Monday Morning, November 10, 2014

2D Materials Focus Topic
Room: 310 - Session 2D+EM+NS+PS+SS+TF-MoM

2D Materials Growth and Processing
Moderator: Thomas Greber, University of Zurich

8:20am 2D+EM+NS+PS+SS+TF-MoM1 Exploring the Flatlands: Synthesis, Characterization and Engineering of Two-Dimensional Materials, *Jun Lou*, Rice University **INVITED**
In this talk, we report the controlled vapor phase synthesis of MoS_2 atomic layers and elucidate a fundamental mechanism for the nucleation, growth, and grain boundary formation in its crystalline monolayers. The atomic structure and morphology of the grains and their boundaries in the polycrystalline molybdenum disulfide atomic layers are examined and first-principles calculations are applied to investigate their energy landscape. The electrical properties of the atomic layers are examined and the role of grain boundaries is evaluated. More importantly, if precise two-dimensional domains of graphene, h-BN and MoS_2 atomic layers can be seamlessly stitched together, in-plane heterostructures with interesting electronic applications could potentially be created. Here, we show that planar graphene/h-BN heterostructures can be formed by growing graphene in lithographically-patterned h-BN atomic layers. Our approach can create periodic arrangements of domains with size that ranging from tens of nanometers to millimeters. The resulting graphene/h-BN atomic layers can be peeled off from their growth substrate and transferred to various platforms including flexible substrate. Finally, we demonstrate how self-assembled monolayers with a variety of end termination chemistries can be utilized to tailor the physical properties of single-crystalline MoS_2 atomic-layers. Our data suggests that combined interface-related effects of charge transfer, built-in molecular polarities, varied densities of defects, and remote interfacial phonons strongly modify the electrical and optical properties of MoS_2, illustrating an engineering approach for local and universal property modulations in two-dimensional atomic-layers.

9:00am 2D+EM+NS+PS+SS+TF-MoM3 Influence of Substrate Orientation on the Growth of Graphene on Cu Single Crystals, *Tyler Mowll*, University at Albany-SUNY, *Z.R. Robinson*, U.S. Naval Research Laboratory, *P. Tyagi, E.W. Ong, C.A. Ventrice, Jr.*, University at Albany-SUNY
A systematic study of graphene growth on on-axis Cu(100) and Cu(111) single crystals oriented within 0.1° from the surface normal and a vicinal Cu(111) crystal oriented 5° off-axis has been performed. Initial attempts to grow graphene by heating each crystal to 900°C in UHV, followed by backfilling the chamber with C_2H_4 at pressures up to $5x10^{-3}$ Torr did not result in graphene formation on either the on-axis Cu(100) or on-axis Cu(111) surfaces. For the vicinal Cu(111) surface, epitaxial graphene was formed under the same growth conditions. By backfilling the chamber with C_2H_4 before heating to the growth temperature, epitaxial graphene was formed on both the on-axis Cu(100) and off-axis Cu(111) surfaces, but not the on-axis Cu(111) surface. By using an argon overpressure, epitaxial overlayers could be achieved on all three Cu substrates. These results indicate that the most catalytically active sites for the dissociation of ethylene are the step edges, followed by the Cu(100) terraces sites and the Cu(111) terrace sites. The need for an argon overpressure to form graphene the on-axis Cu(111) surface indicates that the Cu sublimation rate is higher than the graphene growth rate for this surface. This research was supported in part by the NSF (DMR-1006411).

9:20am 2D+EM+NS+PS+SS+TF-MoM4 Synthesis of Large Scale MoS_2-Graphene Heterostructures, *Kathleen McCreary*, *A.T. Hanbicki, J. Robinson, B.T. Jonker*, Naval Research Laboratory
A rapidly progressing field involves the stacking of multiple two-dimensional materials to form heterostructures. These heterosctructures have exhibited unique and interesting properties. For the most part, heterostructure devices are produced via mechanical exfoliation requiring the careful aligning and stacking of the individual 2D layered components. This tedious and time consuming process typically limits lateral dimensions to micron-scale devices. Chemical vapor deposition (CVD) has proven to be a useful tool in the production of graphene and has very recently been investigated as a means for the growth of other 2D materials such as MoS_2, $MoSe_2$, WS_2, WSe_2 and hexagonal boron nitride. Using a two-step CVD process we are able to synthesize MoS_2 on CVD grown graphene. AFM, Raman spectroscopy, and Photoluminescence spectroscopy of the MoS_2-graphene heterostructure show a uniform and continuous film on the cm scale.

