2D Materials

Room A216 - Session 2D+EM+MI+NS-MoM

Properties of 2D Materials including Electronic, Magnetic, Mechanical, Optical, and Thermal Properties I

Moderator: Jeehwan Kim, Massachusetts Institute of Technology

8:20am **2D+EM+MI+NS-MoM-1 Extreme Fatigue Life of Graphene**, ***Teng Cui***, *S Mukherjee, P Sudeep, G Colas, J Tam,* University of Toronto, Canada*; P Ajayan,* Rice University*; C Singh, Y Sun, T Filleter,* University of Toronto, Canada

Materials can fail when subjected to cyclic loading at stress levels much lower than the ultimate tensile strength or yielding limit, which is known as mechanical fatigue. Understanding the fatigue behavior is critical for any emerging material in order to evaluate its long-term dynamic reliability. Two-dimensional (2D) materials have been widely applied to mechanical and electronic applications, where they are commonly subjected to cyclic stress. However, the fatigue life and underlying damage mechanisms of these atomically thin, nearly defect-free, materials are unknown. Here we show the first fatigue study of freestanding 2D materials, in particular graphene and graphene oxide (GO). Monolayer and few layer graphene and GO were found to all exhibit ultrahigh fatigue life of more than one billion cycles at large stress level in the GPa range. Such a remarkable fatigue life is higher than that of any material reported to date at similar stress levels. Graphene exhibits global and catastrophic fatigue failure preceded by bond reconfiguration near the defective site due to inhomogeneous charge distribution and higher potential energy. Graphene can fracture under cyclic loading but without progressive damage, which is distinct from the fatigue failure mechanism of any other materials. The presence of functional groups on GO imparts a local and progressive fatigue damage mechanism, which fits the macroscopic fatigue convention. The extraordinary fatigue life was found to diminish significantly when the material is scaled up in thickness (10s of layers). This work not only provides new fundamental insights into the widely observed fatigue enhancement behavior of graphene-embedded nanocomposites, but also serves as a starting point for the mechanical dynamic reliability evaluation of other 2D materials.

8:40am **2D+EM+MI+NS-MoM-2 Epitaxial Growth and Thermal Degradation of Monolayer MoS_2 on $SrTiO_3$ Single Crystal Substrates**, ***Peiyu Chen***, *W Xu, Y Gao, P Holdway, J Warner, M Castell,* University of Oxford, UK

Monolayer MoS_2 crystals grown on amorphous substrates such as SiO_2 are randomly oriented. However, when MoS_2 is grown on crystalline substrates, the crystal shapes and orientations are also influenced by their epitaxial interaction with the substrate. In the first part of this talk, we present the results from chemical vapor deposition growth of MoS_2 on three different terminations of single crystal strontium titanate ($SrTiO_3$) substrates: (111), (110), and (001). On all three terminations of $SrTiO_3$, the monolayer MoS_2 crystals try to align their <2 -1 -1 0>-type directions (i.e., the sulfur-terminated edge directions) with the <1 -1 0>-type directions on $SrTiO_3$. This arrangement allows near-perfect coincidence epitaxy between seven MoS_2 unit cells and four $SrTiO_3$ unit cells. On $SrTiO_3$(110), this even distorts the crystal shapes and introduces an additional strain detectable by photoluminescence (PL). Our observations can be explained if the interfacial van der Waals (vdW) bonding between MoS_2 monolayers and $SrTiO_3$ is greatest when maximum commensuration between the lattices is achieved. Therefore, a key finding of this study is that the vdW interaction between MoS_2 and $SrTiO_3$ substrates determines the supported crystal shapes and orientations by epitaxial relations.

