

Graphene Focus Topic

Room: Brazos - Session GR+SS+TF+EM-MoM

Epitaxial Graphene on SiC

Moderator: P.E. Sheehan, Naval Research Laboratory

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Monday Afternoon, October 18, 2010

Graphene Focus Topic

Room: Brazos - Session GR+NS-MoA

Graphene: Chemical Reactions

Moderator: T. Seyller, Universität Erlangen, Germany

2:00pm **GR+NS-MoA1 Chemical Interactions during Thermal Reduction of Multilayered Graphene Oxide**, *M. Acik*, University of Texas at Dallas, *C. Mattevi*, Imperial College London, *C. Gong*, *G. Lee*, *K.J. Cho*, University of Texas at Dallas, *M. Chhowalla*, Imperial College London, *Y.J. Chabal*, University of Texas at Dallas

Graphene/graphite oxide (GO), with its non-stoichiometric chemical structure and highly hygroscopic functionalized graphene backbone, has been of interest for chemical energy storage applications such as supercapacitors and ultracapacitors as well as its reduced form for bioelectronic applications such as sensor networks and for printed electronics. For all these applications, it is important to characterize and control the chemical nature of GO at various stages of thermal reduction. In particular, the formation and evolution of defect structures within GO can greatly impact the resulting properties. Similarly, the properties of species intercalated between individual planes can alter the reduction chemistry. The interplay between intercalated species and defect sites can lead to interesting new chemistry.

To understand these chemical interactions, we have studied the deoxygenation process of both single- and multi-layer(s) of GO and focused on comparing the removal of oxygen upon heating both from the basal plane and the edges, by bringing to bear a number of methods. In particular, we have carried out a series of experiments using *in-situ* IR absorption spectroscopy (FTIR), x-ray diffraction technique (XRD), *ex-situ* raman scattering, thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and x-ray photoelectron spectroscopy (XPS), together with density functional (DFT) calculations and molecular dynamic (MD) simulations of various oxygen structures and resulting electronic states. The IR absorption spectra reveal the formation of ketones, ethers and sp^2 -hybridized C=C as well as a loss of hydroxyls, carboxyls and epoxides upon gradual annealing. They also confirm that defect formation is a direct result of CO_2 and CO formation, and highlight the role of intercalated species, such as water. At higher temperatures ($\sim 850^\circ C$), oxygen is found to remain at the edges of defective sites in a very stable configuration, involving the alignment of edge ether. Overall, the structure of GO upon annealing exhibits interesting, and in some cases unexpected features, which could have a crucial role and applicability to various systems such as vibration-powered energy scavenging, night vision tracking systems and optoelectronics.

*The authors acknowledge funding from the SWAN/NRI program and Texas Instruments.

2:20pm **GR+NS-MoA2 Non-bonding State formed Around Defects on HOPG**, *J. Nakamura*, *T. Kondo*, *J. Oh*, *D. Guo*, *Y. Honma*, *T. Machida*, University of Tsukuba, Japan

Understanding the interface interaction between metal nano-clusters and carbon supports composed of graphite materials is one of the most important needs in the development of carbon related-catalysts. We have studied the carbon support effects on the electrocatalysts for fuel cell as well as the interface interaction using model catalysts of Pt-deposited highly oriented pyrolytic graphite (HOPG) by IETS-STSTM, TPD, and molecular/atomic beam technique. Here, we report the formation of non-bonding state in the vicinity of defects on the HOPG surface. We have measured STS spectra at many different points in the vicinity of the point defect. STS spectra were very different depending on the point of the measurement. In the directions perpendicular to short zigzag edges at the point defect, STS peaks appear near the Fermi level, suggesting the edge state or non-bonding state. The non-bonding state propagates 3-4 nanometers away from the defect with three-fold symmetry. No such a STS peak was observed near the point defect in the other directions. We thus constructed a STS map showing the distribution of the non-bonding state. We also observed spatial "oscillations" in the dI/dV peak position and the intensity. The oscillations have been explained as electron-electron interaction or electron-hole interaction. We currently consider that the non-bonding state is responsible for the chemical reactivity such as adsorption of atom, molecules, and clusters.

References

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2. T. Kondo, J. Nakamura, et al., Phys. Rev. B 80 (2009) 233408.

3. J. Oh, T. Kondo, J. Nakamura, et al., J. Phys. Chem. Lett. 1 (2010) 463.

4. T. Kondo, J. Nakamura, et al., J. Phys. Chem. C 112 (2008) 15607.

2:40pm **GR+NS-MoA3 Opto-electronic Properties of Solution Processable Chemically Derived Graphene Oxide**, *M. Chhowalla*, Rutgers University **INVITED**

A solution based method that allows uniform and controllable deposition of reduced graphene oxide thin films with thicknesses ranging from a single monolayer up to several layers over large areas will be described. Transport of carriers in reduced GO is limited by the structural disorder. However, conductivity of 10^5 S/m and mobilities of ~ 10 $cm^2/V\cdot s$ are sufficiently large for applications where inexpensive and moderate performance electronics are required. The oxidation treatment during synthesis of GO creates sp^3 C-O sites where oxygen atoms are bonded in the form of various functional groups. GO is therefore a two dimensional network of sp^2 and sp^3 bonded atoms, in contrast to an ideal graphene sheet which consists of 100% sp^2 carbon atoms. This unique atomic and electronic structure of GO, consisting of variable sp^2/sp^3 fraction, opens up possibilities for new functionalities. The most notable difference between GO and mechanically exfoliated graphene is the opto-electronic properties arising from the presence of finite band gap. In particular, the photoluminescence can be tuned from blue to green emission. The atomic and electronic structure along with tunable photoluminescence of graphene oxide at various degrees of reduction will be described.

3:40pm **GR+NS-MoA6 Structural Evolution during the Reduction of Chemically Derived Graphene Oxide**, *V.B. Shenoy*, Brown University / Rhode Island Hospital

The excellent electrical, optical and mechanical properties of graphene have driven the search to find methods for its

large-scale production, but established procedures (such as mechanical exfoliation or chemical vapour deposition) are not

ideal for the manufacture of processable graphene sheets. An alternative method is the reduction of graphene oxide, a

material that shares the same atomically thin structural framework as graphene, but bears oxygen-containing functional

groups. Here we use molecular dynamics simulations to study the atomistic structure of progressively reduced graphene

oxide. The chemical changes of oxygen-containing functional groups on the annealing of graphene oxide are elucidated and

the simulations reveal the formation of highly stable carbonyl and ether groups that hinder its complete reduction to

graphene. The calculations are supported by infrared and X-ray photoelectron spectroscopy measurements. Finally, more

effective reduction treatments to improve the reduction of graphene oxide are proposed [1].

[1] Akbar Bagri, Cecilia Mattevi, Muge Acik, Yves J. Chabal, Manish Chhowalla and

Vivek B. Shenoy, Nature Chemistry (in press, 2010).

4:00pm **GR+NS-MoA7 Perfluorographane: Synthesis and Properties**, *J.S. Burgess*, National Research Council, *J.A. Robinson*, Naval Research Laboratory, *M. Zalalutdinov*, SFA, inc, *K. Perkins*, *P.M. Campbell*, *E. Snow*, *B.H. Houston*, *J.W. Baldwin*, Naval Research Laboratory

Graphene was grown by CVD on a copper substrate. The as-grown samples and samples transferred to silicon on insulator (SOI) and SiO_2 substrates were then exposed to XeF_2 gas resulting in fluorination of the graphene sheets. The samples were characterized using XPS and Raman spectroscopies. XPS showed maximum fluorine content in the graphene of 20 % for the graphene on copper and 50 % on SOI. The marked difference is owed to the etching of the silicon layer on the SOI substrate, allowing exposure of the underside of the graphene sheet to the XeF_2 gas and fluorination of both sides of the graphene sheet. The fluorine was removed from the film using both thermal and chemical (hydrazine reduction) methods. Chemical, mechanical, and electrical properties of these materials will also be discussed.

4:20pm **GR+NS-MoA8 Stability and Activity of Pt Nanoclusters Supported on Graphene Monolayers on Ru(0001)**, *O. Alves*, *C. Lorenz*, *H.E. Hoster*, *R.J. Behm*, Ulm University, Germany

Being an atomically thin half-metal and exhibiting moiré-type nm-scale superstructure, graphene monolayers supported on metal single crystals [1-3] can serve as a template for the growth of ordered arrays of nanosized

metallic (electro-)catalyst particles. These particles, which are fabricated by simple metal vapour deposition in ultrahigh vacuum [4-6] and comprise monodispersed Pt clusters seeded on the graphene monolayer on Ru(0001), were found to nucleate preferentially at a unique region in the Moiré unit cell and displayed heights of 1-5 atomic layers and lateral diameters within the range 1-4 nm. The size selectivity of the Pt nanoclusters, jointly with their self-assembled array, assign them as interest and promising system for (electro-)catalytic model studies.

We will report on the activity and stability either of a single graphene monolayer or of the Pt clusters. The graphene layers and the cluster arrays are prepared in ultrahigh vacuum, whilst the potential-dependent reaction studies are measured in a wall-jet type flow cell sited in an electrochemical pre-chamber attached to the main UHV system. Cluster arrays with different total Pt coverages and cluster size distributions were tested as electrodes for elementary reactions as hydrogen evolution/oxidation, CO oxidation, or O₂ reduction. According to STM analyses before and after the electrochemical tests, we discuss in how far the stabilities of clusters of various sizes can be rationalized in terms of reaction conditions and applied potentials. The general electrochemical behaviour of the Pt cluster arrays will be discussed in comparison to bulk Pt. As a main (electro-)catalytic result, we find a surprisingly high activity for hydrogen evolution.

- [1] C. Oshima et al., *J. Phys. Condens. Matter* 9,1 (1997).
- [2] S. Marchini et al., *Phys. Rev. B* 76, 075429 (2007).
- [3] Coraux et al., *Nano Lett.* 8, 565 (2008).
- [4] N'Diaye et al., *New J. Phys.* 11, 103045 (2009).
- [5] Yi Pan et al., *Appl. Phys. Lett.* 95, 093106 (2009).
- [6] K. Donner and P. Jakob, *J. Chem. Phys.* 131 164701 (2009).

4:40pm **GR+NS-MoA9 Writing Graphene Electronics Into Chemically Modified Graphene**, *P.E. Sheehan, Z. Wei*, Naval Research Laboratory, *D. Wang*, Georgia Institute of Technology, *W.-K. Lee, M.K. Yakes*, Naval Research Laboratory, *W.P. King*, University of Illinois at Urbana-Champaign, *E. Riedo*, Georgia Institute of Technology, *A.R. Laracuente, J.A. Robinson, S.G. Walton*, Naval Research Laboratory

Graphene is the most likely carbon-based successor material for CMOS electronics. Recently, interest in chemically modified graphene (CMG) has risen for producing large-scale flexible conductors and for its potential to open an electronic gap in graphene structures. We have developed a means to tune the topographical and electrical properties of several CMGs with nanoscopic resolution by local thermal processing with an AFM tip. Heating converts the CMG back towards graphene with nanoscale resolution. Nanostructures of one CMG, graphene oxide, show an increase in conductivity up to four orders of magnitude as compared to pristine material. Variably conductive graphene nanoribbons have been produced in a single step that is clean, rapid and reliable. Critically, the "carbon skeleton" is continuous across the CMG/graphene boundary. Recent work suggests that ribbons formed this way may be superior to ribbons that were cut.

5:00pm **GR+NS-MoA10 Oxygen Etching of Graphene on Ir and Ru**, *E. Starodub, N.C. Bartelt, K.F. McCarty*, Sandia National Laboratories

We have used low-energy electron microscopy to investigate how graphene is removed from Ru(0001) and Ir(111) by reaction with oxygen. We find two mechanisms on Ru(0001). At short times, oxygen reacts with carbon monomers on the surrounding Ru surface, decreasing their concentration below the equilibrium value. This undersaturation causes a flux of carbon from graphene to the monomer gas. In this initial mechanism, graphene is etched at a rate that is given precisely by the same nonlinear dependence on carbon monomer concentration that governs growth. Thus, during both growth and etching, carbon attaches and detaches to graphene as clusters of several carbon atoms. At later times, etching accelerates. We present evidence that this process involves intercalated oxygen, which destabilizes graphene. On Ir, this mechanism creates observable holes. It also occurs most quickly near wrinkles in the graphene islands, depends on the orientation of the graphene with respect to the Ir substrate, and, in contrast to the first mechanism, can increase the density of carbon monomers. We also observe that both layers of bilayer graphene islands on Ir etch together, not sequentially. Work at Sandia was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U. S. Department of Energy under Contract No. DE-AC04-94AL85000.

