Monday Morning, October 31, 2011

Graphene and Related Materials Focus Topic
Room: 208 - Session GR-MoM

Graphene Growth

Moderator: D.K. Gaskill, U.S. Naval Research Laboratory

8:20am GR-MoM1 Atomic Layer Growth of Graphene, *L. Colombo*, Texas Instruments Incorporated, *C. Magnuson, Y. Hao, X. Li, R.S. Ruoff*, University of Texas at Austin **INVITED**
Graphene has been shown to have unique electronic, chemical and physical properties over the past few years and this is opening many opportunities for its use. However, to date most of the experiments have been performed on graphene exfoliated from natural graphite and the graphene films have been rather small, hundreds of microns squared. Transport properties equivalent to those achieved on exfoliated graphene have also been achieved on layers of graphene on SiC; but this graphene is not easily transferred to other substrates. There is now a need to develop high quality, large area single crystal graphene. Li et al. discovered the growth of graphene on copper metal foils by chemical vapor deposition (CVD) using methane gas which led for the first time to the growth of meter square graphene. The current CVD process can indeed grow very large graphene films but the films are polycrystalline. The domain size for the baseline process is a few tens of microns in diameter and in principle there is pathway to achieving much larger domain size films. Large single crystals, 0.5 mm size, have recently been reported and perhaps we can learn from these results how to extend them to grow even large graphene films with higher quality. The growth mechanisms of graphene and single crystal growth of graphene will be presented and discussed together with a discussion of what the semiconductor industry would need to make graphene a reality.

9:00am GR-MoM3 Graphene on Ni(111): Growth and Defects, *M. Batzill*, University of South Florida, *J. Lahiri*, Brookhaven National Laboratory, *I.I. Oleynik, L. Adamska*, University of South Florida
Using scanning tunneling microscopy (STM), Auger electron spectroscopy (AES), and low energy electron microscopy (LEEM) we have investigated the growth of graphene on Ni(111) surfaces by carbon segregation from the bulk. We reveal two distinct growth modes for graphene growth. Between 480 and 650 °C graphene forms on clean Ni(111) and below 480 °C graphene grows by an in-plane conversion of a surface carbide phase [1,2]. This is the first time that graphene formation is observed by transformation of a surface carbide. STM indicates that a lattice-matched, one-dimensional in-plane domain boundary between graphene and the carbide forms. In the presence of the carbide graphene grows by replacing Ni-atoms with carbon at this interface. In addition to the growth of graphene we will also briefly discuss atomic-scale defects that can be synthesized in Ni-supported graphene. Different adsorption configurations of graphene on Ni will result in domain boundaries that exhibit pairs of pentagonal and octagonal carbon rings [3]. These line defects have similar electronic properties to graphene zig-zag edges but without the dangling bonds.

[1] J. Lahiri, T. Miller, L. Adamska, I.I. Oleynik, M. Batzill Nano Lett. 11, 518 (2011)

[2] J. Lahiri, T. Miller, A.J. Ross, L. Adamska, I.I. Oleynik, M. Batzill New J. Phys. 13, 025001 (2011).

[3] J. Lahiri, Y. Lin, P. Bozkurt, I.I. Oleynik, M. Batzill Nature Nanotechnol. 5, 326 (2010).

9:20am GR-MoM4 Investigating Graphene Nucleation on C-Face SiC via Electron Channeling Contrast Imaging and Raman Mapping, *J.K. Hite*, *J.D. Caldwell, J.L. Tedesco, R.L. Myers-Ward, C.R. Eddy, Jr., D.K. Gaskill*, U.S. Naval Research Laboratory
Epitaxial graphene (EG) has lately garnered enormous interest, due to its high free-carrier mobility and compatibility with semiconductor processing. Furthermore, EG RF field effect transistors have been demonstrated.[1] Current RF device work has been on the Si face (0001) semi-insulating 6H-SiC substrates as EG on this face mainly consists of mono- and bilayer graphene. In contrast, the C-face consists of up to a dozen or more graphene layers and has a rougher morphology. Even so, there is significant interest in obtaining few layer, smooth EG on the C-face of SiC due to its superior mobility (for similar charge density) as compared to growth on the Si-face. However, the growth mechanism of this material is not well understood. Recently, it was shown that C-face EG grown in an argon ambient slows the growth rate and, under certain conditions, results in localized growth of the graphene on the C-face.[2] These localized areas, referred to herein as graphene covered basins (GCBs), create the possibility of investigating the initial stages and mechanism of graphene growth on the C-face of SiC.

