

Friday Morning, November 4, 2011

Surface Science Division
Room: 107 - Session SS-FrM

Surface Science on Graphene

Moderator: I.I. Oleynik, University of South Florida

8:20am **SS-FrM1 Towards Controlled Growth of a Single-Layer of MoS₂**, *D. Sun, W. Lu, D. Kim, J. Mann, L. Bartels*, University of California, Riverside

MoS₂ is a semiconducting material consisting of sulfur-molybdenum-sulfur tripledecker layers loosely bound by van der Waals interactions. MoS₂ has been used technologically for a long time, for instance as lubricant, where similar to graphite its layered character was employed. Recently, its electronic characteristics have attracted increased attention with the finding that it transitions from an indirect bandgap semiconductor at 1.6eV gap to a direct bandgap one at 1.9eV gap at the transition from multilayers to a single layer. A transistor has been constructed from a MoS₂ and shown appreciable properties. The increased bandgap and high fluorescence yield may also suggest applications of the material for photonic or photocatalytic applications.

MoS₂ can be exfoliated mechanically similar to graphene. While this method is simple, it is hard to control and not amendable to mass production of thin films. Solution-based processes have been proposed and may provide a scalable source of a mixture of single and multilayer material. Here we show an alternative avenue for the fabrication of MoS₂ monolayers: growth of MoS₂ on a sulfur-preloaded copper surface. In contrast to all other methods, this route has the potential of providing exclusively monolayer material, as the sulfur source is only available until the substrate is covered. Practically, this approach is related to the growth of graphene monolayers on copper or ruthenium films, where segregation of carbon to the surface is employed in aggregating a carbonaceous layer that transforms into graphene under the correct conditions.

Small MoS₂ triangles of a few nanometers in size have been grown previously on gold in a dilute H₂S atmosphere. Here we show significantly larger patches, tens of nanometers in size. In contrast to gold, copper forms a multitude of sulfur surface coverages and also readily absorbs sulfur into the bulk. Thus, we can preload the substrate with a specific amount of sulfur using an easy-to-handle liquid precursor, benzenethiol. In previous work we have shown that heating to below 400K removes the phenyl group of benzenethiol reliably from copper leaving sulfur coverages behind.

8:40am **SS-FrM2 Oxygen Adsorption on Electronically Modified Graphite Surfaces Studied by Molecular Beam Scattering**, *J.P. Oh, T. Kondo, K. Arakawa, Y. Saito, J. Nakamura*, University of Tsukuba, Japan

The graphite surface consists of π conjugated system. When the π conjugated system is broken, the non-bonding π electronic states are known to form on the surface. Recently, the non-bonding π electronic states at the Fermi level of the graphite-related materials are expected to be the active sites for the specific chemical reaction such as oxygen-reduction reaction in the fuel cell [1]. It is thus important to understand the interaction between an oxygen molecule and the graphite surface for the efficient usage of the graphite-related materials. We have reported previously that the defects induced by Ar⁺ ion bombardment on the graphite surface significantly affect the gas-graphite interaction based on the measurements of the angular intensity distributions of He and Ar beam scattered from the pristine and the defect induced graphite surfaces [2]. The difference in the gas-surface interaction has been ascribed to the local breaking of the π conjugated system of graphite by defect formation. To further investigate the effect of the modification of the graphite electronic states on the gas-surface interaction, especially for the oxygen adsorption, we have measured angular intensity distributions of O₂ from electronically modified graphite surfaces, namely potassium intercalated graphite, nitrogen-doped graphite (graphite bombarded by N₂⁺ ion) and defective graphite (graphite bombarded by Ar⁺ ion). The detail of scattering features as well as the effects of the electronic modification of graphite on the oxygen adsorption will be discussed in detail with our recent STM and STS results.

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[1] S.F. Huang, K. Terakura, T. Ozaki, T. Ikeda, M. Boero, M. Oshima, J. Ozaki and S. Miyata, *Phys. Rev. B*, **80**, 235410 (2009).

[2] J. Oh, T. Kondo, D. Hatake, Y. Honma, K. Arakawa, T. Machida, J. Nakamura, *J. Phys.: Condens. Matter*, **22**, 304008 (2010).