Graphene Focus Topic

Room: Brazos - Session GR+TF-TuM

Characterization, Properties, and Applications

Moderator: M. Chhowalla, Rutgers University

8:00am GR+TF-TuM1 Near-field Scanning Microwave Microscopy of Few-Layer Graphene, N.G. Kalugin, New Mexico Tech

Near-field microwave microscopy can be used as an alternative to atomic-force microscopy or Raman microscopy in determination of graphene thickness. We evaluated the values of AC impedance for few layer graphene. The impedance of mono and few-layer graphene at 4GHz was found predominantly active. Near-field microwave microscopy allows simultaneous imaging of location, geometry, thickness, and distribution of electrical properties of graphene without device fabrication. Our results may be useful for design of future graphene-based microwave devices.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the

United States Department of Energy's National Nuclear Security Administration under contract DE-AC04 94AL85000.

8:20am GR+TF-TuM2 Molecular Simulation of the Indentation of Free-Standing Graphene Films in the Presence of Defects, J.D. Schall, R.V. Petrach, Oakland University

Recent experimental advances in the synthesis of graphene have enabled the construction of free-standing graphene-based "nanobridges" (for example: Shivaraman, Nanoletters, 9, 2009, 3100). This has allowed for the first time to probe the mechanical properties of this unique material directly through experiment. In the past, mechanical properties had been estimated theoretically via various molecular simulation techniques. With these new experimental advances, many new questions arise. To list a few: How do defects affect mechanical properties? How do molecular adsorbates modify these materials? Again, molecular simulation is expected to play a significant part in the future of graphene research. In this talk, results of simulated indentation of free-standing graphene films mimicking recent force-probe experiments will be presented. Simulations are conducted using Brenner's second generation reactive empirical bond order potential. This method allows for accurate determination of mechanical properties and chemical modification of the films. Using indentation and a simple force balance approach, the Young's modulus of a pristine free-standing graphene nano-bridge was estimated to be in excess of 1 Terapascal. Results from films with Stone-Wales defects, vacancies, and chemical adsorbates also will be presented.

8:40am GR+TF-TuM3 Mechanical Characterization of Freestanding Graphenoid Nanomembranes from Self-Assembled Monolayers, X. Zhang, C.T. Nottbohm, A. Turchanin, A. Beyer, A. Götzhäuser, Bielefeld University, Germany

We report on the fabrication and mechanical characterization of novel graphenoid nanomembranes with a thickness of approximately 1 nm. The nanomembranes are prepared from electron cross-linked aromatic self-assembled monolayers (SAMs). The membranes are then transferred to window-substrates (Si) for mechanical characterization. Bulge testing of such freestanding nanomembranes within an atomic force microscope is utilized to investigate their mechanical properties.

A series of biphenyl-based molecules were used to prepare the nanomembranes, such as carbonitrile-biphenyl-trimethoxysilyl (CBPS), biphenyl-thiol (BPT) and nitro-biphenyl-thiol (NBPT). Biphenyl-based nanomembranes have elastic moduli ranging from 6 to 12 GPa. They display outstanding performance in the ultimate tensile strength with values of 400 to 500 MPa, which is several times higher than the values of other carbon based membranes. Furthermore, annealing of the cross-linked nanomembranes in ultra high vacuum systematically increase of the Young's moduli from 10 GPa to ~45 GPa for an annealing temperature of ~1000 K. Strain relaxation lowers the residual strain from 0.9 % to ~0.35 % for temperatures of 800 K and above. This is caused by a structural transformation in which the nanomembrane is converted into nanocrystalline graphene.

9:00am GR+TF-TuM4 Chemical Vapour Deposition (CVD) Growth of Graphene on Copper, C. Mattevi, H.K. Kim, G. Eda, M. Chhowalla, Imperial College London, UK

Uniform large-scale fabrication of graphene thin films with controllable thickness represents a key challenge for integration of graphene into

practical electronic devices. Recently, graphene of high quality has been synthesized by chemical vapor deposition (CVD) on transition metal catalysts [1,2]. The graphene growth by CVD on polycrystalline copper [2] is particularly interesting because it allows single graphene layer over 95% of the surface and the residual 5% is covered by 2-3 layered graphene film. Hence, this is the first [2] reported reproducible method to synthesize uniform graphene thickness over large area. Then the as grown graphene can be transferred by different processes, onto a variety of substrates. An appealing challenge is to selectively obtain different graphene thicknesses over large area, to satisfy different applications. Here we report a detailed study of the multilayer graphene domains that appear in limited regions of the copper surface. The lateral size as well as the graphene thickness and stacking order, has been carefully investigated as a function of copper pre-treatment and growth parameters. In particular the role of the feed stock gas pressure and ratio between the etching gas (H₂) and the precursor (CH₄) has been demonstrated to affect the lateral size and the thickness. Optoelectronic properties of the transferred graphene films onto SiO₂ are also presented.

References

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9:20am GR+TF-TuM5 Structural and Electronic Properties of Graphene Synthesized by Chemical Vapor Deposition, Y. Chen, Purdue University

INVITED

We have studied the structural and electronic properties of large scale (up to several inches) graphitic and graphene thin films synthesized by chemical vapor deposition (CVD) on polycrystalline Ni_{1,2} and Cu₃ foils then transferred onto insulating substrates (SiO₂ on doped Si). For films grown on Ni_{1,2}, structural characterizations by atomic force microscopy (AFM), scanning tunneling microscopy (STM), cross-sectional transmission electron microscopy (XTEM)⁴ and spectroscopic Raman mapping confirm that such large scale graphitic thin films contain both thick graphite regions and thin regions of few layer graphene. The films also contain many wrinkles, with sharply-bent tip and dislocations revealed by XTEM, yielding insights on the growth and buckling processes of the film. Measurements on mm-scale back-gated transistor devices fabricated from the transferred film show ambipolar field effect with resistance modulation ~50% and carrier mobilities reaching ~2000 cm²/Vs. We also demonstrate quantum transport of carriers with phase coherence length over 0.2 μm from the observation of 2D weak localization in low temperature magneto-transport measurements. Our results show that despite the non-uniformity and surface roughness, such large-scale, flexible thin films can have electronic properties promising for device applications. For films grown on Cu₃, we show they consist dominantly of monolayer graphene as indicated by Raman mapping. STM imaging shows monolayer graphene lattice. Low temperature transport measurements are performed on micro devices fabricated from such CVD graphene, displaying ambipolar field effect (with on/off ratio ~5 and carrier mobilities up to ~3000 cm²/Vs) and "half-integer" quantum Hall effect, a hall-mark of intrinsic electronic properties of monolayer graphene. We also observe weak localization and extract information about phase coherence and scattering of carriers by disorder in the graphene. We have measured the thermal conductivity of suspended CVD graphene to be ~3000 W/m-K, comparable with that of exfoliated graphene, by combining electronic transport and Raman thermometry⁵. Finally, I will present some results on graphene layers grown by CVD directly on insulating substrates. Work in collaboration with Q. Yu, H. Cao, L. Jauregui, R. Colby, E. Stach, N. Guisinger and H. Li.

1. Q. Yu *et al.*, *Appl. Phys. Lett.* **93**, 113103 (2008)
2. H. Cao *et al.*, *J. Appl. Phys.* **107**, 044310 (2010)
3. H. Cao *et al.*, *Appl. Phys. Lett.* **96**, 122106 (2010)
4. R. Colby *et al.*, *Diamond Relat. Mater.* **19**, 143 (2010)
5. L. A. Jauregui *et al.*, *ECS Trans.* **28** (5), 73 (2010)

10:40am GR+TF-TuM9 Scanning Tunneling Spectroscopy of a Gated Single-Layer Graphene Device in the Quantum Hall Regime, S. Jung, G.M. Rutter, N.N. Klimov, D.B. Newell, N.B. Zhitenev, J.A. Stroscio, NIST

We have performed scanning tunneling spectroscopy (STS) measurements to investigate Dirac particle interactions and localization by local impurities in a gated single-layer exfoliated graphene device in the quantum Hall

regime at a temperature of 4.3 K. At the Dirac point, electron-hole puddles created by the disorder potential in SiO₂ substrate are observed at zero magnetic field. In an applied magnetic field, the carriers are condensed into well-resolved Landau levels (LLs), whose general evolution as a function of both charge density and magnetic field is well described by the context of ‘massless’ Dirac particles. Tunneling spectroscopy measurements as a function of magnetic field and applied gate potential are shown to give insight into the localization of carriers and their relation to the disorder potential. At low magnetic fields, tunneling spectra display long-range scattering features related to the graphene disorder potential variation. The disorder potential also determines the spatial distribution of LLs in higher magnetic fields. We observe that isolated compressible LL regions surrounded by incompressible strips behave like graphene quantum dots (QDs). Single-electron charging of the QDs is seen as four-fold Coulomb oscillations in individual dI/dV curves. These results show that the plane of the graphene 2DEG breaks into a checkerboard pattern of electron- or hole-rich QDs localized at either maxima or minima of the disorder potential.

11:00am **GR+TF-TuM10 Scanning Tunneling Spectroscopy of Gated Bilayer Graphene Device in the Quantum Hall Regime**, *N.N. Klimov*, CNST/EEEL/NIST and Maryland NanoCenter UMD, *G.M. Rutter*, CNST/NIST, *S. Jung*, CNST/NIST and Maryland NanoCenter UMD, *D.B. Newell*, EEEL/NIST, *N.B. Zhitenev*, *J.A. Stroscio*, CNST/NIST

11:20am **GR+TF-TuM11 Monolayer Graphene on 150mm Substrate**, *H.J. Chung*, *J. Heo*, *H. Yang*, *S.-H. Lee*, *S. Seo*, Samsung Advanced Institute of Technology, Korea

Monolayer graphene over a 150 mm substrate was fabricated using Cu-Ni multilayer growth substrates with Inductively Coupled Plasma-Enhanced Chemical Vapor Deposition (ICPCVD) over 700°C. It was confirmed with Raman spectroscopic mapping after metal etching and transfer process. Over 2000 FETs were fabricated on a 150 mm wafer and on-off ratio and Dirac shift were measured for each device and compared to ones from the graphene grown on Ni substrate. In addition, the result from SPM investigation will be presented.

11:40am **GR+TF-TuM12 Probing the Electronic Structure, Surface Chemistry, and Alignment of Graphene using Soft X-ray Absorption Spectroscopy**, *C. Jaye*, NIST, *V. Lee*, SUNY at Buffalo, *P. Lysaght*, SEMATECH, *S. Banerjee*, SUNY at Buffalo, *D.A. Fischer*, NIST

Graphene, a single layer of graphite packed in a honeycomb lattice, has been the subject of intense scientific research since its discovery in 2004 owing to its remarkable properties such as the half-integer quantum Hall effect, ballistic conduction, and the extremely high mobilities of its charge carriers. Graphene has numerous potential applications in the electronics industry including within ultra-high frequency transistors, electrical interconnects and as a replacement for indium-tin-oxide. Nevertheless, the fabrication of large-area graphene remains a challenge. We present systematic studies of the electronic structure, defect density, and alignment of relatively large-area graphene thin films prepared by a) solution/sonochemical methods and b) chemical vapor deposition (CVD). The solution-chemistry-based approaches have the advantage of ease of scalability, making it an attractive approach for industry. We have been able to achieve the fabrication and transfer of large-area graphene films on both conductive and non-conductive substrates. The fabricated films have been characterized by Raman spectroscopy, near-edge X-ray absorption spectroscopy, and four-point-probe conductivity measurements. This battery of measurements allows evaluation of the role of different reducing agents in reducing graphene oxide to graphene. We have also performed systematic measurements of single- and few-layered graphene grown by CVD onto Cu and Ni substrates. X-ray absorption spectroscopy in particular provides strong evidence for substrate hybridization and rippling of graphene. The ripping of graphene induced during transfer to insulating substrates represents a formidable challenge that will need to be solved since corrugations and electronic asperities in graphene induce local scattering potentials. Finally, we will present some X-ray absorption spectroscopy imaging data showing local electronic asperities in graphene.

