

Graphene and Other 2D Materials Focus Topic Room: 104 B - Session GR+EM+NS+PS+SS+TF-MoM

Growth of 2D Materials

Moderator: T. Ohta, Sandia National Laboratories, B. Ozyilmaz, National University of Singapore

8:20am **GR+EM+NS+PS+SS+TF-MoM1 Using Nitrogenated SiC to Produce Wide-gap Semiconducting Graphene.** *P.I. Cohen, S. Rothwell, University of Minnesota, L.C. Feldman, G. Liu, Rutgers University, E.H. Conrad, F. Wang, Georgia Institute of Technology*

All carbon electronics based on graphene has been an elusive goal. For more than a decade, the inability to produce significant band gaps in this material has prevented the development of semiconducting graphene. While chemical functionalization was thought to be a route to semiconducting graphene, disorder in the chemical adsorbates leads to low mobilities that have proved to be a hurdle in its production. In this work we demonstrate a new approach to produce semiconducting graphene that uses a small concentration of covalently bonded nitrogen, not as a means to functionalize graphene, but instead as a way to constrain and bend graphene. First, about half a monolayer of nitrogen was adsorbed onto a carbon-polar SiC(000-1) surface by annealing in NO. X-ray photoelectron spectroscopy (XPS) indicates that the layer of N that is introduced forms both C=N and C-N bonds that are stable up to 1550C. Then graphene is grown using a controlled silicon sublimation technique, producing, in this case, 3 or 8 layers of graphene. The N coverage and bonding during this process is determined from the XPS signal. After graphene growth the N coverage is about 7 at. % with its bonding unchanged. Examination of the peak intensity in variable energy XPS suggests that the N remains at the interface and there are no other peaks normally associated with either intercalated or substitutional N in graphene. Scanning tunneling microscopy (STM) confirmed that for the case of either 3 layer or 8 layer graphene, N was not present in the top layer. STM, however, showed that the graphene sheet is buckled with 2-4 nm wide folds. The folds can meander and are 5-25 nm long. In addition, atomic resolution images show that the folds are part of a continuous graphene sheet. The implication is that sp³ bonded N at the interface produces this buckling. Finally, angle resolved photoelectron spectroscopy from the buckled, 3-layer graphene is dramatically different than that from pristine 3-layer graphene. With N at the interface, a bandgap of at least 0.7 eV is resolved, presumably due to a finite size effect. For both 3-layer and 8-layer graphene the Fermi velocity is 0.8×10^6 m/s.

9:00am **GR+EM+NS+PS+SS+TF-MoM3 Graphene Growth on C-face SiC in Argon.** *Z. Robinson, G.G. Jernigan, K. Bussmann, R.L. Myers-Ward, V.D. Wheeler, L.O. Nyakiti, U.S. Naval Research Laboratory, S. Oida, J. Hannon, IBM T.J. Watson Research Center, M. Currie, C. Eddy, D.K. Gaskill, U.S. Naval Research Laboratory*

Graphene growth on Si-face SiC has been shown to have improved uniformity when synthesized in an argon environment instead of in UHV. For C-face growth, which is expected to yield graphene with superior electronic properties due to the absence of the interfacial layer, similar progress has not yet been achieved. It has been shown that growth by confinement controlled sublimation, where the C-face SiC is put in a graphite pillbox during growth, can result in improved quality graphene films. However, it remains unclear whether growth by low pressure sublimation (LPS) in a conventional furnace with an argon overpressure can achieve uniformity and thickness control similar to the Si-face. Therefore, a systematic study of SiC surface preparation by hydrogen etching and subsequent graphene growth in argon has been carried out for C-face SiC substrates in a commercially available Aixtron CVD reactor that has been modified for LPS. This reactor exhibits laminar Ar flow and a uniform temperature profile. In this system, which has the advantage of being able to subject different substrates to identical growth conditions simultaneously, it has been found that relatively small differences in the substrate, such as polytype, can have a drastic effect on the resulting graphene film. In fact, growth conditions that result in complete coverage of at least a single layer of graphene on a nominally on-axis 4H substrate have been shown to result in 60% coverage for a nominally on-axis 6H substrate. Therefore, it has been found that optimizing the growth conditions for a particular substrate is crucial if graphene thickness and uniformity are to be controlled. Additionally, it has been suggested that unintentional oxidation of the SiC substrate during growth in high pressures of argon is a potential cause for the non-uniform growth that is observed on the C-face [1]. Several experiments in which LPS grown C-face graphene was transferred to a UHV system equipped with *in situ* XPS have been conducted, and it has