Previously, we had used electron channeling contrast imaging (ECCI) to investigate GCB morphology as a function of GCB size and growth conditions for EG growth on C-face SiC.[3] Threading screw dislocations (TSDs) in the SiC substrate were found to be nucleation sites for GCBs. The TSDs were easily identified at the centers of small EG GCBs (<20 μm diameter). This work shows the evidence that the TSDs fade then disappear with increasing GCB size, suggesting that as the GCBs grow or coalesce to larger diameters the TSDs become buried. Concurrently, Raman mapping experiments determined graphene thickness and quality at GCB genesis; the maximum graphene thickness for TSD detection in the SiC by ECCI was also determined. Initial findings with Raman mapping confirm ECCI results showing that the graphene is thicker in the middle of the GCB. The small GCBs (<20 μm), which exhibit a strong TSD signal, are comprised of roughly 3-4 monolayers of graphene in the center, with decreased thicknesses near the edge. In addition, the Raman 2D spectral linewidth for these small GCBs were correlated with thickness. Atomic force and scanning electron microscopy of the same GCBs were used to obtain correlated morphological details. These results imply that graphene growth is complex on this polar surface of SiC.

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

[2] J.L. Tedesco *et al.*, Appl. Phys. Lett. **96**, 222103, 2010.

[3] J.K. Hite *et al.*, Nano Lett. **11**, 1190, 2011.

9:40am GR-MoM5 Graphene Band Engineering on One-Dimensionally-Modulated SiC Substrate, *K. Nakatsuji, T. Yoshimura*, University of Tokyo, Japan, *K. Morita, S. Tanaka*, Kyushu University, Japan, *F. Komori*, University of Tokyo, Japan
Engineering of the gapless graphene Dirac bands has been studied for understanding and useful applications of distinctive electronic properties due to their chiral nature. It has been theoretically shown that the group velocity of the bands can be tuned anisotropically by external potentials of a few tens nanometer scale. [1] A three-hold anisotropy of the conical band was found for a single-layer graphene modified by adsorbed metal clusters [2] while it was partly masked by the intrinsic trigonal warping of the bands. Here, we report uniaxial deformation of the Dirac cone of the single-layer graphene grown on a vicinal SiC(0001) substrate.

In the experiment, single-layer graphenes were thermally made by annealing in 5 x 10^{-5} Torr N_2 gas at 1970 K for 1 sec on Si-terminated surfaces of nitrogen-doped 6H- and 4H-SiC(0001) substrates vicinal to the [1-100] direction. The tilting angle was either 4 degree for the 6H substrate or 8 degree for the 4H substrate. The terraces were elongated as confirmed by scanning tunneling and atomic force microscopes. The terrace widths in the [1-100] direction were 21 and 13 nm for the 4- and 8-degree-off substrates, respectively, while the width perpendicular to the [1-100] direction was commonly 100 nm.

The shapes of the graphene pi and pi* bands were studied using angle-resolved photoemission spectroscopy (ARPES) at 130 K. The graphene and reconstructed interface structures were confirmed by low energy electron diffraction (LEED) before the ARPES measurements, and we adjusted the orientation of the crystal axes using LEED. The Dirac point was 0.4 eV below Fermi energy E_F as previously observed graphene grown on flat SiC(0001) substrates. The spectrum width of the graphene on the 8-degree-off substrate is larger than that on the 4-degree-off substrate because of the electronic scattering at the curved area of graphene on the substrate step edges as discussed for the graphene on a SiC(0001)substrate vicinal to the [11-20] direction. [3]

The constant-energy ARPES intensity maps of the pi and pi* bands for the graphene on the 4-degree-off substrate are trigonally warped, and almost agree with the previous reports. On the other hand, the intensity maps for the graphene on the 8-degree-off substrate are significantly elongate in the [1-100] direction. The group velocity of the pi* band in the G-K direction parallel to [1-100] is more than 20 % lower than the velocity in the other G-K directions. The velocity reduces in the direction parallel to the substrate slope in contrast to the theoretical prediction.[1]

References

1. C.-H. Park, L. Yang, Y.-W. Son, M. L. Cohen, and S. G. Louie, Nat. Phys. **4**, 213 (2008).

2. S. Rusponi, M. Papagno, P. Moras, S. Vlaic, M. Etzkorn, P.M. Sheverdyaeva, D. Pacile, H. Brune and C. Carbone, Phys. Rev. Lett. **105** 246803 (2010).

