2D Materials
Room 122 - Session 2D-ThM

2D Materials: Defects, Dopants, Edges, Functionalization, and Intercalation

Moderators: Arkady Krasheninnikov, Helmholtz Zentrum Dresden Rossendorf, Germany, **Young Hee Lee**, Sungkyunkwan University, Korea (Democratic People's Republic of)

8:00am **2D-ThM-1 Electronic and Magnetic Properties of Intrinsic Defects in TiS_2**, *P. Keeney,* university of North Florida*; A. Evans, T. Pekarek, J. Haraldsen,* ***Paula Mariel Coelho****,* University of North Florida

Transition metal dichalcogenides (TMDCs) are materials with unique electronic properties due to their two-dimensional nature. Recently, there is a large and growing interest in synthesizing ferromagnetic TMDCs for applications in electronic devices and spintronics. Apart from intrinsically magnetic examples, modification via either intrinsic defects or external dopants may induce ferromagnetism in non-magnetic TMDCs [1-2]. Our study focuses on intrinsic defects in TiS_2, which is a system known for potential applications in energy storage. We use scanning tunneling microscopy (STM) and superconducting quantum interference device (SQUID) magnetometry to characterize the crystal structure and magnetic properties of TiS_2 crystals. Atomically resolved STM images suggest the formation of sulfur vacancies and possibly interstitial defects creating brighter triangular shape regions. Preliminary analysis of magnetic data indicates low-spin paramagnetic response, with a saturated magnetization of ~0.16 emu/g and 80% saturation by ~2.5 T. To rule out ferromagnetism, hysteresis loops were analyzed and showed the coercive field to be zero within experimental error. Concurrently, DFT calculations on formation energy and electronic density were also being performed for proper identification of defect formations. Additionally, simulated STM images were generated by calculations that map the electronic density of the surface for the energetically favorable defects. An initial comparison to experimental STM images corroborates with the initial hypothesis of sulfur vacancies and titanium interstitial defects. Further studies include doping of TiS_2 with transition metals and further investigation of the electronic and magnetic properties of these doped TMDC systems.

[1] Magnetic doping in transition metal dichalcogenides, PM Coelho, J. Phys.: Condens. Matter 36 203001 (2024).

[2] Room-Temperature Ferromagnetism in $MoTe_2$ by Post-Growth Incorporation of Vanadium Impurities, PM Coelho, HP Komsa, K Lasek, V Kalappattil, J Karthikeyan, MH Phan, AV Krasheninnikov, and M Batzill, Adv. Electron. Mater., 1900044 (2019).

8:15am **2D-ThM-2 DFT-Based Investigation of Formation Energies and Properties of 2D TiS_2 with Various Defects**, ***Patrick Keeney****, P. Coelho, J. Haraldsen,* University of North Florida

Titanium disulfide (TiS_2) belongs to a family of materials known as transition metal dichalcogenides (TMDs). These materials exhibit relatively weak van der Waals forces between layers, allowing them to be reduced down to thin films and even one monolayer in thickness. While graphene is the most well researched 2D material, it does not possess a bandgap and thus has limited applications with regard to electronic devices. TMDs often have tunable bandgaps, filling a clear need within 2D materials. They also exhibit sandwich-like structures, with one layer of transition metal atoms sandwiched by two layers of chalcogen atoms.

The most researched applications of 2D TiS_2 are those regarding ion batteries, photovoltaic devices, and spintronics. This study investigates the effects of intrinsic point defects within a 2D (TiS_2) lattice on the electronic and magnetic properties. By comparing post-annealed scanning tunneling microscopy (STM) images with SGGA+U-based density functional theory (DFT) calculations, we examine which defects are more likely to occur by connecting specific geometries that arise from typical intrinsic defects. We also compare a base, benchmarked 2D TiS_2 supercell with supercells containing various point defects, allowing us to interpret the total energy differences and identify which are most energetically favorable.

8:30am **2D-ThM-3 Role of Chalcogen Vacancies and Hydrogen in Bulk and Monolayer Transition-Metal Dichalcogenides**, ***Shoaib Khalid****,* Princeton University Plasma Physics Lab*; A. Janotti,* University of Delaware*; B. Medasani,* Princeton University Plasma Physics Lab

Like in any other semiconductor, point defects in transition-metal dichalcogenides (TMDs) are expected to strongly impact their electronic and optical properties. However, identifying defects in these layered two-dimensional materials has been quite challenging with controversial conclusions despite the extensive literature in the past decade. Using first-principles calculations, we revisit the role of chalcogen vacancies and hydrogen impurity in bulk TMDs, reporting formation energies and thermodynamic and optical transition levels. We show that the S vacancy can explain recently observed cathodoluminescence spectra of MoS_2 flakes and predict similar optical levels in the other bulk TMDs. In the case of the H impurity, we find it more stable sitting on an interstitial site in the Mo plane, acting as a shallow donor, and possibly explaining the often observed n-type conductivity in some bulk TMDs. We also predict the frequencies of the local vibration modes for the H impurity, aiding its identification through Raman or infrared spectroscopy.

