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 5×10^{-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.

Work at Sandia was supported by the Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, U. S. Department of Energy under Contract No. DE-AC04-94AL85000. J.M.W. acknowledges support from the National Science Foundation Graduate Research Fellowship Program.

[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.

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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 10x10µm^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)

Graphene and Related Materials Focus Topic
Room: 208 - Session GR+TF+ET-MoA

Graphene: Electronic Properties and Charge Transport
Moderator: L. Colombo, Texas Instruments Incorporated

2:00pm **GR+TF+ET-MoA1 Electronic and Magnetic Properties of a Graphene Line Defect**, ***D. Gunlycke***, Naval Research Laboratory **INVITED**

Although graphene exhibits excellent electron and thermal transport properties, it does not have an intrinsic band gap, required to use graphene as a replacement material for silicon and other semiconductors in conventional electronics. The band structure of graphene, however, offers opportunities to develop non-traditional applications. One such avenue is to exploit the valley degeneracy in graphene. In this presentation, I will present a two-dimensional valley filter based on scattering of electrons and holes off a recently observed extended line defect. The transmission probability depends strongly on the valley and the angle of incidence of the incident quasiparticles. Quasiparticles arriving at the line defect at a high angle of incidence lead to a valley polarization of the transmitted beam that is near 100%.

I will also discuss results showing that the extended line defect gives rise to ferromagnetically coupled local moments. This ferromagnetism can be understood from a symmetry analysis of the boundary-localized eigenstates. The symmetry requires that the principal moments couple ferromagentically both along and across the line defect, leading to approximately 2/3 more spin-up electrons and than spin-down electrons per repeat unit along the line defect.

This work was supported by the Office of Naval Research, directly and through the Naval Research Laboratory.

2:40pm **GR+TF+ET-MoA3 Hydrogenation Induced Graphene-Metal Contact - Observation of States at Fermi Level**, ***S. Rajasekaran***, Stanford University, *S. Kaya, T. Anniyev,* Stanford Synchrotron Light Source, *F. Yang, D. Stacchiola,* Brookhaven National Laboratory, *H. Ogasawara, A. Nilsson*, Stanford Synchrotron Light Source

Graphene has received tremendous interest due to its unique electronic structure. Manipulating its electronic structure has received considerable interest. Hydrogenating graphene to open a band gap has been proposed and certain groups have demonstrated hydrogenation induced band opening for graphene on metal substrates.

We employed carbon specific soft x-ray spectroscopy (X-ray photoelectron (XPS), X-ray absorption (XAS) and X-ray emission spectroscopy (XES)) and scanning tunneling microscopy (STM) to investigate how hydrogenation changes the geometric and electronic structure of graphene on Pt(111). Graphene growth on Pt(111) is accompanied with Moiré structure due to periodic rippling in the graphene overlayer due to lattice mismatch and weak interaction between graphene and Pt. Hydrogenation leads to complete disappearance of long range order, although STM indicates that ripple periodicity survives even after hydrogenation. We show that hydrogenation of the unit cell of Moiré nano-patterns is accompanied by pinning of the graphene layer to underneath metal substrate. Structural changes involved in the process of hydrogenation induce covalent graphene-metal interaction. Angle resolved XES and XAS make it possible to probe symmetry resolved states in σ and π bond geometry. XES-XAS indicates that the density of states (DOS) of graphene is very similar to that of graphite. Hydrogenation induces significant changes in the electronic DOS, most of which reflect the formation of C-H σ bonds. For disordered hydrogenated graphene, contrary to band opening, we observe states at the Fermi level after hydrogenation which we reason to arise due to graphene metal interaction and localized C-H bonds. This effect is proposed to be a way to tailor its electronic properties as a possible method to form better graphene-metal contact.

3:00pm **GR+TF+ET-MoA4 First-Principles Studies of Atomic and Electronic Structure of Graphene on Sn/Ni(111) Surface Alloy**, ***L. Adamska***, *R.Q. Addou, A. Dahal, M. Batzill, I.I. Oleynik*, University of South Florida

Graphene-substrate interactions can be exploited to modify the electronic structure of free-standing graphene. Although most of the efforts were directed towards investigation of graphene on pure metallic substrates, less is known about properties of graphene grown on surface alloys. Sn/Ni(111) surface alloy is of particular interest because this structure has the surface lattice constant of Ni(111), i.e. almost a perfect match with graphene's lattice constant, and its surface is highly corrugated due to the substantially large atomic radius of Sn compared to Ni. Here we present results of first-priniciples density functional theory investigations of structural and electronic properties of graphene on sqrt(3)xsqrt(3)R(30) Sn/Ni alloy substrate. It was found that the presence of Sn atoms (1/3 monolayer) results in substantial weakening of graphene-substrate interactions, as is evidenced by large graphene-substrate separation. Nevertheless, the electronic structure of graphene is substantially affected by the underlying substrate as is as seen on simulated STM images. The theoretical predictions for the atomic and electronic structures of graphene on Sn/Ni(111) substrate are compared with experimental results.

3:40pm **GR+TF+ET-MoA6 Charge Transport through Graphene: the Role of Metal Contacts**, *M.Y. Chou, M.E. Kindermann,* ***S. Barraza-Lopez***, Georgia Institute of Technology

Graphene is a flat form of carbon only one-atom tick. Formed by two interweaving triangular sublattices, it has two atoms on its unit cell. Under normal conditions the charge carriers in graphene can be described with an effective single-particle picture. They display an isotropic and linear (i.e., conical) electronic dispersion around the charge neutrality level. This dispersion is described by a Dirac-like equation with a pseudo-spin (related to the sublattice degree of freedom) instead of the standard electron spin. The pseudo-spin is responsible in great part for the strongly suppressed back-scattering in graphene that results in coherent quantum charge transport on lengths up to the micrometer scale, making graphene a relevant material for electronic applications. Yet for applications and for electrical measurements metal contacts are patterned onto graphene. Then the two following questions naturally arise: (i) How graphene interacts with these metal contacts? (ii) How this interaction affects the conductance of a metal/graphene/metal junction in comparison with the hypothetical conductance of pristine (and contactless, infinite) graphene?

In this talk I will discuss quantitatively –within a single-particle description– the quantum transport of charges through graphene, with a focus on the signatures that metal/graphene interfaces imprint on the conductance features. The metals considered are normal (i.e., not superconducting), and spin unpolarized. A crucial observation is that not all metal form covalent bonds to graphene. The conductance is obtained as a function of the separation between contacts, the width of the junctions, as well as the thickness of the metal layers when necessary. From these calculations we are able to extract the basic physics involved in transport for all normal metals [1]. Our studies aim towards a comprehensive modeling of graphene devices at the quantitative level.

[1] S. Barraza-Lopez, M. Vanevic, M. Kindermann, and M.-Y. Chou. "Effects of metallic contacts on electron transport through graphene." *Phys. Rev. Lett.* **104**, 076807 (2010); S. Barraza-Lopez, M. Kindermann and M.-Y. Chou. "Charge transmission through short two-terminal graphene junctions with normal bonding metal contacts." (In preparation.)

4:00pm **GR+TF+ET-MoA7 Layer Number Determination and Thickness-dependent Properties of Graphene Grown on SiC**, ***W. Zhu***, *C. Dimitrakopoulos, M. Freitag, Ph. Avouris*, IBM T.J. Watson Research Center

The electronic properties of few-layer graphene grown on the carbon-face of silicon carbide (SiC) are found to be strongly dependent on the number of layers. The carrier mobility is larger in thicker graphene because substrate-related scattering is reduced in the higher layers. The carrier density dependence of the mobility is qualitatively different in thin and thick graphene, with the transition occurring at about 2 layers. The mobility increases with carrier density in thick graphene, similar to multi-layer graphene exfoliated from natural graphite, suggesting that the individual layers are still electrically coupled. The Hall coefficient peak value is reduced in thick graphene due to the increased density of states. A reliable and rapid characterization tool for the layer number is therefore highly desirable. To date, AFM height determination and Raman scattering are typically used since the optical contrast of graphene on SiC is weak. However, both methods suffer from low throughput. We show that the scanning electron microscopy (SEM) contrast can give similar results with much higher throughput.

4:20pm **GR+TF+ET-MoA8 Graphene: Scratching the Surface**, ***M. Fuhrer***, University of Maryland at College Park **INVITED**

Graphene is of interest for its unique electronic structure: electrons in graphene obey the Dirac equation for massless particles, complete with a two-component spinor degree of freedom that mimics the spin of a relativistic particle. But graphene is also composed entirely of surface atoms, making the techniques of surface science useful in studying its properties. I will discuss experiments which combine ultra-high vacuum (UHV) surface science with electronic transport measurements to understand graphene and the adsorbed species on its surface. Surface science techniques can be used to controllably modify graphene's properties: potassium atoms can be deposited to form charged impurity scatterers; ice can be deposited to modify the dielectric environment of graphene and tune the electron-electron interaction strength; and ion irradiation can be used to create atomic vacancies which act as Kondo impurities. Graphene's transport properties are extraordinarily sensitive to surface adsorbates, and can be used to detect e.g. correlations in the positions of potassium atoms at concentrations below 1/1000th of a monolayer, and phase transitions in few-monolayer water.

5:00pm **GR+TF+ET-MoA10 Metallic and Insulating Adsorbates on Graphene***, **K.M. McCreary**, R.K. Kawakami*, University of California, Riverside

While several experiments have separately investigated the doping of graphene by metallic and insulating adsorbates, the transition from metallic to insulating behavior of the adsorbates has not yet been explored. We directly compare the effect of metallic titanium (Ti) and insulating titanium dioxide (TiO_2) on the transport properties of single layer graphene. The deposition of Ti results in substantial *n*- type doping and a reduction of graphene mobility by charged impurity scattering. Subsequent exposure to oxygen largely reduces the doping and scattering by converting Ti into TiO_2. In addition, we observe evidence for short-range scattering by TiO_2 impurities.

5:20pm **GR+TF+ET-MoA11 Electron Transport in Carbon Nanotube - Graphene Contacts***, B. Cook, W. French, **K. Varga***, Vanderbilt University

Graphene and carbon nanotubes are two of the most promising materials for future applications due to their unique properties. Devices combining the two materials are expected to be particularly advantageous. The interface of carbon nanotubes and various metal electrodes has been previously studied, both experimentally (Chen et al. Nano Lett. 2005, Zhang et al. Nano Lett. 2007) and theoretically (Shan et al. PRB 2004, Zhu et al. APL 2006, He et al. APL 2009). These studies focus on the search for materials with a low p-type Schottky barrier. Hybrid graphene-carbon nanotube structures have been previously demonstrated (Tung et al. Nano Lett. 2009). We propose the use of graphene as a electrode material for carbon nanotube based FET devices. To this end the carbon nanotube - graphene contact is investigated with first-principles calculations within density functional theory of the Schottky barrier height (SBH) and transport properties. Total energy and electronic structure calculations are carried out with a plane-wave basis set and the transport characteristics are calculated with a localized atomic orbitals basis within the non-equilibrium Green's function framework. We consider only the side-contact geometry, nanotubes laying atop graphene. The SBH for (5,0), (8,0) and (10,0) nanotubes on graphene is calculated. The transport characteristics of a combined graphene - nanotube device are considered. In the case of small diameter nanotubes (~0.6nm) a SBH of ~0.09 eV is found when graphene contacts are used, much lower than the typical reported values (0.3 eV and higher).

Graphene and Related Materials Focus Topic
Room: 208 - Session GR+EM-TuM

Graphene: Optical Properties, Optoelectonics and Photonics
Moderator: P.E. Sheehan, U.S. Naval Research Laboratory

8:00am **GR+EM-TuM1 Graphene Optoelectronics: From Ultrafast Lasers to Flexible Displays**, ***A.C. Ferrari***, University of Cambridge, UK **INVITED**

The richness of optical and electronic properties of graphene attracts enormous interest. So far, the main focus has been on fundamental physics and electronic devices. However, we believe its true potential to be in photonics, plasmonics and optoelectronics, where the combination of its unique optical and electronic properties can be fully exploited, the absence of a bandgap can be beneficial, and the linear dispersion of the Dirac electrons enables ultra-wide-band tenability [1]. The rise of graphene in photonics and optoelectronics is shown by several recent results, ranging from solar cells and light emitting devices, to touch screens, photodetectors and ultrafast lasers. Despite being a single atom thick, graphene can be optically visualized [2]. Its transmittance can be expressed in terms of the fine structure constant [3]. The linear dispersion of the Dirac electrons enables broadband applications. Saturable absorption is observed as a consequence of Pauli blocking [4,5]. Chemical and physical treatments enable luminescence [1,6]. Graphene-polymer composites prepared using wet chemistry [4-6] can be integrated in a fiber laser cavity, to generate ultrafast pulses, down to 100fs with up to 1 W average power, and enable broadband tunability [4,5]. Graphene-based mode-locked laser are a near term application for this extraordinary material, and can provide simple, low-cost, and convenient light sources for metrology, sensing, medicine and micromachining. Graphene is an ideal transparent flexible conductor. A flexible electrically switchable smart window will be reported, with over 230 contrast ratio, as well as an electro-tactile screen for mobile phone applications. The optoelectronic properties of graphene can be enhanced by combination with plasmonic nanostructures [7], for example in plasmonic-enhanced photovoltage generation [8]

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9:00am **GR+EM-TuM4 Quantum Mechanics-Based Exploration of Graphene-Like Systems to Model Magnetic Resonators**, *X.W. Sha, E.N. Economou,* ***D.A. Papaconstantopoulos***, George Mason University, *M.R. Pederson, M.J. Mehl*, Naval Research Laboratory, *M. Kafesaki*, University of Crete, Greece

Quasi-circular pieces of graphene as well as nanotubes offer the possibility of acting as magnetic resonators to be used in negative refractive index optical metamaterials. The advantage of these graphene pieces is twofold: (a) they are stable even when their size reaches the tens of nanometers; (b) the induced currents in the presence of an AC magnetic field perpendicular to the graphene plane cancel each other in all the interior hexagons and only an edge circular current remains. This current is expected to be ballistic in nature with almost zero resistance. This analog of the split (in the split ring resonators) is expected to be achieved by the substitutional insertion of foreign atoms (e.g. nitrogen atoms). To explicitly and reliably check these ideas we have used the NRLMOL, a first- principles DFT code, in the presence of an AC magnetic field, to calculate the response of various configurations of quasi-circular pieces of graphene with or without the presence of substitutional foreign atoms. In order to be able to extend our calculations to larger systems, of the order of tens of thousands of atoms, we used the NRL-TB method, in which the TB matrix elements were fitted so as to reproduce the energy levels of our DFT approach. Results for the energy levels, some selected eigenfunctions, and the current distribution for several configurations will be presented and evaluated vis-a-vis the intended use as almost lossless magnetic resonators.

9:20am **GR+EM-TuM5 Infrared Optical Conductance of CVD-grown Graphene**, ***J.W. Weber***, *M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

The infrared optical conductance of chemical vapour deposited (CVD) graphene is determined from near normal incidence reflection and transmission Fourier transform infrared measurements in the spectral range of 370-7000 cm^{-1}. The real part of the conductance, up to 2500 cm^{-1} , shows both the effect from doping and finite temperature that was shown for exfoliated graphene.[1,2] The conductance for the range 2500-7000 cm^{-1} is increasing from the value for the universal optical conductance ($\pi e^2/2h$) to 1.5 times this value. This could imply that graphene and bilayer graphene have grown in a 1:1 ratio. The graphene is grown via CVD of methane and hydrogen on Cu-foil and transferred to a glass substrate following the procedure of Li *et al*.[3] A three-phase optical model (air/graphene/glass) is used to simultaneously fit the reflection and transmission data and extract the (Kramers-Kronig consistent) optical conductance. The conductance will be used to compare it with the conductance of CVD-graphene that is exposed to a hydrogen plasma.

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9:40am **GR+EM-TuM6 Optical Properties of Graphene on MgO and SiC Polytypes Determined by Spectroscopic Ellipsometry**, ***A. Boosalis***, *T. Hofmann, S. Schoche, P.A. Dowben,* University of Nebraska - Lincoln, *S. Gaddam, C. Vamala, J. Kelber,* University of North Texas*, V. Darakchieva,* Linköping University, Sweden*, D.K. Gaskill,* U.S. Naval Research Laboratory*, M. Schubert*, University of Nebraska - Lincoln

Wafer-scale production of epitaxial graphene has been demonstrated recently. It has been observed, however, that the highest quality graphene is achieved from exfoliation, while epitaxial graphene exhibits less desirable electronic and optical characteristics. Identifying substrate effects on epitaxial graphene is of paramount contemporary interest for future device production.

We have determined the complex dielectric function of graphene deposited on a number of different substrates using multiple growth techniques. The investigations were performed in the spectral range from 1.5 to 9.5 eV using spectroscopic ellipsometry. The samples studied here include graphene grown on (111) MgO using chemical vapor deposition (CVD) and graphene grown on SiC by sublimation of silicon from the substrate at high temperature. Several different SiC polytypes, including 4H, 3C, and 6H SiC were studied. Distinct differences in the complex dielectric function of graphene are observed as the underlying substrate differs in material composition and polytype. In particular in the spectral region of the exciton absorption peak (4 eV) the complex dielectric function is sensitive to both substrate and growth parameters. We compare our results with those of recent publications of graphene grown by CVD on SiO_2.

