. Importantly, the graphene for the C-face is found to be *thinner* in the areas on top of the islands, consistent with a model in which sublimating Si atoms originate from the interface (and hence thicker graphene implies more material loss). For the Si-face a number of morphological features are found to interrupt the flat, uniform morphology of the graphene, including: surface pits, step bunches, and an apparent "secondary" graphitic surface phase. This secondary phase is observed as locally rough regions in the surface morphology. At low graphene formation temperature these regions can extend substantially over the entire surface, but at higher formation temperatures the regions shrink in size, until they produce only a faint finger-like pattern in the morphology as seen by AFM. We tentatively interpret the secondary phase as arising from excess carbon present *on top* of the surface (as opposed to at the graphene/SiC *interface*, where it would form well-ordered graphene).

4:00pm **GR+SS-MoA7 Nucleation of Epitaxial Graphene on SiC(0001), J.A. Robinson, D. Snyder, R. Cavalero, K. Trumbull, M. Wetherington, E. Frantz, M. LaBella, Z. Hughes, M.A. Fanton**, The Pennsylvania State University Electro-Optics Center

Currently, the most promising route for large area graphene, suitable for standard device fabrication techniques, is the sublimation of silicon from silicon carbide (SiC) at elevated temperatures ( $>1200$  °C). Prior to graphene synthesis, SiC substrates are generally hydrogen etched at elevated temperatures to remove residual polishing damage. However, this process can result in significant step bunching, and lead to large terrace step heights. We utilize various surface preparation conditions, Raman spectroscopy, and atomic force microscopy to investigate the nucleation and growth of epitaxial graphene on SiC(0001). The location of graphene was identified using a WITec confocal Raman microscope (CRM) with a 488 nm laser wavelength, diffraction limited lateral resolution of  $\sim 340$  nm, and spectral resolution of  $0.24$   $\text{cm}^{-1}$ . The physical topography of the SiC substrate and graphene films were determined by atomic force microscopy using a Digital Instruments Nanoscope 3A.

We provide evidence that graphene not only nucleates at terrace step edges in the SiC surface, but also at surface defects such as residual surface damage from chemomechanical polishing, and screw dislocations. Prior to graphene synthesis samples were prepared in four manners: 1) *in situ*

hydrogen (H<sub>2</sub>) etching; 2) *ex situ* potassium hydroxide (KOH) etching; 3) *ex situ* KOH and *in situ* H<sub>2</sub> etching; 4) No etch. Potassium hydroxide selectively etches defect sites on the SiC surface, leaving behind etch pits which serve as macro-defects in the SiC surface. Our monolayer epitaxial graphene was synthesized via Si-sublimation from the Si-face of semi-insulating SiC at 1325°C, 1x10<sup>-6</sup> Torr. These conditions preclude the formation of graphene on SiC(0001) except at terrace step edges and other topological defects, effectively decorating the nucleation sites for subsequent characterization.

Samples with an *in situ* H<sub>2</sub> etch exhibit growth of graphene nearly exclusively at terrace step edges, while KOH etched samples exhibit graphene synthesis primarily at the etch pits and terrace step edges in the SiC surface. Those samples that experience no pre-treatment exhibit the highest surface coverage of any surface preparation, indicating that graphene grown on SiC(0001) nucleates at atomic scale defects on the SiC surface. This work provides evidence that defects in the form of dislocations, terrace step edges, and etch pits act as low energy nucleation sites for the growth of epitaxial graphene on SiC(0001). Finally, this work suggests that the growth of uniform graphene on SiC(0001) will be heavily influenced by the SiC substrate quality.

4:20pm **GR+SS-MoA8 The Effect of Adsorbates on the Electronic Properties of Graphene**, E. Rotenberg, Lawrence Berkeley National Laboratory **INVITED**

Epitaxially grown graphene films with various adsorbates have been prepared and investigated using angle-resolved photoemission spectroscopy (ARPES). Two regimes have been studied, which are differentiated by whether the adsorbates preserve the local symmetry of the graphene unit cell or not. For symmetry-preserving defects, such as adsorbed K or Ca atoms, the charge carriers in the graphene retain their metallic, Fermi liquid character, i.e. they can be described as single, weakly interacting “quasiparticles” with a relatively long lifetime as their energy approaches the Fermi level. (This is in contrast to strongly correlated systems where electron-electron scattering dominates the low energy dynamics) In such samples, ARPES measurements of the valence band can determine details of many-body interactions such as electron-phonon coupling. The second regime is followed by adsorbed atomic H atoms, which break the local lattice symmetry, and, for sufficiently high density, cause a dramatic breakdown in the quasiparticle picture, as evidenced by changes to the valence band spectrum. This, together with an accompanying metal-to-insulator transition, suggests that atomic H localizes the carriers, as described by Anderson’s theory.

\*in collaboration with A. Bostwick, J. L. McChesney, T. Ohta, [LBNL], S. D. Kevan,[U. Oregon] K. V. Emtsev, Th. Seyller [U. Erlangen], and K. Horn [Fritz-Haber Institute]

5:00pm **GR+SS-MoA10 Low Temperature Halogen Assisted Synthesis of Epitaxial Graphene on SiC**, M.A. Fanton, J.A. Robinson, B.E. Weiland, M. LaBella, K. Trumbull, Penn State University

Graphene presents a host of remarkable physical and chemical properties that are uniquely beneficial for the development of nano-scale electronics and chemical sensors. However, high processing temperatures, and the resulting non-uniform surface topography significantly degrades the electronic properties of epitaxial graphene (EG). To minimize these issues a low temperature, atmospheric pressure, synthesis technique was developed that uses halogen species to extract Si from the SiC surface. This significantly minimizes surface roughening, and reduces substrate-induced strain in the graphene layer, which are major factors limiting material and device performance. The synthesis temperature of epitaxial graphene can be reduced to well below 1400°C by exposing the SiC substrate to halogenated (Cl, Br, F) gases. Our preliminary thermodynamic modeling shows that the formation of carbon on the surface of SiC can be accomplished using various halogen-hydrogen gas mixtures. The model shows that carbon formation on the SiC surface can be controlled using a combination of temperature, pressure, and halogen/hydrogen ratio. Using this technique, both the Si-face and C-face of 2” diameter SiC wafers have been graphitized at temperatures as low as 1150°C at a pressure of 600 Torr. Synthesis was accomplished in a SiC CVD reactor from Structured Materials. Temperatures ranged from 1150°C to 1350°C, making the process compatible with Si-based substrates. Growth pressures ranging from 0.1 to 600 Torr were explored, with higher pressures being preferred. The process atmosphere consisted of a mixture of hydrogen, argon, and halogenated gases such as HCl. The formation and structural quality of the epitaxial graphene was characterized using Raman spectroscopy, atomic force microscopy, transmission electron microscopy, and white light interferometry. Structural quality, as assessed by the Raman G’ and D+G peaks, was found to improve as the growth rate decreased and growth temperature increased. Growth rate at a fixed temperature and pressure was readily controlled via the halogen concentration and the halogen/hydrogen ratio as expected from the thermodynamic model. For thick carbon films the

growth rate on the C-face was typically 5 times higher than the growth rate on the Si-face. The impact of the halogen/hydrogen ratio was heavily dependent upon the source of the halogen species, which was also expected from thermodynamics. Transmission electron microscopy showed that the interface between the SiC and graphene was sharp and confirmed the number of layers present that was estimated by Raman spectroscopy. The surface roughness of graphene layers was on the order of 1-3nm.

5:20pm **GR+SS-MoA11 Galvanic Deposition of Au Nanoclusters on Epitaxial Graphene**, M. Cerruti, N. Ferralis, R. Maboudian, C. Carraro, UC Berkeley

Metallization of graphene surfaces are of crucial importance for the fabrication of metal-graphene contacts, and for surface functionalization via metallic nanostructures. In this paper, a novel method of selective deposition of Au clusters on graphene layers grown epitaxially on SiC substrate is presented. The size and the distribution of particles is regulated and fully controlled by the deposition process. From a combined use of scanning electron microscopy, x-ray electron spectroscopy and Raman microscopy, we propose that cluster nucleation takes place at the edges and defects in graphene domains, via oxidation of defects sites. The preferred nucleation indicates that a high level of selectivity is achieved by controlling the quality of the graphene film.

# Tuesday Morning, November 10, 2009

## Graphene Topical Conference

Room: C3 - Session GR+EM+MS-TuM

### Graphene and Carbon-based Electronics

Moderator: J.E. Rowe, North Carolina State University

8:00am **GR+EM+MS-TuM1 Graphene: Quantum Transport in a 2D Membrane**, *C.N. Lau*, University of California, Riverside **INVITED**

Graphene, a two - dimensional single atomic layer of carbon, has recently emerged as a promising candidate for electronic materials, as well as a new model system for condensed matter physics. It also has the double identity of an extraordinary conductor and the thinnest isolated membrane. In this talk I will present our results on both of these aspects: (1) our observation of novel transport phenomena in graphene, including coherent interference of multiply-reflected charge waves and properties of p-n-p junctions in zero and high magnetic fields; and (2) our work on ripple formation and manipulation on suspended graphene sheets. I will conclude the talk with a brief discussion on the fascinating prospect of strain-based graphene engineering.