Tuesday Afternoon, October 19, 2010

Graphene Focus Topic

Room: Brazos - Session GR+TF-TuA

Graphene and 2D Nanostructures

Moderator: Y. Chen, Purdue University

2:00pm **GR+TF-TuA1 Graphene and Its Progeny: from Fundamental Material Properties to Device Applications**, *A.W. Ghosh*, University of Virginia **INVITED**

The incredible material properties of graphene have spurred intense interest among chemists, physicists and engineers towards potentially exciting electronic applications. Much like nanotubes, graphene electrons have high mobilities due to the sharp curvature of their bands at the Gamma point that reduces their effective masses, as well as long scattering lengths due to symmetry selection rules among their pseudospin separated bands. However, a potential problem with graphene is its metallicity, which makes its ON-OFF ratio unacceptable for digital logic. Effort is under way to mitigate this by opening bandgaps through various chemical and electrostatic means. I will argue that any such band-gap opening leads to an inevitable reduction in mobility *even if we manage to do so without affecting its scattering length*. The trade-off arises from a fundamental asymptotic constraint on all graphitic materials (epitaxial graphene, strained graphene, nanoribbons, nanotubes, and bilayer graphene) that pins the high energy electrons away from the Gamma point to an ultimately linear dispersion. However, opening a bandgap by width confinement, e.g. in a nanoribbons, can provide distinct electrostatic if not material advantages. The presence of diffuse boundary conditions at the edges, along with strain and edge roughness, systematically erases any signs of chirality and metallicity in GNRs, making their widths the single arbiter of metallicity. This allows us to envisage wide-narrow-wide (WNW) nanoribbons monolithically patterned out of a single template into both switches and interconnects. The 2-D electrostatics of the source-drain contact edge capacitances improves the gate control, allowing the current to show a highly desirable saturation characteristic. Furthermore, the presence of C-C bonds at the channel-contact interface makes metal induced gap states relatively ineffective in pinning the bands, promoting Ohmic behavior. I will quantify the advantages and disadvantages of WNW devices, and compare with alternate GNR switches, such as utilizing electron focusing in p-n junctions.

2:40pm **GR+TF-TuA3 Electronic Structure of Graphene/BN Heterojunctions formed by Graphene CVD: Doped Graphene**, *C. Bjelkevig, Z. Mi*, University of North Texas, *J. Xiao, P.A. Dowben*, Nebraska Center for Nanostructures and Materials, *S. Gaddam, S. Pokharel, J.A. Kelber*, University of North Texas

Graphene has been grown by chemical vapor deposition of C_2H_4 on a monolayer of h-BN(0001) formed by atomic layer deposition (BCl_3 , NH_3) on Ru(0001). AES, STM and LEED confirm a graphene-like overlayer, with near-zero DOS near the Fermi level, in registry with a BN $R30(\sqrt{3}\times\sqrt{3})$ substrate. Raman spectra reveal graphene "G" and "2D" features with relative intensities indicative of single layer graphene. A large (350 cm^{-1}) redshift in the 2D feature relative to HOPG indicates significant BN-to-graphene charge transfer. The charge transfer is confirmed by photoemission/angle-resolved inverse photoemission spectroscopies (PES/ARIPES), that demonstrate filling of the lowest unoccupied graphene state (π^*) near the Brillouin zone center. These results are in direct contrast to PES/ARIPES results for graphene/Cu, and reported results for graphene/SiC(0001), that show empty graphene π^* states. The data show that the BN layer acts as an n-type dopant for graphene. For the graphene/BN heterojunctions, the ARIPES-determined dispersion of the unoccupied graphene $\sigma^*(\Gamma_1+)$ state yields an effective mass of $0.05 m_e$, in excellent agreement with reported transport measurements on graphene sheets, and indicating that BN doping does not fundamentally alter the graphene electronic structure. The direct growth of graphene on dielectric substrates, and the controlled exploitation of graphene/substrate heterojunction properties, are critical issues for practical device fabrication. The implications of direct CVD of undoped graphene and graphene/BN heterojunctions on high dielectric constant substrates for device applications will be discussed in light of recent results in our laboratories for graphene thermal and free radical-assisted CVD on OH-terminated MgO(111).

Acknowledgements: Work at UNT was supported by the Global Research Consortium of the Semiconductor Research Corporation through Task ID 1770.001, and through ONR under award no. N00014-08-1-1107 through a subcontract with Texas State University at San Marcos. Work at UNL was supported by the Defense Threat Reduction Agency (Grant No. HDTRA1-

07-1-0008), and the NSF "QSPINS" MRSEC (DRM-0820521) at UNL. The authors also thank Luigi Colombo and Adam Pirkle for acquisition of the Raman spectra.

3:00pm **GR+TF-TuA4 Electrical Transport in Graphenoid and Graphene Nanomembranes from Pyrolyzed Self-Assembled Monolayers**, *A. Turchanin*, Univ. of Bielefeld, Germany, *D.H. Weber*, National Metrology Inst., Germany, *M. Bünenfeld*, Univ. of Bielefeld, Germany, *J. Mayer*, Ernst Ruska-Centre for Microscopy, Germany, *C. Kisielowski*, National Center for Electron Microscopy, *T. Weimann*, National Metrology Inst., Germany, *A. Götzhäuser*, Univ. of Bielefeld, Germany

Ultrathin carbon nanomembranes have recently attracted enormous interest. We report a molecular route to the fabrication of a monolayer or few layers of free-standing graphenoid and graphene nanomembranes based on molecular self-assembly, electron processing and pyrolysis. Aromatic biphenyl self-assembled monolayers (SAMs) are cross-linked by electron irradiation. The cross-linking results in mechanically stable graphenoid sheets with the thickness of a single molecule ($\sim 1\text{ nm}$) and arbitrary sized. The graphenoid sheets can be lifted from their surface and transferred to another solid substrate or holey structures, where they become free-standing nanomembranes. Upon annealing (pyrolysis) up to 1300 K the molecular sheets transform into nanocrystalline graphene phase. This transformation is accompanied by a drop of the sheet resistivity from $\sim 10^8$ to ~ 10 k Ω /sq and a 2D insulator to metal transition. We characterize the insulator to metal transition by electrical transport measurements as well as by complementary spectroscopic and microscopic techniques. A plethora of applications of the suggested molecular route to free-standing ultrathin carbon materials is feasible that take advantage from the fact that the large scale fabrication, control over the thickness and nanostructuring are easily controlled.

[1] A. Turchanin, A. Beyer, C. T. Nottbohm, X. H. Zhang, R. Stosch, A. Sologubenko, J. Mayer, P. Hinze, T. Weimann, and A. Götzhäuser: One Nanometer Thin Carbon Nanosheets with Tunable Conductivity and Stiffness, *Adv. Mater.* 21, 1233-1237 (2009)

[2] A. Turchanin, D. Käfer, M. El-Desawy, C. Wöll, G. Witte, and A. Götzhäuser: Molecular Mechanisms of Electron-Induced Cross-Linking in Aromatic SAMs, *Langmuir* 25, 7342-7352 (2009).

[3] C. T. Nottbohm, A. Turchanin, A. Beyer, A. Götzhäuser: Direct e-beam writing of 1 nm thin carbon nanoribbons, *J. Vac. Sci. Technol. B* 27, 3059-3062 (2009).

4:00pm **GR+TF-TuA7 From 2D to 1D - Supramolecular Architectures on Rippled Graphen**, *M. Roos*, *H.E. Hoster*, *R.J. Behm*, Ulm University, Germany

Bis(terpyridine)derivatives (BTP) form highly ordered hydrogen-bonded 2D networks on solid surfaces.¹⁻⁴ The preferred hydrogen bond configurations and thus the resulting structures are steered via the positions of the nitrogen atoms within the BTP molecules. Elaborate synthesis procedures allow varying these positions without altering the footprint shape of the molecules.¹ On smooth surfaces like graphite or metal single crystals, the molecule-substrate interactions play a secondary role for the structures, mainly by determining the orientations of the molecules and thus of the ordered networks.²⁻⁴ In this contribution, we will demonstrate that more pronounced template effects arise for substrates where the molecule-substrate interaction laterally varies at nm-scales. As an example, we will show the ordering behaviour of two different types of BTP molecules on Graphene monolayers grown on Ru(0001). The moiré-type pattern of these surfaces has a periodicity of 3 nm, i.e., in the order of the BTP dimensions and the network meshes they usually form. Submolecularly resolved STM images show that the BTP molecules are confined to the valleys of the graphene ripple structure. We will compare the resulting supramolecular 1D and 2D assemblies to the ordered 2D networks formed by the same molecules on smooth substrates, and we will discuss in how far the template effect can be quantitatively explained by a lateral modulation of the van der Waals interactions due to the height corrugation of the Graphene sheet.⁵

1 C. Meier et al., *J Phys Chem B* 109 (2005) 21015.

2 M. Roos et al., *Phys. Chem. Chem. Phys.* 9 (2007) 5672.

3 H. E. Hoster et al., *Langmuir* 23 (2007) 11570.

4 T. Waldmann et al., *ChemPhysChem* 11 (2010) 1513.5 W. Moritz et al., *Phys. Rev. Lett.* 104 (2010) 136102.

4:20pm **GR+TF-TuA8 Understanding the Functionalization of Graphene by Electron-Beam Generated Plasmas**, *M. Baraket, S.G. Walton, E.H. Lock, J.A. Robinson, F.K. Perkins*, Naval Research Laboratory
Graphene is a single monolayer thick carbon sheet with remarkably high electron mobility. Its unique structural and electronic properties make it an interesting material for nanoscale electronic and sensing devices. The addition of functionalities increases its reactivity toward certain materials and thus broadens its applications. One significant impediment to realizing the potential of graphene is the development of an industrially viable approach to producing precisely engineered functionalities over large areas. In this respect, plasmas are an ideal candidate but problems associated with the large fluxes of high-energy ions are a significant concern. Electron beam generated plasmas, characterized by low incident ion energies (< 5 eV), have been used to functionalize graphene without any damage [1]. We discuss the use of this system to controllably introducing oxygen, hydrogen, fluorine, nitrogen or ammine containing groups at different concentrations. The reversibility of the functionalization via low-temperature annealing will also be discussed. This work was supported by the Office of Naval Research. M.B. appreciates the support of the National Research Council.

[1] M. Baraket, S.G. Walton, E.H. Lock, J. T. Robinson, and F.K. Perkins. The functionalization of graphene using electron beam generated plasmas. *Applied Physics Letters* 96, 231501 (2010)

4:40pm **GR+TF-TuA9 Chemically Tailoring Graphene via Organic Self-Assembled Monolayers**, *M.C. Hersam*, Northwestern University
INVITED

Chemically functionalized semiconductor surfaces have been widely explored due to their potential for enabling molecular electronic and sensing devices that are compatible with conventional microelectronic technology [1]. Thus far, the vast majority of work in this field has focused on established semiconductors including silicon, germanium, and gallium arsenide. Meanwhile, the condensed matter physics community has diverted substantial experimental and theoretical effort to graphene, an emerging electronic material with superlative carrier mobility and exotic charge transport phenomena such as the quantum Hall effect.

In an attempt to unify these two fields, we have been exploring strategies for forming and interrogating organic self-assembled monolayers on graphene surfaces. In particular, we have recently demonstrated that self-assembled monolayers of perylene-3,4,9,10-tetracarboxylic-dianhydride (PTCDA) can be formed on graphene surfaces via gas-phase deposition in ultra-high vacuum (UHV) environments at room temperature [2]. Molecular-scale resolution scanning tunneling microscopy (STM) images reveal long-range order in the PTCDA monolayers, while scanning tunneling spectroscopy (STS) measurements yield distinct electronic features associated with the PTCDA that are not observed on pristine graphene.

In addition to UHV STM characterization, this talk will summarize our most recent efforts to nanopattern self-assembled monolayers on graphene at the sub-10 nm scale. Nanopatterning chemically functionalized graphene presents opportunities for tailoring the electronic and chemical properties of graphene nanoribbons in addition to providing a molecular-scale resolution template for subsequent materials growth on graphene surfaces.

[1] M. A. Walsh and M. C. Hersam, "Atomic-scale templates patterned by ultrahigh vacuum scanning tunneling microscopy on silicon," *Annual Review of Physical Chemistry*, **60**, 193 (2009).

[2] Q. H. Wang and M. C. Hersam, "Room-temperature molecular-resolution characterization of self-assembled organic monolayers on epitaxial graphene," *Nature Chemistry*, **1**, 206 (2009).