9:40am 2D+EM+NS+PS+SS+TF-MoM5 Growth of 2D MoS_2 Films by Magnetron Sputtering, *Andrey Voevodin*, Air Force Research Laboratory, *C. Muratore*, University of Dayton, *J.J. Hu*, Air Force Research Laboratory/UDRI, *B. Wang, M.A. Haque*, Pennsylvania State University, *J.E. Bultman, M.L. Jesperson*, Air Force Research Laboratory/UDRI, *P.J. Shamberger*, Texas A&M University, *R. Stevenson*, Air Force Research Laboratory, *A. Waite*, Air Force Research Laboratory/UTC, *M.E. McConney, R. Smith*, Air Force Research Laboratory
Growth of two dimensional (2D) MoS2 and similar materials over large areas is a critical pre-requisite for seamless integration of next-generation van der Waals heterostructures into novel devices. Typical preparation approaches with chemical or mechanical exfoliation lack scalability and uniformity over appreciable areas (>1 mm) and chemical vapor deposition processes require high substrate temperatures. We developed few-layer MoS_2 growth under non-equilibrium magnetron sputtering conditions selected to minimize the MoS_2 nucleation density and maximize 2D growth of individual crystals [1]. In this process, the thermodynamically driven tendency to form islands is accomplished by maximizing atomic mobility through the control of incident flux kinetic energies, densities, and arriving angle to the substrate while avoiding defect formation (i.e., vacancy creation by sputtering of S atoms). Amorphous SiO_2, crystalline (0001) oriented Al_2O_3, and (002) oriented graphite substrates were used to grow few monolayer thick MoS_2 films. Continuous 2D MoS_2 films were produced over 4 cm^2 areas. They were composed of nano-scale domains with strong chemical binding between domain boundaries, allowing lift-off from the substrate and electronic transport measurements with contact separation on the order of centimeters. Their characteristics were similar to few-layer MoS_2 films produced by exfoliation with a direct band gap in thin samples of approximately 1.9 eV from photoluminescense spectra. The electron mobility measured for as-grown MoS_2 films was very strongly dependent on film thickness and substrate choice.

[1] "Continuous ultra-thin MoS2 films grown by low-temperature physical vapor deposition", C. Muratore, J.J. Hu, B. Wang, M.A. Haque, J.E. Bultman, M. L. Jesperson, P.J. Shamberger, A.A. Voevodin, Applied Physics Letters (2014) in press.

10:00am 2D+EM+NS+PS+SS+TF-MoM6 Formation of Graphene on the C-face of SiC{0001}: Experiment and Theory, *Jun Li, G. He, M. Widom, R.M. Feenstra*, Carnegie Mellon University
There are two {0001} surfaces of SiC, the (0001) surface known as the "Si-face", and the (000-1) surface or "C-face". The formation of graphene (by heating the SiC to 1100 – 1600 ° C in various gaseous environments) has been studied for both surfaces, although it is much better understood on the Si-face. In that case, an intermediate C-rich layer, or "buffer layer" forms between the graphene and the SiC crystal. This buffer layer has 6√3x6√3-R30° symmetry; its structure is well established,[1] and it acts as a template for the formation of subsequent graphene layers. In contrast, graphene formation on the C-face is much less well understood. More than one interface structure between the graphene and the SiC has been observed,[2,3] and, with one notable exception,[4] the quality of the graphene formed on the C-face is generally lower than that for the Si-face.

