2D Materials Focus Topic
Room: 212C - Session 2D+EM+IS+MC+NS+SP+SS-WeA

Dopants and Defects in 2D Materials
Moderator: Daniel Gunlycke, Naval Research Laboratory, Zenghui Wang, Case Western Reserve University

2:20pm **2D+EM+IS+MC+NS+SP+SS-WeA1 The Effect of Defect Density on the Mechanical Properties of Graphene**, ***Jonathan Willman***, *J.M. Gonzales*, University of South Florida, *R. Perriot*, Los Alamos National Laboratory, *I.I. Oleynik*, University of South Florida

Recent experiments involving nanoindentation of graphene have demonstrated counterintuitive weakening of Young's modulus with increasing concentrations of point defects in graphene in contradiction to previous investigations. To fully resolve these inconsistencies we perform large-scale molecular dynamics simulations of nanoindentation under conditions of Atomic Force Microscopy (AFM) nanoindentation experiments. The reliable description of interatomic interactions is achieved by using recently developed screened environment-dependent bond order (SED-REBO) potential. The elastic properties of the defective graphene, the breaking strength and the mechanisms of fracture under indenter are investigated as a function of type of point defects as well as their concentration.

2:40pm **2D+EM+IS+MC+NS+SP+SS-WeA2 Investigation of Grain Boundaries in CVD Grown MoS$_2$**, ***Kolyo Marinov***, *D. Ovchinnikov, D. Dumcenco, A. Kis*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

We present the characterization of grain boundaries in polycrystalline CVD-grown MoS$_2$ films. Epitaxial growth on sapphire substrates is achieved leading to preferred orientation of the domains, which is confirmed by transmission electron microscopy experiments. Using Scanning Kelvin probe microscopy the local potential drop across the three predominant types of grain boundaries in field effect transistors is investigated. These measurements demonstrate that the interfaces between single grains do not degrade the electrical conductivity, which is due to the well aligned growth of the single domains. Furthermore, the relatively high mobility of electrons in the polycrystalline material stays constant even in devices with channels of 80 μm containing multiple grains, separated by grain boundaries. Our approach is a step forward to fabrication of large-area, uniform and high quality single-layer CVD MoS$_2$.

3:00pm **2D+EM+IS+MC+NS+SP+SS-WeA3 Polycrystalline 2D Materials: Atomic Structure and Electronic Transport Properties**, ***Oleg Yazyev***, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**

Grain boundaries and dislocations are intrinsic topological defects of polycrystalline materials, which inevitably affect their physical properties. In my talk, I will discuss the structure of topological defects in two-dimensional (2D) materials such as graphene and monolayer transition metal dichalcogenides (TMDCs) [1].

I will first introduce a general approach for constructing dislocations in graphene characterized by arbitrary Burgers vectors and grain boundaries covering the complete range of possible misorientation angles. By means of first-principles calculations we address the thermodynamic properties of grain boundaries revealing energetically favorable large-angle configurations as well as dramatic stabilization of small-angle configurations via the out-of-plane deformation, a remarkable feature of graphene as a two-dimensional material [2]. Both the presence of stable large-angle grain-boundary motifs and the out-of-plane deformation of small-angle configurations have recently been observed by scanning tunneling microscopy [3].

In the rest of my talk, I will focus on the electronic transport properties of polycrystalline 2D materials. Ballistic charge-carrier transmission across periodic grain boundaries is governed primarily by momentum conservation. Two distinct transport behaviors of such grain boundaries in graphene are predicted − either perfect reflection or high transparency with respect to low-energy charge carriers depending on the grain boundary periodicity [4]. It is also shown that certain periodic line defect structures can be engineered and offer opportunities for generating valley polarized charge carriers [5]. Beyond the momentum conservation picture we find that the transmission of low-energy charge carriers can be dramatically suppressed in the small-angle limit [6]. Unlike graphene, TMDCs combine a two-valley electronic band structure with strong spin-orbit effects. The latter can be employed for creating spin-polarized currents and adds yet another conservation law in the electronic transport across regular defects such as the frequently observed inversion domain boundaries [7,8].

