# Thursday Morning, October 31, 2013

**Graphene and Other 2D Materials Focus Topic**
**Room: 104 B - Session GR+AS+NS+SS-ThM**

## 2D Materials: Nanostructures
**Moderator:** T.F. Heinz, Columbia University, D. Xiao, Carnegie Mellon University

**8:00am GR+AS+NS+SS-ThM1 Density Functional Theory Studies of Mechanical and Electronic Properties in 2-D Superlattices Made of Carbon and Boron Nitride Domains**, *C.V. Ciobanu*, Colorado School of Mines

Using density functional theory approaches, we have studied the energies and stresses for edges of SiC and BN nanoribbons and for domain boundaries of graphene-BN superlattices.The SiC and BN armchair nanoribbons show pronounced edge relaxations, which obliterate the 3-family oscillatory behavior of the edge stress reported for graphene. Our calculations show small boundary stresses in graphene-BN superlattices, suggesting that such domain boundaries will not experience severe deformation. We have also found that the C-terminated and Si-terminated zigzag edges in SiC nanoribbons have different compressive stresses which results in different rippling behavior of these edges. Furthermore, we have studied the spin-dependent bandgap in superlattices and investigated its dependence, for each spin component, on the domain width and magnitude and direction of applied strains. These investigations suggest the possibility of opening of a bandgap in one spin component but not the other, a behavior which could be controlled by the synthesizing domains with different widths and by applying strains of prescribed magnitude and directions

**8:20am GR+AS+NS+SS-ThM2 Enclosing, Isolation and Electron Microscopy of Encapsulated Microscopic Objects Using Graphene Oxide Membranes**, *A. Yulaev, A. Kolmakov*, Southern Illinois University Carbondale

We report on a new drop casting technique for facile and gentle encapsulation of micro and nano objects at arbitrary substrates by electron (photon) transparent graphene oxide membranes. The encapsulation is based on a droplet formation around the encapsulated object and relies on the effect of facile water permeability through the surface segregated quasi 2D network of graphene oxide microflakes. The process of encapsulation was studied using a set of model objects and micro-structured surfaces such as nanowires, inorganic droplets, micro-bubbles, pollen and micro-organisms. Two specific regimes of encapsulation, such as wrapping and isolating, can be realized via controlling the hydrophobicity of the substrates. Several specific phenomena, such as object compression, primary and secondary encapsulation were observed. Finally, the electron microscopy and analysis of the encapsulated objects, image contrast formation mechanism, beam broadening and attenuation are discussed. The technique can find an application in forensic science, histology and environmental remediation.

**8:40am GR+AS+NS+SS-ThM3 "Princess and the Pea" at the Nanoscale: Wrinkling and Unbinding of Graphene on Nanoparticles**, *M. Yamamoto*, University of Maryland, *O. Pierre-Louis,* Univ. Lyon 1-CNRS, France, *J. Huang,* University of Maryland, *M.S. Fuhrer,* University of Maryland & Monash University, Australia, *T.L. Einstein, W.G. Cullen*, University of Maryland

Thin membranes exhibit complex responses to external forces or geometrical constraints. A familiar example is the wrinkling instability, exhibited by human skin, plant leaves, and fabrics, resulting from the relative ease of bending versus stretching. We have carried out a systematic study of the wrinkling instability of graphene membranes supported on $SiO_2$ substrates with randomly placed silica nanoparticles [1]. At small nanoparticle density, monolayer graphene adheres to the substrate and is highly conformal over the nanoparticles, detached only in small regions around them. With increasing nanoparticle density, and decreasing nanoparticle separation to about 100 nm, graphene's elastic response dominates substrate adhesion, and the elastic stretching energy is reduced by the formation of wrinkles which connect the protrusions. Above a critical nanoparticle density, the wrinkles form what is evidently a percolating network across the sample. As the graphene membrane is made thicker, delamination from the substrate is observed. Since the wrinkling instability acts to remove inhomogeneous in-plane elastic strains through out-of-plane buckling, our results can be used to place limits on the possible in-plane strain magnitudes that may be created in graphene to realized strain-engineered electronic structures.

[1] M. Yamamoto et al., Phys. Rev. X 2 (2012) 041018.