9:00am **SS-FrM3 Interaction and Thermal Stability of Oxygen Species in Graphene Oxide and Graphene Defects**, *M. Acik, C. Gong, G. Lee, K. Cho, C. Mattevi, M. Chhowalla, Y.J. Chabal*, University of Texas at Dallas

INVITED

Graphene devices are based on finite size flakes (e.g. nanoribbons) in contact with dielectrics or other materials, and therefore require control of edges and depend on the control of processing methods (often involving vapor or wet chemistry). Graphene oxide (GO) represents an interesting system from which much can be learned about oxygen interaction with graphene. Furthermore, studying the reduction of GO provides a powerful way to understand the stability of oxygen species and the role of trapped molecules. We have studied both the thermal and chemical reduction of single- and multi-layer GO using *in situ* infrared (IR) absorption spectroscopy under a variety of conditions. For the commonly used as-synthesized GO, we find that water molecules play an important role in both defect formation (evident from CO₂ evolution) and carbonyl-termination of defect edges at intermediate annealing temperatures (150-250 C).² We also find that a very stable edge configuration appears after high temperature anneals (> 850C), involving edge-ether termination of atomically straight zigzag edges and characterized by an anomalously strong IR absorption.³ The situation is dramatically different when water is replaced by alcohols or more complex molecules (e.g. ionic liquids). In general, defect formation is greatly suppressed (no CO₂ evolution) with less carbonyl formation and a reduced density of atomically straight, edge-ether terminated edges. This talk will summarize the current understanding of the mechanisms involved in thermal reduction and suggest pathways for developing stable graphene nanostructures with reasonable electrical properties.

1. Acik et al., Generation and capture of CO₂ and CO in graphite oxide stacks during thermal reduction Mater. Res. Soc. Symp. Proc., **1205E**, 1205 (2010).

2. Acik et al., The Role of Intercalated Water in Multilayered Graphene Oxide. ACS Nano **4**, 5861 (2010).

3. Acik et al., Unusual infrared-absorption mechanism in thermally reduced GO. Nature Materials **9**, 840 (2010).

9:40am **SS-FrM5 Graphene on Pt(111) as a Template for Pt Nanocluster Formation**, *Z. Liang, H. Khosravian, A. Uhl, R. Meyer, M. Trenary*, University of Illinois at Chicago

Graphene on transition metal substrates often forms superlattices that are manifested as Moiré patterns in scanning tunneling microscopy (STM) images. Such graphene superlattices can serve as templates for the formation of periodic arrays of metal nanoclusters with a uniform size distribution, a situation that is ideal for model catalyst studies. We have used an ultra high vacuum (UHV) STM to investigate graphene growth on Pt(111) from precursor hydrocarbon species. Different periodicities in the Moiré patterns are observed corresponding to different orientations of the graphene layer with respect to the Pt(111) lattice. Various graphene orientations are possible because of a relatively weak graphene-Pt interaction. Following Pt deposition onto the graphene-covered areas of the surface, small Pt nanoclusters were observed. While graphene on Pt(111) only weakly interacts with the substrate, which leads to a weak corrugation in the superlattice compared to other transition metals, such as Ru, our results show that even this weak corrugation is sufficient to serve as a template for the formation of mono-dispersed Pt nanoclusters. These Pt nanoclusters are relatively stable and only undergo agglomeration for annealing temperatures above 600 K.

10:00am **SS-FrM6 Ripening Behavior of Pt Clusters on Monolayer Graphene Supported by Ru(0001) and the System's Thermal Stability**, *C.U. Lorenz, A.K. Engstfeld*, Ulm University, Germany, *H.E. Hoster*, Technische Universität München, Germany, *R.J. Behm*, Ulm University, Germany

The Moiré-type nm-scale patterns of graphene monolayers supported by metal single crystals were recently used for the fabrication of ordered arrays of metal nanoclusters by metal vapor deposition under ultrahigh vacuum UHV conditions [1-3]. The corrugation within the adsorption potential of the graphene layer results in virtually monodisperse clusters. These are important for model (electro-)catalysis studies investigating the size dependency of Pt clusters on carbon support.