* This work has been supported by the Swiss NSF, ERC and Graphene Flagship.

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[6] F. Gargiulo and O. V. Yazyev, Nano Lett. **14**, 250 (2014).

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4:20pm **2D+EM+IS+MC+NS+SP+SS-WeA7 Defects Compensation and Refining Optical Luminescence in Organic/Transition Metal Dichalcogenide Heterostructure**, *J.H. Park*, UC San Diego, *A.M. Sanne, H.C.P. Movva*, UT-Austin, *S. Vishwanath*, Cornell University, ***Il Jo Kwak***, UC San Diego, *H. Xing*, Cornell University, *J. Robertson*, University of Cambridge, UK, *S.K. Banerjee*, UT-Austin, *A.C. Kummel*, UC San Diego

Since layered transition-metal dichalcogenides(TMD) have demonstrated novel electronic and optoelectronic property, intense research has focused synthesis and integration into future electronic devices. Unlike graphene, TMD materials have band gaps, and these band structures can be tuned by thickness. However, in many cases, unintentional defects can be observed on TMD giving rise to the degradation of performance in the devices. Even for mechanical exfoliated TMD, there is a high density of defects, such as vacancies. For successful integration of TMD into devices, proper passivation of defects on TMD requires high stability in ambient conditions. In this study, a TiOPc monolayer was employed for passivation of defects to improve electrical and optical properties in TMD devices. Multilayer MoS$_2$ flakes were cleaved in ambient condition and transferred into the UHV chamber; afterwards. TiOPc monolayers were deposited on the MoS$_2$ surfaces by organic molecular beam epitaxy. After deposition, TiOPc forms a monolayer with only few defects, and the TiOPc monolayer structure has square lattice in a 1.5x1.5 nm grid. This crystal structure indicates that each TiOPc in the monolayer is directed outward to vacuum. The deposited TiOPc layer has very high thermal stability on MoS$_2$; the TiOPc layer on MoS$_2$ requires annealing above of 673K for desorption. This high thermal stability indicates there are strong interaction between TiOPc and MoS$_2$ surface. STS shows the band gap of the monolayer is 1.8 eV, while bulk MoS$_2$ has a 1.3eV band gap. Moreover, the Fermi level of TiOPc/bulk MoS$_2$ is shifted to the valence band, consistent with a P type shift. However, bulk MoS$_2$ surface, where less than monolayer of TiOPc was deposited, has Fermi level shifted towards the conduction band, consistent with N type doping. In the single layer MoS$_2$ deposited TiOPc monolayer, threshold bias is shifted from -30 V to near O V, indicating P-doping of MoS$_2$. It can be hypothesized that the work function transition of MoS2 is changed as a function of thickness. Before deposition of the TiOPc monolayer, the defects peak corresponded to S vacancy is displayed at 1.7 eV in photoluminescence. Conversely, the deposition of TiOPc monolayer almost completely suppresses S vacancy peak located 1.7 eV. Moreover, in the single layer MoS$_2$ FET, the on/off ratio is enhanced more than 2 orders magnitude. The similar charge transfer behavior also can be observed in TiOPc/WSe$_2$; on the bilayer WSe$_2$/HOPG, the TiOPc monolayer deposited on the first layer of WSe$_2$ shows the a conduction band shifted Fermi level, while a TiOPc monolayer deposited on the second layer of WSe$_2$ shows a valence band shifted Fermi level.

4:40pm **2D+EM+IS+MC+NS+SP+SS-WeA8 Reactivity and Wettability of PVD Metals on 2D Transition Metal Dichalcogenides**, ***Christopher Smyth***, *S. McDonnell, R. Addou, H. Zhu, C.L. Hinkle, R.M. Wallace*, University of Texas at Dallas

Transition metal dichalcogenides (TMDs) have been studied for years due to their tribological properties, but recent discoveries have illuminated unique opportunities for the use of single or few layer TMDs in electronics, specifically tunnel field effect transistors (TFETs). The properties of FETs fabricated with single and few layer TMDs have been investigated with some degree of success, but it has been shown via in-situ chemical analysis that interface interactions between certain contact metals and the underlying TMD are not fully understood[1,2].

