Monday Morning, October 18, 2010

Graphene Focus Topic
Room: Brazos - Session GR+SS+TF+EM-MoM

Epitaxial Graphene on SiC
Moderator: P.E. Sheehan, Naval Research Laboratory

8:20am **GR+SS+TF+EM-MoM1 Controlling Carriers in Graphene**, ***G.G. Jernigan****, P.E. Thompson, C.S. Hellberg, J.L. Tedesco, V.D. Wheeler, L.O. Nyakiti, P.M. Campbell, D.K. Gaskill*, Naval Research Laboratory

No technique for graphene synthesis yields controllably doped material. Measurements of carrier density and carrier type produce results that are dependent on extrinsic factors. For example, exfoliated graphene and metal-catalyzed graphene on SiO2 often obtain carriers through unwanted charges in the oxide[1] or by gas adsorption[2] making graphene p-type. Similarly, epitaxial graphene on SiC should be n-type due to work function differences with the underlying SiC substrate[3]. Our recent measurements of graphene grown on Si-face SiC show that device processing steps can cause it to switch between carrier types. Additionally, we have found graphene grown on C-face SiC to be highly doped by Si impurities, which can produce either electrons or holes.

We have begun a series of investigations to impart properties after growth on epitaxial graphene formed on Si- and C-face SiC[4-5]. Substitutional incorporation of impurity atoms can lead to doping in a graphene sheet, if their concentration does not drastically affect the pi-network. This can be achieved by selective oxidation to remove C atoms from the graphene lattice and by molecular beam deposition (MBE) of dopants with controllable ultra-low fluxes to fill the C vacancies. It is important to note that Group III and V dopants can maintain the 2D geometry of the graphene sheet without producing an unsaturated bond (as they do when incorporated into the bulk of Si.) Thus, the extra p-orbital electrons from the Group V elements can be added to the graphene pi-network, or Group III elements can provide extra holes, without adversely affecting carrier mobility. Using MBE, we have substitutionally doped graphene with B and P. Ultraviolet photoelectron spectroscopy (UPS) is used to observe shifts in the Fermi level resulting from doping, and we have seen up to a 110 meV shift with 1% B in the lattice of graphene. Discussion of scanning tunneling microscopy (STM) observations of dopant placement and electrical properties will be presented. Density functional theory has been used to compute the density of states for the doped system in support of the STM and electrical measurements.

[1] S. S. Datta, D. R. Strachan, E. J. Mele, and A.T.C. Johnson, Nano Lett. 9 (2009) 7.

[2] Y. Dan, Y. Lu, N.J. Kybert, Z. Luo and A.T.C. Johnson, Nano Lett., 9 (2009) 1472.

[3] T. Filleter, K. V. Emtsev, Th. Seyller, and R. Bennewitz, Appl. Phys. Lett. 93 (2008) 133117.

[4] G.G. Jernigan, et al., Nano Lett. 9, 2605 (2009).

[5] J.L. Tedesco, B.L. VanMil, R.L. Myers-Ward, J.M. McCrate, S.A. Kitt, P.M. Campbell, G.G. Jernigan, J.C. Culbertson, C.R. Eddy, Jr., and D.K. Gaskill, Appl. Phys. Lett., 95, 122102 (2009).

8:40am **GR+SS+TF+EM-MoM2 The Role of Carbon Surface Diffusion on the Growth of Epitaxial Graphene on SiC**, ***T. Ohta****, N.C. Bartelt, S. Nie, K. Thürmer, G.L. Kellogg*, Sandia National Laboratories

Growth of high quality graphene films on SiC is regarded as one of the more viable pathways toward graphene-based electronics. Graphene films are readily formed on SiC by preferential sublimation of Si at elevated temperature. Little is known, however, about the atomistic processes of interrelated Si sublimation and graphene growth. We have observed the formation of graphene on SiC by Si sublimation using low energy electron microscopy, scanning tunneling microcopy, and atomic force microscopy. This work reveals unanticipated growth mechanisms, which depend strongly on the initial surface morphology. Carbon diffusion governs the spatial relationship between Si sublimation and graphene growth. Isolated bilayer SiC steps generate narrow ribbons of graphene by a distinctive cooperative process, whereas triple bilayer SiC steps allow large graphene sheets to grow by step flow. We demonstrate how graphene quality can be improved by controlling the initial surface morphology to avoid the instabilities inherent in diffusion-limited growth. This work is supported by the LDRD program at Sandia Labs and the US DOE Office of Basic Energy Sciences, Division of Materials Science and Engineering (DE-AC04-94AL85000), and was performed in part at CINT (DE-AC04-94AL85000). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Co., for the U.S. DOE NNSA (DE-AC04-94AL85000).