10:40am **GR+EM-TuM9 Plasmon Resonance in Individual Nanogap Electrodes Studied Using Graphene Nanoconstrictions as Photodetectors**, ***S.-F. Shi***, Cornell University, *X. Xu*, University of Washington, *P.L. McEuen, D.C. Ralph*, Cornell University

A plasmonic nanostructure can act like an optical antenna, concentrating light into a deep sub-wavelength volume and enabling manipulation of light-electron interactions at the nanometer scale. Achieving efficient coupling from such antennas to functional electrical devices has been challenging, because the region of field enhancement is so small. We achieve direct electrical read out of the wavelength and polarization dependence of the plasmon resonance in individual gold nanogap antennas by positioning a graphene nanoconstriction within the gap as a localized photodetector. The polarization sensitivities can be as large as 99%, while the plasmon-induced photocurrent enhancement is 2-100. The plasmon peak frequency, polarization sensitivity, and photocurrent enhancement all vary between devices, indicating the degree to which the plasmon resonance is sensitive to nanometer-scale irregularities.

11:00am **GR+EM-TuM10 Large Area Graphene Growth for Optoelectronic Applications**, ***C. Edwards***, *C.L. Berrie, J. Liu, J. Wu*, University of Kansas

Graphene shows great promise for numerous applications within the field of optoelectronics due to its high charge mobility, high optical transmittance, chemical inertness, and flexibility. We are focused on developing large-area graphene sheets that sustain or enhance these characteristics currently present in small-area growth. Chemical vapor deposition of graphene onto various copper substrates has been investigated to understand the role of the substrate in graphene epitaxy and its deposition mechanism. With this understanding it will be possible to use the substrate structure to control the density of surface defects, which is high in current methods for large area fabrication. Also, the effect of nanopatterning and doping graphene grown by chemical vapor deposition has been investigated, and observed improvements in light transmittance and electrical conductivity suggest the potential to favorably modify graphene optical and electrical properties for these applications.

11:20am **GR+EM-TuM11 Stable Chemical Doping of Graphene: Transport, Raman Spectroscopy, SEM, and Transmittance Studies**, ***K. Berke***, *S. Tongay, M. Lemaitre, Z. Nasrollahi, D.B. Tanner, B.R. Appleton, A.F. Hebard*, University of Florida

Since becoming experimentally available by mechanical exfoliation, graphene has been used in various devices such as field effect transistors (FETs), Schottky based solar cells and sensing applications. Although graphene based devices with modest characteristics have been reported, in some of the device geometries a lower graphene sheet resistance with different Fermi level values is still desired. To achieve these ends, graphene's physical properties have been adjusted by *n*- or *p*- chemical doping using $AuCl_3$, Br_2, N_2, and organic solutions. However, these techniques have several drawbacks which prevent their use in devices, namely: environmental instabilities, aging effects and a reduction in optical transparency. Here, we describe our use of a hydrophobic organic complex dopant with strong electronegativity, tight bonding, environmental stability and high optical transmittance which is spin cast onto CVD-prepared graphene films. We observe a typical 75% reduction in sheet resistance upon chemical modification of the graphene. Resistance vs. temperature / magnetic field and Hall measurements imply that the modified graphene sheets are doped, and time-dependent resistance measurements show excellent stability. Using a Horiba Micro Raman instrument we confirm the doping of graphene sheets from the shifts in G and 2D peak positions and intensity ratios. We show transmittance and SEM characteristics of the graphene sheets before and after doping. The presented results may serve as a guide for modification of graphene's properties as desired for various applications.

Graphene and Related Materials Focus Topic
Room: 208 - Session GR+MI-TuA

Graphene: Magnetic Properties and Spin-Dependent Phenomena
Moderator: A.C. Ferrari, University of Cambridge, UK

2:00pm **GR+MI-TuA1 Magnetic Impurities on Graphene**, ***K. Kern***, Max Planck Institute for Solid State Research, Germany **INVITED**

Hybrid systems consisting of transition metal (TM) atoms in contact with graphene are expected to show outstanding magnetic effects, from Kondo screening to long range ferromagnetism due to the large Fermi wavelength in graphene. First recent experimental evidence supports this scenario, however, little is known about the nature of the chemical interaction between TM atoms and graphene, which is the necessary starting point for any advanced application. Here we present recent X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic Circular Dichroism (XMCD) experiments probing the electronic configuration and magnetism of Fe, Co and Ni impurities on graphite and various graphenes. We find a rich physical scenario with marked differences between graphite and silicon oxide supported graphene on one hand and few layer epitaxial graphene on the C-face of silicon carbide on the other hand.

2:40pm **GR+MI-TuA3 Electron Spin Transport in Exfoliated and Epitaxial Graphene Grown on SiC**, ***J. Abel***, *A. Matsubayashi, J.J. Garramone,* University at Albany*, C. Dimitrakopoulos, A. Grill, Sung,* IBM T.J. Watson Research Center*, V.P. LaBella*, University at Albany

Graphene is an ideal candidate for the transport channel in future spintronic devices due to its long spin lifetimes at room temperature. The long lifetime arises due to the small intrinsic spin orbit coupling and low hyper-fine interaction of the electron spins with the carbon nuclei. Non-local Hanle measurement devices were fabricated on epitaxially grown graphene on SiC, provided by IBM, and multi-layer exfoliated flakes. Spin injection and detection were achieved in these devices using cobalt nano-magnets directly deposited on the graphene. Spin precession was observed and the spin lifetimes for the epitaxial graphene were found to be comparable to those found in the exfoliated multi-layer flake. We will also present our measurements of spin relaxation as a function of temperature. The temperature dependence in the spin lifetime observed in the exfoliated flake show a coupling between the magnetic contacts and graphene channel. This is expected due to the lack of a tunnel barrier contact. The comparable spin relaxation times measured in epitaxial graphene fabricated with similar contacts and the multi-layer flake is believed to be caused by a large contact induced relaxation due to the contacts coupling with the graphene channel. The strong coupling effectively removes the spin from the channel.

3:00pm **GR+MI-TuA4 Landau Levels of Dirac Fermions Observed at Zero External Magnetic Fields on Modified Graphite by STS**, ***T. Kondo***, *D. Guo, T. Machida, T. Suzuki, K. Iwatake, S. Okada, J. Nakamura,* University of Tsukuba, Japan

Under the external magnetic field, carriers of graphene are quantized to show an unusual Landau level (LL) energy spectrum due to mass-less Dirac fermions (DFs).[1] The LL energies are not equally spaced and include a characteristic zero-energy state (the n = 0 LL) contrary to the case of normal metals or two-dimensional electron gases. As a result, anomalous quantum Hall effect of graphene has been observed.[2, 3] The quantization of the graphene carrier also occurs without external magnetic field if the appropriate strain is induced.[4,5]Here, we report spontaneous LLs formation of mass-less DFs on potassium intercalated graphite (K-Graphite) and nitrogen-doped graphite (N-Graphite) under zero external magnetic field with the use of scanning tunneling spectroscopy (STS). On the basis of the calculation with the density functional theory, the top-most graphene layer is found to be decoupled with the graphite due to the partial intercalation of potassium atom or nitrogen-doping on graphite. Partially decoupled graphene layer has a sufficient strain to generate the pseudo-magnetic field with about 280 T and 60 T for K-Graphite and N-Graphite, respectively, leading to the LLs formation on the top-most graphene layer on graphite.

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4:00pm **GR+MI-TuA7 Tunneling Spectroscopy of Adsorbed Iron Phthalocyanine on Epitaxial Graphene on SiC(0001)**, ***A.A. Sandin***, *D.B. Dougherty, J.E. Rowe*, North Carolina State University

Graphene may be an ideal material for spin field effect transistors because of its high charge carrier mobility and long spin relaxation times due to small spin-orbit coupling.[1] However, efficient spin injection into graphene requires overcoming conductivity mismatch through the use of tunnel barriers and/or spin filters.[2] It is possible that organic films can serve as tunnel barriers/spin filters with highly tailorable properties. In particular, metal phthalocyanines have recently been shown to exhibit spin dependent interfacial coupling on magnetic electrodes.[3] A study of the coupling and morphology of such molecules on graphene is a crucial first step to understand potential spin enhanced interfaces.

We deposit monolayer iron phthalocyanine (FePc) on both single layer and bilayer epitaxial graphene on the Si-terminated polar face of SiC, named SiC(0001). Scanning tunneling microscopy reveals an adsorbed molecular lattice periodicity of 1.8 nm, close to that of the graphene/SiC buffer layer corrugation periodicity. This lattice spacing is larger than that of FePc adsorbed on a graphite surface that shows a smaller spacing of ~1.4 nm. This implies a stronger interaction of the FePc with epitaxial graphene than expected and is possibly due to the modification of graphene by the SiC substrate. Tunneling spectroscopy has been used to study the occupied and unoccupied electronic states of the absorbed monolayer FePc. Broad unoccupied states indicate significant electronic coupling between the molecules and the graphene and suggest a promising future for molecular strategies for spin injection.

*Supported by the NSF Center for Chemical Innovation: Center for Molecular Spintronics under CHE-0943975.

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4:20pm **GR+MI-TuA8 Atomic Scale Determination of the Bilayer Graphene Energy Gap**, ***S. Jung***, *N.N. Klimov, D.B. Newell, N.B. Zhitenev, J.A. Stroscio*, NIST

We have performed scanning tunneling spectroscopy measurements on a gated bilayer graphene device. In graphene bilayer, a potential asymmetry between the layers induces an energy gap in the electron spectrum. The formation of the energy gap is investigated as a function of carrier density and magnetic field. We found that in zero magnetic field, the reliable determination of the gap can be complicated because of disorder scattering. However, in the quantum Hall regime, the energy gap can be quantitatively determined by measuring the layer-polarized low index Landau levels.

Our scanning tunneling spectroscopy measurements reveal that the microscopic nature of the bilayer gap is very different from what was observed in previous macroscopic measurements or expected from current theoretical models. The potential asymmetry varies spatially in both magnitude and sign on a nanometer length scale, showing strong correlation with the disorder potential. This random pattern of alternating dipole fields is qualitatively consistent with the reduced disorder-induced density fluctuations in the top layer.

4:40pm **GR+MI-TuA9 Atomic, Electronic, and Magnetic Properties of Metal-Graphene Interfaces**, ***I.I. Oleynik***, *L. Adamska, Y. Lin,* University of South Florida, *A. Ross,* Saint Anselm College, *M. Batzill*, University of South Florida

Metal/graphene interfaces play an important role in both surface science studies of the epitaxial growth of graphene on metallic substrates, as well as in metal/graphene contacts in graphene nanoelectronic devices. We present results of first-principles density functional theory (DFT) investigations of structural, electronic, and magnetic properties for graphene/Ni(111) and graphene/Cu(111) interfaces relevant to experimental studies of graphene growth on metallic substrates. The favored interface geometries and binding sites for different interface configurations were identified. Additional adlayers of Ni and Cu were either adsorbed on top of the graphene/metal interface, or placed between the graphene and substrate to model processes of metal intercalation. It was also found that the interaction between graphene/Ni(111) and the top Cu adlayer is much weaker compared to that for a Ni adlayer. The atomic, electronic, and magnetic properties of these interfaces, including induced magnetic moments in graphene/Ni(111), Ni/graphene/Ni(111) systems, are also discussed.

5:00pm **GR+MI-TuA10 Spin-Dependent Scattering from Gated Potential Obstacles in Graphene Systems*, M. Asmar,*** *S. Ulloa*, Ohio University

We study the scattering of Dirac fermions in a sheet of graphene from potential obstacles created by external gates in the presence of both intrinsic and extrinsic spin-orbit (SO) interactions [1]. Obtaining analytical solutions in a real-space representation for the eigenvectors allows us to calculate the phase shifts generated by a finite-size obstacle in the presence of SO interactions [2]. From the phase shifts extracted from these solutions we can calculate the differential, total and transport cross sections. The knowledge of these quantities allows us to obtain the spin-flip and momentum relaxation times. The dependence of both relaxation times on the strength of the SO interaction was analyzed showing comparable relaxation times for relatively large values of energy, while displaying a big difference for small values of energy. The relaxation times of the injected electrons exhibit a number of resonances in energy associated with the structure of the scattering obstacle. In the presence of SO, new resonances appear at energies that depend on the strength of the SO interactions, and as such contain spectroscopic information on the system. It has been shown that the main scattering mechanism in graphene is due to strong defects [3]. Therefore, the analysis performed in our work can help understand the role of SO interactions in the scattering processes in these and related experiments.

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5:20pm **GR+MI-TuA11 Suppression of Weak-Localization Effect in Strained CVD –grown Graphene*, X. Miao*,** *S. Tongay, M. Lemaitre, B.R. Appleton, A.F. Hebard*, University of Florida

We investigate the magnetic field and temperature-dependent transport properties of CVD-grown graphene subjected to different strains. The graphene is transferred to kapton substrates to which a blending force can be applied. In zero magnetic field, the prefactor to the logarithmic-in-temperature conductivity correction decreases by an approximate factor of 3 for strains as high as 0.6 %. There is also a concomitant decrease in diffusivity by a factor of 6. At 5 K we observe negative magnetoresistance for fields up to 0.5 Tesla followed by positive magnetoresistance at higher fields. We attribute the low field negative magnetoresistance to weak-localization and find that it is well described by theory. The strains resulting from the applied blending force inhibit the intervalley scattering more than an order of magnitude and decrease the phase coherence length, thereby leading to a suppression of weak-localization.

5:40pm **GR+MI-TuA12 Simulation of Electron-Ion Dynamics in Pristine and Functionalized Graphene in External Fields*, S. Bubin*,** *K. Varga*, Vanderbilt University

In the framework of real-time real-space time-dependent density functional theory (TDDFT) we have studied coupled electron-ion dynamics in small fragments of graphene, graphane, and fluorinated graphene subjected to short (a few femtoseconds) intense laser pulses or irradiated by energetic ions. The goal of this study is to investigate the possibility of defect creation in graphene and desorption of hydrogen/fluorine from graphene surface. We will present the results of our simulations, discuss the mechanisms that take place, and identify the parameters of the laser or energetic ions necessary for those processes to occur.

Graphene and Related Materials Focus Topic
Room: 209 - Session GR-TuA

Graphene on Dielectrics, Graphene Transfer to Novel Substrates
Moderator: A. Turchanin, University of Bielefeld, Germany

2:20pm **GR-TuA2 A Scanning Tunneling Microscopy and Spectroscopy Study of Artificially Modified Bilayer Graphene*, H. Baek*,** *J. Ha, B. Hwang, J. Kwon,* Seoul National University, Republic of Korea*, J.A. Stroscio,* National Institute of Standards and Technology*, Y. Kuk*, Seoul National University, Republic of Korea

Bilayer graphene has drawn considerable attention due to deviation from Dirac Fermion picture such as anomalous quantum hall effect and a tunable band gap in their spectrum. While a pristine Bernal (AB) stacked bilayer graphene can be synthesized by mechanical exfoliation, growth on a SiC single crystal and epitaxial growth on metal substrates, separate control of the top and the bottom layers has seldom been performed. In this study, artificially modified 2D layers were demonstrated with individually stacked bilayer graphene. Large-area graphene was grown on a Cu foil by chemical vapor deposition (CVD). CVD-grown graphene layers were transferred successively onto insulating substrates with minimum chemical process for realizing bilayer graphene. In this method the mosaic spread between the top and the bottom graphene layers could be varied and an additional thin layer structure could be inserted between the two layers. Artificial bilayer graphene was investigated using scanning tunneling microscopy and spectroscopy. In topographic images and spatially resolved spectrums of local density of states, defect scattering and the misorientation between two graphene layers suggesting weak interaction compared to the AB stacking were found.

3:00pm **GR-TuA4 Dry Transfer of Single Layer Graphene to Polymers*, E.H. Lock*,** *S.G. Walton, M. Baraket, M. Laskoski, S. Mulvaney, W.K. Lee, P.E. Sheehan,* Naval Research Laboratory (NRL)*, D. Hines,* Laboratory for Physical Sciences (LPS)*, J.T. Robinson,* Naval Research Laboratory (NRL)*, J. Tosado, M. Fuhrer*, University of Maryland, College Park

The ability to grow and transfer large area single-layer graphene is critical from both fundamental and applied points of view. The transfer of large area samples will facilitate fundamental studies of graphene's unique properties. It can also allow for the fabrication of three-dimentional structures, electrically insulated graphene bilayers, graphene on previously unexplored substrates and "curved" graphene with non-trivial geometry. Currently, single layer graphene grown via CVD on metal foils is transferred to other substrates via chemical etching of the foil. The transfer process is time consuming, generates chemical waste, and destroys the foils.

