

2D Materials Focus Topic

Room 201B - Session 2D+EM+MN+NS-FrM

Nanostructures including Heterostructures and Patterning of 2D Materials

Moderator: Xiang Zhang, University of California, Berkeley

8:20am **2D+EM+MN+NS-FrM-1 Interfacial Strength and Surface Damage Characteristics of Two-dimensional h-BN, MoS₂ and Graphene**, *Frank DelRio*, National Institute of Standards and Technology; *B Tran Khac, K Chung*, University of Ulsan, South Korea

Two-dimensional (2D) materials such as single- and multi-layer hexagonal boron nitride (h-BN), molybdenum disulfide (MoS₂), and graphene have attracted intensive interest due to their remarkable material properties. In this study, the film-to-substrate interfacial strengths and surface damage characteristics of atomically-thin h-BN, MoS₂ and graphene were systematically investigated via atomic force microscopy (AFM)-based progressive-force and constant-force scratch tests and Raman spectroscopy. The film-to-substrate interfacial strengths of these atomically-thin films were assessed based on their critical forces (*i.e.*, normal force where the film was delaminated from the substrate) as determined from progressive-force scratch tests. The evolution of surface damage with respect to normal force was further investigated using constant-force tests. The results suggested three different steps in the evolution of surface damage. At relatively low normal force, no significant change in topography and friction force was observed, which points to elastic deformation in the scratched area. As normal force increased, the formation of defects in the film and plastic deformation in the substrate were noted. At this stage, although the films have not yet failed, their topography, friction force, crystalline quality, and mechanical strengths were affected, which notably degraded their tribological performance. At normal forces above the critical force, delamination of the film from the substrate occurred. The compressive strain-induced buckling in front of the

AFM tip was the primary source of mechanical instability. As the compressive strain increased, the atomic bonds were compressed, and eventually ruptured. As the number of layers increased, the tribological performance of h-BN, MoS₂, and graphene were found to significantly improve due to an increase in the interfacial strengths and a decrease in the surface damage and friction force. In all, the findings on the distinctive surface damage characteristics and general failure mechanisms are useful for the design of reliable nanoscale protective and solid-lubricant coating layers based on these 2D materials.

8:40am **2D+EM+MN+NS-FrM-2 Optical and Optoelectronic Properties in 2D Homo- and Hetero-junctions**, *Juan Xia*, Nanyang Technological University, Singapore, China

It is well-known that the optical and electronic structures of two-dimensional transition metal dichalcogenide (2D TMD) materials and perovskites often show very strong layer-dependent properties¹. It is less well-known however is that the properties can also be tuned by stacking order, which allows us to build electro and optical devices with the same material and the same thickness. Detailed understanding of the inter-layer interaction will help greatly in tailoring the properties of 2D TMD materials for applications, e.g. in p-n junction, transistors, solar cells and LEDs. Raman/Photoluminescence (PL) spectroscopy and imaging have been extensively used in the study of nano-materials and nano-devices. They provide critical information for the characterization of the materials such as electronic structure, optical property, phonon structure, defects, doping and stacking sequence².

In this talk, we use Raman and PL techniques and electric measurements, as well as simulation to study TMD samples (Figure 1). The Raman and PL spectra also show clear correlation with layer-thickness and stacking sequence. Electrical experiments and ab initio calculations reveal that difference in the electronic structures mainly arises from competition between spin-orbit coupling and interlayer coupling in different structural configurations³. Similar phenomena could also be found in TMD heterostructures.

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[3] Xia, J.; Yan, J.; Shen, Z. X. *FlatChem* 2017, 4, 1-19.

9:00am **2D+EM+MN+NS-FrM-3 Sequential Edge-epitaxy: Towards Two-dimensional Multi-junctions Heterostructures and Superlattices**, *Humberto Rodriguez Gutierrez*, University of South Florida **INVITED**