8:40am **GR+EM+MS-TuM3 Air Induced Suppression of n-Type Conduction in Field-Effect Transistors**, *P. Levesque*, Université de Montréal, Canada, *C.M. Aguirre*, École Polytechnique de Montréal, Canada, *M. Paillet*, *F. Lapointe*, Université de Montréal, Canada, *B.C. St-Antoine*, *P. Desjardins*, École Polytechnique de Montréal, Canada, *R. Martel*, Université de Montréal, Canada

Carbon nanotube, graphene, and organic semiconductor based devices share common features when exposed to atmospheric environment. For carbon nanotube field-effect transistors (FET), the effect is an almost exclusive p-type character in air. N-type conduction can only be observed under certain conditions, for instance when the devices are annealed in vacuum. By performing experiment under controlled atmosphere, we investigated the impact of the chemical nature of the substrate and of gas adsorbates on the field-effect switching behavior of both nanoscale and thin-film nanotube FETs. Our study revealed that the intrinsic material properties are modified and lead to the reduction of n-type conduction when an adsorbed water layer containing solvated oxygen is present on the SiO<sub>2</sub> surface. This finding demonstrates that an electrochemical charge transfer reaction between the semiconducting channel and the aqueous oxygen redox couple is the underlying phenomenon behind the suppression of electron conduction in nanotube devices. The impact of this redox couple on graphene FET explored in this context will also be discussed. We forecast that these redox active species generally influence the transport properties of transistors operating in air and propose a general mechanism that explains behaviors observed in many material systems on SiO<sub>2</sub>/Si substrates, also including nanowires, polymers and organic materials.

9:00am **GR+EM+MS-TuM4 Epitaxial Graphene Device Technology**, *D.K. Gaskill*, U.S. Naval Research Laboratory, *J. Moon*, HRL Laboratories, LLC, *J.L. Tedesco*, U.S. Naval Research Laboratory, *J.A. Robinson*, The Pennsylvania State University, *A.L. Friedman*, *P.M. Campbell*, *G.G. Jernigan*, *J.K. Hite*, *R.L. Myers-Ward*, *C.R. Eddy, Jr.*, U.S. Naval Research Laboratory, *M.A. Fanton*, The Pennsylvania State University

Recently, the world's first graphene RF field effect transistors (FETs) have been fabricated using photolithography on epitaxial graphene (EG) grown on 50 mm SiC semi-insulating wafers. The RF FETs had  $f_{\max}$  of 14 GHz at 5 V<sub>ds</sub> for 2 μm gate widths and results are expected to improve as gate widths are scaled down. Continued research addressing key materials issues is needed to push the performance metrics for devices fabricated on wafer-scale EG significantly higher. Some of these key materials issues are morphology and thickness control, enhanced mobility, uniformity of sheet carrier density and resistivity, and optimizing atomic layer deposition (ALD) of high dielectric constant oxides on EG. In this presentation, we will present details on our approach using Si sublimation from SiC substrates for growing EG on 50.8 and 76.2 mm diameter SiC wafers and discuss the impact of key material issues on RF device performance.

Epitaxial graphene was synthesized using a commercial Aixtron VP508 SiC epitaxial growth reactor on the Si- and C-faces of 4H- and 6H-SiC semi-insulating 0° oriented substrates at temperatures from approximately 1225 to 1700°C and for times ranging from 10 to 300 min. Substrates were 16 x 16 mm<sup>2</sup> coupons and 50.8 and 76.2 mm diameter wafers. Both *in-vacuo* (10<sup>-6</sup> to 10<sup>-4</sup> mbar) and Ar ambient (50-200 mbar) Si sublimation synthesis conditions were investigated. Dielectrics were deposited using a Cambridge NanoTech Savannah 200 ALD system. EG was characterized by a wide

array of tools including atomic force, Nomarski and scanning tunneling microscopies, Raman spectroscopy, Hall effect, and Leighton contactless resistivity and mobility wafer probe.

The growth of EG on 50.8 mm Si-face wafers using the *in-vacuo* process was optimized and excellent relative resistivity uniformity of 2.8% and record 300 K Hall mobilities up to 2700 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> were found. Raman spectroscopy mapping of the 2D peak on the wafers determined: (1) the majority of the film was monolayer EG, (2) two layers of EG could be found at step edges and (3) the EG was continuous across the wafer. RF FETs fabricated using the latest optimized wafer-scale EG exhibited state-of-the-art ambipolar behavior, I<sub>on</sub>/I<sub>off</sub> ratios and peak transconductances. Frequency performance metrics were established for these devices such as  $f_T \bullet L_g$  products of 10 GHz•μm and  $f_{\max}$  of 14 GHz. To our knowledge, the highest field effect mobilities reported to-date have been measured using these devices. We will discuss the impact of key material parameters associated with EG for these record results as well as the impact of Ar ambient controlled graphenization on future RF devices.

9:20am **GR+EM+MS-TuM5 Hydrogen Adsorption at Surfaces of the Epitaxial Graphene on the 6H-SiC(0001)**, *Y. Aoki*, *H. Hirayama*, Tokyo Institute of Technology, Japan

Recently, adsorption of a small amount of atomic hydrogen was reported to transform the exfoliated graphene from highly conductive semimetal into an insulator [1]. In this case, the C-atom is only the site for hydrogen adsorption. However, at the epitaxial graphene on the SiC(0001) substrate, hydrogen could adsorb on both C- and Si-site. Furthermore, the surface structure changes by stages from Si-rich 3x3, √3x√3 to C-rich 6√3x6√3 phase in the epitaxial growth of graphene on SiC substrates [2]. In this study, we investigated the hydrogen adsorption at these surfaces appeared in the way of epitaxial growth of graphene on the Si-terminated 6H-SiC(0001) surfaces.

Experiments were carried out in an ultra-high vacuum apparatus equipped with a Si dozer, a LEED/AES, a TPD (Temperature Programmed Desorption), a hydrogen gas inlet, and a hot W-filament. We prepared the 3x3, √3x√3, and 6√3x6√3 surfaces by heating the sample at 850°C under the Si flux, heating at 1150°C for 3min, and heating at 1250°C for 3min, respectively. We exposed these surfaces to atomic hydrogen, and measured their TPD spectra. Our TPD indicated that the saturation coverage of H was ≈0.1 monolayer (ML) at these surfaces independent of the surface structure. However, the TPD spectrum changed drastically at the stage from 3x3 to √3x√3. The 3x3 surface showed a shoulder at ≈500K, and a dominant peak at 700K, while the √3x√3 and the 6√3x6√3 surface had a single peak at 400K. Comparing to the previous TPD studies at graphite [3], we attributed to the single peak at 400K to the hydrogen desorption from the graphene layer. Meanwhile, the peak at 700K of the 3x3 surface is very close to the hydrogen desorption peak from the Si(111) surface. Both TPD and AES suggests that the π-bonded C-induced benzene ring structure started to grow at the appearance of the √3x√3 surface structure. This interpretation is supported by our electron energy loss spectroscopy (EELS) measurements in which the π-plasmon loss peak of the benzene ring started to evolve at the √3x√3 surface.

[1] Science 323,610(2009), [2]JPC,B208,19912(2004), [3]JCP117,8486(2002)

9:40am **GR+EM+MS-TuM6 Graphitic Carbon Growth on Si(111) from Solid Source Molecular Beam Epitaxy**, *J.C. Hackley*, *D. Ali*, *J. Di Pasquale*, *C.J.K. Richardson*, University of Maryland, College Park

Since the recent discovery of isolated graphene through mechanical exfoliation of bulk graphite, a number of methods have been developed to produce graphene. However, there have been no reports of graphene growth by direct carbon deposition such as solid source molecular beam epitaxy (MBE). Carbonization of a silicon surface is a commonly used first step in the epitaxial growth of SiC films, and is often accomplished by solid source MBE of carbon onto a Si substrate to form a thin SiC buffer layer. Annealing SiC wafers in ultra-high vacuum is a reliable method of producing graphene layers, and is frequently referred to as an epitaxial technique. Consequently, graphene may be synthesized via MBE through a two-step process consisting of first growing SiC, and then annealing this film at high temperatures to desorb Si. A shorter processing route which bypasses the SiC formation would be quite beneficial. In this project, we investigate the growth of graphene directly on Si using solid source MBE at growth temperatures which are much lower than a SiC process.