5:20pm **GR+TF-TuA11 Stability of Continuous Graphene Sheet and Graphene Flake on the Si(111) Surface**, *B.B. Kappes, T.E. Davies*, Colorado School of Mines, *S. Jun*, University of Wyoming, *A.C.T. van Duin*, Penn State University, *C.V. Ciobanu*, Colorado School of Mines

While rapid use of carbon nanostructures in the silicon-based nanoelectronics industry will involve the direct integration of graphene with silicon chips, so far graphene has not been grown on pristine silicon surfaces because usual synthesis routes would likely lead to the formation of stable silicon carbide instead of the precipitation of carbon at the surface. Here we show that if graphene can be deposited on pristine Si(111) surfaces, then it forms moiré superstructures and binds strongly to the substrate over a wide range of in-plane orientations. The binding energies depend on the orientation of graphene as well as the strain applied to achieve commensurability with the substrate; the strongest binding estimated from density functional theory calculations is approximately 1.5 eV/carbon atom. Using molecular dynamics simulations based on bond-order and reactive force field interatomic potentials, we present evidence that graphene remains stable and bonded to the substrate for temperatures up to 80% of the substrate melting temperature. Bonding information, study

of the local density of states, and simulated scanning tunneling microscopy show graphene on Si(111) is semiconducting, with a sizable number of carbon hybridized sp^3 and a bandgap affected by the orientation of graphene with respect to the substrate.

5:40pm **GR+TF-TuA12 Effect of Point-like Defects on the Atomic Structure and Electronic Properties of Graphene Supported on Amorphous SiO₂**, *K.E. Kweon, G.S. Hwang*, University of Texas at Austin
Graphene supported on the common gate dielectric, SiO₂, has been considered as a highly promising candidate for future electronics. Therefore, it is important to understand the interfacial interaction between graphene and SiO₂. Most of the existing theoretical studies have modeled the underlying SiO₂ surface using defective or H-terminated crystalline structures. However, the gate oxide is amorphous and possibly has a number of point-like defects, yet no detailed study has been undertaken on the defect effect. In this talk, based on first principles calculations we present how the SiO₂-graphene binding and consequent graphene electronic structure are influenced by the presence of point-like defects in not only SiO₂ surface but also graphene sheet. We considered six different surface defects on SiO₂; silyl radicals [(≡Si-O)₃Si•], oxy radicals [(≡Si-O)₂Si-O•], silylene center [(≡Si-O)₂Si], silanone [(≡Si-O)₂Si=O], peroxide radicals [(≡Si-O)₃Si-O-O•], and dioxasilirane [(≡Si-O)₂Si-O-Si-O₂], along with defective graphene that contains vacancies. This talk will mainly touch on the pathways and energetics of the defect-mediated graphene binding to SiO₂, and how the covalent graphene-SiO₂ binding affects the electronic properties of graphene.

Graphene Focus Topic

Room: Southwest Exhibit Hall - Session GR-TuP

Graphene Focus Topic Poster Session

GR-TuP1 Electronic and Magnetic Properties of Functionalized Graphene Nano-Ribbons, *Y. Fujii, J. Nakamura*, The University of Electro-Communications (UEC-Tokyo), Japan

Oxidation and reduction are the basic and most important processes for the carbon-based materials as initial processes for producing very thin graphitic materials composed of a single or several graphene layers [1]. Recently, Kosynkin *et al.* have reported that the graphene nano-ribbons (GNRs) can be produced using an oxidative process, and the edges of these GNRs are functionalized by carboxylic acids even after the reduction treatment [2]. On the other hand, it has been well-known that a certain type of GNR with zigzag edges exhibits the so-called flat-band magnetism, which stems from the localized states at the edges [3,4]. In this study, we reveal the electronic and magnetic properties of zigzag GNRs functionalized by carboxyl groups using the first-principles total-energy calculations within the spin density functional theory.

The zigzag GNRs employed in this study have widths from $N=2$ to $N=8$. We have found that the ground state of the GNR with the zigzag edges functionalized by the carboxyl groups is ferromagnetic, if N is even. For the GNR with $N=4$, the ferromagnetic state is more stable by 17 meV per unit cell than the anti-ferromagnetic one. However, if N is odd, the ground state of the functionalized GNR becomes the anti-ferromagnetic: e.g., for $N=3$, the anti-ferromagnetic state is more stable by 12 meV per unit cell than the ferromagnetic one. We have also investigated the energy dispersions of the GNRs. In the anti-ferromagnetic states, the energy bands for both spins are degenerate, and their dispersions near the Fermi level are nearly-flat at the edge of the Brillouin zone, while for the ferromagnetic states, the up-spin and down-spin bands split from each other. The spin density for the ferromagnetic states is localized near the GNR edges. Thus, the onset of the finite magnetic moment of the functionalized GNR is due to the so-called flat-band magnetism.

- [1] S. Horiuchi *et al.*, Appl. Phys. Lett. **84**, 2403 (2004)
- [2] D. V. Kosynkin *et al.*, Nature Lett. **458**, 872 (2009)
- [3] M. Fujita *et al.*, J. Phys. Soc. Jpn. **65**, 1920 (1996)
- [4] J. Nakamura, T. Nitta, and A. Natori, Phys. Rev. B, **72**, 205429 (2005)

GR-TuP2 Aminocaproic Graphene Sheet Synthesized by Solution Plasma, *N. Tsuda, Y. Aoki, J. Hieda, O. Takai, N. Saito*, Nagoya University, Japan

Plasma in gas phase is widely used in many industrial fields such as electronic device manufacturing processes (plasma etching, sputtering, plasma-enhanced CVD, etc.), hard coating processes (ion plating, sputtering, etc.), surface treatment processes (low or atmospheric pressure plasma treatments, sputtering, plasma etching, etc.) and so on. Plasma in solid phase has been utilized finally for surface plasmon resonance (SPR) spectroscopy, nanoparticles, etc., and plasmonics is developing as a new research field. On the other hand, plasma in liquid phase is not generally well-known, although it has been partially utilized in water treatments and electrical discharge machining. The fundamentals of plasma in liquid phase have not been established, including its generation techniques, its state, and activated chemical species. However, it would be reasonable to expect a higher reaction rate under lower-temperature conditions, and the greater chemical reaction variability since the molecular density of liquid is much higher than that of gas phase. So we have named the plasma in liquid phase "solution plasma" because we make variety of plasma by choosing the combinations of solvents and solutes in solutions, and are developing solution plasma processing (SPP). In SPP, aqueous solutions, nonaqueous ones, liquid nitrogen, supercritical fluids, etc. can be utilized as solutions. Recently, we have investigated the features of SPP and the applications such as syntheses of nanoparticles and mesoporous silica, and surface modification of particles.

In this research, graphene sheet were modified by a glow discharge in solution. A pulsed power supply was used to generate discharges. The pulsed width was 2 micro seconds, the repetition frequency was 15 kHz. The electrode was tungsten wire in the diameter of 1 mm with electrode gap of 0.3 mm. ammonium aqueous solution was used as the medium around plasma. Graphene sheets were separated by oxidation. The graphene sheets were added to the ammonium solution and irradiated by glow discharge in the solution. The solution and the productants after the discharge were analyzed by optical emission spectroscopy, IR spectroscopy, Uv-Vis

spectroscopy, AFM, XRD and TEM. After the discharge, the graphene sheets were modified by amino functional groups. Moreover, the aminocaproic acid was grafted into the amino functional groups on graphene sheets. Finally, graphene sheets were solidified because the space of sheets was measured.

GR-TuP3 Investigation of Diffusion Process between Many-Layers Graphene and Metallic Contacts, *A.R. Vaz, CTI/CCS - UNICAMP, Brazil, F.P. Rouxinol, C.F. Fischer, S.A. Moshkalev, UNICAMP, Brazil, J.W. Swart, CTIRA, Brazil*

Nanoscale graphitic carbon forms like nanotubes and few-layer graphene (graphite) or FLG layers have attracted much attention recently due to their unique physical-chemical properties and many potential applications in microelectronics, like sensors, MEMS (micro-electromechanical systems) and interconnections [1]. However, successful applications of these materials in microelectronic devices require development of reliable and compatible technologies for their controlled growth or deposition, manipulation, contacting, processing and measurements of electrical other properties. In particular, mechanisms responsible for formation of high-quality electrical contacts between graphitic layers and metals (this is imperative for applications like interconnections) is poorly understood and need thorough study and optimization. In this work, we studied characteristics of the electrical contacts between FLG and metals like W, Ti, Ni, Cu, Pd and Au. For this, two different techniques were used. First, small flakes of FLG were prepared in solutions and deposited using ac dielectrophoresis [1] over metal electrodes pre-fabricated by photolithography and FIB milling processes that produced 5 μm deep gaps with varying widths (Fig. 1). The thickness of FLG flakes was evaluated using Raman spectra, AFM measurements and SEM images [2]. Then, electrical properties of deposited structures were measured before and after thermal annealing, using 2 terminals I-V method (Fig. 2). Electrical contacts between graphitic layers and metal electrodes were found to improve strongly with annealing. It was also found that metal-FLG contacts give usually the major contribution to the total measured 2-terminals resistance, and the contact resistivities were then evaluated for different metals. Better contacts were achieved using Ti and W electrodes. To study interaction between metals and graphitic layers during annealing (metal diffusion), a special study was undertaken. For this, metal layers of certain thickness were deposited in deep trenches prepared in thick HOPG layers using FIB based lithography followed by deep reactive ion etching of graphite in oxygen with high-density plasma source [3]. Then, after annealing in vacuum, FIB was used to make cross-sections and to study lateral (in-plane) and normal (between planes) diffusion of metal inside the graphite structure. For such study, several microscopy techniques with spatial resolution like EDX, EELS, HRSEM were employed.

- 1 R.Gelamo et al, Chem.Phys.Lett. (2009)
- 2 F.P. Rouxinol et al, to be published
- 3 H. Jansen et al., J. of Micromech. Microeng. 16 (1995)

GR-TuP4 Optoelectronic Properties of Large Area Graphene Thin Films, *C. Mattevi, H.K. Kim, G. Eda, M. Chhowalla*, Imperial College London, UK

A scalable method to isolate graphene on insulating substrates is still a challenge. Recently it has been demonstrated that graphite can be exfoliated in certain solvents [1] and in water-surfactant solution [2] forming a stable colloidal suspension. Amongst several solvents investigated, exfoliation with 1-Methyl-2-pyrrolidone (NMP) has yielded the highest concentration of 1-5 graphene layers [1,3]. Here we present Langmuir-Blodgett (LB) films of pure graphene exfoliated in NMP and their optical and electronic characteristics [3]. For flakes with large lateral size, the films displayed sheet resistance of 5 K Ω /sq and transmittance of 75% at wavelength of 550 nm. Thin film transistor (TFTs) have been fabricated and tested at temperatures ranging from 77 K to 340 K. The field effect measurements displayed high degree of p-doping and this is possibly due to interaction between graphene and residual oxygen functional groups, as suggested by X-ray photoelectron spectroscopy (XPS). Below 150 K, the temperature dependence of the conductivity suggests transport by two-dimensional variable range hopping. Above 180 K, thermal activation of the charge carriers appears to be the dominant mechanism. A clear dependence of the optoelectronic properties with the lateral size of graphene flakes has been observed. A critical analysis on the prospects of improving the electrical

properties of graphene obtained *via* non covalent exfoliation will be discussed.

- [1] Y. Hernandez et al. *Nature Nanotech.* Vol. 3, pp. 563-568, 2008.
- [2] M. Lotya et al. *J. Am. Chem. Soc.* Vol 131, pp.3611-3620, 2009.
- [3] H. Kim et al. *submitted.*

GR-TuP5 Tunneling Spectroscopy of Image Potential Derived States of Epitaxial Graphene on SiC(0001): Sample Annealing Effects, A. Sandin, A. Pronshinske, D.B. Dougherty, J.E. Rowe, North Carolina State University

Constant current tunneling spectroscopy has been used to study the high energy unoccupied electronic structure of single layer and bilayer epitaxial graphene on the Si-terminated face of SiC(0001) prepared with several different sample-annealing conditions that give different thicknesses of graphene film coverage. We identify a series of intense peaks in vertical sample-tip spacing versus voltage as derived from image-potential states of epitaxial graphene. These peaks shift in energy position between single-layer and bilayer graphene in a manner somewhat like the known work function difference (of ~4.4 eV and ~4.6 eV for single-layer and bilayer graphene respectively). We compare the series of image-potential-like-state energies measured experimentally with simple models of the tunneling potential due to a sharp tip protrusion and a flatter average tip radius that shows a variability of the energy series with spatial variation of the potential. In addition, we argue that variability in peak positions for nearly all of the observed image potential derived states arises from the variations in the 3-D tip shape, which then determines the field dependent tunneling potential.

