Wednesday Morning, October 30, 2013

Graphene and Other 2D Materials Focus Topic
Room: 104 B - Session GR-WeM

2D Materials on Metallic Substrates
Moderator: U. Kaiser, University of Ulm, Germany, A. Pasupathy, Columbia University

8:00am **GR-WeM1 Growth of Graphene by Catalytic Dissociation of Ethylene on CuNi(111)**, *P. Tyagi, T.R. Mowll*, University at Albany-SUNY, *Z. Robinson*, Naval Research Laboratory, *C.A. Ventrice, Jr.*, University at Albany-SUNY
Copper foil is one of the most common substrates for growing large area graphene films. The main reason for this is that Cu has a very low carbon solubility, which results in the self-termination of a single layer of graphene when grown using hydrocarbon precursors at low pressure. Our previous results on Cu(111) substrates indicate that temperatures of at least 900 °C are needed to form single domain epitaxial films. By using a CuNi alloy, the catalytic activity of the substrate increases, which allows the catalytic decomposition of the hydrocarbon precursor at lower temperatures. In this study, the growth of graphene by the catalytic decomposition of ethylene on a 90:10 CuNi(111) substrate was attempted. The growths were done in an ultra-high vacuum system by either heating the substrate to the growth temperature followed by introducing the ethylene precursor or by introducing the ethylene precursor and subsequently heating it to the growth temperature. The growth using the former method results in a two-domain epitaxial graphene overlayer. However, introducing the ethylene before heating the substrate resulted in considerable rotational disorder within the graphene film. This has been attributed to the deposition of carbon atoms on the surface at temperatures too low for the carbon to crystallize into graphene.

This research is supported in part by the NSF (DMR-1006411).

8:20am **GR-WeM2 Energies and Lifetimes of Unoccupied Electronic States of Graphene on the Ru(0001) Surface**, *J. Guedde, N. Armbrust, P. Jakob, U. Hoefer*, Philipps-University Marburg, Germany
We present the results of an investigation of energies, dispersion and lifetimes of initially unoccupied electronic states between Fermi and vacuum level of single graphene layers on Ru(0001) obtained by means of time- and angle-resolved two-photon photoelectron spectroscopy (2PPE) [1]. Graphene/Ru(0001) is a particular interesting system because of a relative strong geometrical corrugation of the graphene layer in form of a periodically rippled moiré superstructure caused by the interaction with the Ru surface. The high in-plane polarizability of the graphene sheet and the dissimilar graphene-Ru distances in the hill and valley areas of the moiré superstructure lead to a number of novelties referring to image-potential and interface states as compared to other adsorbate systems on metal surfaces.

In the experiment we identify three image-potential states close to the vaccum level and two interface states at energies of 0.91 and 2.58 eV above the Fermi level. The most strongly bound, short lived and least dispersing image-potential state is suggested to have some quantum-well character with a large amplitude below the graphene hills. The two other image-potential states are attributed to a series of slightly decoupled states. Their lifetimes and dispersions are indicative of almost free-moving electrons, predominantly located in the interconnected valley areas. The two interface states most likely originate both from a surface resonance of Ru(0001) and exhibit different confinement and energy shifts in the valley and hill areas.

These results will be compared with model calculations using a parametrized one-dimensional model potential for a varying graphene/metal distance. It will be shown that the strong attraction of graphene for electrons in combination with its low workfunction lead to the situation that the image-potential states typically originate from the graphene and are modified by the presence of the metal surface. This is in strong contrast to insulating adsorbates on metal surfaces where the adsorbate layer modifies the image-potential states of the metal. The observed interface states, on the other hand, are both assigned to a modified surface resonance of Ru. The different confinement in the hill and valey areas result in distinct energy shift of this resonance that resembles the Shockley surface state observed on the (111) surfaces of the noble metals. This will be underlined by comparing the present results with the energy shift observed for the Shockley surface state of the Ag(111) surface upon adsorption of polycyclic aromatic hydrocarbon layers.

[1] N. Armbrust, J. Güdde, P. Jakob, and U. Höfer, Phys. Rev. Lett. **108**, 056801 (2012).

8:40am **GR-WeM3 Low-Energy Electron Microscopy of Hexagonal Boron Nitride on Nickel**, *P. Mende, Q. Gao, M. Widom, R.M. Feenstra*, Carnegie Mellon University, *A. Ismach, H. Chou, R.S. Ruoff*, University of Texas at Austin
Because of its structural similarity with graphene (~2% lattice mismatch), its atomically smooth surface, and lack of charge traps, hexagonal boron nitride (hBN) serves as an ideal candidate both as a substrate for graphene based devices, as well as an insulating layer in graphene-based heterostructures. Following the success achieved in the growth of graphene by chemical vapor deposition (CVD) on metal substrates, many investigators have pursued similar avenues in the synthesis of hBN. In this work, results are presented of low-energy electron microscopy and µLEED studies of hBN grown on polycrystalline Ni substrates by CVD. Low-energy electron reflectivity (LEER) spectra are acquired from surface regions containing various thicknesses (1 – 6 monolyers) of hBN on Ni. Distinct differences in the spectra are found in the low energy (0 – 10 eV) range, with a series of reflectivity minima observed, and the number of such minima being correlated with the thickness of the hBN. These results are consistent with prior work on multilayer graphene, in which it was demonstrated that interlayer states localized between the graphene layers give rise to the reflectivity minima found in the LEER spectra [1]. Theoretical simulation of the spectra using a first-principles method [1] is used to provide a basis for interpreting the experimental results. With the LEER spectra, it is found that the number of layers in multilayer hBN can be confidently determined, and maps of the hBN thickness over the surface are thus obtained.