An EPI-Model 930 MBE system which has been modified to accommodate a Si electron beam source is used for carbon sublimation onto 3" Si wafers. Our carbon source is a Thermionics rod-fed electron beam gun with a

highly oriented pyrolytic graphite (HOPG) target. Reflective high-energy electron diffraction (RHEED) measurements are used to monitor the carbon film growth in situ. The film bonding structure is investigated ex-situ with x-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and Raman scattering spectroscopy. Film topology is examined ex-situ with scanning electron microscopy (SEM) and atomic force microscopy (AFM). Hall measurements in a Van der Pauw configuration are implemented for electrical characterization of the films. Through preparing the Si surface with seeding layers and choosing an appropriate C flux we have been able to suppress SiC formation and grow graphitic carbon at temperatures < 700°C. Raman scattering measurements show the G mode at ~1600 cm<sup>-1</sup> and the D mode at ~1320 cm<sup>-1</sup> (Fig. 1), as well as weak overtones of these phonon modes. XPS analysis of the C 1s region shows no significant sp<sup>3</sup> carbon bonds, and no SiC formation, which is also verified by FTIR measurements (Fig. 2). SEM and AFM analysis show that the films are smooth and continuous.

We are currently refining our growth process in order to increase graphite grain size and subsequently downscale to 2-dimensional growth. These initial results appear promising for the future development of graphene growth via direct deposition of carbon.

10:40am **GR+EM+MS-TuM9 Epitaxial Graphene: Designing a New Electronic Material.** *W.A. de Heer*, Georgia Institute of Technology **INVITED**

Since 2001 the Georgia Tech epitaxial graphene research team and its collaborators have developed the new field of epitaxial graphene electronics. The current status of epitaxial graphene research will be presented, including the production methods and recent results from various characterization investigations. Methods have been developed to grow continuous multilayered epitaxial graphene (MEG) on the C-face of hexagonal silicon carbide with of up to 100 graphene sheets and its extraordinary transport properties have been demonstrated.

Surprisingly, the properties of MEG are closely related to monolayer graphene rather than graphite, as a result of an unusual rotational stacking of the graphene layers that causes the graphene sheets to electronically decouple. Consequently the electronic band structure of MEG is composed of Dirac cones. The charge carriers are chiral and exhibit a non-trivial Berry's phase. Weak anti-localization and quantum confinement has been demonstrated. Landau level spectroscopy further exhibits record-breaking room temperature mobilities and well resolved Landau levels below 1 T, indicating extremely low carrier densities and good homogeneity of the material. Efforts towards large scale electronic device patterning will be reviewed.

11:20am **GR+EM+MS-TuM11 MORTON S. TRAUM AWARD FINALIST: Room Temperature Molecular-Resolution Characterization of Self-Assembled Organic Monolayers on Epitaxial Graphene.** *Q.H. Wang\**, *M.C. Hersam*, Northwestern University

Graphene has attracted significant attention due to its unique electronic structure, high carrier mobilities, and quantum relativistic phenomena. Epitaxial graphene grown on SiC(0001) is a promising material for next-generation technology because it allows for wafer-scale processing. In order to realize its full potential for a diverse range of devices, the bare graphene sheet must be incorporated with other materials via chemical functionalization schemes. Recent progress reported in the literature include the demonstration of atomic layer deposition of Al<sub>2</sub>O<sub>3</sub> on mechanically exfoliated graphene sheets functionalized by carboxylate-terminated perylene derivatives,<sup>1</sup> and the formation of monolayers of 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) at cryogenic temperatures on epitaxial graphene.<sup>2</sup> In this study, we report the room-temperature formation of self-assembled monolayers of PTCDA on epitaxial graphene.<sup>3</sup> We characterize the molecular ordering and electronic properties of these monolayers using ultrahigh vacuum (UHV) scanning tunneling microscopy (STM). The molecules self-assemble into stable, well-ordered monolayers that are arranged in a herringbone phase with extended domains spanning hundreds of nanometers. At submonolayer coverage, PTCDA forms stable, isolated molecular islands. The molecular ordering is unperturbed by either defects in the epitaxial graphene or atomic steps in the underlying SiC surface. Scanning tunneling spectroscopy (STS) performed on the PTCDA monolayers reveals strong features in the electronic density of states that are distinct from the pristine graphene regions. The demonstration of robust, uniform organic functionalization of epitaxial graphene presents opportunities for exploring self-assembly chemistry on graphene, tailoring the chemical functionality of graphene, and templated growth and deposition of other materials as potential routes toward realizing graphene-based molecular electronic and sensing devices.

\* Morton S. Traum Award Finalist

- <sup>1</sup> X.R. Wang, S.M. Tabakman, and H.J. Dai, *J. Am. Chem. Soc.* **130**, 8152-8153 (2008).
- <sup>2</sup> P. Lauffer, K.V. Emtsev, R. Graupner, T. Seyller, and L. Ley, *Phys. Status Solidi B*, **245**, 2064-2067 (2008).
- <sup>3</sup> Q.H. Wang and M.C. Hersam, *Nature Chemistry*, in press (2009).

11:40am **GR+EM+MS-TuM12 Effects of Reducing Conditions on Conductivity Change of Graphene Oxide.** *H. Asano*, *Y. Shimogaki*, The University of Tokyo, Japan

Graphene is an attractive material for electronic devices since it has remarkable electronic properties, such as super high electron mobility. There are some methods to form graphene on SiO<sub>2</sub>, however, it is difficult to cover SiO<sub>2</sub> substrate fully by flat graphene flakes on a wide area. For example, micromechanical cleavage of graphite can make graphene sheet on SiO<sub>2</sub>, but the largest size of it will be within several micrometers. There is a demand, however, to graphene to use as conductive materials such as wiring material for ULSI interconnects and transparent and conductive electrode for solar cells and flat panel displays. These applications require large area coating and low process temperature. Then, graphene oxide (GO) coating and its reduction to form conductive graphene gets much attention. In the present work, we tried to reduce GO by gas-phase reduction and examined the resistivity change.

To obtain GO dispersion, graphite (Nippon Graphite Industry Co., LTD, SCB-100) was oxidized through the modified Hummer's methods. The dispersion was determined to be 0.965 wt% from the weight change of the dispersion. The dispersion was exfoliated by sonication, diluted by ethanol to 0.20 wt% and spin-coated on SiO<sub>2</sub>/n-Si substrate, which was pre-treated by aminopropyltriethoxysilane (APTES). Spin-coated GO film was dried at room temperature. Reduction of GO film to form graphene was carried out in a vacuum, H<sub>2</sub>, or formic acid ambient. The temperature of the substrate was ranged from 200°C to 1000°C, base pressure was 2.6×10<sup>-7</sup> Torr, pressure of reducing agent (hydrogen or formic acid) was 5 Torr.

Thickness of spin-coated GO film was 30±5 nm and the film contents were 90 at% of C and 10 at% of O. Sheet resistance of the film was decreased by annealing in vacuum. The reciprocal of sheet resistance showed the Arrhenius type behaviour and minimum sheet resistance obtained in our work was 0.7 kΩ/sq. This result suggests some thermal activation phenomena that controls resistivity of GO. Thermal Desorption Spectroscopy (TDS) analysis showed that almost all O atoms were removed at 200°C, but very small amount of H<sub>2</sub>O, CO, CO<sub>2</sub> was also detected above 200°C. The elimination of remaining oxygen as H<sub>2</sub>O, CO, CO<sub>2</sub> at high temperature may be responsible for the Arrhenius type behaviour of the sheet resistance. Sheet resistance became one-third by the reduction using formic acid at 290°C compared with the reduction in vacuum or H<sub>2</sub>. The sheet resistance treated over 700°C did not show any ambient dependency. We will also discuss the chemical bond state change observed by XPS and carrier concentration / mobility change measured by Hall measurement.