GR-TuP6 Characterization of Graphene Films Grown on Cu-Ni Foil by XPS and LEED, D.D. Moody, W. Priyantha, R. Droopad,, C.A. Ventrice Jr., Texas State University - San Marcos, S. Chen, W. Cai, R.D. Piner, R.S. Ruoff, The University of Texas at Austin

Previous studies have shown that monolayer graphene films can be grown on Cu substrates by the catalytic decomposition of methane molecules.[1-5] The solubility of carbon in Cu is negligible at the growth temperatures typically used for graphene growth. This results in the formation of films that self-terminate at a monolayer coverage since there is very little (if any) carbon in the sub-surface region that can precipitate to the graphene overlayer during the cooling phase. Indeed, our prior work suggests that the growth is entirely surface mediated with no contribution from segregation of carbon from the bulk.[2] In an attempt to enhance the catalytic activity of the surface and to grow multilayer graphene rather than solely monolayer graphene, use of a commercial 70%-30% Cu-Ni alloy foil (which also has some Fe and Mn present) has been investigated. Growth was performed in a home-made, cold-wall, chemical vapor deposition (CVD) system [6] at a growth temperature of 1000 ° C (as measured with a pyrometer through a quartz window) with pure CH₄ at a pressure of 8 Torr. To determine the surface alloy composition during the different phases of growth, X-ray photoelectron spectroscopy (XPS) measurements have been performed on the Cu-Ni foil before anneal, after anneal in H₂, and after growth of graphene in a CH₄ environment. XPS measurements were made at both normal emission, and at an exit angle of 50° to enhance the surface sensitivity. Before anneal, the measurements indicate that the surface is Ni-rich and heavily oxidized. After annealing in H₂, only a small amount of oxide remained, and the alloy fraction of the surface region was 21% Ni. This indicates that the outermost layer of atoms is probably Cu, but further study is indicated. Growth of the graphene overlayer resulted in an increase of the Ni composition of the surface region to 28%, with only trace amounts of oxygen present. Low energy electron diffraction (LEED) measurements of the foils showed only diffuse background for the Cu-Ni foils before anneal and after anneal in H₂. The LEED measurements of the foil after graphene growth showed diffraction spots and ring structures at 70 eV, which are attributed to the formation of multidomain graphene. *Support from the Office of Naval Research is appreciated.*

- [1] X. S. Li, et al., *Science* **324**, 1312 (2009).
- [2] X. S. Li, et al., *Nano Letters* **9**, 4268 (2009).
- [3] X. S. Li, et al., *Nano Letters* **9**, 4359 (2009).
- [4] X. S. Li, et al., *ECS Transactions* **19**, 41 (2009).
- [5] W. Cai, et al., *Nano Letters* (in-press).
- [6] W. Cai, et al., *Nano Research* **2**, 851 (2009).

GR-TuP7 Chemical Vapor Deposited Graphene-Based NEMS Resonators, I. Rivera, R. Joshi, J. Wang, University of South Florida

Graphene is a superb structural material for NEMS resonators because of its unique electrical and mechanical properties. Excellent material properties of graphene such as good conductivity, single atomic thickness layers, large surface area, low mass density, and high Young's modulus as compared to

other materials allow optimization of the resonance response to approach the ultimate limit for two dimensional NEMSs. Single device resonator has been studied extensively in the past with very high Q-factor and resonant frequency. However, for device technology, arrays of resonators provide a wider range of applications which appear to be possible in graphene based resonators. Figure 1 summarizes the fabrication process of the graphene resonators and Figure 2 presents a 3D schematic of graphene resonator array, indicating key parts and the materials. We have grown the monolayer quality graphene using thermal chemical vapor deposition method on Ni coated substrates at 1000°C using a mixture of argon, hydrogen and methane as precursor gases. It was observed that growth time and thickness of Ni films are key parameters for controlling the number of layers of graphene. Initial results suggest the formation of 1-5 layers of graphene which was estimated from AFM, TEM and 2D peak intensity of Raman spectra [Figure 3]. Hall Effect data show mobility ~ 1500 cm²/V and resistivity of 2X10⁻⁶ Ω-cm for 3 layer graphene. Graphene was released from Ni by wet chemical etching and the layers were transferred onto SiO₂/Si substrate. In order to employ graphene as a major building block, NEMS resonator structures were created by transferring a patterned graphene layer onto a silicon-on-insulator (SOI) substrate to act as mechanical interconnects. The Si device layer in SOI substrate is patterned by deep reactive ion etching (DRIE) using SiO₂ as hard mask to create the resonator body. An ultra-thin layer of high-k dielectric material is uniformly deposited by atomic layer deposition (ALD) followed by deposition and doping of a poly-Si layer. A lithography process is done to create the shape of the double side electrodes. Thereafter, the graphene is transferred and attached to the resonator bodies to complete the array. Finally, the resonator array is released by removing the buried SiO₂ in the SOI substrate.

Wednesday Morning, October 20, 2010

Graphene Focus Topic

Room: Brazos - Session GR+EM+MS+TF+MI-WeM

Graphene and Carbon-based Devices

Moderator: N.P. Guisinger, Argonne National Laboratory

8:00am **GR+EM+MS+TF+MI-WeM1 Epitaxial Graphene: Effects of Dielectric Overlayers and Device Design on FET Performance.** *M.J. Hollander, R. Cavalero, D. Snyder, M. LaBella, K. Trumbull, Z. Hughes, J. Robinson*, The Pennsylvania State University

The realization of a graphene-based electronic technology necessitates large-area graphene production, as well as the ability to integrate graphene with highly insulating films that act as the gate dielectric in field effect transistors (FETs). Graphene's two dimensional nature allows for phenomenal electronic properties and ultimate scalability, but also makes it susceptible to doping and scattering by charged impurities, dangling bonds, and other defects that may derive directly from choice in gate dielectric and deposition technique. The nature and extent of the effect of the dielectric over-layer on conduction within the graphene channel is of fundamental interest in designing and producing graphene based FETs. Atomic layer deposition (ALD) has proven to be an excellent technique toward the integration of dielectrics with graphene and provides a means to produce high quality films for gate dielectrics at temperatures below 300C, but requires the use of a thin nucleation layer to promote complete coverage and to protect the graphene.

We present results on graphene FETs utilizing various gate dielectrics and various nucleation layers. Graphene was grown epitaxially on 100 mm SiC wafers and processed using standard photolithographic techniques. Al₂O₃ and HfO₂ gate dielectrics were investigated using SiO₂, TiO₂, and Al₂O₃ nucleation layers in various combinations. We show that choice of gate dielectric and nucleation layer can have a dramatic effect on transistor performance and charge carrier mobility. Saturation current, transconductance, and device hysteresis were examined in the fabricated FETs while charge carrier mobility and charge carrier density within the epitaxial graphene were evaluated using Van der Pauw structures. Graphene FETs utilizing Al₂O₃ and SiO₂ seeded dielectrics exhibit the best performance while TiO₂ seeded and unseeded devices exhibit large gate leakage currents resulting in non-functioning FETs. Additionally we provide evidence that the choice of dielectric and seed can significantly impact the Dirac point (minimum conduction), amount of hysteresis, and on/off ratio of the graphene FETs. Trends in saturation current, and transconductance appear to be independent of nucleation layer and gate dielectric choice, indicating that conduction through the channel may be limited by mechanisms independent of the nucleation layer and gate dielectric.

In addition to the aforementioned performance metrics, FET performance after continued application of high electric fields across the channel will be reported. Finally, we examine how choice of channel length and width, along with transistor design, effect performance.

8:20am **GR+EM+MS+TF+MI-WeM2 Graphene Oxide on Patterned Self-Assembly Monolayer for Cancer Marker Detection.** *D.-J. Kim, C.Y. Jung, O.J. Yoon, N.-E. Lee*, Sungkyunkwan University, Republic of Korea, *J.-S. Park*, Korea Electronics Technology Institute, Republic of Korea

Graphene, two-dimensional sheet of sp²-hybridized carbon atom, has received much attention in recent years for many applications such as energy storage and conversion, batteries, fuel cells, optoelectronic device, field-effect transistors, electromechanical resonators, chemical sensors, and biotechnologies. Oxidized form of graphene, graphene oxide, which has functional groups of epoxide, carbonyls, hydroxide, and phenol groups at both sides can also provide various functionalities for biomedical applications because the high densities of defective sites can provide many active sites for electron transfer to biological species, similarly to graphene. In this study, we demonstrate the graphene oxide based immunosensor for cancer marker detection. Graphene oxide pattern was formed selectively on self-assembly monolayer (SAM) pattern formed by using inkjet printing. The hydroxyl terminated ITO electrode was first selectively functionalized by the amine (-NH₂) group by inkjet printing of SAM, and the graphene oxide flakes were adsorbed selectively on the SAM pattern. After immobilization of monoclonal antibody to PSA (prostate specific antigen) which is the biomarker in prostate cancer, the electrochemical performance of immunosensor was evaluated by varying the concentration of PSA-ACT (prostate specific antigen/anti-chymotrypsin) complex. And the PSA polyclonal antibody conjugated with gold nanoparticles was applied to amplification of electrochemical signal because the attachment of

nanoparticles onto electrodes drastically enhances the conductivity and electron transfer from the redox analytes. The results showed that graphene oxide based immunosensor can be possibly applied to the delicate diagnosis of various disease markers as well as PSA at the extremely low level and with ultra-high sensitivity.

8:40am **GR+EM+MS+TF+MI-WeM3 Spintronics in Graphene Based Nanostructures.** *J. Fernández-Rossier*, Universidad de Alicante, Spain
INVITED

Spintronics in graphene has received attention from two complementary points of view. On one side, the small spin orbit coupling and nuclear spin density suggest that graphene should have very long spin relaxation and decoherence times, which would make it suitable for long distance spin transport and, eventually, for spin-based quantum computing. Although small, spin orbit interaction turns graphene into a spin hall insulator, at very small temperatures, so that the edges of graphene should carry spontaneous spin currents. Independently of the above, the zigzag edges of graphene nanostructures, like graphene ribbons and islands, are predicted to present ferromagnetic spin order due to electron electron coupling. In this talk I will discuss the properties of graphene nanostructures when both the spin-orbit coupling and the Coulomb interactions are included. I will show how the combined action of spontaneous spin order and spin orbit coupling results in persistent charge currents flow in the edges of a variety of graphene nanostructures.

9:20am **GR+EM+MS+TF+MI-WeM5 CVD Gate Dielectrics and Bandgap Engineering of Graphene Layers.** *W.J. Zhu, D. Neumayer, V. Perebeinos, P. Avouris*, IBM T.J. Watson Research Center

Graphene is very promising for electronic devices, particularly for analogue high frequency devices due to its high intrinsic mobility. One challenge in graphene devices is the formation of gate dielectrics on graphene due to its hydrophobic nature. We found a new CVD gate insulator that provides uniform coverage on graphene while preserving the channel mobility, thus making it a very promising gate dielectric for graphene devices. We also studied the channel resistance and the modification of the band structure as a function of the vertical electric field near the Dirac (neutrality) points in the fabricated top-gated graphene devices. We found that as the vertical field increases, in bi- and tri-layer graphenes, the band-gap increases, while in multi-layer graphene, the band-overlap increases. The values of band-gap/overlap in bi-, tri- and multi-layer graphenes were estimated using a simple model which takes into account the variations of the surface electrostatic potential at the Dirac/neutrality point.

9:40am **GR+EM+MS+TF+MI-WeM6 Characterization of Devices Fabricated from Electrostatically Transferred Graphene: Comparison with Epitaxial based Devices.** *S.W. Howell, L.B. Biedermann, T. Ohta, T.E. Beechem, W. Pan, A.J. Ross, D.C. Trotter*, Sandia National Laboratories

10:40am **GR+EM+MS+TF+MI-WeM9 Electron Transport in Dual-Gated Mono- and Bilayer Graphene Devices with High-k Dielectrics.** *E. Tutuc, S. Kim, B. Fallah, K. Lee, J. Nah, S.K. Banerjee*, The University of Texas at Austin, *L. Colombo*, Texas Instruments, Inc.
INVITED

A key issue for graphene-based devices is the deposition of thin high-k dielectric layers combined with a minimum electron mobility degradation. Here we examine the carrier transport in mono and bilayer graphene field-effect transistors with top Al₂O₃ and HfO₂ dielectrics. The high-k dielectric films are grown by atomic layer deposition (ALD), and using a 1nm-thick Al interfacial layer in order to create intentional nucleation centers for the ALD. We show that this deposition technique allows the realization of high mobility graphene devices with aggressively scaled top dielectrics. We investigate the carrier mobility dependence on dielectric thickness and temperature in mono-layer graphene field-effect transistors with high-k dielectrics. The electron transport in dual-gated graphene bilayers with Al₂O₃ top dielectric reveals an interesting band-gap energy dependence on transverse electric field and perpendicular magnetic field in this system.