K. Nakatsuji, Y. Shibata, R. Niikura, F. Komori, K. Morita and S. Tanaka, Phys. Rev. B**82** 045428 (2010).

10:00am GR-MoM6 Graphene Growth on Au(111), *J. Wofford*, University of California at Berkeley and Lawrence Berkeley National Laboratory, *E. Starodub, N.C. Bartelt, K. McCarty*, Sandia National Laboratories, *O. Dubon*, University of California at Berkeley and Lawrence Berkeley National Laboratory

Studies on the growth of graphene on metal surfaces indicate that the strength of the interaction between the two materials plays a significant role in determining the evolution and final properties of the resulting film. A number of relatively strongly interacting graphene-metal systems, such as – Ru and –Ir, have been studied comprehensively, but the graphene-Cu system remains the only comparatively weakly interacting combination to have been so scrutinized [1]. Comparisons between graphene growth on Cu and Au provide an opportunity to systematically understand graphene growth on weakly interacting substrates. For example, both Cu and Au have low C solubility, but the mismatch between the lattice of graphene aligned with that of the metal's (111) surface is substantially larger for Au than for Cu. To examine what effect these differences have, we used low-energy electron microscopy (LEEM) to observe graphene growth on Au (111) in UHV by direct deposition of C from a heated graphite rod. Low-energy electron diffraction (LEED) analysis of the pre-growth Au (111) surface showed the characteristic "herringbone" reconstruction peculiar to Au. Graphene islands nucleate rapidly upon exposure to the C flux, suggesting a relatively low equilibrium C adatom concentration on the otherwise bare Au surface. The graphene islands nucleate simultaneously across the surface with a slight preference for nucleation along Au step edges rather than on terraces. The nucleation density is substantially higher than previously observed on other metals, causing inter-island impingement to begin at sub-micron sizes. Similar to Cu, no island growth due to C precipitation from the bulk of the Au occurs during sample cooling. We find that the graphene lattice prefers strongly to be aligned with the Au lattice with a small minority of the domains rotated by 30 degrees. The prevalence of the aligned graphene orientation is particularly surprising due to the substantial lattice mismatch involved and calculations predicting a 30 degree relative rotation is preferred [2,3]. We draw comparisons between the observed rotational structure and those predicted by first principle calculations.

[1] J. M. Wofford, *et al.*, Nano Lett. **10**, 4890 (2010).

[2] M. Vanin, *et al*., Phys. Rev. B **81**, 081408 (2010).

[3] C. Gong, *et al*., J. Appl. Phys. **108**, 123711 (2010).

10:40am GR-MoM8 Synthesizing Pristine Epitaxial Graphene and its Impact on Electronic Properties, *V.D. Wheeler, G.G. Jernigan, N.Y. Garces, L.O. Nyakiti, R.L. Myers-Ward, C.R. Eddy, Jr.*, **D.K. Gaskill**, U.S. Naval Research Laboratory

Epitaxial graphene (EG) enables wafer-scale production needed to realize graphene-based technologies. Since monolayer graphene is all surface, any impurities or adsorbed atoms can alter the graphene by doping, acting as scattering sites which decrease the mobility, and creating additional resistances that degrade device performance. Also, impurities and resist residues can increase ohmic contact resistance and impact the ability to deposit uniform gate dielectrics. Achieving pristine graphene surfaces allows ultimate control over future interface formations and thus improves device performance. In this work, an *in-situ* H_2 anneal is explored to attain the pristine epitaxial graphene required to fully realize the advantages of this material for future electronic applications.

EG was grown on semi-insulating, on-axis, (0001) 6H-SiC substrates in an Aixtron VP508 CVD reactor from 1575 to 1650°C for 60 to 180 min. Initially, samples were grown and cooled in a 100 mbar Ar ambient. Chemical analysis, using x-ray photoelectron spectroscopy (XPS), of the as-grown graphene surfaces showed the presence of both O and excess C impurities. These impurities can dope the EG and reduce the mobility, suggesting the need for methods to obtain pristine surfaces.

To address this need, several post-growth treatments were studied. Unlike exfoliated graphene[1], uncontaminated EG surfaces could not be obtained using a 400 °C Ar/H_2 anneal, and wet chemical cleans reduced the surface impurities. A pristine post-growth EG surface was only accomplished with a 1300 °C UHV anneal for 30 min.