# Tuesday Afternoon, November 10, 2009

**Graphene Topical Conference**  
**Room: C3 - Session GR+TF-TuA**

## **Graphene: Characterization, Properties, and Applications**

**Moderator:** M. Fuhrer, University of Maryland, College Park

2:00pm **GR+TF-TuA1 Graphene Atomic Membranes, P.L. McEuen, Cornell University** **INVITED**

Atomically thin graphene membranes have exceptional electronic, optical, thermal and mechanical properties. Here we discuss our group's measurements on graphene membranes made by either exfoliation, epitaxial growth on SiC, or chemical vapor deposition growth on Ni or Cu. For example, we demonstrate that a monolayer graphene barrier is impermeable to standard gases, including helium. By applying a pressure difference across the membrane, we measure both the elastic constants and the mass. We also discuss mechanical resonators made from graphene, as well as the photocurrent response of graphene optoelectronic devices. We find the photoresponse at a graphene interface junction is photo-thermoelectric, i.e. the laser locally heats the graphene, giving rise to a thermoelectric response. This is in contrast to previous interpretations based on photovoltaic charge carrier separation at local potential variations in the sample. The photo-thermoelectric model accurately describes the temperature and laser power dependence, and also provides a simple way to probe the thermal conductivity of graphene membranes. Work done in collaboration with Scott Bunch, Arend van der Zande, Scott Verbridge, Xiaodong Xu, Nathaniel Gabor, Shriram Shivaraman, Xun Yu, Robert Barton, Jonathan Alden, Lihong Herman, MVS Chandrashekhar, Jiwoong Park, Jeevak Parpia, Harold G. Craighead, and Michael G. Spencer

2:40pm **GR+TF-TuA3 Impact of Argon on the Growth of Epitaxial Graphene, J.L. Tedesco, R.L. Myers-Ward, G.G. Jernigan, U.S. Naval Research Laboratory, J.A. Robinson, The Pennsylvania State University, J.C. Culbertson, P.M. Campbell, J.K. Hite, C.R. Eddy, Jr., D.K. Gaskill, U.S. Naval Research Laboratory**

Epitaxial graphene (EG) grown *in vacuo* on semi-insulating, on-axis 4H- and 6H-SiC substrates has demonstrated morphological problems [1], such as pitting in C-face substrates during *in vacuo* growth. In order to reduce the nonuniformities present in the EG, films were grown in an Ar ambient and compared to *in vacuo* films using substrates sourced from the same wafers. The growths took place in a commercial Aixtron VP508 hot-wall epitaxial SiC growth reactor. The Ar growths were performed using temperatures ranging from 1,500°C to 1,600°C and pressures ranging from 50 to 200 mbar. The *in vacuo* growths took place for temperatures ranging from 1,225°C to 1,700°C and pressures ranging from  $10^{-3}$  to  $10^{-6}$  mbar. The resulting films were characterized with Nomarski and atomic force microscopies, Raman and x-ray spectroscopies, and Hall effect measurements.

Si-face EG films did not form under Ar at temperatures  $\leq 1,500^\circ\text{C}$ , yet *in vacuo* films formed for temperatures above  $\sim 1,400^\circ\text{C}$ . At temperatures  $> 1,500^\circ\text{C}$  under Ar, graphene was successfully grown and, while the morphology was not significantly different from *in vacuo* films, Raman spectroscopy measurements indicated that EG films with improved thickness and strain uniformity were realized. At an Ar growth pressure of 50 mbar, resulting Si-face EG was mostly bilayer graphene, while at 200 mbar, the resulting EG films were predominantly monolayer graphene. X-ray photoelectron spectroscopy measurements indicated that argon-grown EG was thinner than *in vacuo* EG grown at the same temperature.

The morphology of argon-grown C-face films was markedly different from *in vacuo* films. Under Ar, graphene did not grow below  $1,500^\circ\text{C}$ , while *in vacuo* films began to grow at  $1,225^\circ\text{C}$ . For growths at temperatures  $> 1,500^\circ\text{C}$ , the density of substrate pits was reduced significantly and was eliminated in half of the argon-grown films. Furthermore, at temperatures between  $1,500^\circ\text{C}$  and  $1,600^\circ\text{C}$ , ambient-controlled films were incomplete, and the percentage of the substrate covered by graphene increased with growth temperature.

Growth under Ar improved the electrical properties for films on both faces. Mobilities increased by up to 4 times relative to *in vacuo* films, while carrier densities decreased by  $\sim 10$  times. For both *in vacuo* and argon-grown EG, the carrier densities of Si-face EG were at least an order of magnitude less than those of C-face EG films. Furthermore, Hall effect measurements showed that, while *in vacuo* EG films on both faces were

divided between n-type and p-type, argon-grown Si-face EG was generally n-type while argon-grown C-face EG was generally p-type.

[1] B.L. VanMil, *et al.*, Mater. Sci. Forum **615-617**, 211 (2009).

3:00pm **GR+TF-TuA4 Mapping the Electronic Surface Potential of Graphene Grown on Ir(111) and Ru(0001), S. Barja, B. Borca, Universidad Autónoma de Madrid, Madrid, Spain, M. Garnica, IMDEA Nanociencia, Spain, F. Hermanns, J.J. Hinarejos, Universidad Autónoma de Madrid, Madrid, Spain, A.L. Vazquez de Parga, R. Miranda, UAM & IMDEA Nanociencia, Spain**

Moiré patterns are generated by the superposition of two periodic structures with a lattice mismatch. They have been observed by means of Scanning Tunneling Microscopy (STM) on different systems and their interpretation, in some cases, is not straightforward. The influence, at the atomic scale, of these patterns in the local density of states of the overlayer is not clear and can be studied by STM.

The growth of graphene on metallic substrates allow us not only control the periodicity of the Moiré pattern but also tailor the interaction strength between the carbon atoms and the metallic substrate [1]. In this work we compare the results obtained on graphene overlayers grown on two different metallic substrates. We studied graphene/Ir(111) and graphene/Ru(0001) in the former there is a weak interaction between the graphene overlayer and the substrate and in the later the strength of the chemical interaction is modulated by the Moiré pattern.

Field Emission Resonances (FERs), which are detected by STM when applying voltages larger than the work function, can be used to explore with nanometer resolution, the inhomogeneities in the local surface potential landscape. Operating the STM in constant current mode implies a constant electric field between tip and sample and the expected energy position for the FERs is given by the expression founded by Gundlach some time ago [2]. From that expression it is possible to determine experimentally the local work function of the surface. We applied this method to the Moiré pattern formed by graphene grown on Ir(111) and Ru(0001). For graphene on Ir(111) we did not find any modulation in the work function due to the Moiré pattern. On the contrary for graphene on Ru(0001) we have found a difference of 0.25 eV in the work function values depending on the position on the Moiré pattern. For graphene on Ru(0001) we also found that the energy position of the first FER presents strong spatial variations that can be measured by scanning tunneling spectroscopy. In fact, for the graphene/Ru(0001) system, the energy position of the first FER is not easily related with the local work function and is modified by the interaction between graphene and the Ruthenium underneath. The energy position of the higher FERs is only influenced by the variations in the local work function.

[1] A.B. Preobrajenski *et al.*, Phys. Rev. B **78**, 073401 (2008)

[2] K.H. Gundlach, Solid State Electron. **9**, 949 (1966)

4:00pm **GR+TF-TuA7 Graphene Electronics and Optoelectronics, P. Avouris, IBM T.J. Watson Research Center** **INVITED**

Graphene is a single atomic layer, 2-dimensional zero band-gap semiconductor with a high Fermi velocity and a huge electrical mobility approaching  $200,000 \text{ cm}^2/\text{V}\cdot\text{s}$  for a free sheet. The photonic properties of graphene are equally remarkable: the strength of light-graphene interaction over a very wide range of photon energies is 10 to 100 times stronger than that in conventional semiconductors. These unique properties can be employed in both electronic and photonic applications. In my talk I will discuss the basic device physics, fabrication and operating characteristics of high frequency, single layer graphene transistors. Devices with gain up to 50GHz will be demonstrated. I will also present the physics and device results on single and few layer graphene ultra-high bandwidth photodetectors appropriate for optical communications, imaging and other applications.

4:40pm **GR+TF-TuA9 Graphene Growth on Metal Surfaces, E. Loginova, N.C. Bartelt, P.J. Feibelman, K.F. McCarty, Sandia National Laboratories**

Previous work has shown that when elemental carbon is deposited on the Ru(0001) surface, graphene forms from a dense, tightly-bound carbon-adatom gas. Nonlinearity of the graphene growth rate with carbon adatom density suggests that growth proceeds by addition of carbon atom clusters to the graphene edge [1,2]. In this talk, we present the results of low-energy electron microscopy (LEEM) observations of graphene formation when Ru(0001) and Ir(111) surfaces are exposed to ethylene. We find that graphene growth velocities and nucleation rates on Ru have precisely the same dependence on adatom concentration as

in elemental carbon deposition [3]. Thus, hydrocarbon decomposition only affects graphene growth through the rate of adatom formation; for ethylene, that rate decreases with increasing adatom concentration and graphene coverage. Graphene growth on Ir(111) is similar to that on Ru: the growth velocity is the same nonlinear function of adatom concentration (albeit with much smaller equilibrium adatom concentrations, as we explain with DFT calculations of adatom formation energies). When graphene is exposed to oxygen at high temperatures, it is etched. We observe the etching to proceed by the inverse of the graphene growth mechanism, i.e., by cluster detachment.

[1] E. Loginova, N. C. Bartelt, P. J. Feibelman, and K. F. McCarty, *Evidence for graphene growth by C cluster attachment*, *New Journal of Physics* 10 (2008) 093026

[2] K. F. McCarty, P. J. Feibelman, E. Loginova, and N. C. Bartelt, *Kinetics and thermodynamics of carbon segregation and graphene growth on Ru(0001)*, *Carbon* doi:10.1016/j.carbon.2009.03.004

[3] E. Loginova, N. C. Bartelt, P. J. Feibelman, and K. F. McCarty, *Factors influencing graphene growth on metal surfaces*, submitted to *New Journal of Physics* (2009).