Monolayer MoS_2 is also a wide-bandgap semiconductor suitable for use in high-temperature electronics. It is therefore important to understand its thermal stability. In the second part, we uncover the thermal degradation behavior of monolayer MoS_2 supported on $SrTiO_3$ in ultrahigh vacuum (UHV) because of sulfur loss. MoS_2 was found to degrade on the (111), (110), and (001) terminations of $SrTiO_3$ substrates in a similar way. The sulfur loss begins at 700 °C, at which point triangular etch trenches appear along the sulfur-terminated edge directions of the MoS_2 crystals (in scanning tunneling microscopy). The sulfur vacancies can be filled byannealing the crystals in a hot sulfur atmosphere, and the optical properties (by Raman spectroscopy and PL) of monolayer MoS_2 can nearly be fully recovered. At higher UHV annealing temperatures, the remaining Mo is oxidized by the $SrTiO_3$ substrates into MoO_2 and MoO_3. The initial sulfur loss and the formation of MoO_x are confirmed by X-ray photoelectron spectroscopy. The sulfur annealing no longer takes effect when all the Mo has been oxidized, which happens at a temperature between 800 °C and 900 °C in UHV. The MoS_2 crystal shapes are stable upon annealing until the residual MoO_3 particles evaporate at above 1000 °C. This infers that any triangular crystals that look intact under low-magnification optical microscopy and SEM may not mean pristine MoS_2.

9:00am **2D+EM+MI+NS-MoM-3 3D Printed and Injection Molded Polymer Matrix Composites with 2D Layered Materials**, ***Sangram Mazumder***, University of North Texas*; J Catalan,* University of Texas at El Paso*; N Hnatchuk, I Chen,* University of North Texas*; P Perez,* University of Texas at El Paso*; W Brostow, A Kaul,* University of North Texas

The two-dimensional layered materials (2DLMs), MoS_2 and WS_2, as well as three-dimensional (3D) graphite were infused in thermoplastic polymer matrices, specifically acrylonitrile butadiene styrene (ABS) and polyethylene terephthalate glycol (PETG). Two techniques were explored for the production of these composites into dog-bone structures for mechanical testing, which included 3D printing and injection molding. The ductility of the composites was generally seen to decrease with the addition of the fillers compared to the otherwise ductile polymer matrix counterparts. Also, changes in Young's modulus, yield and tensile strengths, as well as percent strain at fracture, were analyzed as a function of filler loadings. The effect of processing technique on microstructures was also investigated by scanning electron microscopy of the fracture surfaces which revealed the presence of microstructural defects in the form of voids in the injection molded samples, which act as stress concentrators in the composite samples. Additionally, dynamic friction data of the composites was measured in an attempt to exploit the traditional, inherent solid phase lubricating properties of the 2DLMs. Graphite was indeed seen to lower dynamic friction in case of 3D printed PETG and injection molded ABS. Also, MoS_2 and WS_2 were found to reduce friction in 3D printed PETG and ABS. Graphite being an intrinsically good conductor, while the other 2DLMs explored, specifically MoS_2 and WS_2 given their semiconducting nature, can also be used as avenues for introducing electrical conductivity within these otherwise insulating parent polymer matrices. Thermal conductivity was also found to increase in both ABS and PETG composites containing graphite, MoS_2 and WS_2, irrespective of their processing routes. The use of 2DLM-based polymer composites remains an area that is bound to open up avenues for a wide range of applications in the future related to wearable electronics and sensors with low-cost additive manufacturing approaches.

9:20am **2D+EM+MI+NS-MoM-4 Semiconducting WS_2 and h-BN Inks for Printing Optically-active Nanodevices**, ***Jay A. Desai***, University of Texas at El Paso*; S Mazumder, A Kaul,* University of North Texas