We have developed method for direct dry transfer of graphene grown on Cu foils to polymers. The method relies on the differential adhesion between graphene, the metal foil, and the receiving polymer. A successful print results when the adhesion of graphene to the polymer surface is stronger than its adhesion to the metal foil. Plasma treatment of polymers allowed for the attachment of perfluorophenylazide (PFPA) linker molecule. The transfer printing was performed by placing the PFPA treated polymer surface in contact with graphene covered Cu foil and applying heat and pressure. Then, the polymer substrate with transferred graphene was separated from the Cu foil. In this talk, details of the printing process along with graphene film characterization will be discussed.

This work was supported by the Office of Naval Research. M. Baraket appreciates the NRL/NRC postdoctoral research fellowship.

4:00pm **GR-TuA7 Studies on Ozone Based Atomic Layer Deposition of High-k Dielectrics on Graphene*, S. Jandhyala*,** *G. Mordi, B. Lee, J. Kim,* University of Texas at Dallas*, P.-R. Cha*, Kookmin University, Korea

Graphene, being a two dimensional material, is one of the most promising alternative channel materials for post-Si generation [1-3]. However, being just one atom thick and having an inert surface, it poses a huge challenge to develop a top-gate dielectric process for graphene-based devices. Several techniques are currently being explored for depositing dielectrics including physical-vapor deposition (PVD), chemical-vapor deposition (CVD) and atomic layer deposition (ALD) after chemical 'functionalization' of graphene (using NO_2 or O_3) or after depositing nucleation layers (such as Al, PTCA, PVA) on graphene [3].

Here, we will present a novel technique developed by our group for depositing ALD high-k dielectrics such as Al_2O_3 on graphene through ozone functionalization [4]. Physisorption of ozone has been claimed to be the plausible mechanism for functionalizing the graphene surface [5]. Based on Langmuir adsorption equation, the amount of ozone adsorbed on graphene can be increased by increasing the partial pressure of ozone. By utilizing this, we have been able to precisely control the dielectric thicknesses and successfully scale dielectrics on graphene down to a thickness of ~3 nm. We employed both AFM on HOPG/graphene and in-situ electrical characterization of graphene-FETs in order to understand the adhesion mechanisms of ozone with graphene, enabling the deposition of ALD dielectrics. For in-situ electrical characterization, we used package-level devices with back-gated graphene devices to detect molecules adsorbed on graphene surface. The observed charge scattering mechanisms and effect on mobility due to the interaction of ozone with graphene as a function of temperature and amount of ozone will be presented. In-situ studies regarding the role of TMA (Tri-methyl Aluminum) will also be discussed based on experiments in actual ALD chambers.

Acknowledgement

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4:20pm **GR-TuA8 Fluorine Functionalization of Epitaxial Graphene for Uniform Deposition of Ultrathin High-κ Dielectrics**, ***V.D. Wheeler***, *N.Y. Garces, L.O. Nyakiti, R.L. Myers-Ward, J. Culbertson, C.R. Eddy Jr., D.K. Gaskill*, U.S. Naval Research Laboratory

Thermal atomic layer deposition (ALD) is a viable approach to attain high-quality ultrathin dielectric films needed for graphene devices, but the hydrophobic nature of the graphene surface inhibits direct application of thermal ALD oxides. Several methods have been explored to render the surface more susceptible to ALD[1-3], but these techniques often result in graphene mobility degradation and/or shifts in the Dirac voltage due to charge in the gate stack. In this work, we investigated a simple dry chemical approach using XeF$_2$to functionalize the graphene surface prior to ALD which results in conformal ultrathin high-κ oxides without degradation of the underlying graphene electrical properties. Epitaxial graphene samples were grown on semi-insulating, on-axis (0001) 6H-SiC substrates using an Aixtron VP508 SiC reactor at 1650°C for 120 min. Fluorination of the graphene was performed in a Xactix X$_3$ etcher operating in pulse mode. Optimum fluorine exposure conditions consisted of six, 20s pulses with constant XeF$_2$ and N$_2$ carrier gas partial pressures of 1 and 35 torr, respectively. X-ray photoelectron spectroscopy (XPS) was used to chemically analyze the functionalized surface prior to oxide deposition. ALD Al$_2$O$_3$ and HfO$_2$ films ($\leq$ 15 nm) were deposited at temperatures between 150 - 225 °C using TMA or TEMAHf and deionized (DI) water precursors. Growth was initiated with 20 DI water pulses. Oxide coverage was characterized with atomic force microscopy and scanning electron microscopy, while graphene mobility changes were observed with van der Pauw Hall measurements. Capacitance-voltage (C-V) measurements were conducted on Ti/Au C-V dots to extract the dielectric constant and electrical quality of the oxide. Initial results show that 15 nm conformal, uniform Al$_2$O$_3$ and HfO$_2$ films are obtained with an optimized XeF$_2$ surface treatment prior to ALD. XPS showed that the optimum XeF$_2$ treatment resulted in ~6% fluorine on the surface and the presence of only C-F bonds which provide ALD reaction sites needed for uniform oxide deposition. Graphene mobilities were maintained, and occasionally increased, implying little impact of the XeF$_2$ treatment or ALD oxide on the underlying graphene properties. Raman spectroscopy reveals no change in the D/G ratio after XeF$_2$ and oxide deposition, verifying that the graphene lattice quality is maintained. The viability of the fluorination method for achieving ultrathin films (<10 nm) will be presented along with electrical C-V data to show the electronic quality of the ALD oxides.

1. Robinson, et.al. *ACSNano* **4(5)** 2667 (2010)

2. Farmer, et. al. *Nano Letters* **9(12)** 4474 (2009)

3. Lee, et.al. *ECS Transactions* **19(5)** 225 (2009)

4:40pm **GR-TuA9 Improving Performance of CVD Graphene Field Effect Transistors by Reducing Water Trapped at the Graphene/Substrate Interface**, ***J. Chan***, *A. Venugopal, A. Pirkle, S. McDonnell, D. Hinojos,* The Univ. of Texas at Dallas, *C. Magnuson, R.S. Ruoff,* The Univ. of Texas at Austin, *L. Colombo,* Texas Instruments Inc., *R.M. Wallace, E.M. Vogel*, The Univ. of Texas at Dallas

Graphene grown by chemical vapor deposition (CVD) provides a promising pathway for large area fabrication of graphene field effect transistor (FET). However, the performance of CVD graphene FETs reported to date is poorer than FETs fabricated using exfoliated graphene. CVD graphene FETs often exhibit strong hysteresis accompanied with low mobility, large positive Dirac point (V_{Dirac}) and large intrinsic carrier concentration. CVD graphene is exposed to a number of aqueous solutions and deionized water when it is transferred to a device substrate. We find that the large V_{Dirac} shift and strong hysteresis observed in CVD graphene FET are largely due to water trapped in the graphene/substrate interface during the transfer process.

In this study, CVD graphene grown on copper is transferred to SiO$_2$ substrates with the following three interfacial conditions: i) normal hydrophilic SiO$_2$, ii) SiO$_2$ with 20nm of Al$_2$O$_3$, and iii) a hydrophobic surface prepared by coating hexamethyldisilazane (HMDS). Device performance, including mobility, V_{Dirac} and intrinsic carrier concentration are compared in ambient as well as in vacuum. Gate hysteresis is analyzed by measurement of time-resolved channel resistance at various back-gate bias voltages. We find that the gate hysteresis is partially reduced by transferring the graphene onto a substrate coated with HMDS. Vacuum pump down and low temperature (80 °C) annealing can remove the remaining gate hysteresis and V_{Dirac} shift. The resulting hole mobility is 5,420cm^2/Vs, which is high compared to most of the CVD graphene mobility values reported in the literature.

As a control experiment, the CVD graphene FET fabricated on untreated SiO$_2$ shows a smaller mobility, a larger V_{Dirac} and a stronger hysteresis compared to the HMDS coated sample. Under vacuum the hysteresis is reduced but remains significant. We believe the remaining hysteresis is due to adsorbates trapped at the substrate/graphene interface. A graphene FET prepared on a substrate with an Al$_2$O$_3$ interface shows less hysteresis than the sample fabricated on an untreated SiO$_2$ surface but more than that of the HMDS coated surface. In order to study the influence of water trapped between the graphene and the substrate, water is intentionally replaced by isopropanol at the end of the transfer process before drying. In samples prepared using this method, hysteresis and V_{Dirac} point shift are both reduced. These results indicate that efforts to prevent trapping of water molecules at the graphene/substrate interface during the transfer process will improve the performance of CVD graphene FETs.

This work was supported by the NRI SWAN center, ONR, NSF and Sandia's LDRD program.

5:00pm **GR-TuA10 Improved Performance of Top-Gated Graphene-on-Diamond Devices**, ***A.V. Sumant***, Argonne National Laboratory, *J. Yu, G. Liu, A. Balandin*, University of California, Riverside

Since the discovery of graphene and realization of its exceptional electronic properties in suspended form, there have been many efforts in fabricating FET-type devices based on single and bilayer graphene on SiO2 substrate. However, performance of these devices is found to be inferior to the expected intrinsic properties of graphene. It has been observed that apart from carrier mobility in graphene, which is sensitive to trapped charges, and surface impurities at the graphene-oxide interface, breakdown current density in graphene depends sensitively on the heat dissipation property of the underlying supporting substrate. Although graphene has extremely high intrinsic thermal conductivity, it is reported that in graphene devices, more than 70% of the heat dissipates through the 300 nm SiO2 on silicon directly below the active graphene channel while the remainder is carried to the graphene that extends beyond the device and metallic contacts. Such a distribution of heat in to the substrate cause undesirable effects on the overall performance of the device. We show for the first time that by the use of thin CVD-grown ultrananocrystalline diamond thin films on silicon in graphene-on-diamond configuration, the heat dissipation can be improved substantially leading to the higher breakdown current density of more than 50% as compared to conventional graphene-on-oxide substrates. We also describe the fabrication of the top-gate graphene-on- diamond devices and discuss their performance. The obtained devices had the carrier mobility ~ 2354 cm2V-1S-1 for holes and ~1293 cm2V-1S-1 for electrons. The obtained results are promising for developing high-performance graphene-on-diamond devices and interconnects for future electronics.

Use of the Center for Nanoscale Materials was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. The work in Balandin group at UCR was supported, in part, by DARPA – SRC Center on Functional Engineered Nano Architectonics (FENA).

5:20pm **GR-TuA11 Growth of Turbostratic Graphene on Sapphire**, ***S. Rothwell***, *P.I. Cohen,* University of Minnesota, *M. Kumar*, National Physical Laboratory, India

Large area turbostratic graphene was grown on the (0001) plane of sapphire by thermal decomposition of acetylene. Sapphire is an attractive substrate since it has a symmetry match and close coincidence lattice match to graphene. It is a good insulator, appropriate for electronics applications, and large single crystal wafers are readily available. We have found that only after overcoming nucleation barriers, high quality graphene can be grown directly on sapphire without transfer. The sapphire was first heated to about 1400 C to obtain a reconstructed sqrt 31x31 R9 surface structure. The reconstruction was monitored in real time via reflection high energy electron diffraction, which was possible due to the low Debye-Waller factor. After obtaining a clean reconstructed surface, the sample was cooled to near room temperature and exposed to 10 Torr of acetylene. The sample was then heated to 1400 C in the presence of acetylene, in order to nucleate growth. At these pressures, sufficient acetylene coverage for growth was maintained during the ramp to high temperatures. Continued exposure to acetylene at 1400 C did not result in further growth. We speculate that at high temperature there is not sufficient residence time for incorporation, thus lower temperature is needed for further growth. Controlling pressure and temperature during a cool down phase becomes the fine control for film thickness. For example, 10 nm thick graphene samples were obtained by cooling in 1 – 7 E-7 Torr of acetylene. Transmission electron diffraction showed very sharp, nearly continuous rings, indicating large domains and no preferential azimuthal rotation between planes. X-ray diffraction showed an increased layer separation of 0.345 nm compared to graphite. Electron energy loss spectroscopy showed bulk-like plasmons or interband transitions, indicative of multilayer graphene. Raman spectra showed 2D/G peak intensity ratios of 0.5 to 1, comparable to literature values for turbostratic graphene. The spectra also exhibit the expected broader highly symmetric 2D peak. Thicker films could be easily lifted from the substrate. Films greater than 100 nm thick exhibited macroscopic ripples while 10 nm thick films were flat. Hydrogen was explored as a means to control growth but was found to rapidly etch graphene and to passivate the room temperature reconstructed sapphire surface. The growth was modeled with a simple rate equation analysis. These results offer a route to large area graphene grown directly on single crystal sapphire wafers.

Partially supported by the University of Minnesota IREE and by the National Physical Laboratory, India

5:40pm **GR-TuA12 Scanning Tunneling Microscopy and Nanomanipulation of Graphene-Coated Water on Mica**, ***J.D. Wood,*** *K.T. He, E. Pop, J.W. Lyding*, University of Illinois at Urbana Champaign

Graphene on ultraflat substrates such as hexagonal boron nitride has shown to suppress charge puddle formation and give high carrier mobility [1,2]. Transfer of graphene to other ultraflat substrates such as muscovite mica might bring about similar transport characteristics. To that end, we place graphene on mica for scanning tunneling microscopy (STM) studies. We grow monolayer graphene on Cu by chemical vapor deposition and support it with polymethyl methylacrylate (PMMA). We clean the film with water baths and transfer it to mica. In contrast to previous atomic force microscopy (AFM) experiments of dry-transferred exfoliated graphene on mica [3,4], our graphene films trap multiple water layers. After a 700 ºC *in situ* degas, we achieve atomic resolution of graphene on water on mica, and we notice that there are at least 3 layers of ordered, bound water on mica [5], due to the wet transfer and the highly hydrophilic mica. We can atomically image graphene monolayers, bilayers, and grain boundaries regardless of the underlying water structure. Additional water layers on top of the bound water are rough, weakly bound, and amorphous. We notice up to 5 layers of graphene-encapsulated water on mica. Using the STM tip, we can nanomanipulate these amorphous layers at high tunneling conditions (>6 V, 1 nA). These water patterns are highly stable, invariant after several days of scanning. Water nanomanipulation under graphene could help elucidate water’s complex bonding structure and charge transfer from graphene to encapsulated species. Further, graphene-coated water can assist in STM-based research of other aqueous-suspended nanostructures.

[1] Xue *et al.*, *Nature Mat.* **10**, 282 (2011); [2] Dean *et al.*, *Nature Nano.* **5**, 722 (2010); [3] Xu *et al.*, Science **329**, 1188 (2010); [4] Lui *et al.*, Nature **462**, 339 (2009); [5] Park *et al.*, *Phys. Rev. Lett.* **89**, 85501 (2002).

Graphene and Related Materials Focus Topic
Room: East Exhibit Hall - Session GR-TuP

Graphene and Related Materials Focus Topic Poster Session

GR-TuP2 Solution Plasma Assisted Surface Decoration of Chemically Converted Graphene Sheet with Various Metallic Nanoparticles, ***K. Sadasue***, *N. Zettsu, T. Ueno, O. Takai, N. Saito*, Nagoya University, Japan

Like the other newly discovered carbon nanomaterials, such as fullerenes and carbon nanotubes, graphene, a monolayer graphite, and its composites have been widely applied to the field of electrocatalysis due to that graphene have unique structures and inherent properties including high specific surface areas, chemical and electrochemical inertness, easy surface modification, higher electron mobility and broad electrochemical windows. Thus, the use of graphene as substrates of catalysts provides a new opportunity for designing and constructing next-generation catalysts. Especially, graphene decorated with metallic nanoparticles can be employed as fuel cell electrocatalysts, in which they plays an important role in improving the charge-transfer efficiency and decreasing the overpotential of electrochemical reactions such as methanol oxidation and oxygen reduction.

However, there are still unresolved issues in practical use, such as durability. In situ growth method is the most widely used method for preparing graphene/metallic nanoparticle composites. Hydrophobic and/or electrostatic interactions are the main driving forces of adsorbing metallic nanoparticles on graphene surfaces. These relatively week binding interaction often gave rise to desorption of the nanoparticles from the graphene surface during charging and discharging operation at high temperature.

Very recently, we reported a fabrication of Pt catalysts supported on carbon nanoballs, as well as characterization of their electrochemical activities (Saito et al.,

J. Vac. Sci. Technol. A, 27(4) pp.826-830). Plausible mechanism has remained a mystery, Pt catalysts were strongly attached to the carbon nanoball surface. The resultant products showed relatively higher durability compared with than that of catalysts prepared by conventionally used approaches. In this work, we demonstrate surface decoration of chemically converted graphene with various metallic nanoparticles by the originally-developed solution plasma processing. Structural characterization and electrochemical activities of the all product was performed by a combination with TEM, XRD, AFM, Raman spectroscopy, and measurements of oxidation-reduction potential [file:///C:/Users/%E5%AE%9A%E6%9C%AB%E4%BD%B3%E7%A5%90/AppData/Roaming/EdMax/Attachment/20110504_133844_dtub14/AVS%20%E3%82%A2%E3%83%96%E3%82%B9%E3%83%88%EF%BC%88%E5%AE%9A%E6%9C%AB%EF%BC%89_revised_zettsu0504.docx] .