5:00pm **GR+TF-TuA10 The Reduction Kinetics of Graphene Oxide Determined by Temperature Programmed Desorption**, *C.A. Ventrice, N.J. Clark, D.A. Field*, Texas State University, *I. Jung, D. Yang*, University of Texas, *H. Geisler*, Texas State University, *R.D. Piner, R.S. Ruoff*, University of Texas

Graphene oxide, which is an electrical insulator, shows promise for use in several technological applications. For instance, individual, monolayer, graphene oxide platelets could be used as dielectric layers in nanoscale electronic devices. Since the electrical, optical, and mechanical properties of graphene oxide can be controlled by chemical modification, films composed of layers of graphene oxide platelets may be used as the active region of chemical sensors. In principle, graphene oxide films could also be used as a precursor for the formation of large-scale graphene films by either thermal or chemical reduction of the graphene oxide. In order to determine the thermal stability and reduction kinetics of graphene oxide, temperature program desorption measurements have been performed on multilayer films of graphene oxide deposited on SiO<sub>2</sub>/Si(100) substrates. The graphene oxide was exfoliated from the graphite oxide source material by slow-stirring in aqueous solution, which produces single-layer platelets with an average lateral size of ~10 μm. From the temperature programmed desorption measurements, it was determined that the primary desorption products of the graphene oxide films for temperatures up to 300 °C are H<sub>2</sub>O, CO<sub>2</sub>, and CO, with only trace amounts of O<sub>2</sub> being detected. Since carbon is lost during the reduction process in UHV, the addition of other carbon containing reactants during the thermal reduction will be needed to regain the electrical and mechanical properties of pristine graphene. An activation energy of 32 ± 4 kcal/mol ( 1.4 eV/molecule) was determined by assuming an Arrhenius dependence for the decomposition process.

5:20pm **GR+TF-TuA11 Covalently Immobilized Graphene: Fabrication, Characterization, and Applications**, *M. Yan, L.-H. Liu, G. Nandamuri, R. Solanki*, Portland State University

We developed a simple method for the covalent immobilization of graphene films on solid substrates using a heterobifunctional coupling agent. The films were robustly attached to the substrate, withstanding extensive solvent extraction and sonication. Large sheets of single and few-layer graphene films were fabricated and characterized with Raman, AFM, and XPS. The method is readily applicable for the fabrication of graphene microarrays. Transistors were also constructed with these materials. The device performance with regard to surface and interface properties will be discussed in this presentation.



# Tuesday Afternoon Poster Sessions

## Graphene Topical Conference Room: Hall 3 - Session GR-TuP

### Graphene Topical Conference Poster Session

#### GR-TuP1 Reduction of Graphene Oxide using Electron Beam Generated Plasmas, *M. Baraket, E.H. Lock, S.G. Walton*, Naval Research Laboratory

Graphene and graphene oxide are the subject of intense research because of their unique structural and electronic properties which are advantageous in a large number of applications including nano-electronic and sensing devices. The amount of oxygen present in graphene oxide sheets strongly modifies their properties. Processes aiming to the reduction of oxygen are a current research interest. Wet-chemical approaches have been successful, but these methods have critical drawbacks in terms of scalability and time consumption. Plasma-based processes are an attractive replacement. The electron beam generated plasma developed by the Naval Research Laboratory provides a unique low electron temperature (< 1 eV) plasma and thus any ions leaving the plasma will do so with low ion kinetic energies at substrates. This novel plasma processing technique allows surface modification without excessive etching or surface damage. Experimental investigation of the reactions between plasmas produced in different gases (Ar, CH<sub>4</sub> and/or H<sub>2</sub> mixtures) and graphene oxide in an effort to reduce the concentration of oxygen will be presented. Material characterizations (chemistry, surface energy and surface roughness) and in-situ plasma diagnostics (electron temperature, plasma density) will also be discussed. This work was supported by the Office of the Naval Research. M.B and E.L. appreciate the support of the National Research Council.

#### GR-TuP2 Covalent Immobilization of Graphene on Solid Substrate, *L.-H. Liu, M. Yan*, Portland State University

Graphene, a two-dimensional atomic thin layer of carbon nanostructure, has emerged as a unique nanoscale material with promising applications in various areas due to its excellent mechanical, electrical, thermal and optical properties. Recently, much attention has been focused on graphene based devices. There is a growing need for developing new, simple, and cost-effective techniques to obtain stable graphene sheets on substrate. We present a simple and efficient method to covalently immobilize graphene on silicon wafers. Large graphene sheets were covalently attached to functionalized wafer surface by a simple heat treatment under ambient condition. The formation of single and multiple layers of graphene were confirmed by Raman spectroscopy, optical and atomic force microscopy. Evidence of covalent bond formation was given by X-ray photoelectron spectroscopy and solvent sonication treatment. In addition, this method can be readily applied to other substrates. This provides a facile approach to the construction of graphene-based integrated circuits on a wide range of substrates. The method offers immense opportunities to investigate how surface and interface chemistry affect the electronic properties and performance of graphene-based electronic devices.

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7. Liu, L., Engelhard, M. H., Yan, M. *J. Am. Chem. Soc.* **128** (43), 14067-14072 (2006).

#### GR-TuP3 Edge Structures of Graphene Nano-Patches Grown on the 6H-SiC(0001) Surface, *I. Kim, C. Hwang, W. Kim*, Korea Research Institute of Standards and Science, Republic of Korea

Graphene nanoribbons (GNR) are currently considered as one of the most promising materials for future nanoelectronic devices due to its exceptional physical properties. We investigated the possibility of the growth of GNR on the vicinal 6H-SiC(0001) surface using Scanning Tunneling Microscopy. We observed the formation of the ribbon-like single-layer graphenes with sharp edge structures at the initial stage of thermal graphitization process of the SiC(0001) surface. However, the overall long-range ordering of the steps of the bare vicinal surface was found out to be lost during graphitization process, and only the local short range ordering of the steps

with graphene layer patches existed on the entire surface. From the atom-resolved STM images, we clearly identified the armchair and zigzag edge structure for several ribbon-like graphene nanostructures, and found out that the zigzag structure were more frequently observed than the armchair structure. Scanning tunneling spectroscopy experiment was also carried out over the graphene nano-patches to examine the local electronic states at the edge structures.

#### GR-TuP4 Graphene on Demand, *P. Sessi*, Politecnico di Milano, Italy, *J.R. Guest, M. Bode, N.P. Guisinger*, Argonne National Laboratory

The ultrahigh vacuum (UHV) scanning tunneling microscope (STM) has been utilized for controllably patterning regions of pristine graphene at the nanometer scale from an otherwise hydrogen saturated surface. We have found that the hydrogen saturation of graphene epitaxially grown on 4H:SiC(0001) is stable at room temperature and completely alters the original electronic properties which are no longer graphene-like. In addition to characterizing the structural and electronic properties of the surface at the atomic-scale, we have utilized the STM as a patterning tool via electron stimulated desorption of hydrogen, leaving behind regions of graphene. The STM enables a significant level of control and subsequent characterization of the graphene patterns at the highest resolution. With spectroscopic techniques we are able to extract electronic information of the patterned graphene regions. For patterned regions that are roughly 20 nm or greater, the inherent electronic properties of graphene are completely recovered. Below 20 nm we start to see dramatic variations in the electronic properties of the graphene as a function of pattern size.

# Wednesday Morning, November 11, 2009

## Graphene Topical Conference

Room: C3 - Session GR+MI-WeM

### Spins in Graphene: Injection and Manipulation

Moderator: O.M.J. van 't Erve, Naval Research Laboratory

8:20am **GR+MI-WeM2 Graphene Extraordinary Magnetoresistive Devices**, *S. Pisana, P.M. Braganca*, Hitachi GST, *M. Pelliccione*, Stanford University, *M. Nishioka, N. Smith, E.E. Marinero, B.A. Gurney*, Hitachi GST

Extraordinary magnetoresistance (EMR) has recently attracted interest for magnetic field sensing applications in the magnetic storage industry [1]. The effect is particularly attractive given the magnitude of its response, which is comparable to current giant magnetoresistive sensors for mesoscopic device sizes, and its lack of thermal magnetic noise, as the structure does not incorporate ferromagnetic materials. EMR devices consist of hybrid semiconductor-metal structures in which the exclusion of current from a metal shunt in a magnetic field modulates the resistance of the device. This functionality can be advantageously combined with the Hall effect with appropriate variations in the device's lead configuration [2].

The EMR response is proportional to the semiconductor's mobility, among other factors. Furthermore, the successful implementation of this type of device for future read sensors in magnetic storage applications restricts the sensing element's position within a few nanometers from the source of magnetic field.