Atomically thin layers are known as two-dimensional (2D) materials and have attracted a growing attention due to their great potential as building blocks for a future generation of low-power and flexible 2D optoelectronic devices. Similar to the well-established 3D electronics, the development of functional 2D devices will depend on our ability to fabricate heterostructures and junctions where the optical and electronic properties of different compounds are brought together to create new functionalities. Vertical heterostructures can be produced by selective van der Waals stacking of different monolayers with distinct chemical composition. However, in-plane lateral heterostructures, where different materials are combined within a single 2D layer, have proven to be more challenging. During the formation of the hetero-junction, it is important to minimize the incorporation of undesired impurities and the formation of crystal defects at the junction that will impact the functionality of the 2D device. When fabricating periodic structures it is equally important to develop the ability to control the domain size of each material. In this talk, we will review different techniques that have been used to create 2D lateral heterostructures of transition metal dichalcogenide compounds. Emphasis will be made in our recently reported one-pot synthesis approach, using a single heterogeneous solid source, for the continuous fabrication of lateral multi-junction heterostructures of TMD monolayers. In this method, the heterojunctions are sequentially created by only changing the composition of the reactive gas environment in the presence of water vapor. This allows to selectively control the water-induced oxidation and volatilization of each transition metal precursors, as well as its nucleation on the substrate, leading to sequential edge-epitaxy of distinct TMDs. This simple method have proven to be effective for continuous growth of TMD-based multi-junction lateral heterostructures, including selenides, sulfides and ternary alloys. Basic devices with field effect transistor configuration were fabricated to study the electrical behavior of these heterojunctions, their diode-like response, photo-response as a function of laser power as well as photovoltaic behavior of the heterojunctions will be discussed.

9:40am **2D+EM+MN+NS-FrM-5 Interpretation of π -band Replicas Observed for Mono- and Multi-layer Graphene Grown on 4H SiC(0001)**, *T Balasubramanian, M Leandersson, J Adell, C Polley*, Lund University, Sweden; *Leif Johansson, R Yakimova, C Jacobi*, Linköping University, Sweden

Graphene has made a major impact on physics due to its large variety of properties. The peculiar band structure of free standing graphene, showing linear dispersion and a Dirac point at the Fermi energy, makes it attractive for various applications. Large-scale epitaxial films have been grown on Si-terminated SiC substrates. However, the electronic structure is influenced when the graphene is laid upon a substrate whose lattice symmetry does not match that of graphene [1,2]. Six replicas oriented around each Dirac cone were observed already in the first ARPES experiments [1] of graphene grown on SiC(0001), and later reported [2] to have around 40 times lower intensity than a main Dirac cone. They were found to have the same relative separation and orientation as the rosette spots observed around the 0th and 1x1 SiC and Graphene spots in the low energy electron diffraction (LEED) pattern and were explained [2] to have similar origin, *i.e.* to originate from photoelectron diffraction.

In two later ARPES investigations [3,4] additional weaker replicas were reported to exist along the Γ -K direction in the Brillouin zone of Graphene. One of them showed the existence [3] only for 1 ML but not 2 ML samples while the other reported [4] the existence in both 1 ML and 3 ML graphene samples. The origin of these replicas were in both cases attributed to a modulation of the ionic potential in the graphene layer/layers induced by the charge modulation of the carbon layer at the interface, *i.e.* the carbon buffer layer. Thus to an initial state effect instead of the earlier proposed final state effect. In both those experiments un-polarized HeI radiation was utilized, so the symmetry of the π -band replicas was not determined. We therefore investigated monolayer and multilayer graphene samples using linearly polarized synchrotron radiation, which allowed us to exploit the so called dark corridor [5] to directly determine the symmetry of the replica cones. Our ARPES data therefore clearly show the origin of these additional replicas observed using He-I radiation and moreover reveal the existence of some weaker replicas not earlier reported. An interpretation of our ARPES data in terms of final state photoelectron diffraction effects is shown to account for the location and symmetry of the π -band replicas observed.

References

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2. E. Rotenberg and A. Bostwick, Synthetic Metals 210, 85 (2015)
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10:00am **2D+EM+MN+NS-FrM-6 Effect of SiC(0001) Substrate Morphology and Termination on Multilayer Hexagonal Boron Nitride Epitaxy by Plasma-Enhanced CBE**, *Daniel J. Pennachio, N Wilson, E Young, A McFadden, T Brown-Heft*, University of California at Santa Barbara; *K Daniels, R Myers-Ward, K Gaskill, C Eddy, Jr.*, U.S. Naval Research Laboratory; *C Palmstrøm*, University of California at Santa Barbara

Despite the prevalent use of hexagonal boron nitride (hBN) in 2D devices as a gate dielectric, tunnel barrier, or substrate, the quality of hBN thin films are typically lacking relative to flakes exfoliated from bulk crystals. To address the challenges of hBN epitaxy, this work studies the growth of hBN on single-crystal epitaxial graphene on SiC(0001) via plasma-enhanced chemical beam epitaxy (PE-CBE). As PE-CBE is conducted in an ultra-high vacuum environment, hBN nucleation, composition, and morphology were able to be examined using a combination of *in-situ*, *in-vacuo*, and *ex-situ* characterization techniques to gain insight into the formation of high-quality hBN films and hBN/graphene heterostructures.