Ex-situ UHV anneals are not practical for manufacturing graphene devices, so we explored a new technique incorporating a H_2 anneal during cool down from growth temperature. First, EG samples were cooled in Ar from growth temperature to 1000°C. Next, Ar was evacuated and H_2 introduced at constant pressure. Samples were annealed at 1000°C for 30 min., cooled in H_2 to 700°C, and then the chamber was evacuated. XPS analysis showed that the EG samples have no O impurities and reduced excess C impurities

compared to Ar cooled samples. Also, the signal from the interfacial layer[2] is reduced, and both the graphene and SiC peaks are shifted to lower binding energies, suggesting a reduction in strain between the EG and the SiC substrate. These samples also had a more inert surface, showing only a small amount of adsorbed O (< 2%) after 3 days in atmosphere. Further, van der Pauw Hall measurements revealed a 2X increase in mobility over Ar cooled samples with no change in the sheet concentration magnitude.

1. Ishigami, et. al. *Nano Letters* **7(6)** 1643 (2007)

2. Jernigan, et. al. *Nano Letters* **9(7)** 2605 (2009)

11:00am GR-MoM9 Growth and Characterization of Graphene Films on Cu(111), *Z.R. Robinson, P. Tyagi, H. Geisler, C.A. Ventrice, Jr.,* University at Albany, *H. Yang, T. Valla,* Brookhaven National Laboratory, *A.A. Bol, J.B. Hannon*, IBM T.J. Watson Research Center

Previous studies have shown that monolayer graphene films can be grown on Cu substrates by the catalytic decomposition of various carbon containing molecules. These films are typically grown on poly-crystalline Cu foils, which have a tendency to recrystallize into a {100} texture during the growth procedure. Since graphene crystallizes in a hexagonal lattice and the {100} surface of a face centered cubic lattice has a square symmetry, this is expected to result in multi-domain graphene growth. Because the Cu(111) surface has hexagonal symmetry and a lattice mismatch of 3.7% with graphene, growth on this surface termination has potential for producing films with a lower defect density.

There have been relatively few studies of graphene growth on single crystal Cu substrates, owing to the fact that hydrocarbon source pressures in the range of 100 millitorr are needed, which is incompatible with most UHV systems. In this study, graphene films were grown on Cu(111) substrates by first preparing the clean surface in UHV by sputtering with inert gas ions followed by annealing. The sample was then transferred to a conventional tube furnace where the graphene film was grown by annealing in forming gas to reduce the surface oxide, followed by annealing in ethylene to produce the graphene film.

The growth morphology of the graphene overlayer was characterized using low energy electron microscopy (LEEM) and low energy electron diffraction (LEED). The LEEM shows a mesa-like surface texture with relatively flat terraces covered with graphene and valleys between the terraces with low carbon coverage. Micro-Raman spectroscopy of the terrace regions produces a signal characteristic of a well-ordered graphene overlayer, whereas the Raman signal in the valleys is much weaker and shows a distinct D-peak. The typical lateral dimension of the terraces was ~10 μm. Micro-LEED performed on the terrace sites shows a sharp Moiré pattern. Conventional LEED, which probes a lateral area of ~1 mm, shows a ring structure with increased intensity in the six high symmetry directions of the Cu(111) substrate lattice. This indicates that for this growth procedure there is a quasi-epitaxial relationship between the graphene overlayer and the Cu(111) substrate with rotational disorder of the graphene from mesa to mesa. Synchrotron-based angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) measurements have been performed to probe the electronic band structure of the graphene overlayer. A linear dispersion has been measured in the K direction with the Dirac point located near the Fermi level.

11:20am GR-MoM10 Graphene Growth on Cu(111), *S. Nie*, Sandia National Laboratories, *J. Wofford,* University of California at Berkeley and Lawrence Berkeley National Laboratory, *N.C. Bartelt,* Sandia National Laboratories, *O. Dubon,* University of California at Berkeley and Lawrence Berkeley National Laboratory, *K. McCarty*, Sandia National Laboratories

Large area graphene growth on copper foils has attracted considerable interest because of the low cost and high graphene quality. However, relatively little is understood concerning the effect of substrate crystallographic orientation on the morphological evolution of graphene islands. Complication arises by the fact that the foil surface texture depends on how the foil is manufactured. In previous work we have examined graphene growth on the commonly occurring (100) surface of cold-rolled Cu foil.[1] However, growth on the Cu(111) surface, another often observed orientation in textured Cu foil was not studied.