In this study we analyze the ripening behavior of Pt clusters (formed at room temperature) on monolayer graphene supported by Ru(0001) at temperatures above 450 K by means of STM. The size distribution change of the clusters gives insight into the rate determining step and into the mechanism of the ripening process. Two different annealing step methods (i: a single sample was successively heated to higher temperatures and ii:

individual samples reproducibly prepared in the same manner annealed to certain temperatures; both methods using the same heating period of 10 min) bring us to the conclusion that Pt cluster ripening between 450 K and 725 K occurs via a mechanism proposed by M. Smoluchowski. Above 725 K we observe indications for a change in the ripening mechanism, where Smoluchowski ripening is likely in competition with Ostwald ripening. Also above 725 K, we observed an adverse influence of the Pt on the stability of the monolayer graphene. Single defects in the otherwise well ordered graphene appeared, which were absent after annealing to lower temperatures.

[1] A.T. N'Diaye et al., *New J. Phys.* **11**, 2009, 103045. [2] Yi Pan et al., *Appl. Phys. Lett.* **95**, 2009, 093106. [3] K. Donner and P. Jakob, *J. Chem. Phys.* **131**, 2009, 164701.

10:20am **SS-FrM7 Mechanisms of Graphene Growth on Metals, N.C. Bartelt**, Sandia National Laboratories **INVITED**

Growth on metal substrates is a promising route for synthesizing high-quality graphene films. In addition, moving electronic applications into the real world requires understanding and controlling the properties of graphene in contact with metals. This talk will focus on the properties and growth mechanisms on several metals distinguished by varying binding strengths to graphene sheets. Mechanistic insight comes from observing growth directly using low-energy electron microscopy (LEEM). On the relatively strongly interacting substrate Ru(0001), graphene grows with a single in-plane orientation from a highly supersaturated sea of C adatoms. On the less interacting substrates Ir(111) and Pd(111), graphene forms several but discrete in-plane orientations. Small but significant differences in graphene's electronic properties (i.e., band structure and work function) result from changes in orientation. On Cu foils, graphene islands nucleate with a large range of orientation. Thus, the weak film-Cu interaction leads to a high defect density. Finally, the mechanism of bilayer graphene growth has been explored. Diffraction analysis reveals that the second graphene layer on Ir(111) grows next to the substrate, not on top of the first layer. This "underlayer" growth mechanism occurs when the carbon source is either segregation from the substrate or deposition on top of the first layer. How this unusual mechanism affects thickness uniformity will be discussed.

This work was supported by the Office of Basic Energy Sciences, Division of Materials and Engineering Sciences of the U.S. Department of Energy under Contract No. DE-AC04-94AL85000.

11:00am **SS-FrM9 Graphene Moiré Polymorphism on Hydrogenated Ruthenium Surfaces, B. Diaconescu**, University of New Hampshire, *F. Hagelberg*, East Tennessee State University, *K. Pohl*, University of New Hampshire

Graphene has aroused tremendous interest due to its remarkable electronic and mechanical properties. The lack of a band-gap, however, causes a serious challenge for implementing graphene as a material for electrical switches and therefore creative ways of inducing this band-gap are needed. We will present a STM/LEED/DFT study of the monolayer graphene on Ru(0001) system in the presence of hydrogen. STM reveals a diverse array of Moiré superlattice sizes ranging from 0.9 to 2.4 nm in the presence of hydrogen adlayer structures, as confirmed by LEED. Density functional theory calculations show a correlation between the Moiré superstructure sizes and the hydrogen coverage and the opening of a band-gap in the graphene/H/Ru(0001) system for some of the Moiré/hydrogen adlayer coverages.

This work was supported by the Nanoscale Science and Engineering Center for High-rate Nanomanufacturing (NSF NSEC-425826) and NSF DMR-1006863.

