2D Materials Technical Group
Room 303 - Session 2D+MI-TuA

2D Materials: Heterostructures, Twistronics, and Proximity Effects

Moderators: Francesca Tavazza, National Institute of Standard and Technology, **Suyang Xu**, Harvard University

2:20pm **2D+MI-TuA-1 Strategies for Controlling Structure and Magnetic Texture in 2D Magnets**, ***Frances Ross,*** MIT; *J. Klein,* MIT, USA **INVITED**

Electronic devices that incorporate two dimensional (2D) materials often require contacting or patterning the 2D layer for their fabrication. This is particularly important when we aim to build exciting new nanoscale magneto-electric devices based on 2D magnetic materials. CrSBr is such a 2D magnet that shows stability in air, giving this material a key advantage in practical device fabrication compared to other, less stable 2D magnets. Here we discuss strategies for controlling the structure and properties of CrSBr and related 2D magnets at the local, nanoscale level. We approach this via transmission electron microscopy, based on promising results for other 2D materials. We first discuss local control of structure. We find that electron beam irradiation in a scanning transmission electron microscope (STEM) induces a surprising structural change, where Cr atoms migrate into the van der Waals gap to create a new phase with layer direction (and, in theory, magnetization) perpendicular to the initial layers. The ability to modulate the magnetization direction deterministically is of great interest for quantum devices. Furthermore, since we find that defects in this material can be optically active and correlated with magnetic order and phases, the ability to use STEM to control individual defects will ultimately help to achieve precise control of the material's properties. We next discuss strategies for contacts. For other 2D materials, the 2D/3D contact resistance is known to improve when the contact layers have fewer grain boundaries. We therefore focus on epitaxial growth of metals and other 3D crystals onto the 2D surface. We show how *in situ* TEM imaging helps to clarify the growth mechanisms and interface structures formed during single crystal or heterostructured metal growth on graphene, hBN and transition metal dichalcogenides. We then explore how nucleation and epitaxy phenomena play out for pristine and patterned CrSBr and other 2D magnets. Overall, we conclude that atomic level structural and chemical modification are crucial for understanding properties and designing devices that use the exciting properties of the new 2D magnets. We suggest that rapidly advancing *in situ* TEM instrumentation promises exciting future opportunities where nanoscale growth and patterning create complex devices based on 2D materials.

3:00pm **2D+MI-TuA-3 Bidirectional Phonon Emission in van der Waals Heterojunctions During Ultrafast Charge Transfer**, ***Aditya Sood,*** Stanford University

Photoinduced charge transfer in van der Waals heterostructures occurs on ultrafast timescales of order 100 fs, despite the weak interlayer coupling and momentum mismatch. Little is understood about the microscopic mechanism behind this fast process and the role of the lattice in mediating it. Here, using femtosecond electron diffraction, we directly visualize lattice dynamics in photoexcited heterostructures of WSe_2/WS_2 monolayers. Following selective excitation of WSe_2, we measure unexpectedly concurrent heating of both WSe_2 and WS_2 on a 1 picosecond timescale, corresponding to an "apparent" interlayer thermal conductance that is >100x larger than that due to phonons alone. Using first-principles calculations, we identify a fast channel, involving an electronic state hybridized across the heterostructure, enabling phonon-assisted interlayer transfer of photoexcited electrons. Phonons are emitted in both layers on femtosecond timescales via this channel, consistent with the simultaneous lattice heating observed experimentally. Taken together, our work indicates strong electron-phonon coupling via layer-hybridized electronic states – a novel route to control energy transport across atomic junctions.

4:20pm **2D+MI-TuA-7 Understanding Structural, Chemical, and Number of Layer-Dependent Properties in 2D Lateral and Vertical Structures for Subsequent Optical Measurements**, *U. Kaiser,* ***Michael Mohn,*** University of Ulm, Germany **INVITED**

Properties of 2D materials can manifest at very different length scales. Charge density waves, magnetic ordering, inter- and intralayer excitons are studied also to understand their atomistic origin. Moreover, starting from exciting properties of low-twist angle graphene, twisted transition metal dichalcogenides are now explored, whereby the future of moiré superlattices is also dependent on reliable twist angle control. In addition, interfaces of transition metal dichalcogenide heterostructures such as Janus monolayers or lateral heterostructures have potential applications in optoelectronics, however very critical for carrier and exciton transport is that they are atomically sharp.

Here we use the low-voltage- spherical and chromatic aberration-corrected transmission electron microscope to measure and introduce structural and chemical variations in free-standing 2D materials on the atomic scale. In-situ and ex-situ optical measurements are performed and together with quantum-mechanical calculations their atomic-structure-based properties are understood.