In this work we investigate graphene growth on single crystal Cu(111) in situ using a carbon evaporator in a low-energy electron microscope (LEEM). We find that graphene first nucleates at defects and impurities. A considerable fraction of the islands is misaligned in plane with the substrate, generating rotational boundaries upon inter-island impingement. Islands are dendritic with distinct lobes, similar to those reported on graphene/Cu(100).[1] However, instead of each lobe being a graphene sheet with a different orientation, all lobes in an individual island form a single crystal. We propose that these dendritic shapes are the result of diffusion-

limited growth. Consistent with this, we find that new island nucleation caused by an increase in the carbon flux occurs equidistant from existing islands. Furthermore, we show that the growth velocity of each lobe is accurately predicted by simulations assuming diffusion limited growth. This diffusion limited growth is in stark contrast with the large carbon attachment barriers seen on Ru and Ir.[2] Unlike graphene growth on Ru(0001) and Ir(111),[2] large densities of carbon adatoms are not detected before island nucleation. Temperature plays an important role in the crystallographic alignment of the graphene film. At high growth temperature (> 900 °C), graphene islands are found closely aligned with Cu, while at low temperature (< 800 °C), increased disorder in the orientation of graphene with respect to Cu(111) is observed in the low-energy diffraction patterns.

1. Wofford, J. M.; Nie, S.; McCarty, K. F.; Bartelt, N. C.; Dubon, O. D., Nano Lett.**, 10**, 4890 (2010).

2. Loginova, E.; Bartelt, N. C.; Feibelman, P. J.; McCarty, K. F., New J. Phys. **10**, 093026 (2008).

11:40am **GR-MoM11 Epitaxial Graphene Growth on Non-Polar 6H-SiC Substrates**, *L.O. Nyakiti, R.L. Myers-Ward, V.D. Wheeler, F.J. Bezares, N.Y. Garces, J.K. Hite, C.R. Eddy Jr., J.D. Caldwell, D.K. Gaskill,* U.S. Naval Research Laboratory

Graphene has attracted recent interest due to its unique electronic properties. Epitaxial graphene (EG) grown on different planes of 6H-SiC can have different morphological and electrical properties. For example, EG grown on the (0001) plane produces single or bilayer regions, step bunched heights of 5–10nm and lower carrier mobility compared to EG on the (000-1) plane that produces multilayer EG with ridge heights up to 80nm. Step bunching introduces conduction anisotropy[1] and poses a challenge to lithography at ≤100nm. To mitigate step heights and improve carrier mobility, we studied the formation of EG on non-/semi-polar surfaces, specifically the (10-10), (11-20), and (03-312). Here, we show the morphology of EG on these non-traditional planes is improved by an order of magnitude compared to vicinal plane growths.

EG samples ($16x16mm^2$) were synthesized on non-polar (10-10), (11-20), and (03-312) substrates. Growth was carried out in an Aixtron VP508 chemical vapor deposition reactor. Prior to EG growth, substrates underwent an *in situ* H_2 etch at 1520°C for 50min., producing a controlled nucleating surface with average RMS of 0.1nm. Subsequent EG growth was conducted under a flowing Ar ambient of 20 standard liters per minute at 100mbar. Micro-Raman spectroscopy contour mapping was used to confirm the presence, thickness and strain variation of EG. Atomic force microscope (tapping mode) and scanning electron microscope was used to extract surface morphology variations.

Initial results show that 15min. of EG growth on (10-10) non-polar surface has horizontal wrinkles, indicative of multiple layers of graphene, peak-to-valley heights ≤5nm, and an RMS of ~0.73nm from a $10x10\mu m^2$ AFM scan. Growth on (11-20) non-polar plane showed the presence of wrinkles (~3nm in height) and an average RMS of 1.1nm. Both (10-10) and (11-20) plane EG do not show the step bunch and terrace morphology typically associated with polar surfaces. While uniform terraces on the (0001) face can be up to several μm wide, the (10-10) and (11-20) plane exhibits smaller terrace widths ~75 and ~115nm, respectively. Finally, EG grown on high order (03-312) plane was observed to have wrinkles as well as vertical ridges that were preferentially oriented parallel to each other and an average RMS of 1.17nm. The distance between the successive ridge peaks was ~500nm. Compared to the RMS values of 2.3 and 3.7nm for EG on (0001) and (000) planes, respectively, all EG films grown on non-/semi-polar orientations were markedly smoother. This work shows that the morphology of EG can potentially be controlled using different SiC orientations.

1.Yakes, M. Y., et al Nano lett. **10,** 1559 (2010)

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