11:20am **SS-FrM10 Modifying Ni(111)/Graphene Interfaces by Sn-Ni Interface Alloy Formation, R.Q. Addou, A. Dahal, L. Adamska, I.I. Oleynik, M. Batzill**, University of South Florida

Graphene growth on metal surfaces (Ni, Pt, Ir, Rh and Cu) has been studied extensively [1]. Ni(111) is special among these metals because it is closely lattice matched with graphene ($a_{\text{graphene}} = 0.246$ nm vs. $a_{\text{Ni(111)}} = 0.249$ nm) allowing the growth of graphene with a single domain and in registry with the substrate [2]. However, compared to most other metal substrates the interaction between Ni and graphene is rather large, resulting in a small metal-carbon distance and a large shift of the graphene π -band compared to freestanding graphene. In order to de-couple graphene from the Ni-substrate other weaker interacting metals such as Cu and Au have been successfully intercalated between the graphene and Ni-substrate [3]. These metals have, however, a different lattice parameter and consequently the registry between the substrate and graphene is lost. Here we demonstrate a new approach that

weakens the metal-graphene interaction without destroying the lattice registry. By intercalating Sn-atoms an ordered $\sqrt{3} \times \sqrt{3}$ R30° Sn-Ni alloy is formed at the interface. The Sn intercalation process is characterized by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). In this alloy Sn substitutes for surface Ni atoms without changing the lattice parameter of the substrate and consequently the registry between the metal substrate and graphene is maintained. DFT simulations indicate that Sn alloying with Ni weakens the interaction of graphene with the metal substrate and consequently increasing the graphene-substrate distance and restoring the graphene π -band close to the position of free-standing graphene. Atomic-resolution scanning tunneling microscopy (STM) imaging reveals that the alloy periodicity is reproduced in the graphene layer, i.e. a $\sqrt{3} \times \sqrt{3}$ R30° superstructure is imposed on the graphene by the alloy substrate. This indicates a variation of the local density of states for C-atoms located on top of Sn-substrate sites compared to Ni-sites. Further experimental and theoretical characterization of the influence of the substrate on the electronic and structural properties of graphene is ongoing.

[1] *J. Wintterlin and M.-L. Bocquet, Surf. Sci.* **603**, 1841-1852 (2009)

[2] *J. Lahiri et al., Nano Lett.* **11**, 518-522 (2010)

[3] *A. Varykhalov et al., Phys. Rev. Lett.*, **101**, 157601 (2008)

11:40am **SS-FrM11 Silicene Epitaxial Sheets: Silicon New Start, P. Vogt**, Aix Marseille Univ, CNRS-CINaM, France and Technische Universität Berlin, Germany, *P. De Padova, C. Quaresima*, CNR-ISM, Italy, *J. Avila, E. Frantzeskakis, M.C. Asensio*, Synchrotron SOLEIL, France, *B. Ealet*, Aix Marseille Univ, CNRS-CINaM, France, *G. Le Lay*, Aix Marseille Univ, CNRS-CINaM, France and CNR-ISM, Italy

We have just synthesized in Marseille silicene sheets [1], i.e., atom-thin two-dimensional graphene-like silicon layers with an in-plane Si-Si interatomic distance of 0.23 nm [2], upon in-situ epitaxial growth on silver (111) surfaces. The honeycomb atomic structure is revealed in Scanning Tunneling Microscopy, while the long-range epitaxial order is confirmed by sharp 4x4 Low Energy Electron Diffraction patterns. Dirac cones at the K and K' points of the silicene Brillouin zone, evidenced in High-Resolution Synchrotron Radiation Angle-Resolved PhotoElectron Spectroscopy measurements, point to massless relativistic fermions with a Fermi velocity of 1.3E6 m/s, as theoretically predicted [3], quite the same as graphene, and four times higher than previously obtained on a one-dimensional grating of silicene nano-ribbons [4]. Density Functional Theory calculations including the Ag(111) substrate confirm the stability of the epitaxial arrangement. The demonstration that silicon can form sheets of silicene, a two dimensional honeycomb structure, which does not exist in Nature, is tantalizing for new Physics. Silicon being the workhorse of electronics industry, this synthesis could have a major impact for novel devices because of the compatibility with existing Si technologies.

[1] P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M.C. Asensio and G. Le Lay, submitted

[2] G. G. Guzman-Verri and L.C. Lew Yan Voon, *Phys. Rev. B* **76**, 75132 (2007).

[3] M. Houssa, G. Pourtois, M. Heyns, V.V. Afanas'ev, and A. Stesmans, *J. Electrochem. Soc.* **158**, H107 (2011)

[4] P. De Padova et al., *Appl. Phys. Lett.*, **96**, 261905 (2010)

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