We first report on advances in TEM sample preparation both for oxygen-sensitive TMDs as well as describe our sample platform to relate atomic defects in 2D materials produced by TEM with subsequent measurements in stacked devices. Then we describe studies on electron-beam-induced defects and observe the migration paths and associated property changes in a variety of single and few-layered free-standing structures of transition metal di-chalcogenides (TMDs) and transition metal phosphorus tri-chalcogenides (TMPTs). We also investigate the twist-angle-dependent moiré pattern formation in bilayers of TMDs by theoretical prediction-followed TEM experiments. From the comparison of monolayer, bi-layer and 2° twisted bilayer experimental images, we determine twist-angle-induced inhomogeneous stacking-related localized strain in the layers as well as the twist-angle-induced changes of the interlayer excitons located in the low-loss range of the EELS spectrum. We further report on the number of layer-dependent electronic properties of Pt-dichalcogenide family. We also show proof-of-principle experiments in which we transfer electron-exposed TMD flakes from a TEM grid to arbitrary substrates and measure the produced defects in photoluminescence and transport measurements. Moreover, the investigated lateral heterostructures show near-atomically sharp junctions with a typical extent of 3 nm for the covalently bonded $MoSe_2$-WSe_2 interface, determined by high-resolution transmission electron microscopy. This explains the considerably narrowed optical transition linewidth in the photoluminescence, reflectance contrast and Raman spectroscopy.

5:00pm **2D+MI-TuA-9 Determination of Band Offsets in Semiconductor Heterostructures (2D/3D) by Using XPS**, ***Mohamed Nejib Hedhili,*** *NG, B. Ooi,* King Abdullah University of Science and Technology, Saudi Arabia

Electrical and optical properties of heterojunction semiconductors are heavily influenced by the relative alignment of their energy band edges at the interface [1]. That is why the knowledge of this alignment is crucial for the design of heterostructure devices. In this regard, high-resolution X-ray photoemission spectroscopy (HR-XPS) has been shown to measure the valence band offset of heterojunction semiconductors quite accurately [2]. In this report, we present a study devoted to the characterization of 2D/ 3D heterojunction semiconductor materials using a myriad of techniques including HR-XPS, scanning transmission electron microscopy (STEM), atomic force microscopy (AFM), micro-Raman, absorbance, and microphotoluminescence spectroscopy.

The samples for this study were prepared by depositing an epitaxial GaN ($In_{0.15}Al_{0.85}N$) thin layer with molecular beam epitaxy (MBE) on chemically vapor deposition (CVD) grown single-layer (SL) MoS_2/c-sapphire (WSe_2/c-sapphire) substrates. The formation of SL of MoS_2 (WSe_2)was crucial to device properties and hence was confirmed by using both STEM and AFM techniques. HR-XPS analysis of samples was performed in two-steps to measure the valence band discontinuity for GaN ($In_{0.15}Al_{0.85}N$) / SL of MoS_2 (WSe_2) heterojunction interface. In first step, the core level binding energies with respect to the valence band maximum in both GaN ($In_{0.15}Al_{0.85}N$) and MoS_2 (WSe_2) bulk films were measured. Second, the subsequent measurements on the separation between Ga (In) and Mo (W) core levels for GaN ($In_{0.15}Al_{0.85}N$) thin layer grown SL-MoS_2 (SL-WSe_2)was measured. The valence band and conduction band offset values are determined.

The band alignment parameters determined here provide a route toward the integration of group III nitride semiconducting materials with transition metal dichalcogenides (TMDs) for designing and modeling their heterojunction-based electronic and optoelectronic devices.

References:

[1] U. Gnutzmann and K. Clausecker, Appl. Phys. 3, 9 (1974).

[2] J. C. Bernède, L. Cattin, P. Predeep, XPS Study of the Band Alignment at the Interface

ITO/CuI, Technology Letters 1 (1), 2 (2014).

5:20pm **2D+MI-TuA-10 Investigation of a Novel Layer-by-Layer Growth Methodology for Surface Metal-Organic Frameworks**, ***Nicholas Stucchi***, Clarkson University

The fabrication of highly ordered and crystalline surface-confined metal-organic frameworks (SURMOFs) has garnered interest in applications such as catalysis, gas storage, and gas separation. At present, the state of the art of SURMOF fabrication is a layer-by-layer (LBL) growth, wherein a functionalized substrate undergoes sequential immersions in solutions of the desired metal or ligand. This LBL strategy is commonly performed using gold substrates modified with carboxylate-terminated self-assembled monolayers (SAMs) which act as an initial nucleation site for the metal cluster. Careful control over deposition conditions and reaction times results in the formation of crystalline SURMOFs with tunable thicknesses. However, this technique is limited to substrates that can undergo the necessary SAM functionalization as well as being highly sensitive to the deposition conditions. I will discuss the development of a new LBL methodology that utilizes a pre-formed covalent-organic framework (COF) on the surface of highly oriented pyrolytic graphite (HOPG) as the template for SURMOF growth. The COF template should have the same geometry and a lattice parameter close to that of the desired SURMOF to minimize the strain of the first few layers. As such, COF-366-Zn was chosen as the template for UiO-67, which has a 3% lattice mismatch between the COF template and MOF. The COF was reacted with isonicotinic acid (INA) in which the pyridine axially coordinates to the zinc centers of the COF and the exposed carboxylate moieties of the INA serve as nucleation sites for the zirconium acetate clusters of UiO-67. The SURMOF was formed following several sequential reactions in the cluster and benezene-1,4-dicarboxylic acid (BDA) ligand solutions. The COF and initial INA binding will be characterized by scanning tunneling microscopy (STM) and Fourier-Transform Infrared (FTIR) spectroscopy. Atomic force microscopy (AFM) will be used to characterize the LBL growth of UiO-67. The crystallinity of the SURMOF will be determined using diffraction techniques.

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