We present our work on dispersions of WS_2 and h-BN using cyclohexanone and terpineol (C/T) as the solvent to subsequently print prototype nanodevices. Current-voltage measurements, Raman spectroscopy, and photoluminescence spectroscopy were used to characterize the properties of these inks produced by various sonication techniques such as horn tip sonication, magnetic stirring and shear mixing. Both photodetector and capactive heterostructure devices were formed with these materials. From this analysis, the photoresponsivity and detectivity of the graphene-WS_2-graphene heterostructure devices were calculated to be ~ 0.86 A/W and ~ 10^{13} J, respectively. Capacitance-voltage (*C*-*V*) and *C*-frequency (*f*) measurements were also conducted, where the *V* was swept from – 6 V to + 6 V, while the change in *C* was measured from *f* ~ 20 kHz up to 3 MHz to gain insights into the nature of the graphene-WS_2 interface. An all-inkjet-printed graphene-h-BN-graphene capacitors were fabricated and leakage current density, $J_{Leakage}$, of up to ~ 0.072 μA/mm^2 and *capacitance density* of up to ~ 2.4 μF/cm^2 is reported. Finally, the influence of temperature, frequency, and LED illumination on the performance of the graphene-h-BN-based capacitor is explored with the help of *capacitance density*-voltage measurements at different parameters to promote the all-inkjet-printed capacitor for photosensitive detector applications.

9:40am **2D+EM+MI+NS-MoM-5 Transparent PEDOT:PSS Based Electro-Chromic/Thermal Devices With Excellent Durability For Applications In Smart Electronics**, ***Hossein Sojoudi***, *S Nemani,* University of Toledo

Thin-film electro-thermal/chromic devices were fabricated by utilizing PEDOT:PSS as the active conductive electrode thin-film and a compliant flexible polyurethane/ glass substrate as the building block. PEDOT:PSS exhibits electrochromic properties by undergoing an electrochemical redox reaction when an external stimulus in the form of electric potential is induced across the film. One major advantage of this technology is that it requires significantly lesser power per unit area and the color switching can be bi-stable in either transparent (oxidation) or dark blue (reduction)

states. This low powered, controlled tuning in transparency of PEDOT:PSS was achieved by coupling doped PEDOT:PSS films with graphene as counter electrode, sandwiched between a solid-state electrolytic medium while maintaining high level of transparencies ~85% at peak oxidation levels. A high color contrast and improved coloration efficiency of 75% coupled with low power densities of 0.96 W/m^2, envisions its used in smart windows and visors. The mechanical self-assembly approach of graphene can be regulated by controlling the wavelength of wrinkles generated by inducing measured pre-strain conditions and regulating the modulus contrast of the materials used, which control the level of transparency, conductivity, and hydrophobic nature of the electrode(s). The transparency of wrinkled few layered graphene with an induced biaxial pre-strain = 0.36 was found to be 95% at 550 nm. We have also harnessed the electrothermal nature of PEDOT:PSS to achieve significant thermal responses at the expense of low power inputs to achieve temperatures as high as ~100°C due to joule heating in the doped PEDOT:PSS thin films. The absorbance and transmittance spectra for PEDOT:PSS were studied using a UV-VIS spectrometer at various oxidation and reduction states by applying biased voltage in the range of 2-5 Volts in varying cycles to determine electrochromic/thermal reversibility under induced strains, and electrothermal nature at various additive concentrations. These exceptional properties of the polymer, coupled with high work-function graphene electrodes can be envisioned to develop in-tandem smart electronic windows with tunable transmittances and heating responses for applications in automobile, aerospace, and service industries.

10:00am **2D+EM+MI+NS-MoM-6 Edge Dominated Graphene/h-BN Lateral Hybrid Nanostructures for Electronic and Spintronic Applications***, Gour P. Das,* IIT Kharagpur India, India

For hybrid 2D nanostructures, the prime challenge is to control the electronic structure of edges that play a dominant role in tuning their structural, electronic, magnetic and other properties. Such heterostructures have been fabricated in-plane as well as perpendicular to the 2D plane, the latter constituting a class known as van der Waals heterosturctures. We have studied, using first principles approach, the electronic structure as well as transport properties of graphene/h-BN lateral hetero-nanoribbons of finite width, in order to probe the role of edge atoms and edge geometry on the resulting device behavior. For example, edge B doped zigzag graphene nanoribbons (ZGNRs) leads to spin filter based device [1]. We have investigated the origin of the spin filtering property in edge B-doped zigzag graphene nanoribbons (ZGNRs) and provide a guide to preparing a graphene based next-generation spin filter based device. While 100% edge B doping in ZGNR results in semiconductor to metal transition, 50% edge B doping shows half-metallicity when doped edge is unpassivated. Zero-bias transmission function of the other configurations shows asymmetric behavior for the up and down spin channels, thereby indicating their possible application potential in nano-spintronics.