GR-TuP3 Synthesis of Carbon Nanoballs, Covered by CNTs with Metallic Conductivity, ***K. Ohno***, *N. Zettsu, T. Ueno, O. Takai, N. Saito*, Nagoya University, Japan

Carbon nanostructures, due to their unique electronic and extraordinary mechanical properties, have been receiving much attention for a wide variety of applications. Especially, highly-conductive carbon nanostructures is a promising candidate supports for heterogeneous catalysts, for use in fuel cells and in metal-air sources of current. Synergetic interaction of the catalyst-nanoparticles with carbon nanostructures exhibits better catalytic parameters than application of carbonaceous materials.

Very recently, we demonstrated a fabrication of platinum catalysts supported on carbon nanoballs (CNBs), as well as characterization of their electrochemical activities (Saito et al., *J. Vac. Sci. Technol. A*, 27(4) pp.826-830). Originally-developed CNB is a highly crystallized nanosized carbon powder with spherical shape. The CNBs can be synthesized by thermal decomposition of ethylene and hydrogens under argon stream. Diameter of CNB can be tuned from 200 to 700nm by changing the mixing ratio of H_2. Platinum nanoparticles were densely loaded on the CNBs surface under modified solution plasma processing of CNBs and Pt ions with stabilizing agents. We obtained 1.6-fold incr ease in the electrochemical activity of Pt/CNBs system (0.26cm^2/mg) compared with that of conventionally-used Pt/C system (0.16cm^2/mg).

In this work, we propose newly developed CNBs, covered by carbon nanotubes (CNTs) with metallic conductivity in order to reduce contact resistance between neighboring CNBs in electrodes. We grew CNTs from various shaped Fe, Ni nanocrystals deposited onto an individual CNB, and subsequently decorated the surface of the CNBs with Pt nanoparticles as a catalyst by using solution plasma processing. The ratio of metallic to semiconducting CNTs of our all products was evaluated by Raman spectroscopy.

GR-TuP5 Soluble Precursor Synthesis of Grapheme and Graphene Nanoribbons, ***L.M. Tolbert***, *C.L. Henderson, J. Vargas, J. Baltazar, J. Kowalik*, Georgia Institute of Technology

Graphene is currently produced typically through one of three routes: (1) some combination of mechanical and chemical exfoliation of graphite, (2) high temperature processing of SiC, or (3) through high-temperature catalytic methods on metal surfaces using simple carbon precursors such as methane. We are investigating and developing methods for synthesis of graphene through a molecular approach, in which the molecular precursors used already possess most of the C=C bonds necessary for graphene formation. A limitation of such approaches is that many of the precursors, e.g., pentacene, are only sparingly soluble and thus have difficulty being solution coated or have low volatility that prevent vapor phase deposition. Thus we have been investigating the use of soluble precursor molecules which form the grapheme templates at higher temperatures or in the presence of catalysts. In particular, one approach toward solubilization that is under investigation is the use of reversible Diels-Alder chemistry to produce soluble grapheme precursor adducts. After solution coating of the materials onto appropriate substrates, the cycloaddition can be reversed at modest temperatures to produce the desired polyaromatic precursor and subsequently processed into grapheme through a further chemical or thermal consolidation. This presentation will review our progress to date in developing such techniques and will demonstrate the ability to form graphene from such approaches at relatively moderate temperatures. A discussion of the effect of choice of precursor on the ability to consolidate the material into graphene and its resulting quality will be presented.

GR-TuP6 Formation of Graphene Films and Patterned Structures through Deposition of Graphene Oxide on Patterned Aminosilane Monolayers, ***C.L. Henderson***, *L.M. Tolbert, H.-W. Chu, J. Baltazar, J. Kowalik*, Georgia Institute of Technology

Graphene is currently produced typically through one of four routes: (1) some combination of mechanical and chemical exfoliation of graphite, (2) oxidation of graphite to form grapheme oxide which is subsequently deposited onto surfaces and reduceed to grapheme, (3) high temperature processing of SiC, or (4) through high-temperature catalytic methods on metal surfaces using simple carbon precursors such as methane. Some applications for grapheme would benefit from low temperature methods (<400 ^{0}C), and the first two methods mentioned above can inherently provide access to such low processing temperatures. However, simple exfoliation of graphite has only been demonstrated to produce relatively small, poorly controlled grapheme flakes that are not easily processed due to their limited solubility in solvents and lack of methods for further assembly into larger structures. Therefore, we have been investigating the ability to utilize grapheme oxide (GO) flakes as a soluble grapheme precursor that can be assembled onto surfaces to form both continuous grapheme films and directly form patterned grapheme microstructures. We will present a process in which we deposit and pattern aminosilane monolayers on a substrate, pattern them using lithographic techniques, and utilize such aminosilane patterns to control where GO assembles on the surface and subsequently is reduced to form grapheme. It will be demonstrated that by producing aminosilane monolayers that are dense and which possess a large fraction of non-hydrogen bonded amine terminal groups, continuous grapheme oxide and grapheme films and microstructures can be assembled on substrates. It will be shown that by subjecting the resulting assembled grapheme on such aminosilane layers to modest thermal treatments, that stable n-doped grapheme can be produced. The materials produced via such methods will be discussed in terms of their spectroscopic (e.g. Raman) and electrical properties (e.g. I-V curves for FET devices, carrier concentrations, mobilities, etc.)

GR-TuP7 Graphene Layer-By-Layer Growth on Co_3O_4 (111) at 1000 K by Molecular Beam Epitaxy, ***M. Zhou***, *F. Pasquale, J. Kelber*, University of North Texas, *A. Boosalis, M. Schubert, P.A. Dowben*, University of Nebraska - Lincoln

We report layer-by-layer growth of macroscopically continuous and uniform graphene sheets on Co_3O_4(111) at 1000 K by carbon molecular beam epitaxy (MBE) from a graphite rod source. The direct growth of graphene on dielectric substrates is an essential step in the practical and scalable production of graphene-based devices. Co_3O_4(111) films 3 monolayers (ML) thick were formed from surface segregation of dissolved oxygen after deposition ~ 40 Å Co grown on Al_2O_3(0001) substrates at 750 K in UHV. Epitaxial Co_3O_4(111) films, as characterized by Auger spectroscopy and LEED, were formed by subsequent annealing to 1000 K in UHV, and exhibit th a O-O surface nearest neighbor distance of 2.8 Å, in good agreement with literature. The evolution of the Auger electron C(KVV) lineshape during carbon MBE indicates sp^2 hybridization, and layer-by-layer growth up to at least 3 ML average thickness. LEED spectra indicate that the sp^2 (111) graphene overlayer is incommensurate with the Co_3O_4(111) substrate. The graphene-related diffraction spots remain sharp from a coverage of 0.4 ML up to 3 ML, indicating that the graphene sheets are azimuthally in registry with each other. Exposure of the 3 ML graphene/Co_3O_4(111)/Co(111) sample to ambient results in no observable change in Auger or LEED spectra, indicating macroscopically continuous graphene sheets. Subsequent acquisition of XPS spectra in a separate chamber yields a graphite-characteristic asymmetric C(1s) peak at 284.9 eV binding energy, indicating graphene → oxide charge transfer, as observed for graphene/SiC and graphene/MgO. A $\pi \rightarrow \pi^*$ satellite feature is also observed. Spectroscopic ellipsometry measurements carried out in a separate system confirm the presence of a $\pi \rightarrow \pi^*$ resonance, and similarities with the optical absorption of graphene/SiC are observed. Raman spectra acquired at different, macroscopically separated sample areas indicate a uniform 3ML graphene film thickness. These results also strongly suggest that other non-polar (111) transition metal oxide surfaces with similar O-O nearest neighbor distances may act as suitable substrates for graphene growth at moderate temperatures, opening the way to controlled direct growth of high quality graphene on a variety of dielectric substrates, with materials and processing temperatures readily compatible with Si CMOS integration.

Graphene and Related Materials Focus Topic
Room: 208 - Session GR+MN-WeM

Graphene: Mechanical and Thermal Properties, Graphene MEMS and NEMS
Moderator: J. Rabe, Humboldt University Berlin, Germany

8:00am **GR+MN-WeM1 Graphene Atomic Membranes: From Patchwork Quilts to Atomic Drums**, ***P.L. McEuen***, Cornell University **INVITED**

Graphene is the world's first atomic membrane, a robust, one-atom thick freestanding layer of sp2-bonded carbon. The physical properties of these membranes straddle the border between soft and hard condensed matter. They are strong but highly flexible, with bending stiffness comparable to a lipid bilayer but stretching stiffness similar to diamond. Meter-scale polycrystalline graphene films can now be produced cheaply and easily, opening the door to applications in both science and technology. In this talk we will present new results on the structural and physical properties of this remarkable 2D material, including the first STEM images of graphene grain boundaries and the patchwork-quilt-like structure of graphene grains. We also discuss experiments on atomic drums made with graphene membranes that can be actuated and probed either electrically or optically. Unlike for traditional MEMs and NEMs, we find that stiction and entropy are key parameters in determining the drum's vibration frequency.

8:40am **GR+MN-WeM3 Nanomechanics of Graphene: Non-Linear Response, Fracture, and Crack Propagation**, ***R. Perriot***, *Y. Lin*, University of South Florida, *X. Gu*, Aalto University School of Science and Technology, Finland, *V.V. Zhakhovsky, I.I. Oleynik*, University of South Florida

Recent nanoindentation experiments on graphene have revealed its exceptional strength, making it an excellent candidate for the design of nano devices such as MEMS and pressure sensors. Therefore, it is critical to understand the mechanical properties of graphene, and its response to a wide range of loading pressures beyond the elastic regime. In this work we performed molecular dynamics (MD) simulations of the nanoindentation of graphene membranes by a spherical indenter. The indentation curves (load *vs.* indentation depth) obtained from simulations revealed two regimes of response: linear for smaller, and non-linear for larger indentation depths respectively. The MD results are in good agreement with the theory of elastic plates and recent experiments. Using the kinetic theory of fracture, we were able to determine the breaking strength of graphene and its dependence on the indenter radius. MD simulations also provided an atomic-scale description of the breaking process, which occurs through crack formation and propagation in graphene.

9:00am **GR+MN-WeM4 The Effect of the Environment on Electrical and Mechanical Properties of Graphene**, ***K. Bolotin***, Vanderbilt University

Every atom of graphene, a monolayer of graphite, belongs to the surface. Therefore, the environment of graphene -- the substrate onto which graphene is deposited and the coating on top of graphene -- intimately affects the properties of graphene. In this talk, we demonstrate that both mechanical and electrical properties of graphene can be tuned by varying the environment of graphene.

To study the mechanical properties of graphene, we developed a novel technique that is based on measuring the temperature-dependent deflection of a "bimetallic" cantilever composed of graphene and silicon nitride or gold layers. We demonstrate that the built-in strain, the substrate adhesion force and even the thermal expansion coefficient of graphene depend on the substrate under it.

To study the electrical properties of graphene in various environments, we developed a technique to fabricate electrically contacted multiterminal *suspended* graphene devices that are submerged into liquids. We explore the dependence of electron mobility of graphene on dielectric constant and ionic concentration of liquids surrounding graphene. We find that ions in liquids can cause strong scattering in graphene and that very large values of mobility (>40,000 cm^2/Vs) can be achieved in ion-free liquids.

9:20am **GR+MN-WeM5 Nanoscale Friction and Adhesion Behavior of Graphene: The Effect of Sliding History**, ***X.-Z. Liu***, *Q. Li, B. Zhang, R.W. Carpick*, University of Pennsylvania

As a prominent example of a two-dimensional (2-D) material, graphene has drawn much attention because of its extraordinary physical properties. However, in contrast to its electronic and thermal properties, the mechanical and tribological properties of graphene remained poorly understood. These properties are interesting scientifically because of the extremely high strength and low defect density of the bonds, and the intrinsically wrinkled structure of graphene. These properties are important for integrating graphene with devices. We studied the friction and adhesion between nanoscale single-asperity tips and exfoliated graphene sheets using atomic force microscopy (AFM). We have previously reported that friction on few-layer graphene (and other 2-D materials) depends on the number of layers[1], whereby the friction is higher for fewer layers. The layer-dependence is associated with the presence of a "strengthening" effect, where the static friction force builds up as scanning proceeds, most evident for the thinnest layers. This suggested that the increase was due to the build-up of a puckered area in front of the tip due to the high compliance of the graphene and adhesion with the tip. However, adhesion between the tip and graphene, measured by regular AFM force-displacement spectroscopy, does not change appreciably when the layer number changes. This result agrees with trends obtained from finite element method (FEM) simulations. However, we observed that both friction and adhesion exhibit a contact history dependence. For friction on single layer graphene, the strengthening is not present initially, but rather, it gradually builds up as the tip is rastered over the surface. This suggests that the puckered structure requires repeated scanning before it geometrically develops to a point where friction is enhanced. In addition, we find that adhesion is enhanced if it is measured without breaking the tip-graphene contact after sliding the AFM tip over the same area for a sufficient distance. This sliding-history dependence was not observed on bulk graphite or SiO2 substrates, and thus appears to be yet another unique feature of the tribological behavior of atomic sheets These two observations strongly suggest that the geometric structure of the sheet and the contact area it makes with the tip is significantly affected by the sliding history.

[1] Lee, C., Q. Li, W. Kalb, X. Liu, H. Berger, R. Carpick, and J. Hone, *Frictional Characteristics of Atomically Thin Sheets.* Science, 2010. **328** (5974): p. 76.

10:40am **GR+MN-WeM9 Molecular Dynamics Simulations of Melting of Graphene**, ***B. Steele***, *V.V. Zhakhovsky, R. Perriot, I.I. Oleynik*, University of South Florida

It has long been predicted by Peierls, Landau, and Mermin that infinite two-dimensional solids are unstable and should melt at any finite temperature. The stability of graphene, a two-dimensional layer of carbon atoms, is thus explained by the presence of an additional degree of freedom that allows it to buckle in the third direction normal to the 2-D perfect plane. We performed large-scale molecular dynamics (MD) simulations of graphene melting in order to provide a fundamental insight into the stability of graphene, as well as to investigate the nature of the defects naturally created by thermal excitations at high temperatures. We will discuss the types of defects appearing before melting, the atomic-scale mechanisms of melting, and the nature of the resulting carbon melt. In addition, the graphene melting in 3D space *versus* 2D-constrained melting is also discussed. The importance of a proper description of chemical bonding in graphene at high temperatures is illustrated using different interatomic potentials: the reactive bond order (REBO) potential and the newly developed screened environment dependent SED-REBO. Comparisons with other recent simulations of graphene melting (including those using the LCBOPII potential for carbon) are also presented.

11:00am **GR+MN-WeM10 Inhomogeneous Strain in Monolayer Epitaxial Graphene**, ***D.A. Schmidt***, Ruhr-University Bochum, Germany, *T. Ohta, L.B. Biedermann, T.E. Beechem, S.W. Howell, G.L. Kellogg*, Sandia National Laboratories

We report a large in-plane compressive strain (up to 0.5%) and its inhomogeneous variation at micrometer length scale in single layer graphene films on silicon-carbide (SiC) (0001). The strain, due to the difference in lattice constants and thermal expansion coefficients of graphene and SiC substrate, is probed using Raman scattering. We show that both the growth mechanism and the relaxation along the mismatched symmetry of the graphene and underlying substrate can affect the exact amount of local strain. The large compressive strain implies that monolayer graphene is tightly grafted to the underlying interface layer and SiC substrate; otherwise it would delaminate to relieve the strain. The magnitudes of the structural strain and its local variation are significant and need to be taken into account for electronics applications based on the graphene-SiC(0001) system.

The Raman microscope was supported under BMBF grants 05KS7PC2. D. A. S acknowledges support within the BMBF funded projects 05KS7PC2 and 05K10PCA. The work was also supported in part by the LDRD program at SNL and the US DOE Office of Basic Energy Sciences' Division of Materials Science and Engineering (Contract No. DE-AC04-94AL85000). Part of this work was performed at CINT (Contract No. DE-AC04-94AL85000). SNL is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Surface Science Division
Room: 109 - Session SS2-WeM

Chemisorption on Metal & Oxide Nanoparticles
Moderator: B. Roldan Cuenya, University of Central Florida

8:00am **SS2-WeM1 Temperature Program Desorption and X-ray Photoelectron Spectroscopy Study of Cu_x on CeO_2/YSZ (111)**, ***J.C. Lofaro, Jr.***, Stony Brook University, *M.G. White*, Stony Brook University and Brookhaven National Laboratory

Energy research has increased in importance in the past decade due to our growing understanding of climate science and rising oil prices. Many catalysts center around expensive and rare transition metals, such as Pt and Pd, supported on oxide substrates. However, copper, a relatively cheap and abundant metal, supported on metal oxides has been used as a heterogeneous catalyst in industrial settings for various chemical processes.[1,2] Recent works have shown that copper nanoparticles supported on metal oxides (ZnO, CeO_2, TiO_2) have higher activity for the water gas shift reaction (WGSR) as well as other important chemical reactions when compared to their individual components.[3,4] Understanding how these complex catalysts work on a fundamental level will allow for the design and implementation of more efficient and selective systems in the future. Here, using a homemade thermal evaporator, a model system of copper nanoparticles deposited on CeO_2 films (200 nm thick) grown on YSZ (111) single crystals is used. X-ray photoelectron spectroscopy (XPS) is used to characterize the oxidation state of supported copper nanoparticles and temperature programmed desorption (TPD) is used to probe their reactivity and thermal stability. Copper coverages ranging from 0.25ML to 1ML are investigated. Carbon monoxide and water are used as probe molecules since they are the reactants involved in the WGSR. We have found that copper's stability is highly temperature dependent and have found evidence of its encapsulation by the support.