Our results show that the chalcogen vacancies are deep acceptors and cannot lead to n-type or p-type conductivity in monolayer TMDs. Both the (0/-1) and (-1/-2) transition levels occur in the gap, leading to paramagnetic charge states S=1/2 and S=1, respectively, in a collinear-spin representation. We discuss trends in terms of the band alignments between the TMDs, which can serve as a guide to future experimental studies of vacancy behavior.

8:45am **2D-ThM-4 Defect-engineered High-gain WS_2 Photodetector after 10 MeV Proton Irradiations**, ***Joonyup Bae****, D. Lee, S. Kwak, J. Kim, W. Lee,* Seoul National University, Republic of Korea

As silicon-based electronics approach their physical limitations, two-dimensional (2D) transition-metal dichalcogenides (TMDs) have emerged as potential alternatives due to their unique mechanical and electrical properties. Among TMDs, WS_2 exhibits layer-dependent bandgaps and impressive electron and hole mobilities. However, to effectively integrate 2D TMDs into advanced applications, reliable doping strategies must be developed.

Conventional ion implantation doping methods used in silicon and GaAs-based semiconductors are not suitable for 2D TMDs due to lattice damage and high post-annealing temperatures. Alternative techniques, such as substitutional doping and charge transfer doping, have been explored but face limitations related to high-temperature processes and dopant carrier concentration control.

This study investigates the n-type doping effect of high-energy proton beam irradiation on intrinsic n-WS_2 using various fluences. Previous studies have focused on post-fabricated devices, making it difficult to isolate the specific interactions between the substrate and TMD materials. By examining the effects of proton irradiation on bulk WS_2 crystals, this study aims to understand the intrinsic impacts with different proton fluences on 2D WS_2.

Electrical properties, defect state formation, and work function variations were assessed using transmission line measurement, Raman spectroscopy, low-temperature photoluminescence spectroscopy, and Kelvin probe force microscopy. Density Functional Theory (DFT) calculations suggest that sulfur vacancies generated by proton irradiation contribute to the formation of defect states near the conduction band, facilitating an n-type doping effect.

To validate the effects of proton beam irradiation-induced defects, multilayer WS_2 photodetectors exposed to varying proton fluences were fabricated. Increasing proton fluence led to a significant improvement in internal photo-gain under 530 nm wavelength illumination, attributable to the creation of mid-gap states. This proton-mediated doping technique offers insights into the direct effects of high-energy protons on WS_2, potentially informing the development of advanced ultra-large-scale integration devices with controllable proton irradiations.

This work was supported by the Korea Research Institute for defense Technology planning and advancement (KRIT) grant funded by Defense Acquisition Program Administration (DAPA) (KRIT-CT-21-034).

9:00am **2D-ThM-5 Doping Transition Metal Dichalcogenides by Low Energy Ion Irradiation**, *W. Blades,* Juniata College*; F. Bastani, E. Truhart, K. Burns,* ***Petra Reinke****,* University of Virginia

Transition metal dichalcogenides (TMD) MX_2 offer unique and versatile functionality for a wide range of electronic, photonic, and quantum devices. It remains a significant challenge to achieve electronic or magnetic doping. In conventional semiconductors such as Si, or III-V materials ion implantation is well-established as a versatile method of doping but TMDs are much more susceptible to damage. We introduce a new concept termed “backdoor doping” which mimics low energy ion irradiation with an energy below 50 eV with the goal of doping of the metal sub-lattice with a wide range of elements while at the same time minimizing damage.

We combine experimental studies of defects in TMDs with computational models describing the ion-matter interactions, and defect signatures using

DFT. We will compare defects created by (i) annealing, (ii) ion irradiation, and (iii) plasma exposure in a semiconducting and a metallic TMD (e.g. MoS_2, TaS_2). We observed defects created by annealing in WSe_2 with scanning tunneling microscopy and spectroscopy (STM, STS) and density functional theory (DFT). Initially chalcogen vacancies dominate but larger, extended defects with multiple damaged bonds develop rapidly. The defects introduce numerous states in the gap and damage the structural and bonding integrity of the TMD layer. A small background pressure of the chalcogen might help to repair broken M-X bonds and offer a path to defect repair. We will systematically compare the different modes of defect formation using experiment and DFT modeling. If time permits, STEM (scanning transmission electron microscopy) will be included for detailed structural and phase information.