It was found that utilization of high growth temperature ($>1400^{\circ}\text{C}$) and nitrogen plasma flux (5×10^{-6} Torr background pressure) resulted in improved multilayer hBN film morphology over lower temperature (1300°C) depositions and CBE growths without nitrogen plasma flux. PE-CBE also produced more stoichiometric films than CBE without plasma at temperatures above 1400°C , as determined by *in-vacuo* X-ray photoelectron spectroscopy (XPS). *In-situ* reflection high energy electron diffraction (RHEED) showed streaky diffraction patterns persisting throughout several nanometers of PE-CBE hBN growth, indicative of a smooth, epitaxial film. Crystallinity and epitaxial arrangement of hBN nuclei were examined by *in-vacuo* and *ex-situ* scanning probe microscopy (SPM).

Scanning probe spectroscopy provided information on the electrical properties of the hBN films relative to bulk values.

The epitaxial alignment of the hBN/graphene/SiC(0001) heterostructure was studied by RHEED and by comparing nuclei edge alignment, as measured with SPM or scanning electron microscopy, to the substrate lattice orientation. It was found that the rotational alignment of the hBN nuclei depended on the substrate surface morphology. Nuclei on the $(6\sqrt{3} \times 6\sqrt{3})R30^{\circ}$ SiC surface reconstruction, a graphene-like buffer layer, aligned directly to the buffer layer, while hBN nuclei on 4° off-cut epitaxial graphene substrates showed preferential alignment to substrate macrosteps rather than the graphene lattice. These $\sim 25\text{nm}$ high macrosteps were then examined by cross-sectional transmission electron microscopy (TEM), which showed that the epitaxial graphene and hBN conformally blanketed the macrostep facets despite the macrostep's effect on nuclei orientation. The macrostep-directed nucleation outlined in this work provides a potential route to controlling the hBN/graphene rotational alignment during van der Waals epitaxy, an important variable for modulating electronic properties in this 2D system.

10:20am **2D+EM+MN+NS-FrM-7 Nanoelectromechanical Drumhead Resonators from 2D Material Bimorphs**, *Sun Phil Kim, J Yu, E Ertekin, A van der Zande*, University of Illinois at Urbana-Champaign

Atomic membranes of monolayer 2D materials represent the ultimate limit in size of nanoelectromechanical systems. Yet, new properties and new functionality emerge by looking at the interface between layers in heterostructures of 2D materials. In this talk, we demonstrate the integration of 2D heterostructures as nanoelectromechanical systems and explore the competition between the mechanics of the ultrathin membrane and the incommensurate van der Waals interface. We fabricate electrically contacted, 5-6 μm circular drumheads of suspended heterostructure membranes of monolayer graphene on monolayer molybdenum disulfide (MoS_2), which we call a 2D bimorph. We characterize the mechanical resonance through electrostatic actuation and laser interferometry detection. The 2D bimorphs have resonance frequencies of 5-20 MHz and quality factors of 50-700, comparable to resonators from monolayer or few layer 2D materials. The frequencies and eigenmode shape of the higher harmonics display split degenerate modes showing that the 2D bimorphs behave as membranes with asymmetric tension. The devices display dynamic ranges of 44 dB, but there is a strong dependence of the dissipation on the drive. Under electrostatic frequency tuning, devices display small tuning of $\sim 20\%$ compared with graphene

resonators $> 100\%$. In addition, the tuning shows a recoverable kink that deviates from the tensioned membrane model for atomic membranes, and corresponds with a changing in stress of 0.014 N/m . One model that would account for this tuning behavior is the onset of interlayer slip in the heterostructure, allowing the tension in the membrane to relax. Using density functional theory simulations, we find that the change in stress at the kink is much larger than the energy barrier for interlayer slip of 0.0001 N/m in a 2D heterostructure, but smaller than the energy barrier for an aligned bilayer of 0.034 N/m , suggesting local pinning effect at ripples or folds in the heterostructure. Finally, we observe an asymmetry in tuning of the full width half max that does not exist in monolayer materials. These findings demonstrate a new class of NEMS from 2D heterostructures and unravel the complex interaction and impact of membrane morphology, and interlayer adhesion and slip on the mechanics of incommensurate van der Waals interfaces.