In another related study [2], we have systematically varied the number of C-C or B-N units present in the graphene/*h*-BN hetero nanoribbon (G/BNNR), and have investigated their electronic as well as magnetic properties. Systems with both N or B terminated edges, undergo a semiconductor-to-semimetal-to-metal transition with the increase in the number of C-C units for a fixed ribbon width. The spin density distribution indicates significant localization of the magnetic moments at the edge carbon atoms, that gets manifested when the number of C-C units is greater than 2 for most of the structures.

** Work done in collaboration with Soubhik Chakrabarty, Tisita Das, Ranjit Thapa and Yoshiyuki Kawazoe.*

References :

[1] “Origin of spin polarization in an edge boron doped zigzag grapheme nanoribbon: a potential spin filter”, Soubhik Chakrabarty, A H M Abdul Wasey, Ranjit Thapa and G. P. Das, Nanotechnology **29**, 345203 (2018).

[2] “Tuning the electronic and magnetic properties of graphene/h-BN hetero nanoribbon: A first-principles investigation”, Tisita Das, Soubhik Chakrabarty, Y. Kawazoe and G. P. Das, AIP Advances **8**, 65111 (2018)

10:40am **2D+EM+MI+NS-MoM-8 Engineering Interfaces in the Atomically-Thin Limit***, Deep Jariwala,* University of Pennsylvania **INVITED**

The isolation of a growing number of two-dimensional (2D) materials has inspired worldwide efforts to integrate distinct 2D materials into van der Waals (vdW) heterostructures. While a tremendous amount of research activity has occurred in assembling disparate 2D materials into “all-2D” van der Waals heterostructures, this concept is not limited to 2D materials alone. Given that any passivated, dangling bond-free surface will interact with another via vdW forces, the vdW heterostructure concept can be extended to include the integration of 2D materials with non-2D materials that adhere primarily through noncovalent interactions. I will present our work on emerging mixed-dimensional (2D + nD, where n is 0, 1 or 3) heterostructure devices. Two distinct examples of gate-tunable p-n heterojunctions with anti-ambipolar field efect will be presented. The anti-ambipolar field effect observed in the above systems is also shown generalized to other semiconducting heterojunction systems and extended over large areas with practical applications in wireless communication circuits. Recent work on high performance 2D/3D triodes will also be presented.

The second part of talk will focus on engineering interfaces on photovoltaic devices from 2D semiconductors such as transition metal dichalcogenides (TMDCs).High efficiency inorganic photovoltaic materials (e.g., Si, GaAs and GaInP) can achieve maximum above-bandgap absorption as well as carrier-selective charge collection at the cell operating point. Experimental demonstration of light confinement in ultrathin (< 15 nm) Van der Waals semiconductors (MoS_2, WS_2 and WSe_2) leading to nearly perfect absorption will be demonstrated concurrently with record high quantum efficiencies. Ongoing work on addressing the key remaining challenges for application of 2D materials and their heterostructures in high efficiency photovoltaics which entails engineering of interfaces and open-circuit voltage will be presented in addition to on going work on probing of buried metal/semiconductor interfaces with sub 50 nm resolutions as well as near field luminescence spectroscopy. I will conclude by giving a broad perspective of future work on 2D materials from fundamental science to applications.