9:00am **GR+SS+TF+EM-MoM3 Epitaxial Graphene on SiC(0001)**, ***T. Seyller***, Universität Erlangen, Germany **INVITED**

The properties of graphene, its fabrication, and its application are very active fields of research. The large carrier mobility and prospects for room-temperature ballistic transport raise hopes for application of graphene in electronic devices. Applications, however, demand growth methods suitable for producing graphene layers on a wafer scale. While this goal is impossible to reach with mechanical exfoliation, epitaxial graphene (EG) grown on the basal plane surfaces of silicon carbide (SiC) offers a much better prospective. In this talk I shall review studies of the structural, electronic, and transport properties of EG grown on SiC by solid-state decomposition at elevated temperatures. The first part describes a study of the electronic structure and structural properties of EG which can conveniently be determined using surface science techniques. In the second part I demonstrate how the growth of EG is improved by going from the traditional growth environment, namely ultrahigh vacuum, to an Argon atmosphere. The latter method leads to vastly improved EG films with properties similar to those of exfoliated graphene. Finally I shall discuss how the interface between SiC and graphene can be controlled by intercalation of foreign atoms.

9:40am **GR+SS+TF+EM-MoM5 Structural Defects in Epitaxial Graphene Layers Synthesized on 4H-SiC(000-1) Substrate - Transmission Electron Microscopy (TEM) Studies**, *J. Borysiuk*, University of Warsaw, Poland, ***S.K. Krukowski***, Polish Academy of Sciences, Poland

Main structural defects in graphene layers, synthesized on the carbon-terminated face, i.e. SiC($000\underline{1}$) face of 4H-SiC substrate, are discussed. The discussed structures include in-plane edge dislocations, grain boundaries, puckers, etc. These defects are investigated using High Resolution Transmission Electron Microscopy (HRTEM), revealing their atomic arrangement. The mechanism of creation of such defects, in relation to the misalignment to the underlying crystallographic structure of the SiC substrate is elucidated. The relation between the SiC surface structure, including the presence of the single atomic steps, the sequences of atomic steps, and also the macrosteps, and the emergence of edge dislocations or boundaries between the regions having different crystallographic orientation in the graphene layers, is shown. In addition, the structures containing different stacking sequences of carbon atoms in the graphene layers are presented. The presented C-layers stacking includes AA, AB, ABC sequences, and also the stacking close to turbostratic stacking.

10:00am **GR+SS+TF+EM-MoM6 Controlling the Growth Rate of Graphene on Silicon Carbide**, ***D.B. Torrance****, D.L. Miller, M. Phillips, H. Tinkey, E. Green, P.N. First*, Georgia Institute of Technology

Controlled thermal decomposition of silicon carbide is so far the most effective method for growing high-quality graphene epitaxially and at the wafer scale. In this work we simultaneously study the graphenization of SiC(0001) and SiC(000-1) as a function of temperature and buffer-gas pressure in a custom-built ultrahigh vacuum (UHV) induction furnace. The buffer gas is modeled as a homogeneous diffusion medium using kinetic theory. In-situ characterization by both Auger electron spectroscopy and low-energy electron diffraction (LEED) was used to determine the pressure- and temperature-dependent growth rate of graphene layers. Sample quality was further assessed ex-situ using a variety of techniques such as Raman spectroscopy and scanning tunneling microscopy.

10:40am **GR+SS+TF+EM-MoM8 Evidence of Screw Dislocations in Epitaxial Graphene Islands**, *J.K. Hite, J.C. Culbertson,* Naval Research Laboratory, *J.L. Tedesco,* National Institute of Standards and Technology, *M.E. Twigg, A.L. Friedman, P.M. Campbell, R.L. Myers-Ward,* ***C.R. Eddy, Jr.****, D.K. Gaskill*, Naval Research Laboratory

Epitaxial graphene (EG) has lately garnered enormous interest, due to its high free-carrier mobility and compatibility with semiconductor processing. In fact, the first EG RF field effect transistor has been demonstrated.[1] However, the growth mechanism of this material is not well understood. Current RF device work has been on the Si polar face of (0001) semi-insulating SiC substrates as EG on this face mainly consists of 1 monolayer of graphene. In contrast, the C-face consists of a dozen or more graphene layers and has a rougher morphology. Yet, there is significant interest in obtaining few layer, smooth EG on the C-face of SiC due to its better electrical properties as compared to the Si-face. Recently, it was shown that C-face EG grown in Ar ambient slows the growth rate, and under certain conditions results in islanding of the graphene on the C-face.[2] These islands open the possibility of investigating the initial stages of graphene growth.