This work was supported by STARnet, a Semiconductor Research Corporation program sponsored by MARCO and DARPA.

[1] R. M. Feenstra, et al., Phys. Rev. B **87**, 041406(R) (2012).

9:00am **GR-WeM4 Intercalation of C_{60} at the Interface of CVD Graphene and Copper**, *E. Monazami*, University of Virginia, *P. Rudolf, L. Bignardi*, University of Groningen, Netherlands, *P. Reinke*, University of Virginia
The unique properties of graphene are coveted for application in electronic devices but doping and opening of a bandgap while retaining the integrity of the Dirac cone, remains a challenge. The electronic properties of graphene can be modified through the interaction with adsorbates or the substrate, which has also been exploited to achieve moderate doping of the graphene layer. In our study we present the intercalation of fullerene molecules at the interface between copper and graphene as a method to electronically decouple graphene from the metal substrate, introduce a controlled strain field and create a topographic superlattice.

Our presentation focuses on the synthesis of the intercalated fullerene layer, and the local impact of intercalated fullerenes on the strain and deformation of the graphene layer. The intercalation is achieved by depositing 10-20 ML of C_{60} on graphene, which was grown on a polycrystalline Cu-substrate. The C_{60}-graphene-Cu sandwich is annealed at 400-500° C in UHV and subsequently imaged with Scanning Tunneling Microscopy (STM) and Spectroscopy (STS) conductivity maps at room temperature. The graphene-Cu system was studied separately to ascertain that the impact of Cu crystallinity and annealing on graphene's topographic and electronic structure is minimal. The role of temperature and Cu-structure on the intercalation process will be discussed in detail, and we will introduce specific indicators in the STM and STS signature to ascertain C_{60} intercalation. Recent experiments strongly suggest that a temperature around 400° C leads to the formation of regular, crystalline intercalated C_{60} layer, while higher temperatures favor an irregular, amorphous arrangement of the molecules.

The intercalation of C_{60} molecules leads to the modulation of the graphene topography due to the mechanical deformation and strain around a fullerene molecule. The graphene is detached from the Cu-substrate in the vicinity of C_{60} moleculesand the Fermi level is shifted with respect to the Dirac point indicating a local p-type doping at the graphene-fullerene contact. The local electronic properties are controlled by the intercalated molecules offering a new approach to manipulating of charge distribution in graphene. The intercalation leads to a considerable increase in the density of graphene wrinkles, which is attributed to the reduction of graphene adhesion. We will present a cohesive model, which integrates the impact of C_{60} intercalation on graphene strain, adhesion, and electronic structure.

9:20am **GR-WeM5 Controlled Synthesis of Heterostructures of 2D Materials**, *P.W. Sutter*, Brookhaven National Laboratory   **INVITED**
The ability to combine materials in heterostructures with controlled interfaces has become one of the foundations of modern materials science.

Two-dimensional (2D) crystals, such as graphene, hexagonal boron nitride, and a family of metal dichalcogenides, represent a new class of systems that offer unique opportunities for materials integration. Heterostructures that combine different 2D materials in layer stacks or as several tightly interfaced components in a single, atomically thin membrane promise tunable properties and extended functionality, and raise fundamental questions on interface formation, intermixing, strain, polarity, etc., in a new context at reduced dimensionality.

I will discuss recent advances in developing the synthesis and processing of heterostructures of 2D materials on metal substrates, derived primarily from real-time observations by surface electron microscopy, complemented by high-resolution scanning probe microscopy and in-situ spectroscopy. Focusing on the integration of graphene [1,2] with hexagonal boron nitride [3], I will discuss progress toward meeting key challenges in the controlled formation of 2D heterostructures: Atomically precise thickness and stacking control in superlattices [4], and the creation of atomically sharp line interfaces in heterogeneous monolayer membranes [5]. Our combined findings establish a powerful toolset for the scalable fabrication of 2D heterostructures for research and applications.

References

[1] P. Sutter, J.I. Flege, and E. Sutter, Nat. Mater. **7**, 406 (2008).

[2] P. Sutter and E. Sutter, Adv. Funct. Mater. (2013), DOI: 10.1002/adfm.201203426 and references therein.

[3] P. Sutter, J. Lahiri, P. Albrecht, and E. Sutter, ACS Nano **5**, 730 (2011).

[4] P. Sutter, J. Lahiri, P. Zahl, B. Wang, and E. Sutter, Nano Lett. **13**, 276 (2013) .

[5] P. Sutter, R. Cortes, J. Lahiri, and E. Sutter, Nano Lett. **12**, 4869 (2012).