11:20am **GR+EM+MS+TF+MI-WeM11 In-situ X-ray Photoelectron Spectroscopy Studies of Ozone-based ALD Al₂O₃ Dielectrics on Graphite and Graphene.** *A. Pirkle, S. McDonnell*, University of Texas at Dallas, *L. Colombo*, Texas Instruments, Inc., *R.M. Wallace*, University of Texas at Dallas

We present a study of ozone-based atomic layer deposition (ALD) of Al₂O₃ films on graphene and bulk graphite. Uniform deposition of scalable device-quality high-k dielectrics on graphene is a substantial hurdle for the implementation of conventional FET devices as well as novel device

structures exploiting the unique transport properties of graphene. Trimethylaluminum (TMA) / O₃ processes are found to result in uniform Al₂O₃ depositions on graphite and graphene surfaces (1), in contrast to common TMA / H₂O-based processes which result in nonuniform nucleation at defects and step edges.

In order to further examine the nature of interactions between TMA / O₃ and graphene, we utilize *in-situ* x-ray photoelectron spectroscopy (XPS) coupled via a UHV transfer line to an ALD reactor. Morphology of deposited films is also examined *ex-situ* using atomic force microscopy (AFM). We examine the impact of several parameters on Al₂O₃ deposition. Choice of deposition temperature is critical, as etching of graphene by O₃ is observed at elevated temperatures (2) but dielectric quality is degraded at low temperature (3). We also examine the impact of surface condition on Al₂O₃ composition particularly with regard to partially reacted TMA precursor molecules; various surface treatments are employed to approximate realistic device processing conditions. Finally, the effect of variations in purge time between ALD precursor pulses is studied; a reduction in deposition with increased purge time indicates that weakly bonded precursor molecules (TMA and O₃) are easily desorbed from the graphene surface.

This work is supported by the NRI SWAN and MIND centers.

1: B. Lee, et. al., Appl. Phys. Lett. 92 (20), 203102 (2008)

2: G. Lee, et. al., J. Phys. Chem. C 113 (32), 14225 (2009)

3: S. K. Kim, et. al., J. Electrochem. Soc. 153 (5), F69 (2006)

Wednesday Afternoon, October 20, 2010

Graphene Focus Topic

Room: Brazos - Session GR+MS-WeA

Low Dimensional Carbon Device Manufacturing

Moderator: A.C. Diebold, The University at Albany-SUNY

2:00pm **GR+MS-WeA1 Material Properties of Epitaxial Graphene in RF Devices**, *D.K. Gaskill*, U.S. Naval Research Laboratory, *J.S. Moon*, HRL Laboratories, LLC, *G.G. Jernigan*, *J.C. Culbertson*, *J.L. Tedesco*, U.S. Naval Research Laboratory, *J. Robinson*, The Pennsylvania State University, *P.M. Campbell*, *N. Garces*, *V.D. Wheeler*, *J.K. Hite*, *R.L. Myers-Ward*, *C.R. Eddy, Jr.*, *A.L. Friedman*, U.S. Naval Research Laboratory, *M. Fanton*, The Pennsylvania State University **INVITED**

The advent of the world's first epitaxial graphene (EG) RF field effect transistors (FETs), grown on semi-insulating SiC wafers, has generated tremendous interest in the electronics community since devices can be fabricated using conventional photolithographic approaches [1]. Recently, RF FETs have shown an f_{max} of 14 GHz at 5 V_{ds} for a 2 μm gate width and better results are expected as gate widths are scaled down. To push the performance metrics for wafer-scale EG FETs significantly higher, key materials issues must be addressed. Some of these issues are morphology and thickness control, enhanced mobility, uniformity of sheet carrier density and resistivity, and substrate defects. Here we describe NRL-HRL-Penn State approach in the DARPA CERA program for forming EG via Si sublimation from SiC wafers and the impact of material issues on RF device performance will be discussed.

Epitaxial graphene was synthesized using an Aixtron VP508 reactor on the Si- and C-faces of 4H- and 6H-SiC semi-insulating 0° oriented substrates from 1225 to 1700°C and for 10 to 300 min. Samples were 50.8 and 76.2 mm wafers and 16 x 16 mm² witnesses. Both *in-vacuo* (10⁻⁶ to 10⁻⁴ mbar) and Ar ambient (50-200 mbar) sublimation conditions were investigated. Growth conditions resulted in continuous EG on Si-face witnesses < 1 nm thick as measured by atomic force microscopy, x-ray photoelectron spectroscopy and Raman spectroscopy, whereas growth on C-face witnesses could be varied, depending upon growth conditions, from island formation to continuous sheets > 10 nm thick. Using the witness samples, 300 K mobilities over 2,100 and 27,000 cm²V⁻¹s⁻¹ were found for 10x10 μm² sized Hall patterns for EG on the Si- and C-face of SiC, respectively.

The growth of EG on 50.8 mm Si-face wafers resulted in excellent relative resistivity uniformity of 2.8% and 300 K Hall mobilities up to 2,700 cm²V⁻¹s⁻¹ were found. Raman spectroscopy mapping of the 2D peak on the wafers determined: (1) the majority of the film was monolayer, (2) two layers of EG could be found at step edges and (3) EG was continuous across the wafer. RF FETs exhibited state-of-the-art ambipolar behavior such as electron field-effect mobility of 6,000 cm²V⁻¹s⁻¹ with I_{on}/I_{off} ratio of 19 and peak transconductance of 600 mS mm⁻¹ per 1 fF μm² gate oxide capacitance. The f_r•L_g performance metric of 10 GHz•μm was established. Additionally, we will discuss our recent work on EG growth on 76.2 mm wafers as well as the impact of morphological features and Ar ambient controlled graphenization on future RF devices.

Supported by DARPA CERA (N66001-08-C-2048) and ONR.

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

2:40pm **GR+MS-WeA3 In situ Growth, Microscopy, and Spectroscopy of Graphene Films**, *J. Hannon*, IBM T.J. Watson Research Center **INVITED**

I will describe *in situ* low-energy electron microscopy (LEEM) studies of graphene synthesis on SiC and polycrystalline Ni substrates. Using spatially-resolved electron diffraction (LEED-IV), we have determined the atomic structure, layer thickness, and stacking sequence of individual graphene domains with sub-micron precision. Using spatially-resolved electron energy loss spectroscopy (EELS), we have correlated the local electronic and atomic structure. I will discuss how these measurements aid in interpreting transport measurements from these same samples. This work was performed in collaboration with Ruud Tromp.

4:00pm **GR+MS-WeA7 High-frequency Transistors from Wafer-scale Epitaxial Graphene**, *Y.-M. Lin*, IBM T.J. Watson Research Center **INVITED**

Graphene has generated enormous research interest because of its unique physical and electronic properties. In particular, a large part of the research interests and activities arise from the high intrinsic carrier mobility and saturation velocity in graphene that may lead to higher-frequency electronic devices/circuits than can be achieved by conventional semiconductor

materials. Here we present the top-gated graphene transistors fabricated on two-inch graphene wafer.

Graphene was epitaxially grown on the Si face of a high-purity semi-insulating SiC 4H(0001) wafer by thermal decomposition, yielding a film of 1-2 layers of graphene over the entire wafer. The as-grown graphene film possesses an electron (*n*-type) carrier density of ~ 3x10¹² cm⁻² and a Hall-effect mobility between 1000–1500 cm²/V.s. In order to preserve the intrinsic mobility of graphene in the top-gated device structure, an interfacial polymer layer was spin-coated on the graphene prior to the oxide deposition. The carrier mobility of top-gated Hall bar devices varied between 900-1520 cm²/V.s across the two-inch wafer, indicating that little degradation in graphene mobility.

The cutoff frequency *f*_T is obtained from the high-frequency S-parameters measurements, which signifies the highest frequency at which a transistor can propagate an electrical signal. For a gate length of 550 nm, the measured *f*_T ranges between 20 to 53 GHz. For a shorter gate length of 240 nm, *f*_T as high as 100 GHz was measured. This 100 GHz cutoff frequency is the highest speed achieved to date for any type of graphene devices, including exfoliated and CVD -grown graphene. Further enhancement in the device performance is expected to be achieved by continued improvements in the electrical characteristics of epitaxial graphene and the gate length scaling.

*In collaboration with K. Jenkins, D. Farmer, C. Dimitrakopoulos, H.-Y. Chiu, A. Valdes-Garcia, A. Grill, and P. Avouris.

4:40pm **GR+MS-WeA9 Graphene-on-SiC and Graphene-on-Si MOSFETs on 75 mm Wafers**, *J.S. Moon*, *D. Curtis*, *M. Hu*, *S. Bui*, *D. Wheeler*, *T. Marshall*, HRL Laboratories, LLC, *D.K. Gaskill*, *P.M. Campbell*, Naval Research Laboratory, *P. Asbeck*, University of California at San Diego, *G.G. Jernigan*, *J.L. Tedesco*, *R.L. Myers-Ward*, *C. Eddy Jr.*, Naval Research Laboratory, *X. Weng*, *J. Robinson*, *M. Fanton*, Penn State University **INVITED**

In this talk, we present recent progress in epitaxial graphene n-MOSFETs and p-MOSFETs on both SiC and Si substrates for graphene-on-SiC and graphene-on-Si technologies. Both graphene MOSFETs were fabricated in a self-aligned manner on 75 mm wafers and exhibited gate-controlled ambipolar characteristics. For the graphene MOSFETs on SiC substrates, the graphene was grown by Si-sublimation of Si-face 6H-SiC substrates in a commercial Aixtron VP508 epitaxial reactor. For the graphene MOSFETs on Si substrates, the graphene was synthesized by graphitizing a thin 3C-SiC layer grown on float-zone Si (111) substrates using a halogen process. Figure 1 shows sheet resistance maps of 3-inch graphene-on-SiC and graphene-on-Si wafers. Typical Hall mobility ranges from 500 to 2000 cm²/Vs depending on electron carrier density. Both graphene MOSFETs were fabricated with a gate oxide layer and metal gate stack. The gate length was 3 μm. The graphene-on-SiC MOSFETs showed excellent I-V saturation behavior as shown in Figure 2(a). Figure 2(b) shows measured ambipolar behaviors with n-type MOSFET at V_{gs} = 0 V, while p-type behaviors are observed at V_{gs} < -1.5 V. An I_{on}/I_{off} ratio of 33 was measured. Figure 2(c) shows measured peak transconductance of 600 mS/mm at V_{ds} = 3 V. Figure 3 shows the extrinsic field-effect mobility of 6000 cm²/Vs for electron and of 3200 cm²/Vs for hole obtained at an effective electric field of ~0.27 MV/cm, approaching Dirac point. The measured graphene field-effect mobility is eight to 10 times higher than that of ITRS Si n-MOSFETs and ~80 times higher than that of ultra-thin-body SOI n-MOSFETs.

The graphene-on-Si MOSFETs are fabricated in a similar manner. Figure 4 shows measured transfer curves of graphene-on-Si MOSFETs, showing ambipolar behaviors with the Dirac point close to zero gate bias, unlike the graphene-on-SiC MOSFETs. The on-state current is measured at 50 to 125 mA/mm with I_{on}/I_{off} ratio of 3 to 2, respectively. This is the highest performance observed among graphene-on-Si technologies so far. RF performance of graphene FETs will be discussed. This work was supported by DARPA, monitored by Dr. M. Fritze, under SPAWAR contract number N66001-08-C-2048.

The views, opinions, and/or findings contained in this article/presentation are those of the author/presenter and should not be interpreted as representing the official views or policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the Department of Defense.

[1] C. Berger *et al.*, Science, vol. 312, p. 1191, 2006; J.S. Moon *et al.*, IEEE EDL, vol 30, p650, 2009

Thursday Morning, October 21, 2010

Graphene Focus Topic

Room: Brazos - Session GR+AS+TF-ThM

Graphene Synthesis on Metals

Moderator: A.W. Ghosh, University of Virginia

8:00am **GR+AS+TF-ThM1 Contrast Behavior of Carbon Adatom Diffusion and Nucleation in the Initial Stage of Graphene Epitaxial Growth on Stepped Metal Surfaces**, *H. Chen, W. Zhu*, University of Tennessee at Knoxville; Oak Ridge National Laboratory, *Z. Zhang*, Oak Ridge National Laboratory; University of Tennessee at Knoxville

Using first-principles calculations within density functional theory, we study the energetics and kinetics of carbon adatom diffusion and nucleation on three stepped metal surfaces: Ir(111), Ru(0001) and Cu(111). We find that on the flat surfaces, two carbon atoms repel each other on Ir(111) and Ru(0001), while they prefer to form a dimer on Cu(111). Moreover, the step edges on Ir and Ru surfaces cannot effectively trap single carbon adatoms either, whereas it is strongly favorable to form carbon dimers at the step edges. The different behaviors are attributed to the competition between C-C bonding and different types of C-metal bonding, and the picture is generalized to other C-on-metal systems with predicted results. These findings provide an insight into the understanding of experimentally observed carbon nucleation in the initial stage of graphene epitaxial growth on metal surfaces.