11:20am **2D+EM+MI+NS-MoM-10 Ultrasoft Slip-mediated Bending in Few-layer Graphene***, Jaehyung Yu, E Han, E Annevelink, J Son, E Ertekin, P Huang, A van der Zande,* University of Illinois at Urbana-Champaign

A challenge and opportunity in nanotechnology is to understand and take advantage of the breakdown in continuum mechanics scaling laws as systems and devices approach atomic length scales. Such challenges are particularly evident in two-dimensional (2D) materials, which represent the ultimate limit of mechanical atomic membranes as well as molecular electronics. For example, after more than a decade of study, there is no consensus on the bending modulus of few layer graphene, with measured and predicted values ranging over two orders of magnitude, and with different scaling laws. However, comparing these studies is challenging because they probe very different and often fixed curvatures or magnitudes of deformation. To unravel the discrepancy, a systematic measurement of bending stiffness versus deformation is needed. The results have practical implications on predicting and designing the stiffness of many 2D mechanical systems like origami/kirigami nanomachines, stretchable electronics from 2D heterostructures, and resonant nanoelectromechanical systems.

In this study, we combine atomistic simulation and atomic scale imaging to theoretically and experimentally examine the bending behavior of few-layer graphene. First, we experimentally probe the nanoscale bending by laminating few-layer graphene over atomically sharp steps in boron nitride and imaging the cross-sectional profile using aberration-corrected STEM. Second, we use DFT simulations to examine the bending of few-layer graphene under compression. By measuring the nanoscale curvatures, we extract the simulated and experimental bending modulus while varying both the number of layers and the degree of nanoscale curvature.

We find remarkable agreement between the theory and experiment and observe an unexpected curvature dependent bending stiffness of few-layer graphene that deviates from continuum scale bending mechanisms. We find that the bending stiffness of few layer graphene versus curvature corresponds with a gradual change in scaling power with thickness from cubic to linear. We find that the transition in scaling behavior originates from a transition from shear, slip and the onset in superlubricity between the graphene layers at the van der Waals interface, verified by a simple Frenkel-Kontorova model. Our results provide a unified model for the bending of 2D materials and show that their multilayers can be orders of magnitude softer than previously thought, among the most flexible electronic materials currently known.

11:40am **2D+EM+MI+NS-MoM-11 Experimental Study on Vanadium Oxides Films by Sputtering**, ***Chuan Li,*** National Yang Ming University, Taiwan, Republic of China*; J Hsieh,* Ming Chi University of Technology, Taiwan, Republic of China*; C Su,* National Yang Ming University, Taiwan, Republic of China

Vanadium is noteworthy for its multivalence states of the four adjacent oxidation states 2–5. The oxides of vanadium(II-V) presents various colors in aqueous solution as $[V(H_2O)_6]^{2+}$ (lilac), $[V(H_2O)_6]^{3+}$ (green), $[VO(H_2O)_5]^{2+}$ (blue) and $[VO(H_2O)_5]^{3+}$ (yellow). Because of the broad range of oxidation states, vanadium oxides can be both an amphoteric oxide and an oxidizing/reducing agent. Thus vanadium oxides are used as precursors and catalysts as well in many industrial processes.

By its nature of multivalence, vanadium oxides have been widely used in devices for memory, photonics, and optoelectronics. Through articulately harnessing on phase transitions between metal and compound, vanadium oxides can be produced with specific properties for targeted functions. For example, one of the stoichiometric oxides, VO_2, vanadium dioxide is thermochromic which a phase change occurs at a temperature above 68°C from the semiconducting monoclinic microstructure to the almost conductive tetragonal structure. Correspondingly the high optical transmittance in the range of near-infrared also switches to high reflectance.

In this study, we fabricate vanadium oxide thin films by sputtering using vanadium targets by adjusting the oxygen flow rate to have amorphous vanadium oxides. The temperature during deposition is room temperature. To monitor the chamber condition, optical emission spectrometer is employed to record the optical spectra change following different oxygen flow rates fed into the chamber. To have a crystalline phase of as-deposited films, a rapid thermal annealing process is set up and the time and temperature of annealing shall be investigated to determine the appropriate operational range.

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