11:00am **GR-WeM10 Growth and Characterization of Single Layer MoS$_2$ and Mo$_2$S$_3$ on Cu(111): Toward an Inverted Catalyst**, *W. Lu, C.S. Wang, D. Sun, Q. Ma, D. Kim, J. Wyrick, J. Mann, Y. Zhu, L. Bartels, S. Bobek*, University of California, Riverside

Single layer MoS$_2$ can be exfoliated mechanically similar to graphene. This presentation shows an alternative avenue for the fabrication of MoS$_2$ monolayers at comparatively low temperature and mild conditions through sulfur loading of a copper substrate using thiophenol followed by the evaporation of Mo atoms and annealing. In addition, this method allows the growth of ordered Mo$_2$S$_3$ films and Mo$_6$S$_6$ nanowires. Using anthraquinone and formic acid as test molecules, we titrate the various MoS$_x$ and copper-based structures presented on our substrate in order to determine their affinity for adsorbate interactions. We will also report on ongoing catalytic/TPD investigations of these films.

11:20am **GR-WeM11 Ultrafast Charge Transfer at Graphene Monolayers on Ni(111) and Other Substrates**, *D. Menzel,* Technical University Muenchen, Germany, *P. Lacovig,* Sincrotrone Trieste, Italy, *R. Larciprete,* CNR Inst. for Complex Systems, Italy, *M. Dalmiglio,* Sincrotrone Trieste, Italy, *K.L. Kostov,* Bulgarian Academy of Sciences, Bulgaria, *S. Lizzit*, Sincrotrone Trieste, Italy

The unique electronic properties of graphene (Gr) are being investigated vigorously with the entire arsenal of surface science. Nevertheless the dynamics of excited states remote from the Dirac cone range are still not well known, even though they should be important for photochemistry on Gr and for contact formation in electrochemistry. In a late breaking contribution at the AVS meeting last year we have reported our preliminary results on the investigation of ultrafast charge transfer at Gr monolayers on substrates with strongly varying coupling, using the well-established core-hole-clock method with adsorbed argon [1]. We have shown [2] that decoupled layers, irrespective of the way of decoupling, show the same rather slow charge transfer despite the high empty DOS at the relevant energies about 1.5 eV above the Dirac point. This slowdown has been tentatively explained by the local charge accumulation interfering with CT, similar to dynamical Coulomb blockade [3]. On Ru(0001) the much faster CT, graded depending on the location on the periodically buckled Gr layer, has been explained by the degree of hybridisation of Gr empty states with substrate states. The results on the Gr "hills" on Ru(0001) and on Pt(111), which are characterized by considerably faster CT than on the decoupled layers, show that these layers - often assumed to be essentially bound only by Van der Waals forces - must also exhibit considerable hybridisation. We have now extended our investigation to Gr on Ni(111) which, due to the good lattice match, is a flat layer and does not possess a Dirac cone, so that good coupling and fast CT should be expected. The results however, show CT much slower than on the Gr "valleys" on Ru, and about as fast as on the Gr "hills" on Ru. We will discuss this unexpected result in terms of hybridising states and the surface DOS. Another interesting finding is that oxygen intercalation acts very differently on Gr/Ni(111) from Gr/Ru(0001). While on Gr/Ru it fully decouples the Gr layer [2], for Gr/Ni much faster CT persists.

[1] See, e.g., D. Menzel, Chem. Soc. Rev. 37, 2212 (2008), and references therein.

[2] Lizzit et al., AVS-59, abstract #1538. S. Lizzit et al., ACS Nano (in press), DOI: 10.1021/nn4008862

[3] C. Brun et al., Phys. Rev. Lett. 108, 126802 (2012).

11:40am **GR-WeM12 Growth Kinetics of Monolayer Graphene on Pd(111)**, *H.S. Mok,* University of California at Los Angeles, *A. Ebnonnasir,* Colorado School of Mines, *S. Nie, N.C. Bartelt, K.F. McCarty,* Sandia National Laboratories, *C.V. Ciobanu,* Colorado School of Mines, *S. Kodambaka*, University of California at Los Angeles

Using *in situ* low energy electron microscopy (LEEM) observations along with density functional theory (DFT) calculations, we investigated the growth kinetics of monolayer graphene on Pd(111). All of our experiments were carried out on carbon-containing Pd(111) single crystals. Graphene layers were grown by cooling the sample to temperatures below 900 °C during annealing the sample in ultra-high vacuum. LEEM images and electron reflectivity data were acquired during graphene growth as a function of incident electron energy and annealing time. From the LEEM images, we measured the time-dependent changes in areas of graphene islands. From the electron reflectivity data, we determine the work functions of graphene-covered and graphene-free regions on the surface as a function of time. Interestingly, the work functions of graphene-free regions decrease (increase) during the growth (dissolution) of graphene. DFT calculations show that Pd work function can change due to the formation of metastable carbides and precipitation of C adatoms on the surface. Based upon our results, we suggest that graphene layers grow out of C atoms intercalated at the graphene-Pd interfaces.

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