been found that UHV anneals of up to 1200 °C were necessary in order to desorb the oxygen. Following the anneal, exposure to atmospheric conditions resulted in the return of only ~20% of the original oxygen concentration. This suggests that a robust oxide which is stable at high temperature may be influencing the graphene growth process. A detailed LEED, LEEM and STM study has been initiated to determine the effect that this oxygen has on the graphene film's properties and new results will be presented.

References:

[1] L. Srivastava, G. He et al., Phys. Rev. B 82, 235406 (2010)

9:20am **GR+EM+NS+PS+SS+TF-MoM4 Microscopic Control of Epitaxial Graphene on SiC(111) and SiC(100) Thin Films on a Microfabricated Si(100) Substrate.** *H. Fukidome, T. Ide, M. Suemitsu, Y. Kawai, Tohoku University, Japan, T. Ohkouchi, M. Kotsugi, T. Kinoshita, JASRI/SPring-8, Japan, T. Shinohara, N. Nagamura, S. Toyoda, K. Horiba, M. Oshima, University of Tokyo, Japan*

Graphene is the promising material for the next-generation devices due to its excellent electronic properties. We have developed epitaxy of graphene on SiC thin films on Si substrates (GOS) toward fusion of graphene with Si-based electronics. We have found that structural and electronic properties of graphene are tuned by crystallographic orientation of the Si substrates [1,2]. This result indicates that, in combination with Si microfabrication technologies, the electronic properties of GOS may be tuned by microfaceting Si surface [3].

A Si(100) substrate was fabricated by combining electron-beam lithography [3] and alkaline etching which produces (111) and (100) microfacet on the Si(100) substrate. On the microfabricated Si(100) substrate, SiC thin films were grown by using gas-source MBE, followed by graphitization in vacuum at 1500 K. Microscopic characterization of graphene was performed by using 3D NanoESCA for microscopic XPS (micro-XPS) and low-energy electron microscope for microscopic low-energy electron diffraction (micro-LEED). Vibrational and bandstructure characterization was done by Raman microspectroscopy.

The micro-LEED observation reveals that graphene is Bernal stacked on the SiC(111)/Si(111) facet, while it is non-Bernal stacked on the SiC(100)/Si(100) microfacet. The observation is in consistent with the previous result on the epitaxy of graphene on non-fabricated SiC(111)/Si(111) and SiC(100)/Si(100) [1, 2]. The variation of the stacking is explained by the micro-XPS observation. The buffer layer which works as a template for the epitaxy of graphene exists only in between graphene and the SiC(111)/Si(111) microfacet. The existence of the buffer layer is also confirmed by cross-sectional transmission electron microscopy observations. Furthermore, Raman microscopy reveals that the band dispersion (splitting) microscopically changes depending on the variation of the stacking with the microfacet.

Our work can open a new way to microscopically tune control of electronic properties of graphene, semiconductive or metallic, which can make graphene devices multi-functionalized on Si substrates.

One of the authors (H. F.) acknowledges a financial support by KAKENHI (23560003).

References: [1] H. Fukidome et al., J. Mater. Chem. 21 (2011) 17242. [2] H. Fukidome et al., Appl. Phys. Exp. 4 (2011) 115104. [3] H. Fukidome et al., Jpn. J. Appl. Phys. 51 (2012) 06FD02.

9:40am **GR+EM+NS+PS+SS+TF-MoM5 STM Studies on Direction-Selective Epitaxial Graphene: Growth Mechanism and Moiré Superstructures.** *H. Lim, Y. Kim, RIKEN, Japan*

Chemical vapor deposition on a Cu surface is one of the feasible methods for industrial applications, because large-area monolayer graphene film can be achieved.¹ However, grain boundaries and wrinkle formation in the graphene film are known to reduce the electrical performance of graphene. An atomic scale understanding of the growth mechanism on a Cu substrate is therefore of great importance for the synthesis of higher-quality graphene films.