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8:20am **SS2-WeM2 X-ray Photoelectron Spectroscopy and Scanning Tunneling Microscopy Characterization of the Active Edge Sites of MoS_2 Nanoclusters**, *A. Tuxen, S. Porsgaard, H. Goebel, F. Besenbacher,* ***J.V. Lauritsen***, Aarhus University, Denmark

The atomic and electronic structure of MoS_2 nanoclusters is of considerable interest due to the catalytic application of MoS_2 in e.g. hydrotreating catalysis of crude oil and in photocatalysts and hydrogen evolution reactions. Previous atom-resolved STM results have shown in great detail that both the overall morphology and in particular the edge structure of MoS_2 nanoclusters, which are known to contain the most catalytically active sites for hydrotreating and H_2 dissociation, adopt a structure which is very dependent on the conditions under which the cluster are kept. Under sulfiding conditions, atom-resolved STM images show that the MoS_2 nanoclusters expose fully sulfide edges, whereas activation by H_2 or mixed H_2/H_2S exposures show that sulfur vacancies and S-H form on the cluster edges reflecting the MoS_2 catalyst in its active state. To dynamically follow such structural changes at the MoS_2 edges induced e.g. by hydrotreating reaction conditions we have here combined high-resolution x-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) studies of single-layer MoS_2 nanoclusters with a well known structure. The XPS studies done on well-characterized samples reveal a set of edge specific core level shifts in the Mo3d photoemission peak that can be uniquely associated with the fully sulfide edges, edge with S vacancies or fully reduced edges. The XPS fingerprint thus allows us to dynamically follow changes between the catalytically active states of MoS_2 when exposed to sulfiding of sulforeductive conditions. Preliminary *in-situ* XPS results on the same MoS_2 samples obtained under a 10^{-2} torr H_2 atmosphere on the Ambient Pressure X-ray Photoelectron Spectroscopy on beamline 11.0.2 of the Advanced Light Source Berkeley show a characteristic sequence of sulfur reduction steps on the catalytically interesting edges followed by decomposition of MoS_2 at higher temperatures. The present studies thus successfully shows that XPS in combination with STM can be successfully used as a tool to characterize the chemistry of highly dispersed active sites of well-defined nanoclusters, such as the active edges on MoS_2.

8:40am **SS2-WeM3 Charge-Mediated Chemisorption on Supported Clusters**, ***M. Sterrer***, Fritz-Haber-Institute of the Max-Planck-Society, Germany **INVITED**

Among the many factors that influence catalytic activity of supported metal clusters, the effects of size and charge state of the clusters are most frequently discussed, e.g., in CO oxidation over supported gold. In this contribution, I will present results of our recent experimental efforts to characterize metal clusters supported on single-crystalline model oxide surfaces, using Au on MgO thin films as example. Using a combination of various surface science techniques including low-temperature scanning tunneling microscopy, infrared spectroscopy, X-ray photoelectron spectroscopy, and electron paramagnetic resonance, the properties of supported Au atoms and clusters were addressed in detail. Starting with the unusual CO chemisorption behavior of single Au atoms on the perfect MgO(001) surface, I will move on and show how the charge state of Au particles on the MgO surface, which in most cases is inferred from distinct CO chemisorption features, may be influenced by modification of the oxide surface, e.g. by their interaction with defects or hydroxyl groups, or by the MgO film thickness.

9:20am **SS2-WeM5 The Structure and Chemical Activity of Two-dimensional Gold Islands on Single-layer Graphene/Ru(0001)**, ***L. Liu***, Texas A&M University, *Y. Xu,* Oak Ridge National Laboratory, *Z. Zhou,* Texas A&M University, *Q. Guo,* Chinese Academy of Sciences, China, *Z. Yan, Y. Yao,* Texas A&M University, *L. Semidey-Flecha,* Oak Ridge National Laboratory, *D.W. Goodman*, Texas A&M University

Single-layer graphene supported on transition metals provides a unique substrate for synthesizing metal nanostructures due to the high crystallographic quality, thermal stability, and chemical inertness of the graphene. Contrary to its formation of three-dimensional (3-D) nanoclusters on graphene supported on a SiO_2 substrate, Au forms two-dimensional (2-D) islands on graphene moiré/Ru(0001). These Au islands maintain their 2-D structures up to 1 monolayer (ML) equivalent of Au dosage and are stable at room temperature. Our scanning tunneling microscopic study further shows that the 2-D Au islands are most likely two layers high, and conform to the graphene moiré in the lateral direction. Spin- and angle-resolved photoemission studies indicate even though these Au islands are largely electronically isolated, a weak through-graphene coupling exists between the Au islands and the Ru(0001) substrate. The structure for these 2-D Au islands and the corresponding electronic band structures are proposed based on DFT calculations.

Parallel studies using polarization modulation infrared reflection absorption spectroscopic (PM-IRAS) and high resolution electron energy loss spectroscopic (HREELS) indicate that CO adsorbs on these 2-D gold islands at 85 K with a characteristic CO stretching feature at 2095 cm^{-1} for a saturation coverage. Preliminary data obtained by dosing molecular oxygen onto this CO pre-covered surface suggest that the 2-D gold islands catalyze the oxidation of CO. These electron-rich, weakly coupled 2-D Au islands provide a unique platform to study the intrinsic catalytic activity of low-dimensional Au nanostructures.

9:40am **SS2-WeM6 Spatially Resolved Measurements of Catalytic Activity on Variable-Composition Pd-Cu and Pd-Cu-Au Thin Films using a Microfluidic Reactor Array**, ***P. Kondratyuk***, *G. Gumuslu,* Carnegie Mellon University, *B.D. Morreale,* National Energy Technology Laboratory, *J.B. Miller, A.J. Gellman*, Carnegie Mellon University

A new experimental approach to mapping the relationship between composition and catalytic activity in metal alloy catalysts is presented. We apply this methodology to study H_2-D_2 exchange reaction on Pd-Cu and Pd-Cu-Au alloys. The activity measurements were performed on thin alloy films deposited in such a way that the elemental composition varied continuously across the film. We refer to these films as composition spread alloy films (CSAFs). CSAFs were prepared by co-deposition of Pd, Cu and Au onto a molybdenum substrate under UHV conditions. The top-layer and near-surface composition of the CSAFs were determined by low-energy ion scattering (LEIS) and X-ray photoemission spectroscopy (XPS) respectively. The activity of the alloy films in the H_2-D_2 exchange reaction was analyzed at atmospheric pressure using a 100-channel glass microfluidic device. During the spatially-resolved activity measurements, the microfluidic device delivers reactant gases to a 10x10 array of measurement points on the CSAF surface covering an area of 1 cm^2, each measurement point corresponding to a different catalyst composition. After coming in contact with the catalyst, the gases are withdrawn for mass-spectrometric analysis through a separate set of channels. The activity-composition relationship can then be established by correlating the XPS (or LEIS) data with the product concentration in each channel of the microfluidic device.

10:40am **SS2-WeM9 Surface Structure Dependence by Monofaceted CeO_2 Nanoparticles: Catalytic Oxidation Reactions**, *M. Li, Z. Wu, F.C. Calaza, D.R. Mulllins,* ***S.H. Overbury***, Oak Ridge National Laboratory

Reducibility of pure and doped CeO_2 is of interest in emission control catalysts because of the ability of the CeO_2 to store and supply oxygen during oxidation catalysis. But, it is not known how the structure or crystallographic termination of the CeO_2 affects the catalytic reaction rates and selectivity. Using CeO_2 nanoparticles with controlled shapes including cubes, octahedra and rods that are terminated on (100), (111) and (110) surfaces respectively, we have investigated this structure dependence. Temperature programmed desorption, temperature programmed reaction, flow reactor rates, and in situ DRIFTS were used to probe adsorption states, desorption, reaction, oxidation rates and product selectivity for CO and ethanol oxidation. Results show pronounced differences between the three different morphologies. All morphologies show evidence of surface ethoxide species at room T, but during subsequent TPD, the DRIFTS exhibits variation in surface species between the different surfaces with evidence for formation of adsorbed acetaldehyde and acetate. Temperature induced changes in the C-H stretching regions, different also for each polymorph, suggest competing dehydrogenation and dehydration of surface species. Desorption temperatures and product distributions also vary. The ratio of H_2/H_2O, and the H_2 peak desorption temperature is highest for the octahedra, consistent with its highest vacancy formation energy and therefore least available oxygen. This ratio is lowest for high surface area multi-faceted nanoparticles, and its variability has important implications for tailoring and understanding CeO_2 catalysts or supports for production of H_2 in ethanol fuel cells. Product profiles during TPR of ethanol in O_2 were also dependent upon the surface structure. Octahedra show the highest selectivity to acetaldehyde and an onset of H_2 evolution above 400 °C while the cubes and rods showed lower temperatures for the onset of H_2, indicating that the hydrogen is evolved by two different pathways on different shaped ceria. Similarly, in a steady state flow reactor, the ratio of selective oxidation product (acetaldehyde) to the total oxidation product (CO_2) followed the order (111) > (100) > (110). Such results provide a basis for fundamental understanding of how surface coordination, bonding, decomposition and reaction are affected by the atomic structure of an oxide surface, especially important for reducible oxides.

Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, US DOE.

11:00am **SS2-WeM10 Tuning the Adsorption Properties of an Oxide Material Via Doping: Au Clusters onto Cr-doped MgO(001) Films**, ***F. Stavale***, *N. Nilius, H.-J. Freund*, Fritz-Haber-Institute of the Max-Planck-Society, Germany

The doping of metal oxides has been explored in several investigations with the aim to prepare better materials for catalysis, optics and electronic applications. Doping of wide-gap oxide materials can be realized by the controlled introduction of various types of lattice defects, including point defects such as oxygen vacancies, line defects (e.g. grain boundaries and dislocations) and impurity atoms. In this study, we have exploited photon-scanning tunneling microscopy used in imaging as well as in cathode-luminescence mode to investigate Au clusters supported on thin, single crystalline MgO(001) and Cr-doped MgO(001) films grown on Mo(001). First of all, we have prepared Cr-doped MgO films on a Mo(001) support as a model system for a transition-metal doped wide-gap insulator with interesting applications in catalysis. To elucidate the role of the Cr in the MgO matrix, the morphological and optical properties of the system were analyzed as a function of the Cr load, using the STM. The Cr was incorporated into the film either by Cr-Mg co-deposition in oxygen or post-evaporation followed by an annealing step. From the distinct light emission properties of the doped oxide, a detailed picture has been developed on the Cr^{+3} position inside the MgO lattice and the associated modifications in the electronic structure. The role of the Cr dopants on the adsorption behaviour of the oxide film was investigated by depositing small amounts of Au. While on pristine MgO films, Au nucleates into 3D particles, mainly 2D aggregates form on the doped oxide support. We assign this change in the Au growth mode to charge transfer processes from the Cr centres into the Au clusters and will discuss possible consequences on the chemical activity of the doped metal-oxide system.

11:20am **SS2-WeM11 Hydrogen Adatom Manipulation on the Rutile TiO_2(110) Surface using LT-STM**, ***P. Sutter***, *D. Acharya, N. Camillone III*, Brookhaven National Laboratory

Characterization and control of the structure of TiO_2 surfaces at the single-atom level are vital to the development of a fundamental understanding of the chemistry and physics of this technologically important oxide. In this work we investigate the use of a low-temperature scanning tunneling microscope (LT-STM) tip to manipulate individual hydrogen adatoms on the rutile TiO_2(110) surface at 77 K. We show that applied voltage pulses are effective for transferring hydrogen atoms from the surface to the STM tip with single-atom control. This tip-induced 'desorption' is useful for unambiguously distinguishing between surface hydroxyls (OH_{br}) and bridging oxygen (O_{br}) vacancies—two common surface defects whose appearance in STM images is quite similar. In addition we show that individual atoms can be redeposited on the surface precisely at selected O_{br} sites, allowing for the controlled preparation of arbitrary hydrogen adatom assemblies. Such control is a prerequisite for the investigation of the structural dependence of surface photo- and thermal reactivity at the single-molecule level.

11:40am **SS2-WeM12 Reaction of Water with Terminal Hydroxyls on TiO_2(110) Surface**, ***I. Lyubinetsky***, *Y.G. Du*, Pacific Northwest National Laboratory, *N.A. Deskins*, Worcester Polytechnic Institute, *Z. Zhang*, Baylor University, *Z. Dohnalek, M. Dupuis*, Pacific Northwest National Laboratory

We report a combined experimental and theoretical investigation of the reaction of molecular water with terminal hydroxyls (OH_t's) on reduced TiO_2(110)-(1x1) surface at 300 K. We show that OH_t's have a significant effect on the water reactivity and extract molecular-level details about the underlying reaction mechanisms. By tracking the same surface area with high-resolution scanning tunneling microscopy before and after water exposure, we demonstrate that there are two distinctive reaction pathways involving multiple proton transfers [1]. For water interaction with OH_t on an adjacent Ti row, the proton can be transferred through bridging oxygen to OH_t, which leads to the formation of a new water molecule and apparent across-row motion of OH_t due to O scrambling. This process further manifests the existence of the equilibrium between molecular and dissociated states of water on TiO_2(110) [2]. If H_2O interacts with OH_t along the same Ti row, fast multi-step OH_t motion along the Ti row is observed. Our density functional theory results show that this process is caused by the fast diffusion of (OH_t + H_2O) pairs, whereby the underlying mechanism involves proton transfer and H_2O hopping over OH_t.

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[2] Y. Du, N. A. Deskins, Z. Zhang, Z. Dohnálek, M. Dupuis, and I. Lyubinetsky, Phys. Rev. Lett. 102 (2009) 096102.

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

Graphene Characterization including Microscopy and Spectroscopy

Moderator: J.T. Robinson, Naval Research Laboratory

2:00pm **GR-WeA1 Scanning Probe and Optical Microscopy and Spectroscopy of Graphenes on (sub-) Molecular Layers on Atomically Flat Substrates***, **J. Rabe**, N. Severin, P. Lange, M. Dorn, S. Eilers*, Humboldt University Berlin, Germany **INVITED**

Graphenes were used to cover solid substrates, including silicon wafers and atomically flat mica, pre-coated with molecularly thin liquids as well as single macromolecules. Optical reflection microscopy was employed to identify single graphenes on optically transparent substrates in optical reflection microscopy with a contrast of more than 12% [1]. A combined fluorescence and scanning force microscopy study revealed that that graphene is not only a highly conductive and transparent electrode, but also a most effective barrier to protect conjugated polymers against degradation through water and oxygen [2]. Time resolved pump-probe spectroscopy revealed ultrafast nonequilibrium carrier dynamics [3]. Finally, scanning force and electrostatic force microscopy, and also STM/STS were used to characterize structure and electronic properties of single graphenes with molecules either on top or below the graphene, revealing a remarkable stability of the elctronic properties of these hybrid systems.

[1] M. Dorn, P. Lange, A. Chekushin, N. Severin, J.P. Rabe, *J. Appl. Phys.* 108 (2010) 106101.

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2:40pm **GR-WeA3 Scanning Tunneling Microscopy and Spectroscopy of Suspended Graphene Membranes**, ***N.N. Klimov***, PML/CNST/NIST and Maryland NanoCenter UMD*, S. Jung*, CNST/NIST and Maryland NanoCenter UMD*, N.B. Zhitenev*, CNST/NIST*, D.B. Newell*, PML/NIST*, J.A. Stroscio*, CNST/NIST

The discovery of graphene, a unique two-dimensional electron system with extraordinary physical properties, has ignited tremendous research activity in both science and technology. Graphene interactions with a substrate such as, for example, SiO_2/Si are known to strongly limit the electrical performance of graphene devices. Suspended graphene devices, where the interaction with substrates can be strongly reduced, have been studied by macroscopic transport measurements and shown to have a 10-fold increase in mobility. However, a detailed investigation of electronic properties of suspended graphene on a microscopic scale is still missing. In this talk we present a scanning tunneling microscopy/spectroscopy (STM/STS) study of free-standing graphene membranes. The device was fabricated from a graphene flake exfoliated over an array of 1 µm holes etched in SiO_2/Si substrate. Electronic spectra of both suspended and supported regions of single-layer graphene can be probed using STM/STS in a perpendicular magnetic field with varying back gate voltages applied to the Si substrate. We found that both the scanning probe tip and applied back gate voltage induce mechanical deformations in the suspended graphene membrane, which, in turn, influences the graphene electronic spectrum. The significant differences found in the electronic spectra of suspended and non-suspended graphene will be discussed.