In this study, the wettability and reactivity of various metals with a number of bulk TMDs (MoS$_2$, HfSe$_2$, SnSe$_2$, etc.) were investigated. Multiple samples were processed in parallel to ensure that all sample sets saw identical metal depositions. The metal-TMD interface was monitored in-situ using X-ray photoelectron spectroscopy (XPS) and metal film topography was imaged using atomic force microscopy (AFM). For some low work function metals, noticeable differences in interface chemistry were found between samples that saw high vacuum rather than UHV metal e-beam depositions.

Significant variations in compatibility between contact metal and TMD were discovered. These variations were dependent upon the metal-TMD pair and the base pressure of the chamber prior to metal deposition. Au exhibits far superior wettability on $MoSe_2$, where uniform thin films were achieved, compared to $ReSe_2$, on which Au grows as clusters. Au wettability varies between that of thin films and clusters for the other TMDs studied. An Au thin film deposited on $SnSe_2$ results in the formation of reaction products such as Sn metal, as evidenced by the evolution of different chemical states in the Sn 3*d* spectrum after deposition. Reactions between MoS_2 and Sc producing Mo metal occur when Sc is deposited in UHV instead of HV. These results provide further understanding for the critical interface between Sc and TMD in high performance TFETs.

This work was supported in part by NSF Award No. 1407765, the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA, and by the Southwest Academy on Nanoelectronics (SWAN) sponsored by the Nanoelectronic Research Initiative and NIST.

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5:00pm **2D+EM+IS+MC+NS+SP+SS-WeA9 Defects and Boundaries in 2D Materials: Correlating Electronic Properties to Atomic Structures***, **An-Ping Li***, Oak Ridge National Laboratory **INVITED**

The quest for novel two-dimensional (2D) materials has led to the discovery of hybrid heterostructures of graphene and other 2D atomic films, which provide us fascinating playground for exploring defects and boundaries in a variety of atomic layers. Even in graphene itself, there usually exist large amount of extended topological defects, such as grain boundaries and changes in layer thickness, which divide graphene into grains and domains. These interfaces and boundaries can break the lattice symmetry and are believed to have a major impact on the electronic properties, especially the transport, in 2D materials.

Here, we report on the electronic and transport properties of two types of defects studied by STM and multi-probe scanning tunneling potentiometry with a focus on the correlations to their atomic structures. The first type of defect is the monolayer-bilayer (ML-BL) boundaries in epitaxial graphene on SiC. By measuring the transport spectroscopy across individual ML-BL graphene boundaries, a greater voltage drop is observed when the current flows from monolayer to bilayer graphene than in the reverse direction, displaying an asymmetric electron transport upon bias polarity reversal [1, 2]. Interestingly, this asymmetry is not from a typical nonlinear conductance due to electron transmission through an asymmetric potential. Rather, it indicates the opening of an energy gap at the Fermi energy. Another type of defect is 1D interface in hexagonal boron nitride (hBN) and graphene planar heterostructures, where a polar-on-nonpolar 1D boundary is expected to possess peculiar electronic states associated with edge states of graphene and the polarity of hBN [2]. By implementing the concept of epitaxy to 2D space, we grow monolayer hBN from fresh edges of monolayer graphene with lattice coherence, forming a 1D boundary [3]. STM/STS measurements reveal an abrupt 1D zigzag oriented boundary, with boundary states about 0.6 eV below or above the Fermi level depending on the termination of the hBN at the boundary [4]. The boundary states are extended along the boundary, and exponentially decay into the bulk of graphene and hBN. The origin of boundary states and the effect of the polarity discontinuity at the interface will be discussed.

This research was conducted at the Center for Nanophase Materials Sciences, which is DOE Office of Science User Facility.

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3 L. Liu, et al., *Science***343**, 163 (2014).