Herein, we present the direction-selective growth of epitaxial graphene (EG) on a Cu(111) surface. All EGs had an identical $R0^\circ$ rotational angle with respect to the lattice direction of Cu(111), although it is distinguished from the general understanding that graphene grown on weakly-interacting metal surfaces generally shows various rotation angles.² The EG growth mechanism was also elucidated with microscopic evidence of characteristic step edge formation of the Cu layers underneath individual EGs. We also observed various kinds of Moiré patterns in EGs with an identical rotational angle. The variety of Moiré patterns, even with an identical rotational angle, cannot be explained by conventional analysis showing that different

rotational angles induce the different types of Moiré patterns. We suggest a “compressive strain” effect to explain the various Moiré superstructures observed in the atomically-resolved STM images.

1. Li, X.; Cai, W.; An, J.; Kim, S.; Nah, J.; Yang, D.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S. *Science* **2009**, *324*, (5932), 1312-1314.

2. Batzill, M. *Surf. Sci. Rep.* **2012**, *67*, (3-4), 83-115.

10:00am **GR+EM+NS+PS+SS+TF-MoM6 Epitaxial Graphene on Ag(111)**, *B.T. Kiraly*, Northwestern University, *E. Iski*, Argonne National Laboratory, *A.J. Mannix*, Northwestern University, *B. Fisher*, Argonne National Laboratory, *M.C. Hersam*, Northwestern University, *N.P. Guisinger*, Argonne National Laboratory

Graphene plasmonics has recently combined near field optics with the exotic properties of graphene to demonstrate remarkable optical, biochemical, and optoelectronic architectures capable of extreme light concentration and manipulation, highly efficient photoconversion, and single molecule detection. Graphene's unique electronic structure and chemical stability make it an optimal platform to interface with both light and matter; however, current devices are limited by the low-throughput or non-pristine processing steps to produce either the exfoliated or CVD transferred graphene, respectively. In this regard, it would be highly useful to grow a layer of graphene directly on top of a plasmonic metal substrate.

In this work, we report the novel growth of graphene on a bare Ag(111) single crystal. Growth was accomplished by evaporating atomic carbon onto a Ag(111) surface at elevated temperatures under ultra-high vacuum (UHV) conditions. The growth was verified and examined in-situ via scanning tunneling microscopy (STM)/scanning tunneling spectroscopy (STS) and further qualified via ex-situ Raman spectroscopy, scanning electron microscopy (SEM), and x-ray photoelectron spectroscopy (XPS). While the minimal C solubility in Ag suggests similar growth behavior to other noble metals (Cu, Au), this growth mode demonstrates markedly different signatures: nanoscale dendritic features, both terrace and step nucleation, strong electronic scattering at the graphene boundaries, and highly mobile Ag adatoms interacting with the graphene growth front. Furthermore, the growth was carried out at temperatures (600°C-700°C) much lower than the temperatures commonly used for conventional chemical vapor deposition (CVD) techniques (>1000°C) and it could be extended to a variety of weakly interacting substrates, including non-metals. All the observed growth was electronically characterized as single-layer graphene, and was further supported by the narrow full-width half-maximum (FWHM) of the 2D Raman band. All the observed growth was electronically characterized as single-layer graphene, and was further supported by the narrow full-width half-maximum (FWHM) of the 2D Raman band. A 65% decrease in the Ag-O peak in the O1s spectrum reveals that the graphene layer protects the underlying silver from environmental degradation. Two predominant Moiré patterns were observed in the graphene; their periodicity was ~1.55nm and ~0.95 nm corresponding to lattice offsets of ~4.5° and ~13°, respectively. Finally, the graphene grown on Ag is weakly bound to the surface indicated by the stark contrast between the dI/dV spectra of the graphene and bare silver surface. The graphene-Ag system demonstrated in this study could immediately be applied to tip-based molecular spectroscopies and will lead to the development of more advanced hybrid graphene plasmonics.