10:40am **2D+EM+MN+NS-FrM-8 Atomically-precise Graphene Etch Masks for 3D Integrated Systems from 2D Material Heterostructures**, *Jangyup Son*, University of Illinois at Urbana-Champaign; *A van der Zande*, University of Illinois at Urbana-Champaign

Atomically-precise fabrication methods are critical for the development of next-generation technologies in which electronic, photonic, and mechanical devices approach the atomic scale. In no area is this challenge more apparent than in nanoelectronics based on two-dimensional (2D) heterostructures, in which van der Waals (vdW) materials, such as graphene, hexagonal boron nitride (hBN), and transition metal dichalcogenides (TMDs), are integrated stacked to form functional electronic devices with nanometer thicknesses. A major challenge in the assembly of vdW heterostructure devices is the difficulty of patterning and individually connecting each molecular layer.

In this presentation, we demonstrate the use of graphene as a highly selective, atomically-thin etch mask and etch stop in van der Waals heterostructures. We also show the advantages of graphene etch masks (GEM) through advanced device demonstrations. We demonstrate that most inorganic 2D materials, such as hBN, TMDs, and black phosphorus (BP), are efficiently etched away by exposing those to XeF_2 gas at room temperature. In contrast, instead of getting etched, atomically-thin monolayer graphene is chemically functionalized (*i.e.* fluorographene (FG)) under XeF_2 exposure due to the formation of sp^3 bonds by the addition of fluorine atoms onto the graphene surface. Based on this, we used exfoliated (and CVD) graphene layer as etch mask for patterning other 2D layers in micro (and macro) scale vdW heterostructures. We also demonstrate the use of this selective etching and GEM in mainly two different applications: 3D-integrated heterostructure devices with interlayer vias and suspended graphene mechanical resonators. First, we fabricate an electrical device having buried contacts in a 2D material heterostructure. Holes were etched through the top layer of hBN in an encapsulated BN-G-BN heterostructure to locally expose the buried graphene layer and contacts were fabricated by evaporating metal electrodes on the exposed graphene regions. The resulting encapsulated graphene device shows a low contact resistance of $\sim 80 \text{ ohm}\cdot\text{mm}$ ($n = -2 \times 10^{12} \text{ cm}^{-2}$) at room temperature, leading to high carrier mobility of $\sim 140,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is comparable to the electrical properties of state-of-the-art edge contacted graphene devices. Second, we fabricate a suspended graphene membrane by vapor phase etching of a BP thin film supporting graphene. We show that the graphene membrane behaves as a nanomechanical resonator with a frequency of 5.24 MHz and quality factor of ~ 255 , comparable to graphene NEMS prepared on conventional substrates.

11:00am **2D+EM+MN+NS-FrM-9 Insights into the O Atom Adsorption and O₂ Dissociation on Halogenated Graphene Surfaces**, *Reynaldo Geronia*, University of the Philippines Diliman; *A Padama*, University of the Philippines Los Baños, Philippines; *J Ocon*, University of the Philippines Diliman, Philippines; *P Chuang*, University of California, Merced

Oxygen reduction reaction (ORR) usually depends on precious metal-based catalysts like platinum and its alloys to facilitate its sluggish kinetics. The high cost of these materials however limits the employment of ORR-based technologies in commercial applications like fuel cells and metal-air batteries. Interestingly, recent works have demonstrated that doped metal-free carbon catalysts, such as graphene-based materials, can facilitate adsorption of ORR intermediate species [1]. This motivates us to investigate the interaction of oxygen atom and oxygen molecule on halogenated graphene systems.

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In this work, we performed density functional theory (DFT) based calculations to investigate the stability of coplanar and non-coplanar halogen (X = F, Cl, Br, I) doped monovacant graphene systems. The stability of halogenated-graphene is strongly influenced by the size of halogen dopant as well as the geometry of the vacancy [2]. The calculated adsorption properties of atomic [3] and molecular oxygen on halogenated graphene systems, on the other hand, signifies the possibility of O₂ dissociation. We note that the dissociation of the molecule results to the distortion of the geometric structure of the substrate. This leads mostly to the formation of dangling and bridging C-O bonds along the edge of the graphene monovacancy which could have facilitated the dissociation of the molecule. Depending on the halogen, adsorption of oxygen can strengthen or weaken existing C-X bonds, due to differences between the abilities of oxygen and halogens to induce charge transfer and to participate in π bonding with carbon. These findings are expected to increase our understanding of novel graphene-based materials, which are currently being developed with the aim of reducing the use of noble metals as catalysts in fuel cells.

References:

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