**9:00am GR+AS+NS+SS-ThM4 Chemical Properties of Ultrathin MgO(100) Films: The Role of Interfaces and Dopants**, *T. Risse*, Freie Universität Berlin, Germany*, A. Gonchar*, Fritz-Haber-Institut der MPG, Germany

The ideal (100) surface of MgO being the prototype of a ionic oxide is considered rather inert with respect to chemical interactions. Recent theoretical and experimental evidences show that this perception may have to be significantly altered if ultrathin films of only a few monolayer in thickness or transition metal doped systems are considered.[1-3]

To address these questions thin and ultrathin single crystalline MgO(100) films grown on Mo(100) were investigated. On the one hand we will discuss the properties of ultrathin MgO films between 4 and 10 ML thickness focusing on the adsorption properties of molecular oxygen. While molecular oxygen is thought to be weakly physisorbed on bulk stoichiometric MgO(100) surfaces, the stoichiometric surfaces of the thin films bind oxygen much stronger, showing a desorption only above 300 K. In addition, electron spin resonance spectroscopy done under ultrahigh vacuum conditions show that these oxygen molecules are in fact O2- radical species on the surface, being created by a charge transfer from the metal substrate onto the oxygen molecule. Spectroscopic evidence for structural modifications of the MgO surface namely polaronic distortions will be discussed.

The situation on the ultrathin film will be compared to transition metal doped MgO(100) films, which are thick enough (typically around 20 ML) to ensure that charge transfer from the metal substrate does not occur. We will discuss the geometric and electronic properties of the transition metal dopants focusing on Mo ions and discuss their impact on the redox chemistry which occurs on the MgO(100) surface.

References

[1] Hellman, A.; Klacar, S.; Grönbeck, H. J. Am. Chem. Soc. 2009, 131, 16636

[2] Frondelius, P.; Häkkinen, H.; Honkala, K. Phys. Chem. Chem. Phys. 2010, 12, 1483.

[3] Stavale, F.; Shao, X.; Nilius, N.; Freund, H. J.; Prada, S.; Giordano, L.; Pacchioni, G. J. Am. Chem. Soc. 2012, 134, 11380.

**9:20am GR+AS+NS+SS-ThM5 The Self-assembly of Carbon Atoms on Catalyst Surface—Mechanism of Carbon Nanotube and Graphene Chemical Vapor Deposition (CVD) Growth**, *F. Ding*, The Hong Kong Polytechnic University, Hong Kong Special Administrative Region of China **INVITED**

Carbon nanomaterials, such as fullerene, carbon nanotubes (CNT) and graphene have drawn great interests due to their intriguing properties and the unlimited applications. Although the technologies of their synthesizing and using them for many applications have been greatly advanced, their formation mechanisms are still not very clear to us. In this talk, I will address two issues regarding (i) the chirality control in SWCNT growth and (ii) the epitaxy of graphene chemical vapor deposition (CVD) growth: **(i)** Encouraged by the dream of synthesizing carbon nanotubes (CNTs) with identical chiral indexes (n,m), the growth mechanism of CNTs has been overwhelming explored both theoretically and experimentally for nearly two decades. By developing a new version of potential energy surface (PES) and a hybridized atomic simulation method, we are able to simulate the nucleation and growth of perfect SWCNTs and the kinetics that controls the chirality assignment in CNT growth has been revealed. Based on this understanding, two strategies that may lead to chirality control in SWCNT synthesis, using high melting solid catalysts and varying the SWCNT's chirality during growth, are proposed. **(ii)** The epitaxial CVD growth on catalyst surface is the most promising method of synthesizing high quality, large area graphene. The key issue that how the orientation of the synthesized graphene is determined is crucial for both experimental design and growth control. Here three modes of graphene CVD growth, on terrace, near metal step, and the embedded growth are proposed and explored by the ab initio method. It is revealed that CVD graphene tends to be embedded on soft catalyst surfaces (e.g., Cu and Au) while the on terrace growth dominates the growth on the rigid catalyst surface (e.g., Ru, Ir, Rh). The graphene grown via on terrace mode may align along with different orientations while the graphene grown via the embedded mode or near metal step mode has only two potential orientations. Based on this understanding, many experimental puzzles are well understood and the

strategies of growing high quality graphene on various catalyst surfaces are proposed.