10:40am **GR+EM+NS+PS+SS+TF-MoM8 A Universal Scheme to Convert Aromatic Monolayers Into Functional Carbon Nanomembranes**, *A. Angelova*, *H. Vieker*, *N.J. Weber*, *D. Matei*, University of Bielefeld, Germany, *S. Kurasch*, *U. Kaiser*, University of Ulm, Germany, *K. Müllen*, Max Planck Institute for Polymer Research, Germany, *A. Götzhäuser*, *A. Turchanin*, University of Bielefeld, Germany

The engineering of free-standing nanomembranes with molecular or atomic thickness and with well-defined structural and functional properties is a challenge for materials research. Here we present a broadly applicable scheme to create mechanically stable carbon nanomembranes (CNMs) with a thickness of ~0.5 to ~3 nm. Monolayers of polyaromatic molecules (oligophenyls, hexaphenylbenzene and polycyclic aromatic hydrocarbons) were assembled and exposed to electrons that crosslink them into CNMs; subsequent pyrolysis converts the CNMs into graphene sheets. In this transformation thickness, porosity and surface functionality of the nanomembranes are determined by the monolayers, and structural and functional features are passed on from the molecules through their monolayers to the CNMs and finally on to the graphene. Our procedure is scalable to large areas and allows the engineering of ultrathin nanomembranes by controlling the composition and structure of precursor molecules and their monolayers.

11:00am **GR+EM+NS+PS+SS+TF-MoM9 Hydrogenation of Monolayer and Bilayer Graphene and Nanodiamond Growth on Ni(111) Substrate**, *I.I. Oleynik*, *L. Adamska*, *M. Batzill*, University of South Florida

Hydrogenation of a few layer graphene is known to result in the change of sp² to sp³ hybridization, which can be exploited to grow nanodiamond thin films. First-principles studies of hydrogenated monolayer, bilayer, and trilayer graphene, supported on Ni(111) substrate are performed using first-principles density functional theory. The monolayer graphene and AB-stacked bilayer graphene are shown to rehybridize to form sp³ bonds, thus promoting the formation of nanodiamond thin films. Structural, electronic and magnetic properties of the hydrogenated monolayer, bilayer, and trilayer graphene are discussed.

11:20am **GR+EM+NS+PS+SS+TF-MoM10 Graphene-based, Graphene-derived, and New Carbon Materials**, *R.S. Ruoff*, The University of Texas at Austin

INVITED

Graphene-based materials are of interest because of their electronic and thermal transport, mechanical properties, high specific surface area, and that they can act as an atom thick layer, barrier, or membrane, among other reasons. Our micromechanical exfoliation approaches [1,2] conceived of in 1998 yielded multilayer graphene and one paper described in detail how monolayer graphene could be obtained [1]. Three main research areas of our group are: (i) Growth of large area graphene on metal substrates, characterization and physical properties, and studies of devices having such CVD-grown graphene as a central component; (ii) Generation, study, and use of chemically modified graphene ‘platelets’ (typically derived from graphite oxide) including as dispersed in liquids forming colloids, and powders derived from such colloids or separately generated by microwave or thermal treatment of graphite oxide; (iii) Generation and study of new types of carbon derived from graphene-based precursors, such as *activated microwave expanded graphite oxide* (‘AMEGO’)[3].

Here, I will focus on growth of graphene and h-BN from research projects underway in my group and also *briefly* describe what I think are some important new directions in carbon and *first row element* research, for the next 10-20 years, that will introduce new issues involving interfaces for these new material classes that have not yet been made experimentally [4].

Current or prior support of our work by the W. M. Keck Foundation, NSF, DARPA ‘iMINT’, DARPA ‘CERA’, ONR, SWAN NRI, ARO, AEC, DOE, and the SRC, is appreciated.

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3. Zhu, Yanwu; Murali, Shanthi; Stoller, Meryl D.; Ganesh, K. J.; Cai, Weiwei; Ferreira, Paulo J.; Pirkle, Adam; Wallace, Robert M.; Cychoz, Katie A.; Thommes, Matthias; Su, Dong; Stach, Eric A.; Ruoff, Rodney S. *Carbon-Based Supercapacitors Produced by Activation of Graphene*. *Science* **332**, 1537-1541 (2011).

4. Ruoff, Rodney S. *Personal perspectives on graphene: New graphene-related materials on the horizon*. *MRS Bulletin* **37**, 1314-1318 (2012).

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