Graphene, a single atom-thick layer of graphite, is a promising electronic material, given its high mobility, high current carrying capabilities and linearly dispersive electronic bands [3]. These qualities make it a promising candidate for magnetic field sensing in an EMR device, allowing for the conceptually smallest magnetic spacing in a structure that is free from thermal magnetic noise.

In this work, we outline the first implementation of graphene EMR devices. We will discuss their mesoscopic fabrication and demonstrate response that is comparable to current magnetic field sensors. Devices with minimum feature of 150 nm (Figure 1) show signals above 2 mV in magnetic fields of 350 Oe at room temperature. The results are summarized in the context of future magnetic field sensors for terabit density data storage.

[1] Solin, S. A.; Thio, T.; Hines, D. R. & Heremans, J. J.; *Science* **289**, 1530 (2000)

[2] Boone, T. D.; Smith, N.; Folks, L.; Katine, J. A.; Marinero, E. E. & Gurney, B. A.; *IEEE Electron Device Letters* **30**, 117 (2009)

[3] Geim, A. K. & Novoselov, K. S.; *Nature Materials* **6**, 183 (2007)

8:40am **GR+MI-WeM3 Electronic Spin Transport and Spin Precession in Single Graphene Layers at Room Temperature**, *B.J. van Wees, N. Tombros*, University of Groningen, the Netherlands **INVITED**

I will give an overview of electron spin injection, spin transport, spin precession and spin manipulation in graphene. The focus will be on recent experiments on single graphene field effect devices with ferromagnetic contacts. The use of the so-called non-local geometry allows a detailed investigation of various aspects of spin injection and spin transport.

I will first give a basic introduction into the "standard model" for spin transport and show how it can be applied to carbon systems, in particular graphene. The Bloch equations will be explained, which describe the processes of spin diffusion, drift, precession and relaxation. Following that will discuss that:

a) Spins can be transported through a graphene layer with a spin relaxation length of about 1.5 micrometer. By applying a perpendicular magnetic field Hanle spin precession can be studied and information about spin relaxation and the carrier diffusion can be obtained [1].

b) By applying a large DC electric field the transport of spins between injector and detector can be manipulated (sped up or slowed down) using carrier drift [2].

c) The spin relaxation is found to be slightly anisotropic, with spins directed perpendicular to the graphene plane relaxing faster than spins directed in the plane [3].

d) Spins can be injected into graphene with an injection efficiency up to 20 percent. This injection efficiency can be enhanced by a current bias which takes the carriers away from the injecting contacts. In this way injection efficiencies up to 38% have been achieved [4].

e) We have observed a scaling between the spin relaxation times and lengths and the carrier mobility in graphene [5,6]. I will discuss the

possibility that in intrinsic graphene (where the carriers are only scattered by electron-phonon interaction) spin relaxation lengths of 100 micrometer in graphene at room temperature might be possible, and even longer ones at lower temperatures. Related to that I will discuss the potential of graphene for future spintronics applications.

[1] N. Tombros et al., *Nature* **448**, 571 (2007)

[2] N. Tombros et al., *Phys. Rev. Lett.* **101**, 046601 (2008)

[3] C. Jozsa et al., *Phys. Rev. Lett.* **100**, 236603 (2008)

[4] C. Jozsa et al., *Phys. Rev. B* **79**, 081402 R (2009)

[5] M. Popinciuc et al., submitted to *Phys. Rev. B*.

[6] C. Jozsa et al, in preparation.

9:20am **GR+MI-WeM5 Quantum Hall Effect in Suspended Graphene Devices**, *S.Y. Jung, N.N. Klimov*, NIST and University of Maryland, College Park, *J.A. Stroscio, D.B. Newell, N.B. Zhitenev*, National Institute of Standards and Technology

High carrier mobility and long coherence lengths are one of the main attributes which have attracted so much attention to graphene as a new electronic material. Recent studies have shown that the mobility in graphene is extremely sensitive to disorder, particularly coming from substrate interactions [1]. Substrate interactions can be minimized or possibility eliminated by fabricating suspended graphene devices [2]. In this presentation, we present results where we systematically study the quantum Hall effect in suspended graphene devices varying device geometry and disorder. Suspended graphene devices allow for a broad range of particular realizations of the disorder potential. Magnetotransport properties are investigated at various temperatures and with respect to the influence of current annealing. Device geometries with two- and four-probe terminals and different aspect ratios are compared and the effects of disorder potential modifications are discussed.

[1] J. Martin et al, *Nature Phys.* **4**, 144 (2008).

[2] K. I. Bolotin et al, *Phys. Rev. Lett.* **101**, 096802 (2008).

9:40am **GR+MI-WeM6 Spin Injection and Transport in Single Layer Graphene**, *W. Han\*, K. Pi, K. McCreary, W. Bao, C.N. Lau, R. Kawakami*, University of California, Riverside

Single-layer graphene (SLG) is an attractive material for spintronics due to its tunable carrier concentration and polarity, weak spin-orbit coupling, its quasi-relativistic band structure with symmetric electron and hole bands. We fabricated the SLG spin valves using transparent Co/SLG contacts and studied the spin dependent properties by non-local magnetoresistance (MR) measurements at room temperature. Hanle effect confirms that the non-local signal originates from spin injection and transport and gives a spin relaxation time of ~84 ps and a spin diffusion length of ~1.5  $\mu\text{m}$ . Spacing dependence of the non-local MR indicates a spin diffusion length of ~1.6  $\mu\text{m}$  and a spin injection/detection efficiency of 0.43. Gate voltage dependence shows that the non-local MR is proportional to the conductivity of the SLG, which is the predicted behavior for transparent ferromagnetic/nonmagnetic contacts. Bias dependence of the non-local MR reveal an electron-hole asymmetry in which the non-local MR is roughly independent of bias for electrons, but varies significantly with bias for holes.

10:40am **GR+MI-WeM9 Spin Polarized Electrons in Graphene Nanoribbons**, *Y.-W. Son*, Korea Institute for Advanced Study, Korea **INVITED**

In this talk, I will discuss the electronic and magnetic properties of graphene nanoribbons with homogeneous edge structures. Several calculation methods including self-energy corrections and/or strong Coulomb interactions are introduced to study magnetic orderings and their robustness along the zigzag shaped edges on both sides of graphene nanoribbons. I will also discuss special interplays between external electric fields and magnetic orderings in graphene nanoribbons and a possible realization of half-metallic phase in conventional experimental setups with various substrates or molecular adsorptions.

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\* Falicov Student Award Finalist

11:40am **GR+MI-WeM12 Observation of Charge Puddles and Edge Effect in a Graphene Device by Scanning Gate Microscope**, *J.S. Chae*, Seoul National University, Korea, *S.Y. Jung*, *N.B. Zhitenev*, *J.A. Stroscio*, National Institute of Standards and Technology, *Y. Kuk*, Seoul National University, Korea

Despite the recent progress in understanding the geometric structure of defects and edge atoms and their role in the transport property in a graphene sheet, there has been no report showing direct correlation between them. That is because the structural studies were performed using microscopic tools such as scanning tunneling microscopy and other electron microscopies, while the transport property measurement was done macroscopically in a two or four terminal device with a back gate. Scanning Gate Microscope (SGM) is a unique microscopic tool with which the local electronic structure and the transport property of a device can be measured simultaneously. A SGM uses a conducting tip to apply an electric field locally and measures the transport current through two or four contacts and utilizes the same tip to measure the geometric structure in Atomic Force Microscopy (AFM) mode. In this experiment, we observed a conductance change originated from the spatial distribution of charge puddles with a length scale of  $\sim 100\text{nm}$  in a graphene device, very similar to the previously reported results<sup>1)</sup> measured with AFM with a single electron transistor tip. We discovered that the charge puddles can be detected only when the local Fermi level of a gated area by the tip bias is near the Dirac point. We also discovered that there is strong conductance enhancement when the tip is placed along the edges of a graphene device. We think that this edge effect can be explained by the fact that there is a strong charge accumulation at the edges in a charged graphene<sup>2)</sup>

1) J. Martin, N. Akerman, G. Ulbricht, T. Lohmann, J. H. Smet, K. von Klitzing & A. Yacoby, *Nature Physics*, **4**, 144 (2008)

2) P.G. Silvestrov and K.B. Efetov, *Phys. Rev. B* **77**, 155436(2008)

# Wednesday Afternoon, November 11, 2009

## Graphene Topical Conference

Room: C3 - Session GR+AS-WeA

## Graphene: Surface Characterization

Moderator: P. Sheehan, Naval Research Laboratory

### 2:00pm GR+AS-WeA1 Tuning the Properties of Dirac Fermions in Graphene, A. Lanzara, University of California, Berkeley INVITED

