

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 μ -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 cm^2/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 ~ 340 nm, and spectral resolution of 0.24 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 (H₂) etching; 2) *ex situ* potassium hydroxide (KOH) etching; 3) *ex situ* KOH and *in situ* H₂ 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, 1x10⁻⁶ 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* H₂ 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.

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