8:20am **GR+AS+TF-ThM2 Density and Height Distribution of Ru and Bimetallic Pt/Ru Nanoclusters Self-Assembled on Ru(0001) Supported Monolayer Graphene**, *A.K. Engstfeld, S. Beckord, H.E. Hoster, R.J. Behm*, Ulm University, Germany

The Moiré-type nm-scale patterns of graphene monolayers on metal single crystals were recently shown to allow facile fabrication of ordered arrays of virtually monodisperse metal nanoclusters by simple metal vapour deposition in UHV [1-3]. In view of a potential utilization as model systems in electrocatalysis, we have tested the possibility of preparing Ru and bimetallic PtRu clusters by an analogous procedure. This included an extended study on the growth behaviour of the pure Ru clusters. Statistically evaluated STM images indicate that density and height distribution of Ru clusters are largely independent from the evaporation rate at room temperature. Lower/higher cluster densities along with larger/smaller cluster sizes were only achieved by higher/lower substrate temperatures during evaporation. For a given temperature, the lateral density of Ru clusters is higher than that of Pt clusters. Hence, the fabrication of bimetallic clusters can be performed more reliably when Ru is deposited first. We discuss in how far the found growth behaviour can be understood using classic nucleation theory.

8:40am **GR+AS+TF-ThM3 From Perfect Graphene to Cluster Superlattices**, *T. Michely*, University of Cologne, Germany **INVITED**

Through pyrolysis of hydrocarbons on noble metal surfaces monolayer graphite – graphene – is readily formed. Using scanning tunneling microscopy (STM) and low energy electron microscopy (LEEM) we investigate the temperature dependent growth and the nature of point and line defects in the graphene layer on Ir(111). We identify heptagon-pentagon pairs of carbon atom rings to accommodate for slight misalignments of graphene domains, and wrinkles in the graphene layer for the mismatch in thermal expansion of graphene and Ir. After a systematic optimization of the growth procedure we obtain a single sheet of well oriented graphene on Ir(111) with a minimum of point and line defects.

Angle resolved photo emission finds graphene on Ir(111) to be only marginally doped and to display the characteristic Dirac cone at the K-point of the graphene Brillouin zone. The absence of hybridization of Ir and graphene states is consistent with the weak graphene - Ir interaction, as inferred from the large graphene - substrate separation as measured by the X-ray standing wave method and calculated by density functional theory including van der Waals interactions. The moiré resulting from the incommensurate epitaxy of graphene on Ir(111) gives rise to a large graphene supercell. In the graphene electronic structure it is reflected by the opening of minigaps at the boundaries of the induced mini-Brillouin zone.

The graphene moiré with Ir(111) is an active template allowing one to grow superlattices of metal clusters (Ir, Pt, Au, W, Fe, Re, Co, etc), spatially and thermally stable below 450 K. The graphene moiré enables also patterned adsorption of molecules and the template effect is not limited to the Ir(111) substrate. Based on STM and XPS measurements as well as density functional theory calculations it is proposed that at geometrically defined locations within the supercell and if sandwiched between substrate and

cluster metal the graphene rehybridizes from sp^2 graphitelike to sp^3 diamondlike bonding, resulting in strong covalent bonds between metal and graphene. The relevance of the graphene template effect for nanocatalysis, nanomagnetism and electrochemistry will be outlined.

9:20am **GR+AS+TF-ThM5 Graphene on Pd(111): In situ Low-Energy Electron Microscopy Studies of Growth Kinetics and Structure – Work Function Relationship**, *S. Kodambaka, Y. Murata*, University of California Los Angeles, *E. Starodub, N.C. Bartelt, K.F. McCarty*, Sandia National Laboratories

Using *in situ* low-energy electron microscopy, we investigate the dynamics of graphene layer formation and the relationship between domain structure and its work function on Pd(111). We observe, in real time, the nucleation and growth of graphene islands during cooling via surface segregation of C atoms from the Pd bulk. Interestingly, we observe rapid motion of Pd substrate surface steps during graphene growth. Using low-energy electron diffraction, we identify at least five different orientations (domains) of monolayer graphene islands on the surface. We determine their relative orientations with respect to the substrate as approximately 2° , 6° , 11° , 19° , and 26° . We measured electron reflectivity (image intensity) values for each of the domains as a function of incident electron energy. From this data, we extracted the work functions of graphene domains which are found to vary with the domain orientation. Our results suggest that the substrate-graphene interactions influence the growth kinetics as well as the electronic structure of graphene.

9:40am **GR+AS+TF-ThM6 Second-Layer Graphene on Ir(111) – Relating Growth Mechanism to Physical and Electronic Structure**, *S. Nie*, Sandia National Labs, *A.L. Walter*, Lawrence Berkeley National Lab and Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *E. Starodub, K.F. McCarty, K. Thürmer*, Sandia National Labs, *K. Horn*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *A. Bostwick*, Lawrence Berkeley National Lab, *N.C. Bartelt*, Sandia National Labs, *E. Rotenberg*, Lawrence Berkeley National Lab

An interesting question is how the second layer of graphene grows on transition-metal substrates. First-layer graphene on Ir(111) [1] exists with four discrete in-plane orientations relative to substrate directions [2]. Thus, this system offers potential to better understand the relationship between second-layer growth and first-layer structure. We use low-energy electron microscope (LEEM) to characterize where the second-layer graphene forms on Ir(111) covered by domains of differently oriented first-layer graphene. We find that the second layer does not grow easily where the lattice of the first-layer graphene is aligned with the lattice of the substrate. Instead the second-layer graphene forms most easily where the first-layer graphene is rotated, by 30° , for example. Angle-resolved photoemission spectroscopy (ARPES) confirms this strong preference. So how does the orientation of the first layer control the growth of the second layer? ARPES and Raman spectroscopy provide insight, revealing that the rotated variants of first-layer graphene are even less strongly bound to the substrate than the more abundant, non-rotated variant [3]. This information suggests the following growth mechanism. Carbon atoms segregating from the substrate build up in concentration under the first layer. The second layer nucleates and grows where it is easier to debond the first layer from the substrate, that is, under the rotated first-layer domains. Electron diffraction also reveals that the second graphene layers are usually but not always aligned with the first-formed layer. Finally, we will discuss the doping of the different types of second-layer graphene, as revealed by ARPES.

This work was supported by the Office of Basic Energy Sciences of the US DOE under Contracts No. DE-AC04-94AL85000 (SNL) and No. DE-AC02-05CH11231 (LBL).

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[3] I. Pletikoscic, M. Kralj, P. Pervan, R. Brako, J. Coraux, A. T. N'Diaye, C. Busse, and T. Michely, *Phys. Rev. Lett.* 102, 056808 (2009).

10:40am **GR+AS+TF-ThM9 Graphene on Transition Metals – Growth and Interfacial Processing**, *P. Sutter, E. Sutter*, Brookhaven National Laboratory **INVITED**

Graphene has been used to explore the fascinating properties of two-dimensional sp^2 bonded carbon, and shows great promise for applications. A key bottleneck lies in synthesizing the required starting material: structurally perfect, macroscopically large graphene sheets with uniform thickness, into which active device structures can be patterned.

Epitaxial growth on transition metals has recently become one of the most promising methods for large-scale graphene synthesis. Here we discuss the fundamental mechanisms of graphene growth on ruthenium [1] and platinum [2], both single crystals and polycrystalline thin films, studied by a combination of *in-situ* surface microscopy methods. Real-time observations by low-energy electron microscopy (LEEM) show that epitaxy on Ru(0001) produces arrays of macroscopic monolayer graphene domains, whose coalescence is followed by the formation of large bilayer areas in a controlled layer-by-layer fashion. LEEM imaging together with diffraction, selected-area angle resolved photoemission spectroscopy (micro-ARPES), and scanning tunneling microscopy provide unique insight into the interaction between graphene and transition metal substrates, key to the synthesis of high-quality graphene [2, 3].

Beyond large-scale synthesis, potential applications of graphene will require novel approaches to processing and functionalization. We will highlight experiments by real-time surface microscopy to understand chemical reactions at graphene-metal interfaces, which may become part of novel processing strategies for graphene devices.

Work performed under the auspices of the U.S. Department of Energy under contract No. DE-AC02 98CH1-886.

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11:20am **GR+AS+TF-ThM11 Real-time Analysis of Graphene Growth on Polycrystalline Copper Foils**, *J.M. Wofford*, University of California at Berkeley and Lawrence Berkeley National Lab, *S. Nie, N.C. Bartelt, K.F. McCarty*, Sandia National Laboratories, *O. Dubon*, University of California at Berkeley and Lawrence Berkeley National Lab

Despite the potentially significant technological impact of graphene synthesis on Cu, little is understood about both the growth kinetics of this system and the morphology of the resulting heterostructure. We use low-energy electron microscopy (LEEM) to observe directly the UHV growth of graphene on polycrystalline Cu foils by the electron-beam evaporation of carbon. The temperatures required to synthesize highly ordered graphene simultaneously induce significant Cu sublimation and step flow, leading to a dynamic growth surface. As a result a complex interdependence develops between the graphene growth behavior and Cu surface morphology, with the graphene islands limiting Cu step mobility, and Cu step bunching distorting the propagation of the graphene growth front. This interplay becomes increasingly dramatic over time as the inhomogeneous sublimation of Cu leads to considerable surface roughening. In addition, the graphene islands are not compact in shape. Instead, the islands are ramified, consisting of several distinct lobes extending from a common nucleation site. Diffraction analysis reveals that each constituent lobe has a different in-plane orientation relative to the copper grain below and that the growth velocity of a given lobe depends strongly on its orientation relative to the underlying Cu at the growth front. We will describe the relationship between the orientation-dependent growth velocity and the local atomic geometry at the edge of the graphene sheet. Finally, the implications of this unexpected nucleation and growth mechanism on the formation of high-quality graphene films on Cu foils are evaluated.

Work at Sandia was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U. S. Department of Energy under Contract No. DE-AC04-94AL85000. Work at LBNL was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. JMW acknowledges the support from an NSF fellowship.

11:40am **GR+AS+TF-ThM12 Moiré Superstructures of Graphene on Faceted Nickel Islands**, *Y. Murata*, University of California Los Angeles, *V. Petrova*, University of Illinois at Urbana-Champaign, *B.B. Kappes, A. Ebnommasir*, Colorado School of Mines, *I. Petrov*, University of Illinois at Urbana-Champaign, *Y.-H. Xie*, University of California Los Angeles, *C.V. Ciobanu*, Colorado School of Mines, *S. Kodambaka*, University of California Los Angeles

Using scanning tunneling microscopy and spectroscopy, in combination with density functional theory (DFT), we investigated the morphology and electronic structure of monolayer graphene grown on the (111) and (110) facets of three-dimensional nickel islands on highly oriented pyrolytic graphite substrate. We observed hexagonal and stripe moiré patterns with periodicities of 22 Å and 12 Å, respectively, on (111) and (110) facets of the Ni islands. Graphene domains are also observed to grow, as single crystals, across adjacent facets and over facet boundaries. We suggest that the unexpected observation of moiré patterns of graphene on lattice-matched Ni(111) and the formation of single-crystalline domains across

different surface orientations are a consequence of the kinetic limitations of growth, rather than of the strength of the C-Ni interactions. Scanning tunneling spectroscopy data indicate that the graphene layers are metallic on both Ni(111) and Ni(110), in agreement with the DFT calculations. We attribute this behavior to strong hybridization between the *d*-bands on Ni and the *p* bands of carbon. Our findings point to the possibility of preparing large-area epitaxial graphene layers even on polycrystalline Ni substrates.