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5:40pm **2D+EM+IS+MC+NS+SP+SS-WeA11 Metal Ion Intercalated 2D Materials as Transparent Electrodes***, **Jiayu Wan*****, W. Bao, F. Gu,* University of Maryland, College Park*, M. Fuhrer,* Monash University, Malaysia*, L. Hu*, University of Maryland, College Park

Transparent electrode materials are critical for optoelectronic devices such as touch screen and solar cells. Graphene has been widely studied as transparent electrodes for its unique physical properties. To further boost the performance of graphene based transparent electrodes, we novelized Li-ion intercalation in graphene, and achieved highest performance of carbon based transparent electrodes.[1] Transmission as high as 91.7% with a sheet resistance of 3.0 ohm/sq is achieved for 19-layer LiC_6, which corresponds to a figure of merit ($Sigma_{dc}/Sigma_{opt}$) at 1,400, significantly higher than any other continuous transparent electrodes. The unconventional modification of ultrathin graphite optoelectronic properties is explained by the suppression of interband optical transitions and a small intraband Drude conductivity near the interband edge. To achieve low cost, large scale graphene-based transparent electrodes, we further developed Na-ion intercalated printed reduced graphene oxide (RGO) film[2]. Unlike pristine graphene that inhibits Na-ion intercalation, the larger layer-layer distance of RGO allows Na-ion intercalation, leading to simultaneously much higher DC conductivity and higher optical transmittance. The typical increase of transmittance from 36% to 79% and decrease of sheet resistance from 83 kohms/sq to 311 ohms/sq in the printed network was observed after Na-ion intercalation. Compared with Li-intercalated graphene, Na-ion intercalated RGO shows much better environmental stability, which is likely due to the self-terminating oxidation of Na ions on the RGO edges. This study demonstrated the great potential of metal-ion intercalation to improve the performance of graphene-based materials for transparent conductor applications.

Reference

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6:00pm **2D+EM+IS+MC+NS+SP+SS-WeA12 Oxygen Reduction Reaction on Nitrogen-doped Graphene***, **Jun Nakamura***,* The University of Electro-Communications (UEC-Tokyo), Japan*, A. Ichikawa, H. Matsuyama, A. Akaishi*, The University of Electro-Communications (UEC-Tokyo)

Recently, several groups have reported high oxygen reduction reaction (ORR) activities in nitrogen-doped carbon nanomaterials which are candidates of metal-free catalysts for ORR [1]. Lee et al. have successfully fabricated nitrogen-doped graphene with the high ORR activity in acid media [2]. It has been confirmed that local atomic configurations of dopants in nitrogen-doped graphene are classified into three functional groups (pyrrole-like, pyridine-like, and graphite-like configurations) [3,4]. However, the mechanism of the ORR on the nitrogen-doped graphene has not fully understood.

In this work, we examine the ORR on the nitrogen-doped graphene containing the graphite-like N in a basal plane using first-principles calculations. In general, the ORR occurs mainly two pathways: The two-electron pathway (2e-) that is reduced to hydrogen peroxide (H2O2), and the direct four-electron pathway (4e-) that reduces to water (H2O). Thermodynamic electrode potentials of each process at standard conditions are about 0.68V (2e-) and 1.23V (4e-), respectively. In case of the associative mechanism for the two- and four- electron reduction pathways, the electrocatalytic activity is governed by the stability of reaction intermediates like OOH*, OH*, and O* (where "*" refers to a surface site). Free energies of the reaction intermediates have been calculated based on the computational hydrogen electrode model suggested by Nørskov et al. [5]. We have taken account of effects of electrode potential, Ph of a solution, a local electric field in double layer, and water environment.

We have constructed energy diagrams at several electrode potentials on the basis of the first-principles calculations. It has been shown that the 2e- and 4e- reduction processes proceed at potentials up to about 0.5V and 0.8V, respectively. This means that we can control the reduction pathway for the nitrogen-doped graphene with the graphite-like N. Proton-electron transfer to OOH* (the 2e- pathway), and the formation of OOH* (the 4e- pathway) are confirmed to be the rate-limiting steps, respectively. Density dependence of N on the ORR activity will also be discussed in the presentation.

References

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