3:00pm **GR-WeA4 Moiré Twist and Absence of Chirality in Graphene on Ru(0001)**, *K.L. Man, **M.S. Altman***, Hong Kong University of Science and Technology, China

The strength of the interaction between graphene and a supporting metal substrate is revealed in its influence on electronic structure and properties. Knowledge of structure is of elementary importance for understanding the nature of this interaction. The structure of a single layer of graphene (g) on the Ru(0001) surface has been controversial, beginning with the elementary matter of its lateral periodicity. It was eventually shown using surface x-ray diffraction (SXRD) that a superstructure forms from the moiré-like superposition of (25x25) graphene on (23x23) Ru units [1]. Although corrugation was detected within the supercell, the predominant origin of corrugation in this system, whether physical or electronic, has been disputed. Intriguing evidence from SXRD was also put forth that g/Ru(0001) exhibits chirality, whereby the weakly bound, protruding regions of a physically corrugated graphene layer are rotated in-plane by up to two degrees [2]. We have investigated single layer g/Ru(0001) using low energy electron microscopy (LEEM) and micro-low energy electron diffraction (µLEED) in order to verify the existence of chirality. Chirality should give rise to differences between the intensities of diffraction spots mirrored across the high symmetry directions. However, this broken mirror symmetry will be very difficult to detect using laterally averaging techniques such as SXRD because of the presence of two chiral enantiomers and two terminations of the hcp substrate. Using LEEM and µLEED we have successfully obtained diffraction information from an area with a diameter of 250 nm within a single surface termination. While no evidence is found with such high spatial resolution diffraction measurements that confirms chiral features within the unit cell, we do in fact observe rotation or twist of the moiré-like superposition over long length scales. Moiré twist causes the entire ensemble of satellite diffraction spots around each integer order spot to rotate as a group about their respective stationary foci. When the µLEED beam is scanned across the surface, the rotation angle undulates randomly. The data also suggest that the ground state configuration comprises a graphene layer that is slightly rotated with respect to the underlying substrate surface. Conceivably, the orientational variations that are observed here over sub-micron length scales might produce a signature in laterally averaging measurements that could be construed as evidence of chiral features on the short length scale within the unit cell.

[1] D. Martoccia *et al.*, Phys. Rev. Lett. **101**, 126102 (2008).

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4:00pm **GR-WeA7 Scanning Tunneling Microscopy Study on a Graphene Layer Grown on a Single-crystal Cu(111) Surface by Using Chemical Vapor Deposition***, **W. Kim**,* Korea Research Institute of Standards and Science, Republic of Korea*, K.-E. Yang,* KRISS and Chunnam National Univ., Republic of Korea*, K. You, S.J. Kim, E.K. Seo, C. Hwang*, Korea Research Institute of Standards and Science, Republic of Korea

We investigated the surface atomic structure of a graphene layer grown on a single-crystal Cu(111) surface by using a chemical vapor deposition method. The low-energy electron diffraction pattern shows a clear ring structure, which indicates the existence of multiple domains with different in-plane orientations. In the scanning tunneling microscopy(STM) experiment, two domains showing different Moiré patterns and a domain boundary between them are observed. The misorientation angle between the domains was estimated from the quantum interference pattern around the domain boundary and the atom-resolved image of each domain. In the STM images of the domain boundary, the chain of protrusions was observed, which indicates the existence of localized electronic states originated from the pentagon or heptagon structures at the boundary.

4:20pm **GR-WeA8 Interface Structure of Graphene on SiC(000-1)**, ***N. Srivastava**, G. He, R.M. Feenstra*, Carnegie Mellon University

The graphene/SiC interface structure is quite well understood on the SiC(0001) surface (the *Si-face*) but the situation is less clear on the SiC(000-1) surface (the *C-face*). For the C-face some groups report a 3×3 and/or 2×2 interface structure with weak interaction with the underlying substrate.[1] A single study however found an interface layer that was strongly bonded to the SiC.[2] We demonstrate that the interface layer on the C-face depends on the means of graphene formation. For graphitization in vacuum we observe a 3×3 interface in agreement with other groups. However for graphitization in a Si-rich environment we observe a new interface indicative of a buffer layer similar to that seen on the Si-face.

In this work, graphene films are formed by heating the C-face in vacuum or in a disilane environment. It is found that different interface structures occur for the two preparation conditions. In particular, in 5×10^{-5} Torr of disilane we find a graphene-like buffer layer forming at the interface, analogous to the well known behavior of the Si-face. We therefore find that graphene formation on the C-face and Si-face are not so much different (although they appear to be when using vacuum preparation): A buffer layer that acts as a template for graphene formation exists in both cases, so long as equilibrium conditions are employed (i.e. with the disilane environment).

Studies are performed using atomic force microscopy (AFM), low-energy electron diffraction (LEED), and low-energy electron microscopy (LEEM). For graphene prepared in vacuum, LEED patterns show a characteristic 3×3 pattern together with graphene streaks. In contrast, for the graphene produced in 5×10^{-5} Torr of disilane, LEED patterns reveals a complex $\sqrt{43}\times\sqrt{43}$-R±7.6° arrangement. This structure is somewhat similar to the well known $6\sqrt{3}\times6\sqrt{3}$-R30° “buffer layer” of the Si-face, with satellite spots surrounding the primary Si spots, and is interpreted as arising from a C-rich buffer layer with 8x8 graphene unit cells on the SiC (with rotation angle of ±7.6° rather than 30° for the Si-face). After air exposure the $\sqrt{43}\times\sqrt{43}$-

R±7.6° pattern changes, with the intensity of the graphene streaks increasing and the √43×√43 spots themselves disappearing and being replaced by √3×√3-R30° spots. This latter behavior is interpreted as oxidation of the SiC surface beneath the buffer layer,[3] again similar to what occurs on the Si-face. LEEM reflectivity curves on the surface reveal features similar to those for the 6√3×6√3-R30° layer on the Si-face.[4] Importantly, selected area diffraction on those surface areas, after oxidation, reveals a wavevector magnitude precisely equal to that of graphene, thus proving that a decoupled buffer layer does indeed exist on the surface. It is argued that the C-face buffer layer represents the equilibrium structure of the interface, whereas the 3×3 interface forms due to kinetic limitations.

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[4] Hibino et al., Phys. Rev. B **77**, 075413 (2008).

4:40pm **GR-WeA9 Thermionic Emission of Graphene on Metal Surfaces**, ***E. Starodub***, *N.C. Bartelt, K. McCarty*, Sandia National Laboratories

We employ low-energy electron microscopy (LEEM) to study the thermionic emission of graphene on representative metals, Ru(0001) and Ir(111). In traditional LEEM, an image is produced using low-energy electrons reflected from a surface. The unique capabilities of LEEM allow us to image directly electrons thermionically emitted from graphene at high temperatures, above 1100K, using the same imaging optics. Due to the strong dependence of emission current on temperature, given by the Richardson-Dushman equation, we determine the work function of graphene-covered Ru(0001) and Ir(111) surfaces. The work function of graphene on Ru(0001) is determined to be 3.4 ± 0.1 eV, which is considerably smaller than work function of clean Ru (5.4 eV) and graphene (4.6eV). The obtained value is in good agreement with the result of first principles calculations, 3.6 eV [1], where strong graphene/metal interaction leads to significant film-to-substrate charge transfer and, as a result, reduced work function.

In contrast to the strong interaction with Ru, graphene bounds weakly to the Ir surface reducing the work function. The work functions of graphene on Ir(111) measured for two in-plane orientations on the Ir surface [2], R0 and R30, are 4.5 ± 0.1 eV and 4.7 ± 0.1 eV, respectively. Thus, the in-plane orientation noticeably changes the work function on Ir. It is consistent with our previous observation of the effect of electronic structure on orientation by electron reflectivity [3] and ARPES [4] .

Our finding shows that graphene has another application in addition to be a promising candidate for future electronics. One-monolayer graphene on metals such as Ru and Ir can be used as a chemically inert electron emitter with large surface area and low work function, comparable to lanthanum hexaboride, LaB_6.

Acknowledgement: This work is supported by the Office of Basic Energy Science, Division of Materials Sciences and Engineering of the U.S. DOE under Contract No. DE-AC04-94AL85000.

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5:00pm **GR-WeA10 Imaging Epitaxial Graphene on SiC(0001) using STM with Functionalized W Tips**, ***S.H. Rhim***, *Y. Qi, G.F. Sun, Y. Liu, M. Weinert, L. Li*, University of Wisconsin-Milwaukee

Epitaxial graphene on SiC(0001) is studied using scanning tunneling microscopy with W tips functionalized by transition metal (Cr, Fe) coating, which enables the imaging of states within a few meV of the Fermi level that are not accessible with conventional W tips. Modeling of these tips using X/W(110) (X=Cr, Fe, W) by first-principles calculations indicates that states responsible for enhanced tunneling are located 0.4~0.6 eV above and below E_F for Fe/W tips, and 0.3 eV above E_F for Cr/W tips. Further calculations show that the formation of an apex atom is not stable for W/W(110) or Fe/W(110) tips, but is stable for Cr/W(110) tips, resulting in point-like iso-density of states contours that are ideal for the selective imaging of the complex electronic properties of the epitaxial graphene on SiC(0001).

5:20pm **GR-WeA11 Hydrogenation of Epitaxial Graphene on 6H-SiC(0001): The Formation of Hydrogen-Vacancy Complex**, *Y. Liu, M. Weinert,* ***L. Li***, University of Wisconsin-Milwaukee

In this work, we have studied the hydrogenation of epitaxial graphene on 6H-SiC(0001) by Ar/H_2 plasma at room temperature. Two predominant types of defects are observed, and their atomic and electronic structures are studied by scanning tunneling microscopy/spectroscopy (STM/STS) and first principles calculations. The results suggest that vacancies are created with hydrogen atoms trapped nearby between the graphene sheets, forming H-vacancy complexes. In addition, changes in the electronic structures of the defects are also observed during STM imaging, which can be attributed to the dissociation and recombination of these complexes by the electric field of the STM tip. These results and their impact on the gap opening in hydrogenated graphene will be presented at the meeting.

5:40pm **GR-WeA12 Many-Body Interactions in Quasi-Freestanding Graphene**, ***D.A. Siegel****, *C.H. Park,* University of California, Berkeley, *C.G. Hwang,* Lawrence Berkeley National Laboratory, *J. Deslippe,* University of California, Berkeley, *A.V. Fedorov,* Lawrence Berkeley National Laboratory, *S.G. Louie, A. Lanzara*, University of California, Berkeley

Until recently it had been extremely difficult to experimentally address one of the most fundamental questions about graphene: How do the quasiparticles behave in neutral graphene, i.e. when the chemical potential coincides with the Dirac point energy? Here we address this question by investigating graphene on a particularly interesting substrate, the carbon face of SiC, with high-resolution angle-resolved photoemission spectroscopy (ARPES). We present the first direct measurements of the self-energy in graphene near the neutrality point, and show that the many-body physics in graphene differ from those of an ordinary metal. These exciting findings set a new benchmark in our understanding of many-body physics in graphene and a variety of novel materials with Dirac fermions.

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* Morton S. Traum Award Finalist

Graphene and Related Materials Focus Topic
Room: 208 - Session GR+NS+PS+SS-ThM

Graphene: Surface Chemistry, Functionalization, Plasma Processing and Sensor Applications
Moderator: G.G. Jernigan, U.S. Naval Research Laboratory

8:00am **GR+NS+PS+SS-ThM1 Tailoring Graphene's Properties through Chemistry*, J.T. Robinson***, Naval Research Laboratory **INVITED**

Graphene's unique electron transport properties have motivated intensive research and development to mold it into the electronic material of the future. However, graphene can be much more than an electrical switch. Its high structural integrity and chemical flexibility enable extensive control of its optical, mechanical, and electronic properties. The most scalable and inexpensive route to modify these properties is chemical functionalization. Consequently, chemically modified graphenes (CMGs) have emerged as a system of materials whose many attractive properties complement and extend those of unmodified graphene.

In this talk I will describe efforts at NRL to synthesize and characterize new CMGs as well as first steps towards applications such as sensors and nanomechanical resonators. To begin, I will discuss the interaction of small molecules (CCl_4, CS_2, H_2O and acetone) with single-layer graphene under steady-state conditions using infrared multiple-internal-reflection. Adsorption-induced changes in the IR spectra suggest the formation of in-plane strain, where we observe important differences arising between species that form liquid-like layers under steady-state conditions and those that do not. Second, I will discuss graphene oxide, a well known derivative of graphene that has a rich ensemble of oxygen-based functional groups and related defects. These defects are readily tunable through chemical or thermal treatments and facilitate the formation of vapor and bio-sensors with parts-per-billion and nanomolar sensitivities, respectively. Third, I will discuss the stoichiometric addition of fluorine atoms to graphene and describe their resulting properties. Experiments indicate fluorinated graphene derivatives become highly resistive and optically transparent, while DFT calculations show band gaps open depending on the fluorine coverage and ordering. Finally, through combining these two material systems, I will discuss the fabrication and performance of CMG-based nanomechanical resonators. Through chemical modification, the frequency of CMG-based resonators is tunable over 500% and their quality factors can exceed 20,000 at room temperature.

8:40am **GR+NS+PS+SS-ThM3 Water Splits Epitaxial Graphene on Ru(0001) from Domain Boundaries*, X. Feng***, *S. Maier, M. Salmeron*, Lawrence Berkeley National Laboratory

Epitaxial growth of graphene on metal substrates has recently been demonstrated as a rational synthesis route for producing macroscopic graphene domains and may hold the key to realizing the potential of large-scale applications. However, the epitaxial graphene is generally polycrystalline, with domain boundaries that may severely affect its structure and properties. Here we report that water adsorption splits epitaxial graphene on Ru(0001) and results in nanoscale graphene flakes at temperatures as low as 90K. Scanning tunneling microscopy studies indicated that the splitting starts primarily from domain boundaries followed by water intercalation underneath graphene. The mechanism proposed is that Ru-induced water dissociation provides hydroxyl species that break the graphene starting at the dangling and stretched bonds at the boundaries.

9:00am **GR+NS+PS+SS-ThM4 Novel Strategies for the Chemical Functionalization of Graphene: Towards Graphene/Molecular Nanosheet Heretostructures*, A. Turchanin***, *C.T. Nottbohm, Z. Zheng, M. Schnietz, A. Beyer,* University of Bielefeld, Germany*, M. Heilemann, M. Sauer,* Julius-Maximilians-University Würzburg, Germany*, A. Gölzhäuser*, University of Bielefeld, Germany

Chemical functionalization of graphene is essential for implementations of the 2D carbon sheets in various functional devices (e.g. chemical and biochemical sensors, nanoelectromechanical components, etc.) and for tuning their electrical properties. However, the functionalization is difficult to achieve due to the chemical inertness of graphene sheets with high structural quality. On the other hand, ultrathin (~1 nm) molecular nanosheets made from self-assembled monolayers (SAMs) possess well-defined chemical groups intrinsically. Moreover, due to the directionality of the constituting molecules both faces of the free-standing nanosheets -*Janus nanomembranes*- can be independently and specifically functionalized. Simple mechanical stacking of the nanosheets allows fabricating ultrathin layered structures with tunable physical and chemical properties. Upon annealing these stacks are converted into graphene sheets with adjusted thickness. The engineering of graphene/nanosheet heterostructures opens up novel routes towards chemically functionalized graphene sheets for functional applications. A potential of this approach will be discussed.

Z. Zheng, C.T. Nottbohm, A. Turchanin, H. Muzik, A. Beyer, M. Heilemann, M. Sauer, A. Gölzhäuser, "Janus nanomembranes: A generic platform for chemistry in two dimensions", *Angew. Chem. Int. Ed.* 49 (2010) 8493-8497

C.T. Nottbohm, A. Turchanin, A. Beyer, R. Stosch, A. Gölzhäuser, "Mechanically stacked 1 nm thick carbon nanosheets: 2D layered materials with tunable optical, chemical, structural and electrical properties", *Small* 7 (2011) 874-883

A. Turchanin, D. Weber, M. Büenfeld, C. Kisielowski, M. Fistul, K. Efetov, R. Stosch, T. Weimann, J. Mayer, A. Gölzhäuser, "Conversion of self-assembled monolayers into nanocrystalline graphene: structure and electric transport", *ACS Nano* 5 (2011) DOI: 10.1021/nn200297n

9:20am **GR+NS+PS+SS-ThM5 Biosensors Based on Chemically Modified Graphene*, R. Stine***, *J.T. Robinson, P.E. Sheehan, C.R. Tamanaha*, U.S. Naval Research Laboratory

The sensitive and specific detection of biomolecules without using a label is a long-standing goal of the biosensors community. Several promising advances of the past several years formed biological field effect transistors (bioFETs) that have as the gate nanoscale materials such as nanowires and carbon nanotubes. The nanoscale dimensions of these materials allow the small charges associated with biomolecules to significantly change conduction through the gate. These conduction changes can be correlated with solution concentration to give precise readouts. While bioFETs are a promising way forward, there are many processing difficulties associated with these 1-D materials that inhibit large scale, reproducible fabrication of devices. Here, we will discuss our efforts to develop biosensors based on 2-D chemically modified graphene. These devices impart the sensitivity gains seen from other nanoscale materials, but offer a configuration that is amenable to processing techniques that are common in the semiconductor industry. We will focus primarily on chemically modifying graphene for attachment of biomolecular probes. Devices utilizing both graphene and graphene oxide will be covered, and surface spectroscopic studies of the material modification will be discussed. Successful results for the detection of specific DNA hybridization will also be presented, with detection limits that compare favorably with the best results reported from nanowire bioFETs.