Graphene, a one atom thick layer of carbon, the supposedly ideal Dirac material, has been under the radar of theorists and experimentalist for many decades. Although novel physical properties were envisioned, graphene, as any other 2D material, was presumed not to exist in its free state because of long wavelength fluctuations will easily destroy purely 2D membranes. The recent success in isolating a single sheet of graphene has certainly challenged this view. In this talk I will present our experimental work in this field using a combination of spectroscopic and microscopy tools. I'll present experimental evidence of what drives the stability of a graphene membrane and show comparison between exfoliated and epitaxial graphene. I will then discuss the nature of fermions in graphene sheets and how their peculiar electronic structure can be tuned by engineering small terraces of graphene down to nm size, where the physics gets dominated by quantum confinement. The implications of our study on the properties of Dirac materials and their potential role for applications are discussed

### 2:40pm GR+AS-WeA3 Growth of Semiconducting Graphene on Pd(111), S. Kodambaka\*, S.-Y. Kwon, University of California, Los Angeles, C.V. Ciobanu, Colorado School of Mines, V. Petrova, J. Barenco, University of Illinois, V.B. Shenoy, Brown University, V. Gambin, Northrop Grumman Space and Technology, I. Petrov, University of Illinois INVITED

We report *in situ* variable-temperature scanning tunneling microscopy studies of graphene growth on Pd(111) during ethylene deposition at temperatures between 723 and 1023 K. We observe the formation of monolayer graphene islands, 200-2000 Å in size, bounded by Pd surface steps. Surprisingly, the topographic image contrast from graphene islands reverses with tunneling bias, suggestive of a semiconducting behavior. Scanning tunneling spectroscopy measurements confirm that the graphene islands are semiconducting, with a bandgap of  $0.3 \pm 0.1$  eV. Using density functional theory calculations, we attribute this phenomenon to the breaking of hexagonal symmetry due to a strong interaction between graphene and the nearly commensurate Pd substrate. Our findings suggest the possibility of preparing semiconducting graphene layers for future carbon-based nanoelectronic devices via direct deposition onto strongly interacting substrates.

### 4:00pm GR+AS-WeA7 Electronic Corrugation of Rippled Graphene Grown on Ru(0001), B. Borca, S. Barja, Universidad Autonoma de Madrid, Spain, M. Garnica, IMDEA Nanociencia, Spain, J.J. Hinarejos, Universidad Autonoma de Madrid, Spain, A.L. Vazquez de Parga, R. Miranda, UAM & IMDEA Nanociencia, Spain

By means of Scanning Tunneling Microscopy/Spectroscopy (STM/STS) we investigate the electronic and structural modulation of epitaxial graphene grown on Ru(0001). The difference in lattice parameter between graphene and Ru(0001) induces in the graphene overlayer a Moiré pattern with hexagonal order and a lateral periodicity of around 3nm. The bonding with the substrate occurs through the hybridization of C *p*-states with Ru *d* states. Photoelectron spectroscopy shows that the bonding between the graphene and the metallic substrate is not carbidic and the graphene is doped with electrons from the substrate [1].

The hybridization between the carbon and ruthenium atoms changes inside the unit cell [2]. Measuring *dI/dV* maps we observe inhomogeneities in the charge distribution, i.e., electron pockets, in some areas of the ripples. This inhomogeneity can be understood with the help of a tight-binding model which incorporates a periodic potential associated with the structural ripples that induces a shift of the electronic levels and a corresponding charge transfer from conduction to valence bands for some atoms and the opposite in the others [3].

The influence of the modulated electronic structure in the STM images is quite strong. Large differences in corrugation values were measured in the STM images taken exactly in the same spot and changing the bias voltage applied between tip and sample. A compilation of data measured with different tips and different samples show that the apparent corrugation of the Moiré superstructure is essentially constant (0.1 nm) in the interval from

-3V to -1V and diminish as the voltage goes from -1V up to +2V (0.03 nm). For a bias voltage higher than +2.5V, the contrast of the Moiré is inverted. By means of STS we measured, spatially resolved, the surface unoccupied density of states. The *dI/dV* spectra show that the contrast inversion is due to the presence of a strong peak at 3V above the Fermi level in the lower areas of the Moiré structure.

These results demonstrate that the electronic effects in this system are strong enough to overcome the actual geometric corrugation of the graphene layer.

[1] F. J. Himpsel *et al.*, Surf. Sci. Lett. **115**, L159 (1982)

[2] A.B. Preobrajenski *et al.*, Phys. Rev. B **78**, 073401 (2008)

[3] A. L. Vázquez de Parga *et al.*, Phys. Rev. Lett. **100**, 05680 (2008)

### 4:20pm GR+AS-WeA8 Mapping the Geometric and Electronic Structures of Epitaxial Graphene, B. Wang, M. Caffio, R. Schaub, University of St Andrews, UK

A single layer of graphite is known as graphene [1]. It is acknowledged that graphene is a candidate for future electronic devices when supported. Hence a detailed understanding of its geometric and electronic properties is essential. Many studies have in common the observation of moiré superstructures with parameters depending on the mismatch between graphene and substrate [2]. However, an in-depth characterization of the monolayer and its interaction with the support has so far been hampered by experimental limitations, and is strongly debated. We report on a low temperature STM study of graphene grown by low-pressure CVD of ethylene on Rh(111).

Topography measurements show that the C-Rh interactions lead to distortions of the ideal, free-standing graphene, resulting into two sets of superstructures: one is characterized by a coincidence lattice expanded to  $(12 \times 12)/(11 \times 11)$ , while the other is contracted to  $(11 \times 11)/(10 \times 10)$ . The coexistence of several graphene superstructures on a transition metal substrate is in contrast to previous reports. Both superlattices exhibit remarkable coherence lengths, in excess of 1000 nm. However, high-resolution images allow us to precisely monitor the registry of the C atoms with respect to the underlying substrate, revealing that the atomic arrangements are subject to local distortions. Resonance transmission microscopy and spectroscopy, in combination to DFT calculations, were further used to obtain deeper insight into the altering environment at the graphene/Rh(111) interface. Our results show how variations of the local work function within the overlayer unit cell provide invaluable information on the electronic coupling between graphene and Rh(111) substrate.

[1] K.S. Novoselov *et al.*, Nature **438**, 197 (2005)

[2] J. Coraux *et al.*, Nano Letters **8**, 565 (2008)

### 4:40pm GR+AS-WeA9 Rotational Domains of Graphene on Ir(111), S. Nie, E. Loginova, K. Thürmer, N.C. Bartelt, K.F. McCarty, Sandia National Laboratories

We use scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), and low-energy electron microscopy (LEEM) to study four different orientations of single-layer graphene sheets on Ir(111). The most-abundant orientation (R0) has been previously characterized in the literature [1]. While less prevalent than R0, the three additional structures can still occur as relatively large domains, tens of microns in spatial extent. We find that the four types of graphene differ simply in how the graphene sheets are oriented relative to the in-plane directions of the Ir lattice. That is, the four types of graphene are rotational variants, similar to the rotational variants of graphene on Pt(111) [2,3]. Using selective-area LEED, we find the graphene sheets in the other three variants to be rotated by approximately 14°, 18.5° and 30° (R30), respectively. The R30 structure is studied in detail with STM. Compared with the R0 structure, R30 has much less height corrugation. We propose atomic models for the new variants. The moiré structures can be classified using simple geometric rules involving the different periodic and quasiperiodic structural motifs. In addition, LEEM reveals that linear defects form in the graphene sheets during cooling from the synthesis temperature. STM shows that the defects are ridges where the graphene sheets locally delaminate as the Ir substrate contracts. We will describe the factors that control the relative abundance of the different variants.

[1] A. T. N'Diaye, J. Coraux, T. N. Plasa, C. Busse, and T. Michely, New J. Phys. **10**, 16 (2008).

[2] T. A. Land, T. Michely, R. J. Behm, J. C. Hemminger, and G. Comsa, Surf. Sci. **264**, 261 (1992).

[3] M. Sasaki, Y. Yamada, Y. Ogiwara, S. Yagyu, and S. Yamamoto, Phys. Rev. B **61**, 15653 (2000).

\* Paul Holloway Award Winner

5:00pm **GR+AS-WeA10 Deposition and Characterization of HfO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> Dielectrics for Graphene-Based Devices**, *A. Pirkle*, University of Texas at Dallas, *L. Colombo*, Texas Instruments Incorporated, *R.M. Wallace*, University of Texas at Dallas

We present a study of dielectric deposition on graphene and bulk graphite for nanoelectronic device applications. Recent studies have demonstrated that the chemically inert nature of the graphene surface presents challenges to uniform deposition of high quality dielectrics by conventional deposition techniques including ALD. These issues are compounded by the ultrathin nature of graphene, as any covalent bonding that disturbs the underlying graphene lattice is likely to induce scattering and degrade mobility.