In this work we provide new experimental and theoretical results that allow us to understand graphene formation on the C-face of SiC. Experimentally, by heating the SiC in a disilane environment, we map out the phase diagram of different surface and interface structures that form on the SiC as a function of disilane pressure and sample temperature. New surface structures that develop just prior to the graphene formation are observed. With additional heating, graphene forms on the surface, but some remnant of the surface structure prior to the graphene formation is believed to persist at the graphene/SiC interface. From first-principles theory, we find that the hydrogen in the disilane environment plays a critical role in the surface/interface structures that form. Experimentally, for disilane pressures below $5x10^{-5}$ Torr, we find a 2x2 surface structure forming prior to graphene formation. From theory we identify this structure as consisting of a silicon adatom together with a carbon restatom on the surface, with H-termination of those atoms being possible but not necessary. At higher disilane pressures we observe a 4x4 structure, and we identify that as consisting of a lower density of Si adatoms than the 2x2, now with at least some of the adatoms and restatoms being H-terminated. With graphene formation, this structure converts to the observed √43x√43-R± 7.6° interface structure. At higher disilane pressures we theoretically predict the formation of a surface consisting simply of H-terminated carbon restatoms. Experiments are underway to observe that surface, along with subsequent graphene formation on the surface.

(1) Y. Qi et al., PRL **105**, 085502 (2010).

(2) F. Hiebel et al., PRB **78**, 153412 (2008).

(3) N. Srivastava et al., PRB **85,** 041404 (2012).

(4) W. A. de Heer et al., PNAS **108**, 16900 (2011).

10:40am **2D+EM+NS+PS+SS+TF-MoM8** **Graphene on Hexagonal Boron Nitride Heterostacks Grown by UHV-CVD on Metal Surfaces**, *Juerg Osterwalder, S. Roth, A. Hemmi,* University of Zurich, Switzerland, *F. Matsui,* Nara Institute of Science and Technology, Japan, *T. Greber*, University of Zurich, Switzerland **INVITED**
Chemical vapor deposition (CVD) performed under ultra-high vacuum conditions on single-crystal metal surfaces enables the growth of large-area and high-quality graphene and hexagonal boron nitride (h-BN) single layers. We explore the CVD parameter space of precursor pressure and temperature in order to go beyond the self-saturating single-layer growth, or to grow heterostacks of the two materials. Formed layers are characterized structurally by LEED, STM and x-ray photoelectron diffraction. On Cu(111) a graphene layer could be grown on a pre-deposited single layer of h-BN when using 3-pentanone as a precursor at a pressure of 2.2 mbar and a substrate temperature of 1100 K [1]. On Rh(111) the same procedure leads to incorporation of carbon into the metal surface layers, while a graphene layer is formed only upon a second high-pressure dose [2]. In both cases the heterostructures show clearly the stacking sequence and structural and ARPES signatures of graphene on h-BN but are far from defect-free.

[1] S. Roth et al., Nano Lett. 13, 2668 (2013).

[2] S. Roth, PhD Thesis, Department of Physics, University of Zurich (2013).

11:20am **2D+EM+NS+PS+SS+TF-MoM10** **Kinetics of Monolayer Graphene Growth by Carbon Segregation on Pd(111)**, *Abbas Ebnonnasir, H.S. Mok, Y. Murata,* University of California at Los Angeles, *S. Nie, K.F. McCarty,* Sandia National Laboratories, *C.V. Ciobanu,* Colorado School of Mines, *S. Kodambaka*, University of California at Los Angeles
In this research, using in situ low-energy electron microscopy and density functional theory calculations, we elucidate the growth kinetics of monolayer graphene on single-crystalline Pd(111). In our experiments, carbon saturated Pd(111) samples were cooled down from 900 °C to segregate carbon on the surface in the form of graphene. Upon cooling the substrate, graphene nucleation begins on bare Pd surface and continues to occur during graphene growth. Measurements of graphene growth rates and Pd surface work functions along with DFT calculations establish that this continued nucleation is due to increasing C adatom concentration on the Pd surface with time. We attribute this anomalous phenomenon to a large barrier for attachment of C adatoms to graphene coupled with a strong binding of the non-graphitic C to the Pd surface.

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