Acknowledgements: R.S. is an employee of Nova Research Inc., Alexandria, VA, USA. This project received support from the Defense Threat Reduction Agency-Joint Science and Technology Office for Chemical and Biological Defense.

9:40am **GR+NS+PS+SS-ThM6 Controllable Defect Healing and N-doping of Graphene by CO and NO Molecules*, B. Wang***, Vanderbilt University*, S.T. Pantelides*, Vanderbilt University and ORNL

Point defects alter strongly the physical and chemical properties of graphene, e.g. they degrade electrical transport and enhance chemical reactivity. Defects could also be used to achieve graphene functionalization, e.g. N atoms, as n-type dopant, can be introduced to obtain n-type graphene. Thus, controllable defect healing and N-doping in graphene would be very valuable for potential device applications. Here we report first-principles molecular dynamic simulations that suggest a procedure for defect healing and N-doping with fast dynamics and low thermal budget. Vacancies in graphene can be healed by sequential exposure to CO and NO molecules. A CO molecule gets adsorbed at a vacancy site and a NO molecule subsequently removes the extra O by forming NO_2, which desorbs quickly resulting in a defect-free graphene sheet. Controllable N-doping can be achieved by sequential vacancy creation (e.g. by electron or ion beam) and subsequent exposure to NO molecules at room temperature. NO molecules are trapped at vacancies and other NO molecules remove the extra O atoms simultaneously, leaving N atoms incorporated in graphene. Both reactions (healing and doping) are exothermic. We suggest that a combination of CO and NO molecules can potentially provide simultaneous healing and doping. Adjusting the ratio could fine-tune the N-doping level. The proposed strategy introduces no extra defects and is promising for graphene-based electronic materials in radiation environments. Finally, we propose that NH_3, which is normally used in experiments to introduce N atoms, may not be a good choice for N-doping since the dissociated H atoms can be trapped at vacancies and act as impurities that increase the resistivity of graphene.

This work was supported by DTRA Grant No. HDTRA1-10-1-0016 and the William A. and Nancy F. McMinn Endowment at Vanderbilt University. The calculations were performed at ORNL's Center for Computational Sciences.

10:40am **GR+NS+PS+SS-ThM9 Aptamer Modified Graphene Bio Sensor*, K. Maehashi*,** *Y. Ohno, K. Matsumoto*, Osaka University, Japan

Since graphene has high mobility and a large surface area, it is suitable for the application of the high sensitive sensor. In the present paper, we have first succeeded in the selective detection of the bio molecule such as IgE using the aptamer modified graphene FET.

The graphene was formed using the conventional mechanical exfoliation method on the SiO 2 /Si substrate. The source and drain electrode were formed by the electron beam lithography and Ti/Au evaporation. The silicon rubber pool was formed on the fabricated graphene FET, and phosphoric buffer solution was poured into the silicon rubber pool. The Ag/AgCl reference electrode was introduced into the phosphoric buffer solution, which works as a top gate electrode for the graphene FET.

As a first step of the biosensor, three bio molecule such as Immunoglobulin E(IgE), Streptavidin(SA), and Bovine serum albumin(BSA) were introduced into the phosphoric buffer solution of pH of 6.8, and the change of the drain current of the graphene FET was detected. In this case, the IgE and SA shows the decrease of the drain current, while the BSA the increase of the drain current. Because, in the phosphoric buffer solution of pH of 6.8, IgE and SA are positively charged, while BSA negatively charged. Therefore, the hole current of the graphene FET change the drain current following the charge of the bio molecule. As a result, bare graphene FET can detect the bio molecule following the charge of the molecule, but it dose not have the selectivity

As a second step, in order to get the selective sensing of the bio molecule, the surface of the graphene was modified by the IgE aptamer, which was connected to graphene using the linker(1-pyrenebutanoic acid succinimidyl ester). IgE aptamer was known to selectively couple to IgE. When the BSA and SA were introduced into the phosphoric buffer solution on the aptamer modified graphene FET, there occurred no change in the drain current, while the IgE was introduced in the solution, the drastic decrease of the drain current was observed. This means the BSA and SA do not couple to IgE aptamer, and only IgE couple to the IgE aptamer on the grapehne FET. Therefore, the selective sensing of the IgE was successfully carried out.

We have first succeeded in the selective sensing of IgE using the modified graphene FET.

11:00am **GR+NS+PS+SS-ThM10 A Molecular Dynamics Study of Chemical Modification of Graphene Oxide Sheets*, T. Liang*,** *B. Devine, S.R. Philllpot, S.B. Sinnott*, University of Florida

Graphene, the single-layered graphite, has attracted tremendous attention owing to its fascinating physical properties. One of the main obstacles in this field is to find an efficient and consistent approach to produce graphene sheets in large quantities. In addition to the mechanical exfoliation method, many chemical approaches have been developed to synthesize graphene on a large scale. The key intermediate product in these chemical approaches is the graphene oxide sheets, which are often heavily oxygenated with hydroxyl or epoxide functional groups on the surface and carbonyl or carboxyl groups at the edge. However the energetic and kinetics associated with graphene oxide sheets have not been elucidated in detail due to the inherent chemical complexity of the system. Here, a new dynamic charge empirical potential is presented that is used in classical molecular dynamics simulations to elucidate the dynamics of graphene oxidation and the resulting influence on their mechanical and structural properties. In addition, the oxygenating and hydrogenating processes of defective graphene sheets at room temperature in addition to elevated temperatures are presented. The findings are compared to the results of first principles density functional theory findings and to experimental data.

11:20am **GR+NS+PS+SS-ThM11 Enhancing and Controlling the Chemical Reactivity of Epitaxial Graphene via Growth Induced Strain, *J.E. Johns,*** Northwestern University*, Md.Z. Hossain,* Gunma University, Japan*, M.C. Hersam*, Northwestern University

The high electrical and thermal conductivity of graphene, as well as its two dimensional nature, has led to its rapid incorporation into any practical applications including high frequency analog transistors and transparent conductors. However, many other potential applications, such as excitonic switches, psuedospin devices, or digital logic circuits, require covalent chemical modification of graphene. Due to the chemical inertness of its pi bonded network, previous methods for covalently modifying graphene have required extreme, irreversible conditions including acidic treatments, high energy radical polymerization, and ion beam implantation. Here we present an alternative method for increasing the chemical reactivity of graphene by systematically altering the compressive strain of epitaxial graphene (EG) on SiC(0001). Depending on its annealing history, EG has been shown to have a compressive strain of 0% to 1% due to a mismatch of thermal expansion coefficients with the underlying buffer layer and silicon carbide substrate. Using differing thermal treatments, we show that the amount of strain in EG can be tailored, as verified by characteristic peak shifts of the 2D Raman band. The resulting chemical reactivity of the strained EG is studied at the atomic-scale using ultra-high vacuum scanning tunneling microscopy following reversible gas phase reactions of EG with oxygen and fluorine. These results suggest a new method for controlling the electronic properties of graphene, and provide fundamental insight into the nature of chemical bonding on EG.

11:40am **GR+NS+PS+SS-ThM12 Plasma-based Functionalization of Graphene with Primary Amines for Biomaterials Applications*, S.G. Walton*,** *M. Baraket, S.C. Hernandez, R. Stine, W.K. Lee, C.R. Tamanaha, P.E. Sheehan, J.T. Robinson, C.E. Junkermeier, T.L. Reinecke*, Naval Research Laboratory (NRL)

Graphene, a sp^2-structured monolayer of carbon atoms, has attracted much interest for its fundamental science and its potential in many device applications. By tailoring its surface chemistry, material properties can be regulated and thus broaden the number of potential applications. In this work, we demonstrate that by chemically functionalizing graphene the electrical properties and its interaction with adsorbates may be controlled. Electron beam generated plasmas produced in ammonia-containing gas, is used to controllably introduce nitrogen and primary amines. A study of the chemical, electrical and structural properties of the chemically-modified graphene at different functional group concentrations is discussed. In addition, the use of amine-functionalized graphene as a bio-sensing platform for DNA detection using a field-effect-transistor-based sensor is demonstrated. This work is supported by the Office of the Naval Research.

Graphene and Related Materials Focus Topic
Room: 208 - Session GR+TF+NS-ThA

Graphene Nanoribbons and Related Structures
Moderator: Y.J. Chabal, University of Texas at Dallas

2:00pm **GR+TF+NS-ThA1 Rationally Patterned Large-Area Semiconducting Graphene Materials from the Top-Down and the Bottom-Up**, *N. Safron, M. Kim, P. Gopalan,* ***M. Arnold***, University of Wisconsin-Madison **INVITED**

We are experimentally investigating self-assembling lithography (e.g. block co-polymer and nanosphere lithography) to create nanostructured graphene materials with feature sizes below what is easily achieved using optical and electron-beam lithography (< 20 nm), with the motivation of opening up a technologically relevant band gap in graphene. We are particularly interested in a novel form of semiconducting graphene that we call nanoperforated graphene, which consists of graphene perforated by regular hexagonal arrays of nanoscale holes. Unlike nanoribbons, nanoperforated graphene advantageously retains a large-area two-dimensional form factor. In this talk, we will discuss the inter-relationship between the physical structure of nanoperforated graphene and its electronic properties, with specific emphasis on how its band gap experimentally varies with feature size and how charge transport is affected by structure (including the role of edge defects and the observation of single-electron charging effects). We will also report on efforts in our group to realize nanostructured graphene materials with well controlled edge structure and superior properties via scalable and rationally controlled bottom-up growth that avoids top-down etching without sacrificing arbitrary pattern forming ability.

2:40pm **GR+TF+NS-ThA3 Quantum Pumping in Graphene Nanoribbons**, ***T. Kaur,*** Ohio University, *L. Arrachea,* Universidad de Buenos Aires, Argentina, *N. Sandler*, Ohio University

The interest in the development of devices at the nanoscale has intensified the search for mechanisms that provide tailored control of transport properties while reducing effects of heat dissipation and contact resistance. For instance, *charge pumping* is one of the current generating methods that allows for minimizing the effects of contact resistance. *Charge pumping* is the mechanism used to generate DC currents in open-quantum systems by applying local de-phased time-dependent potentials.

We analyze the properties of non-equilibrium zero-bias current through nano-ribbons using tight-binding Hamiltonians and the *Keldysh formalism*. This theoretical treatment, based on non-equilibrium Green's function techniques, is the most appropriate one to address questions for systems in non-linear, out of equilibrium conditions. We develop a numerical implementation for the models described below in a wide range of non-equilibrium regimes.

After reviewing results for quantum pumping in a one-dimensional chain attached to two reservoirs, with two local single-harmonic potentials oscillating in time, we study finite-width ribbons of square and graphene lattices. The transmission function reveals the value of the *resonant frequency* and explains how the quantum charge pumping works. We analyze the dependence of the *DC current* as a function of different parameters such as chemical potential, pumping amplitude, frequency, etc. In addition, the role of reservoirs is fully described. Pumped currents can also be generated by application of laser fields. We present the comparison between these two pumping methods. Possible extensions for disordered systems will be discussed.

3:00pm **GR+TF+NS-ThA4 First-principles Study of Field Emission from Graphene Nanoribbons**, ***J. Driscoll***, *K. Varga*, Vanderbilt University

A real-space, real-time implementation of time-dependent density functional theory [1,2,3] is used to study electron field emission from graphene nanoribbons. The structures are shown to be good field emitters with spatial variation of the emission current influenced by the presence of passivating hydrogen. The nanoribbons are seen to produce slightly lower currents than nanotubes formed from the ribbons. Spin-polarized field emission from carbon nanotubes has been calculated with and without Fe adsorbates (atoms and clusters). It was observed that various adsorbates cause the separation of density into spin-polarized regions. The calculations predict that carbon nanotubes with various adsorbates can be used as spin-polarized current sources. The spin-polarized results for nanotubes will be compared to similar

calculations for graphene nanoribbons.

References

[1] J.A. Driscoll and K.Varga, Phys. Rev. B 80, 245431 (2009).

[2] J.A. Driscoll, S. Bubin, W. French, and K. Varga (submitted).

[3] J.A. Driscoll, B. Cook, S. Bubin, and K. Varga (submitted).

Acknowledgments

This work is supported by NSF grant CMMI0927345.

3:40pm **GR+TF+NS-ThA6 Quantum Transport Properties of Modified Graphene Nanoribbons with Boron Nitride Domains at the Nanoscale**, ***A. Lopez-Bezanilla***, Oak Ridge National Laboratory

Carbon-based systems are being widely investigated as potential candidates for nanoelectronic interconnects and transistors. The control of electric current is, therefore, an important challenge in nanostructures engineering. The possibility of creating hybrid one-atom thick layers containing C, B and N atoms have attracted much attention as they can provide an efficient way to create new materials with properties complementary to those of graphene and h-BN.

Here we present a theoretical methodology and study of charge transport through GNRs with BN domains randomly distributed along the ribbon surface. We resort to both first principles calculations, to obtain a suitable parametrization of the electronic structure, and a transport approach based on the ab initio results to explore conduction regimes through large and disordered systems. The quantum transport modeling is based on the Green's function formalism, combining an iterative scheme for the calculation of transmission coefficients with the Landauer's formula for the coherent conductance.

Our results describe how the conductance of the hybrid systems is altered as a function of incident electron energy and BN domain density. We explore the transport regimes comparing different degrees of BN doping and BN domain size for ribbons of various widths and lengths on the order of the micrometer. A comparison with other types of defects such as atoms in epoxy configuration and functional groups covalently attached to the ribbon surface will be also discussed.

4:00pm **GR+TF+NS-ThA7 Simple and Scalable Route for the 'Bottom-Up' Synthesis of Few-Layer Graphene Platelets and Thin Films**, ***K. Coleman***, University of Durham, UK

Graphene has generated much interest owing to its exceptional electronic properties and high mechanical strength. This has enabled new types of electronic devices and composite materials to be envisaged. The main problem is the availability of the material and the difficulties associated with its synthesis. Here we present a simple, convenient and scalable chemical vapour deposition method involving metal alkoxides in ethanol to produce few-layer graphene platelets. The graphene platelets have been fully characterised using TEM, SEM, AFM, XPS and XRD. The methodology used has the added flexibility in that it can be used to grow conducting transparent thin films on inert substrates such as silicon wafer and quartz glass. Importantly, no heavy metal catalysts were required to produce the few-layer graphene platelets or graphene films and all non-carbon by-products are soluble in water.

4:20pm **GR+TF+NS-ThA8 Approaching the Intrinsic Bandgap in Suspended High-Mobility Graphene Nanoribbons**, *M.-W. Lin, C. Ling,* Wayne State University, *L.A. Agapito, N. Kioussis,* California State University Northridge, *Y. Zhang, M.-C. Cheng,* Wayne State University, *W.L. Wang, E. Kaxiras,* Harvard University, ***Z.X. Zhou***, Wayne State University

We report the first variable-temperature electrical-transport study of suspended ultra-low-disorder GNRs with nearly atomically smooth edges. Suspension of the GNRs not only removes the substrate influence but also allows a thorough removal of impurities, including those trapped at the interface between the GNR and the substrate, leading to a substantial increase of the carrier mobility. We observe high mobility values over 3000 $cm^2\ V^{-1}\ s^{-1}$ in GNRs that are ~ 20 nm wide, the highest reported to date on GNRs of similar dimensions. Furthermore, we demonstrate that the activation gap extracted from the simple activation behavior of the minimum conductance and residual carrier density at the charge neutrality point approaches the intrinsic bandgap in ultra-low-disorder GNRs. Comparison of the bandgap values of multiple samples shows that the bandgap in our ultra-low-disorder samples is approximately inversely proportional to the ribbon width, consistent with theoretical predictions. On the other hand, non-negligible disorder in GNRs obscures the observation of the intrinsic bandgap in transport measurements. In addition, the size of the bandgap derived from the transport measurements is in *quantitative* agreement with the results of our complementary tight-binding calculations for a wide range of chiral angles characterizing the GNR structure, suggesting that the underlying electronic origin of bandgap enhancement is the magnetism of the zigzag edges.