Thursday Afternoon, October 21, 2010

Graphene Focus Topic

Room: Brazos - Session GR+AS+TF+MI-ThA

Graphene: Surface Characterization

Moderator: P. Sutter, Brookhaven National Laboratory

2:00pm **GR+AS+TF+MI-ThA1 Scanning Tunneling Microscopy and Spectroscopy of Impurities on a Gated Graphene Device**, *R.T. Decker, V.W. Brar, M.H. Solowan, Y.C. Wang, A. Zettl, M.F. Crommie*, University of California Berkeley **INVITED**

Understanding the scattering properties of electrons in graphene is important for controlling the behavior of different graphene nanostructure-based devices. Here we report a scanning tunneling microscopy (STM) and spectroscopy (STS) study of impurities on a single monolayer of graphene. In our experiments the graphene is placed on a layer of insulating SiO₂ that sits above a doped silicon back-gate electrode. We will discuss our observations of the electronic local density of states of impurities, as well as how these properties respond to electrical gating of the graphene monolayer with respect to the silicon back-gate electrode.

In particular, we will show that the combination of the back-gate voltage and the STM tip-gating effect allows the controlled ionization of the impurity when the resonance sweeps through the Fermi energy. The influence of this induced Coulomb potential on the electrons in graphene in the vicinity of the impurity will be discussed.

2:40pm **GR+AS+TF+MI-ThA3 Graphene Defect States in a Magnetic Field Studied by Scanning Tunneling Spectroscopy**, *K.D. Kubista, D.L. Miller, M. Ruan, W.A. de Heer, P.N. First*, Georgia Institute of Technology, *G.M. Rutter, J.A. Stroscio*, National Institute of Standards and Technology

We present tunneling differential conductance (dI/dV) spectra and 2D conductance maps acquired over both positive and negative defects in magnetic fields up to 8 T. The measurements were performed on multilayer epitaxial graphene using scanning tunneling microscopy and spectroscopy at 4 K under ultrahigh vacuum conditions. Landau level drift states are found to follow the local potential (determined independently at near-zero magnetic field), but near a negatively-charged defect a bound (or quasibound) state originates from the $n = -1$ Landau Level. The defect state Stark shifts and finally ionizes under the influence of the STM tip electric field.

3:00pm **GR+AS+TF+MI-ThA4 Atomic-Scale Maps of Quantum Hall States in Epitaxial Graphene**, *D.L. Miller, K.D. Kubista*, Georgia Institute of Technology, *G.M. Rutter*, National Institute of Standards and Technology, *M. Ruan, W.A. de Heer, P.N. First*, Georgia Institute of Technology, *J.A. Stroscio*, National Institute of Standards and Technology

When a perpendicular magnetic field is applied to a graphene sheet, the resulting eigenenergies (Landau Levels or LLs) have a nonlinear energy distribution that includes a four-fold degenerate zero-energy state (LL₀). Maps of the energy-resolved local density of states (LDOS) acquired via cryogenic scanning tunneling spectroscopy (STS) provide atomic-scale imaging of the LL spatial distribution. Focusing on LL₀, we use STS maps to image the *localized* and *extended* quantum Hall states. Unexpectedly, we find atomic-scale variations of the LDOS above a critical magnetic field. We attribute this to an energy gap in LL₀ and show how it depends on the local A-B lattice symmetry. The gap is observed only within patches of at least a few magnetic lengths in size, which forces the splitting to "turn off" below the critical field. This behavior implies a breaking of the local sublattice symmetry imposed by moiré layer stacking.

3:40pm **GR+AS+TF+MI-ThA6 Imperfect Graphene: Point Defects, Edges, Dislocations and Grain Boundaries**, *O.V. Yazyev*, University of California, Berkeley **INVITED**

In two dimensions, properties of materials can be heavily affected by defects. In this talk, I will review our recent efforts directed towards understanding various types of structural irregularities in graphene.

Firstly, I will present the results of theoretical studies of the magnetism induced by point defects and edges in graphene and graphite. We show that in graphene single-atom defects such as vacancies and hydrogen chemisorption induce the spin-polarized defect states [1, 2]. The coupling between the magnetic moments is either ferromagnetic or antiferromagnetic, depending on whether the defects correspond to the same or to different sublattices of the graphene lattice, respectively. These results are able to clarify some experimental observations of high-temperature ferromagnetism in proton-irradiated graphite. Similarly, zigzag edges of

graphene are predicted to induce spin-polarized edge states which can serve as a basis for novel spintronic devices. We address the question of the spin correlation length at finite temperatures in this one-dimensional magnetic system and establish the limitations of the proposed spintronic devices [3].

Then, I will talk about our latest results on dislocations and grain boundaries in graphene [4], topological defects which are still not well understood despite the growing number of experimental observations. We introduce a general approach for constructing dislocations in graphene characterized by arbitrary Burgers vectors as well as grain boundaries, covering the whole range of possible misorientation angles. By using ab initio calculations we investigate thermodynamic, electronic and transport properties of grain boundaries, finding energetically favorable large-angle symmetric configurations, strong tendency towards out-of-plane deformation in the small-angle regimes, pronounced effects on the electronic structure, and two distinct behaviors in the electronic transport [5] - either perfect reflection or high transparency for low-energy charge carriers depending on the grain boundary structure. Our results show that dislocations and grain boundaries are important intrinsic defects in graphene which may be used for engineering graphene-based functional devices.

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4:20pm **GR+AS+TF+MI-ThA8 Spectroscopic Ellipsometry for Thickness Measurement and Optical Dispersion Modeling of CVD-Grown Graphene**, *F.J. Nelson, V.K. Kaminen, A.C. Diebold*, The University at Albany-SUNY

Graphene has attracted much research over the past several years due to its electrical and mechanical properties. It is a prime candidate for electronic and optoelectronic devices, yet much of the research has utilized the exfoliation, or "scotch-tape" technique of sample preparation. More scalable growth methods have been investigated, such as the thermal decomposition of SiC, and the resulting graphene films have properties dependent on their fabrication parameters. One potentially scalable technique is that of hydrocarbon gas-based CVD onto metallic substrates. Here, we report on the ellipsometric measurement of Few-Layer-Graphene (FLG) grown on copper foils and subsequently transferred to a different substrate (i.e. glass). One of the challenges with development of a dispersion model for FLG is that the CVD graphene has many "grains" inside the measured area while previous reports of exfoliated graphene were done on single crystal samples. The work explores finding an average thickness, as well as the optical dispersion modeling, of the graphene layers on different substrates, such as SiO₂/Si and glass slides.

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Park, J.-S.: GR+EM+MS+TF+MI-WeM2, **11**
Perebeinos, V.: GR+EM+MS+TF+MI-WeM5, **11**
Perkins, F.K.: GR+TF-TuA8, **8**
Perkins, K.: GR+NS-MoA7, **3**
Petraich, R.V.: GR+TF-TuM2, **5**
Petrov, I.: GR+AS+TF-ThM12, **16**
Petrova, V.: GR+AS+TF-ThM12, **16**
Phillips, M.: GR+SS+TF+EM-MoM6, **1**
Piner, R.D.: GR-TuP6, **10**
Pirkle, A.: GR+EM+MS+TF+MI-WeM11, **11**
Pokharel, S.: GR+TF-TuA3, **7**
Priyantha, W.: GR-TuP6, **10**
Pronshinske, A.: GR-TuP5, **10**

— R —

Riedo, E.: GR+NS-MoA9, 4
Rivera, I.: GR-TuP7, **10**
Robinson, J.: GR+EM+MS+TF+MI-WeM1, 11;
GR+MS-WeA1, 13; GR+MS-WeA9, 13
Robinson, J.A.: GR+NS-MoA7, 3; GR+NS-MoA9,
4; GR+TF-TuA8, 8
Roos, M.: GR+TF-TuA7, **7**
Ross, A.J.: GR+EM+MS+TF+MI-WeM6, 11
Rotenberg, E.: GR+AS+TF-ThM6, 15
Rouxinol, F.P.: GR-TuP3, 9
Rowe, J.E.: GR-TuP5, **10**
Ruan, M.: GR+AS+TF+MI-ThA3, 17;
GR+AS+TF+MI-ThA4, 17
Ruoff, R.S.: GR-TuP6, 10
Rutter, G.M.: GR+AS+TF+MI-ThA3, 17;
GR+AS+TF+MI-ThA4, 17; GR+TF-TuM10, 6;
GR+TF-TuM9, 5

— S —

Saito, N.: GR-TuP2, 9
Sandin, A.: GR-TuP5, 10
Schall, J.D.: GR+TF-TuM2, 5
Seo, S.: GR+TF-TuM11, 6
Seyller, T.: GR+SS+TF+EM-MoM3, **1**
Sheehan, P.E.: GR+NS-MoA9, **4**
Shenoy, V.B.: GR+NS-MoA6, **3**
Snow, E.: GR+NS-MoA7, 3
Snyder, D.: GR+EM+MS+TF+MI-WeM1, 11
Solowan, M.H.: GR+AS+TF+MI-ThA1, 17
Song, Y.J.: GR+SS+TF+EM-MoM9, **2**
Soukiasian, P.: GR+SS+TF+EM-MoM10, 2
Starodub, E.: GR+AS+TF-ThM5, 15; GR+AS+TF-
ThM6, 15; GR+NS-MoA10, 4

Stroscio, J.A.: GR+AS+TF+MI-ThA3, 17;
GR+AS+TF+MI-ThA4, 17; GR+SS+TF+EM-
MoM9, 2; GR+TF-TuM10, 6; GR+TF-TuM9,
5
Sutter, E.: GR+AS+TF-ThM9, 15
Sutter, P.: GR+AS+TF-ThM9, **15**
Swart, J.W.: GR-TuP3, 9

— T —

Takai, O.: GR-TuP2, 9
Tedesco, J.L.: GR+MS-WeA1, 13; GR+MS-
WeA9, 13; GR+SS+TF+EM-MoM1, 1;
GR+SS+TF+EM-MoM8, 1
Thompson, P.E.: GR+SS+TF+EM-MoM1, 1
Thürmer, K.: GR+AS+TF-ThM6, 15;
GR+SS+TF+EM-MoM2, 1
Tinkey, H.: GR+SS+TF+EM-MoM6, 1
Torrance, D.B.: GR+SS+TF+EM-MoM6, **1**;
GR+SS+TF+EM-MoM9, 2
Trotter, D.C.: GR+EM+MS+TF+MI-WeM6, 11
Trumbull, K.: GR+EM+MS+TF+MI-WeM1, 11
Tsuda, N.: GR-TuP2, **9**
Turchanin, A.: GR+TF-TuA4, 7; GR+TF-TuM3, 5
Tutuc, E.: GR+EM+MS+TF+MI-WeM9, **11**
Twigg, M.E.: GR+SS+TF+EM-MoM8, 1

— V —

van Duin, A.C.T.: GR+TF-TuA11, 8
Vaz, A.R.: GR-TuP3, **9**
Ventrice Jr., C.A.: GR-TuP6, 10
Vizzini, S.: GR+SS+TF+EM-MoM10, 2

— W —

Wallace, R.M.: GR+EM+MS+TF+MI-WeM11, 11
Walter, A.L.: GR+AS+TF-ThM6, 15
Walton, S.G.: GR+NS-MoA9, 4; GR+TF-TuA8, 8

Wang, D.: GR+NS-MoA9, 4
Wang, J.: GR-TuP7, 10
Wang, Y.C.: GR+AS+TF+MI-ThA1, 17
Weber, D.H.: GR+TF-TuA4, 7
Wei, Z.: GR+NS-MoA9, 4
Weimann, T.: GR+TF-TuA4, 7
Weng, X.: GR+MS-WeA9, 13
Wheeler, D.: GR+MS-WeA9, 13
Wheeler, V.D.: GR+MS-WeA1, 13;
GR+SS+TF+EM-MoM1, 1
Wofford, J.M.: GR+AS+TF-ThM11, **16**

— X —

Xiao, J.: GR+TF-TuA3, 7
Xie, Y.-H.: GR+AS+TF-ThM12, 16

— Y —

Yakes, M.K.: GR+NS-MoA9, 4
Yang, H.: GR+TF-TuM11, 6
Yazyev, O.V.: GR+AS+TF+MI-ThA6, **17**
Yoon, O.J.: GR+EM+MS+TF+MI-WeM2, 11

— Z —

Zalalutdinov, M.: GR+NS-MoA7, 3
Zettl, A.: GR+AS+TF+MI-ThA1, 17
Zhang, X.: GR+TF-TuM3, **5**
Zhang, Z.: GR+AS+TF-ThM1, 15
Zhitenev, N.B.: GR+TF-TuM10, 6; GR+TF-TuM9,
5
Zhu, W.: GR+AS+TF-ThM1, 15
Zhu, W.J.: GR+EM+MS+TF+MI-WeM5, **11**