Electron channeling contrast imaging (ECCI) has previously been used to investigate threading dislocations in semiconductors such as GaN and SiC.[3,4] In this work, ECCI is used for the first time to investigate graphene island morphology as a function of island size and growth conditions. Using this characterization tool, single threading screw dislocations (TSDs) have been found in the center of small EG islands (>20μm diameter). ECCI images confirm that these small graphene islands are forming in hexagonal recesses below the surface of the SiC substrate. For larger islands, the evidence of TSDs disappears suggesting that as the islands grow or coalesce to larger diameters either the TSD becomes buried or no longer contributes to growth. Once the islands become this large, the graphene begins to grow above the SiC surface, unlike the smaller islands. After removal of the EG by various methods, TSDs are still observed in the centers of the pits formed by the small island graphene growth. After some removal efforts, many pits retained small triangles of graphene around the TSD . These results are consistent with Raman and AFM maps of the islands that demonstrate that the centers of the islands are much deeper and the graphene thicker than the surrounding graphene. The evidence of TSDs in the centers of these C-face EG islands strongly suggests that these dislocations serve as nucleation sites for EG growth, where the TSD may provide an escape pathway for sublimated silicon atoms during the growth process.

[1]J.S. Moon *et al.*, IEEE Electron Dev Lett **31**, 260, 2010

[2]J.L. Tedesco *et al*., Appl Phys Lett, in press

[3]Y.N. Picard *et al*., Scripta Materiala **61**, 773, 2009

[4]Y.N. Picard *et al*., Appl Phys Lett **90**, 23401, 2007

11:00am **GR+SS+TF+EM-MoM9 Direct Measurement of the Energy Gaps Involved in the Lifting of the Valley and Spin Degeneracies in Epitaxial Graphene**,
***Y.J. Song**, A.F. Otte,* CNST/NIST; Maryland NanoCenter UMD*, D.B. Torrance, Y. Hu, P.N. First, W.A. de Heer,* Georgia Institute of Technology*, J.A. Stroscio*, CNST/NIST

Landau levels on epitaxially grown graphene were recently mapped both spatially and energetically using scanning tunneling spectroscopy in magnetic fields at 4 K [1]. In this talk we present new measurements, made at ≈10 mK, of all four electron states resulting from the lifting of the fourfold spin- and valley-degeneracy of the $N = 1$ Landau level in applied magnetic fields. We show that the energy splitting from the broken valley degeneracy is ten times larger than electron spin splitting in our samples. When the Fermi level lies inside the four-fold Landau manifold, significant electron correlation effects result in an enhanced valley splitting at even filling factors, and an enhanced electron spin splitting at odd filling factors. Most surprisingly, we observe new many body states with top-layer Landau level filling factors 7/2, 9/2, and 11/2.

[1] David L. Miller, Kevin D. Kubista, Gregory M. Rutter, Ming Ruan, Walt A. de Heer, Phillip N. First, and Joseph A. Stroscio, Science **324**, 924-927 (2009).

11:20am **GR+SS+TF+EM-MoM10 Morphology of Epitaxial Graphene on SiC: Nano-Objects, Nano-Cracks, and Ribbons**,
***S. Chiang**,* Univ. of California at Davis*, N. Camara,* IMB-CNM-CSIC, Spain*, S. Vizzini, D. Martinotti,* CEA-Saclay, France*, H. Oughaddou,* Univ. de Cergy-Pontoise & CEA Saclay, France*, H. Enriquez,* Univ. de Paris-Sud/Orsay & CEA-Saclay, France*, Ph. Godignon,* IMB-CNM-CSIC, Spain*, J. Camassel,* GES, UMR-CNRS, France*, P. Soukiassian*, Univ. de Paris-Sud/Orsay & CEA-Saclay, France

We use scanning tunneling microscopy/spectroscopy (STM/STS) and low energy electron microscopy (LEEM) to investigate epitaxial graphene grown under vacuum on a 4H-SiC(000-1)-C-face substrate and self-organized parallel graphene ribbons grown in a furnace on a 6H-SiC(000-1) C-face sample covered by a graphite cap. On the vacuum grown graphene, we observed two types of nanostructures including nano-objects and nano-cracks. The results reveal that these nano-objects are located at the graphene/SiC interface leading to electronic interface states. Their height profiles suggest that these objects are made of packed carbon nanotubes confined vertically and forming mesas at the SiC surface. We also find nano-cracks covered by the graphene layer that, surprisingly, is not broken going deep into the crack, with no resulting electronic interface state. Therefore, unlike the above nano-objects, these cracks should not affect the carrier mobility. LEEM has been used to observe the formation of graphene ribbons grown on SiC in a furnace. The morphology and distribution of the ribbons has been examined, and their typical size is about 1 μm wide and 10 μm long.

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