In this study, Al, Hf and Si are deposited by electron beam evaporation and subsequently oxidized. We also examine deposition of dielectrics by reactive electron beam evaporation in the presence of a partial pressure of oxygen in the vacuum chamber. Chemical interactions with the substrate are analyzed by means of *in-situ* x-ray photoelectron spectroscopy (XPS) before and after oxidation. Any presence of carbide bonding (AlC, HfC, SiC) is likely to degrade mobility, and we examine the conditions under which carbide bonds are formed. The oxidized films are also characterized by *ex-situ* Raman spectroscopy, particularly with regard to the formation of D-band states that are indicative of damage to the graphene lattice during deposition or oxidation. Surface morphology of the deposited films is studied using atomic force microscopy (AFM), particularly with regard to uniformity as pertinent to thickness scaling.

This work is sponsored by the NRI SWAN center.

5:20pm **GR+AS-WeA11 Large Area Graphene Formed by the Catalytic Exfoliation of Natural Graphite with Invar Alloy**, *J.C. Sung*, KINIK Company, Taiwan, *K. Chang, K. Hsu*, National Taipei University of Technology, Taiwan, *M. Sung*, Advanced Diamond Solutions, Inc.

Graphene is the ideal material for many dream applications, such as single electron transistors, field emission sources [1], light through electrodes, clothing solar cells, terra hertz surface acoustic wave (SAW) filters, wall paper displays, UV light emitting diodes, atomic gas sensors, DNA or antigen wafers...etc. However, a practical method to fabricate meter-sized graphene is still beyond imagination. We made use the mechanism of diamond synthesis in liquid phase and produced graphene of several hundreds microns. Such graphene revealed silk-like tenderness with transparent folding lines. This promising process appears scalable for making device-sized graphene in the near future. This paper also presented many intriguing aspects related to the growth of large graphene. We also proposed a new hypothesis of graphene formation by the catalytic exfoliation of graphite in molten iron group alloys.

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Hite, J.K.: GR+EM+MS-TuM4, 5; GR+TF-TuA3, 7  
Honma, Y.: GR-MoM11, 2  
Hsu, K.: GR+AS-WeA11, 13  
Hughes, Z.: GR+SS-MoA7, 3  
Hwang, C.: GR-MoM3, 1; GR-TuP3, 9

## — I —

Iwasaki, Y.: GR-MoM11, 2

## — J —

Jang, C.: GR+SS-MoA4, 3  
Jernigan, G.G.: GR+EM+MS-TuM4, 5; GR+SS-MoA3, **3**; GR+TF-TuA3, 7  
Jung, I.: GR+TF-TuA10, 8  
Jung, S.Y.: GR+MI-WeM12, 11; GR+MI-WeM5, **10**

## — K —

Kawakami, R.: GR+MI-WeM6, 10  
Kedzierski, J.: GR+SS-MoA6, 3  
Kim, I.: GR-TuP3, 9  
Kim, W.: GR-TuP3, **9**  
Klimov, N.N.: GR+MI-WeM5, 10  
Kodambaka, S.: GR+AS-WeA3, **12**  
Kondo, T.: GR-MoM11, 2  
Kuk, Y.: GR+MI-WeM12, 11  
Kwon, S.-Y.: GR+AS-WeA3, 12

## — L —

LaBella, M.: GR+SS-MoA10, 4; GR+SS-MoA7, 3  
Lanzara, A.: GR+AS-WeA1, **12**  
Lapointe, F.: GR+EM+MS-TuM3, 5  
Lau, C.N.: GR+EM+MS-TuM1, **5**; GR+MI-WeM6, 10  
Levesque, P.: GR+EM+MS-TuM3, **5**  
Lim, S.: GR-MoM3, 1  
Liu, L.-H.: GR+TF-TuA11, 8; GR-TuP2, **9**  
Lock, E.H.: GR-MoM5, 1; GR-TuP1, 9  
Loginova, E.: GR+AS-WeA9, 12; GR+TF-TuA9, 7  
Luxmi, L.: GR+SS-MoA6, 3

## — M —

Maboudian, R.: GR+SS-MoA11, 4  
Marinero, E.E.: GR+MI-WeM2, 10  
Martel, R.: GR+EM+MS-TuM3, 5  
Mastrogiovanni, D.: GR-MoM4, 1  
Mattevi, C.: GR-MoM4, **1**  
McCarty, K.F.: GR+AS-WeA9, 12; GR+TF-TuA9, 7  
McCreary, K.: GR+MI-WeM6, 10  
McEuen, P.L.: GR+TF-TuA1, **7**  
Miller, S.: GR-MoM4, 1  
Miranda, R.: GR+AS-WeA7, 12; GR+TF-TuA4, 7  
Mkhoyan, A.: GR-MoM4, 1  
Moon, J.: GR+EM+MS-TuM4, 5  
Mun, J.: GR-MoM3, **1**  
Myers-Ward, R.L.: GR+EM+MS-TuM4, 5; GR+TF-TuA3, 7

## — N —

Nakamura, J.: GR-MoM11, 2  
Nandamuri, G.: GR+TF-TuA11, 8  
Newell, D.B.: GR+MI-WeM5, 10  
Nie, S.: GR+AS-WeA9, **12**

Nishioka, M.: GR+MI-WeM2, 10

## — O —

O'Donnell, S.: GR-MoM8, 2  
Oh, J.: GR-MoM11, 2

## — P —

Paillet, M.: GR+EM+MS-TuM3, 5  
Pelliccione, M.: GR+MI-WeM2, 10  
Petrov, I.: GR+AS-WeA3, 12  
Petrova, V.: GR+AS-WeA3, 12  
Pi, K.: GR+MI-WeM6, 10  
Piner, R.D.: GR+TF-TuA10, 8  
Pirkle, A.: GR+AS-WeA10, **13**  
Pisana, S.: GR+MI-WeM2, **10**

## — R —

Reinke, P.: GR-MoM8, **2**  
Richardson, C.J.K.: GR+EM+MS-TuM6, 5  
Robinson, J.A.: GR+EM+MS-TuM4, 5; GR+SS-MoA10, 4; GR+SS-MoA3, 3; GR+SS-MoA7, 3; GR+TF-TuA3, 7  
Rotenberg, E.: GR+SS-MoA8, **4**  
Ruoff, R.S.: GR+TF-TuA10, 8; GR-MoM1, 1

## — S —

Schaub, R.: GR+AS-WeA8, 12  
Sessi, P.: GR-TuP4, 9  
Shenoy, V.B.: GR+AS-WeA3, 12  
Shimogaki, Y.: GR+EM+MS-TuM12, 6  
Smith, N.: GR+MI-WeM2, 10  
Snyder, D.: GR+SS-MoA7, 3  
Solanki, R.: GR+TF-TuA11, 8  
Son, Y.-W.: GR+MI-WeM9, **10**  
Srivastava, N.: GR+SS-MoA6, 3  
St-Antoine, B.C.: GR+EM+MS-TuM3, 5  
Stroschio, J.A.: GR+MI-WeM12, 11; GR+MI-WeM5, 10; GR+SS-MoA1, **3**  
Sun, Y.: GR+SS-MoA6, 3  
Sung, J.C.: GR+AS-WeA11, **13**  
Sung, M.: GR+AS-WeA11, 13  
Sutter, E.A.: GR-MoM6, 1  
Sutter, P.W.: GR-MoM6, 1  
Suzuki, T.: GR-MoM11, 2

## — T —

Tedesco, J.L.: GR+EM+MS-TuM4, 5; GR+SS-MoA3, 3; GR+TF-TuA3, **7**  
Thürmer, K.: GR+AS-WeA9, 12  
Tischler, J.G.: GR+SS-MoA3, 3  
Tombros, N.: GR+MI-WeM3, **10**  
Trumbull, K.: GR+SS-MoA10, 4; GR+SS-MoA7, 3

## — V —

van Wees, B.J.: GR+MI-WeM3, 10  
Vazquez de Parga, A.L.: GR+AS-WeA7, **12**; GR+TF-TuA4, 7  
Ventrice, C.A.: GR+TF-TuA10, **8**

## — W —

Wallace, R.M.: GR+AS-WeA10, 13  
Walton, S.G.: GR-MoM5, **1**; GR-TuP1, 9  
Wang, B.: GR+AS-WeA8, 12  
Wang, Q.H.: GR+EM+MS-TuM11, **6**  
Watahiki, K.: GR-MoM11, 2  
Weiland, B.E.: GR+SS-MoA10, 4  
Wetherington, M.: GR+SS-MoA7, 3  
Williams, E.: GR+SS-MoA4, 3

## — Y —

Yan, M.: GR+TF-TuA11, 8; GR-TuP2, 9  
Yang, D.: GR+TF-TuA10, 8

## — Z —

Zhitenev, N.B.: GR+MI-WeM12, 11; GR+MI-WeM5, 10