**10:40am GR+AS+NS+SS-ThM9 Graphene Nanostructures: Top-down vs. Bottom-up Approaches**, *A. Sinitskii*, University of Nebraska-Lincoln
**INVITED**

Graphene, a two-dimensional carbon allotrope, is often considered as a complement or even replacement for silicon in many electronics applications. However, the absence of an electronic bandgap in graphene prevents its use in logic devices. According to the theoretical studies, a bandgap compared to that in silicon (1.1 eV) could be found in narrow graphene nanoribbons (GNRs) that have atomically precise armchair edges and widths less than 2 nm. Different top-down approaches, such as a combination of electron-beam lithography and dry etching, sonochemical method, nanowire lithography, and unzipping of carbon nanotubes, typically yield ribbons with widths > 10 nm and have a limited control over the edge structure in GNRs. Several recent studies have also focused on the development of bottom-up chemical approaches for narrow GNRs. Most of these methods are based on a polymerization of pre-synthesized molecular precursors followed by a cyclodehydrogenation. The reported bottom-up techniques could yield narrow atomically-engineered GNRs that are currently unachievable by any top-down approach, stimulating further research and development of new synthetic methods for GNRs. However, several problems still need to be solved, such as a limited length of synthetic GNRs, their poor solubility, difficulties with their precise placement on dielectric substrates for device fabrication, etc.

In this talk I will review recent efforts to synthesize GNRs with an emphasis on a comparative analysis of top-down and bottom-up approaches. I will also discuss a recently developed bottom-up approach for gram quantities of narrow GNRs that are less than 2 nm wide and have atomically precise armchair edges. These GNRs could be conveniently deposited from solution on any substrate, such as Si/SiO2, mica and Au(111), for further studies. The GNRs were characterized by different techniques, including NMR, UV-vis-NIR and Raman spectroscopy, XPS, EDX, PES/IPS, SEM, AFM and STM. These data suggest that GNRs obtained by this novel synthetic approach could be promising for applications in field-effect transistors with high on-off ratios. Also, since these GNRs could be synthesized in gram quantities and at a very high yield, they could be used for bulk applications, including coatings, composites and photovoltaic devices.

**11:20am GR+AS+NS+SS-ThM11 Exfoliation, Sorting, and Applications of Few Layer Graphene Sheets**, *X. Chen*, Northwestern University

Graphene is one of the strongest, lightest and most conductive materials known so far. The common approach to prepare single layer graphene sheets is the reduction of graphene oxide which is made with well-known Hummer method. Due to the high level of the defects, the conductivity and the mechanical strength are significantly decreased comparing to the pristine graphene sheets. CVD growth is a very promising method to prepare large scale and high quality of graphene. It is still a challenge to transfer the sheet to insulate substrates. The liquid exfoliation of graphite without chemical modification is still desired for the electronics-grade graphene sheets. We are developing a simple and efficient exfoliating method to produce high quality and large scale graphene material.

The starting material is expandable graphite. This material is a product of flake graphite reacting with intercalation reagents in order to migrate between the graphene layers in a graphite crystal and remain as stable species. The materials were heat treated and then dispersed in N-Methyl-2-pyrrolidone (NMP). After the sonication and centrifuge process, the graphene sheets have been characterized by SEM, TEM, AFM, XPS, and Raman.

The material was treated at 450 ºC for 30 min in nitrogen atmosphere and was changed to be very fluffy. The XPS shows that the carbon has a narrow peak and it indicates the fraction of bonding to oxygen is negligible. The result shows that most graphite is pristine and not oxidized by the intercalation process. The exfoliated graphene sheets have been observed with AFM and TEM. The result shows that the majority of the sheets are several layer thick and submicrometer to several micrometers long. The Raman measurement was also carried out on these few layer sheets and the result shows the D band is negligible and it indicates that these graphene sheets have little defects. Besides the electronics applications of these few layer graphene sheets, they also have potential applications in conductive composite. The result of the composite of graphene sheets and polystyrene will also be discussed.

**11:40am GR+AS+NS+SS-ThM12 Interaction of Copper Nanoparticles with Graphene Membrane**, *L.W. Huang*, *C.S. Chang*, Academia Sinica, Taiwan, Republic of China

We obtained atomically clean graphene membrane by annealing free-standing graphene in ultra-high vacuum transmission electron microscopy (UHV-TEM). Copper (Cu) nanoparticles formed by in-situ e-beam deposition of Cu atoms onto the clean graphene surface. The interaction between individual metal nanoparticles and this exceptional clean suspended graphene membrane was demonstrated by the stabilization and uniform distribution of Cu nanoparticles on the graphene surface. After carefully analyzing, we report the individual metal nanoparticle induced local strain field on the graphene membrane. The result is crucial to understand the structural effect and charge transfer between graphene and Cu nanoparticles.

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