4:40pm **GR+TF+NS-ThA9 Fabrication of Polymer-Protected Graphene Nanoribbons by Thermal Dip-Pen Nanolithography (tDPN),** ***W.K. Lee****, J.T. Robinson, R. Stine, A.R. Laracuente,* Naval Research Laboratory, *W.P. King,* University of Illinois at Urbana Champaign, *P.E. Sheehan*, Naval Research Laboratory

The lithographic patterning of graphene nanoribbons (GNRs) to engineer band gaps has gained much attention as one path to realizing graphene-based devices. We employed thermal dip-pen nanolithography (tDPN)[1] to pattern GNRs on CVD single-layer graphene (SLG) that had been transferred onto a SiO_2 substrate. In tDPN, a heatable AFM cantilever regulates the deposition of an ink through controlled melting, much like a nanoscale soldering iron. tDPN has been successful at depositing polymers ranging from semiconductors to insulators on a variety of surfaces. To create the nanoribbons, we deposited polystyrene (PS) ribbons via tDPN on a SLG film between the source and drain electrodes. The areas of the graphene not protected by the polymer were then modified to isolate thin graphene nanoribbons. We show that the PS protected ribbon was the only conductive pathway for active device. This method allows a wide range of nanoribbon widths to be created and avoids electron beams which can damage graphene. The impact of the polymer choice on conductivity as well as the choice of isolation will discussed. For instance, we find that the PS ribbon can serve not only as an etch mask to pattern GNRs but also a stable dopant layer. The detailed fabrication and characterization of these structures will be presented.

1. WK Lee, et al. (2010) “Maskless Nanoscale Writing of Nanoparticle-Polymer Composites and Nanoparticle Assemblies using Thermal Nanoprobes”, *Nano Letters, 10, 129*

5:00pm **GR+TF+NS-ThA10 Edge Termination of Modified Graphene Oxide during Thermal Exfoliation*****, M. Acik******,** *Y.J. Chabal*, The University of Texas at Dallas

Nanopore formation in carbon materials (e.g. exfoliated nanostacks of graphite) has been widely studied through mechanical exfoliation, intercalation, electrochemical separation, chemical or thermal exfoliation of graphite oxide (GO) via expansion with partial oxygen removal. Amongst all these methods, exfoliation of modified graphene (GO), a solution-processable precursor compound where aromatic and heterocyclic rings with embedded oxygen functionalities exist, by thermal processing still remains elusive for the following reasons: (1) poor control of GO composition (initial oxygen content), (2) poor understanding of the chemical composition, (3) unknown role of oxygen, adjoining oxygen interactions, and edge termination with oxygen. Infrared absorption spectroscopy coupled with *in-situ* thermal annealing process [1] makes it possible to examine the chemical changes taking place during thermal reduction to identify and understand interacting molecular environment and the edge functionalization. To unravel the complex mechanisms leading the removal of oxygen in GO, we have performed *in-situ* transmission infrared absorption spectroscopy (IRAS) measurements of graphene/graphite oxide (GO) thin and bulk films upon thermal annealing (60-850°C) in vacuum (10^{-3}-10^{-4} Torr). Control of the edge geometry of finite-sized modified graphene flakes depends very much on the control of the processing methods. This edge reconstruction further determines electronic, electric, optical and mechanical properties of the exfoliated modified graphene flakes. Therefore, we not only perform studies deriving a thermal reduction mechanism, but also examine the edge reconfiguration with oxygen. We report here the observation of a surprisingly strong IR absorption band that occurs only upon thermal reduction of GO. After annealing at 850°C in vacuum, the strong enhancement of the new IR active absorbance band is observed at ~800 cm^{-1}[2]. The intensity of this band is 10-100 times larger than what is expected for the oxygen content of the reduced GO, namely between 5 and 8 at.%. This band is assigned to a specific oxidation state, involving oxygen located in the basal plane (forming C-O-C bonds) and at *atomically straight* edges of reduced graphene. The large enhancement in IR absorption is attributed to the direct participation of electrons, induced by the asymmetric C-O-C stretch mode displacement. These findings open new possibilities in the field of nanoelectronics for all sensor and energy storage applications. [1] M. Acik, *et al.* J. Am. Chem. Soc. (2011), *in preparation*. [2] M. Acik, *et al.* Nat. Mater. 9, 840-845 (2010).

5:20pm **GR+TF+NS-ThA11 Study of Ridges on Epitaxial Graphene on 6H-SiC(0001),** ***Y.Y. Li****, Y. Liu, L. Li*, University of Wisconsin-Milwaukee

The graphitization of hexagonal SiC surfaces provides a viable alternative for the synthesis of wafer-sized graphene for mass device production. During the later stages of growth, ridges are often observed on the graphene layers as a result of bending and buckling to relieve the compressive strain between the graphene and SiC substrate, which also introduce ripples in the otherwise atomically flat graphene sheet. In this work, we show, by atomic resolution STM imaging, that ridges are in fact bulged regions of the graphene layer, forming one-dimentional (nanowire) and zero-dimentional (quantum dot) nanostructures. We further demonstrate that their structures can be manipulated and even new ones created by the pressure exerted by the STM tip during imaging. These results and their impact on the electronic properties of epitaxial graphene on SiC(0001) will be presented at the meeting.

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* Morton S. Traum Award Finalist

Graphene and Related Materials Focus Topic
Room: 208 - Session GR+MS+EM-FrM

Graphene Device Physics and Applications
Moderator: M. Arnold, University of Wisconsin-Madison

8:20am **GR+MS+EM-FrM1 Fabrication and Characterization of Graphene p-n Junction Devices,** ***J.U. Lee***, University at Albany-SUNY **INVITED**

Graphene is a newly discovered material composed of two-dimensional array of hexagonal carbon atoms. It has a number of unique electronic properties, the most remarkable of which is the zero band-gap light-like linear electronic dispersion, giving rise to Dirac fermions. This feature can be used to make devices based on previously unexplored physical properties. For example, in analogy to optics, we describe new devices based on *optics-like manipulation of electrons*.

Our devices are based on graphene and bi-layer graphene *p-n* junctions doped using electrostatic doping techniques from buried split gates. In the present context, graphene *p-n* junctions do not rectify, i.e. behave as semiconductor diodes. Instead, in graphene p-n junctions, carriers launched from a point contact from one side of the junction are able to refocus back to a point on the other side of the junction. This behavior, known as the Veselago effect, can be the basis for new logic devices for replacing Si CMOS. In addition, using the same platform, we describe interconnect structures that can be reconfigured. Together, we envision a new circuit paradigm based on components that seamlessly reconfigure between devices and interconnect components.

In this talk, we describe the details of graphene *p-n* junction fabrication and characterization, and circuits that are enabled by the *p-n* junction devices. The devices are fabricated at CNSE’s state-of-the-art 300mm Si wafer fabrication line using processing techniques that leave atomically flat top oxide surface above the patterned split gates. For characterizing the p-n junctions, we perform transport and SPM measurements.

9:00am **GR+MS+EM-FrM3 Assembled Bilayer Graphene for Electronic Applications,** ***G.G. Jernigan***, *T.J. Anderson, J.T. Robinson, J.D. Caldwell, M.D. Ancona, V.D. Wheeler, L.O. Nyakiti, J. Culbertson, A.L. Davidson, A.L. Friedman, P.M. Campbell, D.K. Gaskill*, U.S. Naval Research Laboratory

Graphene has shown successful application in RF transistors and frequency doublers where its high mobility and high saturation velocity translate into operation at high frequencies while utilizing little power. However, a major detraction to graphene development for other device applications is that it does not have a band gap. The lack of a band gap means that graphene’s current cannot be turned off. Bilayer graphene is regarded as one possible solution to this problem, since bilayer graphene is capable of developing a band gap if the symmetry of the system can be broken. That said, bilayer graphene (from exfoliation or growth) forms a highly ordered A-B stack of the two graphene sheets resulting in little to no band gap, unless a high electric field can be applied.

In this presentation, we will demonstrate a novel method for creating bilayer graphene where a single layer of CVD graphene grown on Cu is bonded to a single layer of epitaxial graphene grown on Si-face SiC. This process results in a bilayer system that has a built-in asymmetry that yields unique physical and electrical properties not previously observed. For example, we demonstrate that the transfer of CVD graphene to epitaxial graphene results in a smoother morphology than transfer onto SiO2 and that bonding of CVD graphene to epitaxial graphene can avoid the damage caused by the drying step necessary in the poly (methyl methacrylate) transfer method. X-ray photoelectron spectroscopy and Raman microscopy demonstrate that the sheets are coupled together but strained differently, in contrast to a naturally formed bilayer. Electrical characterization of Hall devices fabricated on the novel bilayer show higher mobilities and lower carrier concentrations than the individual CVD graphene or epitaxial graphene sheets alone. Modeling of the electric field produced by opposite doping in the graphene sheets will also be presented, as CVD graphene is typically p-type and epitaxial graphene is typically n-type.

10:00am **GR+MS+EM-FrM6 Rectification at Graphene / Semiconductor Junctions: Applications Beyond Silicon Based Devices,** ***S. Tongay***, *X. Miao, K. Berke, M. Lemaitre, B.R. Appleton, A.F. Hebard*, University of Florida

Schottky barriers are crucial and necessary device components of metal-semiconductor field effect transistors (MESFETs) and high electron mobility transistors (HEMTs). Here, we report on the formation of Schottky barriers at graphene-multilayer graphene/semiconductor junction interfaces which have been characterized by current density vs. voltage (J-V) and capacitance vs. voltage (C-V) measurements. After graphene transfer onto various semiconductors such as Si, GaAs, GaN and SiC, we observe a strong rectification at the interface, i.e., high (low) resistance in the reverse (forward) bias directions. The J-V characteristics have been analyzed using thermionic emission theory and the extracted barrier height values are consistent with the Schottky-Mott model. When capacitance is plotted as $1/C^2$ vs V, a linear dependence is observed, which by extrapolation to the intercept identifies a built in potential that is consistent with the Schottky barrier height extracted from J-V measurements. Graphene's low Fermi energy together with its robust thermal, chemical, structural and physical properties provide numerous advantages when used to form Schottky barriers in device applications: namely, voltage tunability of the Schottky barrier height, stability to high temperatures, resistance to impurity diffusion across the interface, and the use of absorbates to chemically tune the Fermi energy and hence the Schottky barrier height.

10:20am **GR+MS+EM-FrM7 Imaging of Electron Beam Induced Current in Epitaxial Graphene,** ***S. Mou***, *J. Boeckl, W.C. Mitchel, J.H. Park,* Air Force Research Laboratory, *S. Tetlak,* Wyle Laboratories, *W. Lu*, Fisk University

It has been known and observed that there forms a Schottky junction between graphene and SiC in epitaxial graphene due to the work function difference and the charge transfer between them. As a result, it is viable to apply the electron beam induce current (EBIC) technique on the epitaxial graphene directly due to the fact that it needs a built-in field and ample electron generation volume to generate EBIC. EBIC is an important characterization technique, which identifies electrically active impurities/defects, detects local built-in field, and measures minority carrier diffusion length. In this paper, we use a FEI SEM equipped with a current amplifier to investigate the spatial mapping of EBIC generation and collection in a two terminal geometry. The incident electron beam generates excited electron-hole pairs in SiC and the minority carriers are collected through the Schottky junction before flowing into graphene. EBIC imaging reveals mesoscopic domains of bright and dark contrast areas due to local EBIC polarity and magnitude, which is believed to be the result of spatial fluctuation in the carrier density in graphene. We also investigate the electron energy dependence, which modulates the EBIC magnitude. With an analytical drift-diffusion current model, we are able to extract the minority carrier diffusion length in the SiC, which is on the order of micro meter and agrees well with other published data.

10:40am **GR+MS+EM-FrM8 Potassium-Ion Sensors Based on Valinomycin-Modified Graphene Field-Effect Transistors,** ***Y. Sofue***, *Y. Ohno, K. Maehashi, K. Inoue, K. Matsumoto*, The Institute of Scientific and Industrial Research, Osaka University, Japan

Highly sensitive ion sensors based on valinomycin-modified graphene field-effect transistors (VGFETs) have been developed to selectively detect K ions, which are an essential element for biological activity including human life. Graphene single-layers were obtained by mechanical exfoliation. Graphene FETs were fabricated by conventional e-beam lithography and lift-off method on a thermally grown SiO_2 layer. To demonstrate selective detection of K ions, the graphene channels were covered with ion selective membrane, which consisted of polyvinyl chloride and valinomycin. Transfer characteristics of VGFETs in a 100 mM Tris-HCl buffer solution with various KCl concentrations over the range from 10 nM to 1.0mM. With increasing K ion concentration, the solution-gated voltage at the Dirac point shifted toward negative direction. The shifts are due to the accumulation of positively charged K ions surrounded by valinomycin on the graphene surfaces. The electrostatic potential of graphene surfaces exhibit a rather linear dependence on log[K]. These results indicate that VGFETs effectively detected K ions with concentration from 10 nM to 1.0 mM. To investigate selectivity in VGFETs, Na-ion concentration dependence was also measured. The transfer characteristic in VGFETs remained almost constant over the Na ion concentration range between 10 nM and 1.0 mM. These results indicate that VGFET selectively detected K ions with high sensitivity.

11:00am **GR+MS+EM-FrM9 Band-gap Generation by using Ionic-Liquid Gate in Bilayer Graphene,** ***Y. Yamashiro***, *Y. Ohno, K. Maehashi, K. Inoue, K. Matsumoto*, Osaka University, Japan

Electric fields were applied to a bilayer graphene to generate a band gap using an ionic-liquid gate instead of the general top-gate structures. The ionic-liquid gate can apply higher electric field than other type of the gates because of its large capacitance and electric strength. In this abstract, the graphene layers were extracted from kish graphite by a mechanical exfoliation and were put on highly *n*-doped Si substrates covered with a 300-nm-thick SiO_2 layer. Side-gate electrodes were patterned approximately 20 mm away from the channels. An ionic liquid (DEME-TFSI) was put on the bilayer graphene and the side-gate electrode. Electrical characteristics at 300 K revealed that the electrical double layer in the ionic-liquid, which works as a very thin insulator, had 200 times larger capacitance than a 300-nm-thick SiO_2 layer. The thickness of electrical double layer was estimated to be 3.75 nm. In electric field dependence measurements, an increase in a sheet resistance of the bilayer grapheme channel was clearly observed with increasing the magnitude of electric field in bilayer graphene. On the other hand, the increase in the sheet resistance didn't appear in the monolayer- and trilayer- graphene. That is why the increasing of the sheet resistance was caused by a band gap generated in ionic-liquid gated bilayer graphene by the electric field.

11:20am **GR+MS+EM-FrM10 Electronic Transport in Hydrogenated Graphene Films**, ***B.R. Matis****, J.S. Burgess,* NRC/NRL Postdoctoral Associate*, A.L. Friedman, J.T. Robinson,* Naval Research Laboratory (NRL)*, F.A. Bulat,* Sotera Defense Solutions, Inc.*, B.H. Houston, J.W. Baldwin*, Naval Research Laboratory (NRL)

Graphene films grown by chemical vapor deposition on copper foils and exfoliated graphene flakes were hydrogenated using low kinetic energy plasma processing. The film sheet resistance can be tuned over a wide range (1 kΩ/square – 300 kΩ/square), increasing proportionally with hydrogen coverage. Variable temperature measurements demonstrate a transition from semi-metallic behavior for graphene to semiconducting behavior for hydrogenated graphene. Sheet resistance measurements as a function of temperature also suggest the emergence of a band gap in the hydrogenated graphene films. Interesting surface doping effects will be discussed in conjunction with the location of the charge neutrality point. This work was supported by the Office of Naval Research.

11:40am **GR+MS+EM-FrM11 First-principles Study of Electronic Properties of Two Dimensional Carbon and Boron Nitride Nanomaterials**, ***S. Mukherjee***, S.N. Bose National Centre for Basic Sciences, India

First principles pseudopotential plane wave method was used to study ground state electronic properties of Graphene, hexagonal Boron Nitride (h-BN), Graphene doped with Boron and Nitrogen, and multilayers of Graphene and h-BN. Our results on doped Graphene indicate that upon electron (hole) doping, the Dirac-point in the electronic bandstructure shifts below (above) the Fermi level and a gap appears at the high-symmetric K-point. Upon co-doping of Graphene by both Boron and Nitrogen a small energy gap between the conduction and valence band appears at the Fermi level, making the CBN nanomaterial a narrow band semiconductor. The energy gap depends sensitively on the degree of doping and on the thickness of CBN layer. These results are in agreement with recent experimental measurements [1,2]. Our bandstructure calculations on the multilayers of Graphene and h-BN indicate that these nanostructured multilayers exhibit semiconducting behaviour with band gap in the range 60-600 meV depending on the relative orientation and thickness of the layers. (Author: Sugata Mukherjee, work done in collaboration with T.P. Kaloni)

1. X. wang et al, Science **324**, 768 (2009)
2. L. Cie et al, Nature Materials **9**, 430 (2010).

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