The low energy ion irradiation is achieved by using a "sandwich structure" made of a TMD layer which is capped with a thin metal layer made of the desired dopant. For proof of concept we are using Au and Fe metal layers. The sandwich structure is irradiated from the metal layer side and the projectile (a noble gas ion with an energy <5 keV) will initiate a collision cascade. The collision cascade is adjusted to eject metal atoms from the thin layer into the TMD while limiting transmission of the projectile. The defect formation in the metal is modeled with SRIM/TRIM (stopping and range of ions in matter) and SDTrimSP which are Monte Carlo simulations of collision events in matter. These simulations predict the energy of ions leaving the metal layer and entering the TMD. The TMD layer is then studied with STM to assess the defect inventory, XPS to understand compositional variations, and other methods to fully characterize the TMD.

9:15am **2D-ThM-6 Atomic-scale Manipulation of Two-dimensional Materials with Ion Beams: From Aberration-corrected STEM to Monochromated EELS**, ***Kory Burns**, T. Alem, E. Truhart,* University of Virginia, USA*; C. Smyth,* Sandia National Laboratories, USA*; S. McDonnell,* University of Virginia, USA*; T. Ohta,* Sandia National Laboratories, USA*; J. Hachtel,* Oak Ridge National Laboratory, USA

Heterogeneities can be selectively engineered in 2D materials from the interaction of charged projectiles at varying velocities, angle of incidences, and stage temperatures. These heterogeneities exist as intrinsic structural defects, impurities in lattice sites, topological disorder, and strain-driven interfaces. So, how can we study these defects in detail to correlate their impact on materials properties? In this talk, aberration-corrected scanning transmission electron microscopy (STEM) is combined with monochromatic electron energy loss spectroscopy (EELS) to combine unprecedented spatial resolution with world-class energy resolution from an electron probe to decouple the nature of bosons arising from subtle heterogeneities. On-axis EELS, where our bright field disc is perfectly aligned with the EELS entrance aperture, leaves our signal being dominated by dipole scattering, so we get a delocalized signal. To get a localized signal from adatoms and vacancies in our material, we must go off-axis to suppress the long-range signals and highlight hyperbolic phonon polaritons. Hereby, off-axis EELS is employed, where a bright-field disc is electrically shifted outside of the EELS entrance aperture by the projector lenses such that a portion of the dark field disc now enters the spectrometer window to give information on the impact scattering in the off-axis regime. We use the selection rules inside an electron microscope to decouple the optical transitions arising from single anomalies in 2D materials. Ultimately, this work not only pushes boundaries in electron microscopy, but provides avenues to the entire scientific landscape on decoupling the defect-property relationship in solids for the better design of next-generation nanoelectronics.

9:30am **2D-ThM-7 MoSSe/MoSeS Janus Crystals: Nanoscale Defects and Composition Misconceptions Revealed Through Cross-Correlated AFM and TERS Imaging**, ***Andrey Krayev**,* HORIBA Scientific*; T. Zhang,* MIT*; L. Hoang,* Stanford University*; N. Mao,* MIT*; A. Mannix, E. Pop,* Stanford University*; J. Kong,* MIT

In this talk we'll present the results of an extensive collaborative project aimed at the cross-correlated nanoscale AFM (atomic force microscopy) and TERS (tip enhanced Raman scattering) characterization of various defects appearing in the course of synthesis of Janus transition metal dichalcogenides (TMDs). Optoelectronic and catalytic properties of Janus TMDs differ from normal TMDs, thus Janus materials are of great interest for the research community.

In the course of our study, we characterized MoSSe and MoSeS Janus materials derived from MoS_2 and $MoSe_2$ correspondingly via the cold plasma-assisted replacement of the top chalcogen layer. Preliminary Raman characterization of the as-synthesized crystal performed in a single point with the single excitation wavelength (532nm) showed weak Raman peaks of the precursors, what was misinterpreted as incomplete conversion to Janus material.

Cross-correlated AFM and TERS imaging revealed that the precursor monolayers, both MoS_2 and $MoSe_2$ featured noticeable number of nanoscale bi-, tri- and higher number of layer islands. These islands have been identified in the Janus crystals transferred to gold or silver via the Kelvin probe imaging and their composition was confirmed by TERS imaging even for the islands of just 20-30 nm in diameter. It was these multi-layer islands which were responsible for the weak Raman bands of the precursor.

The morphology of the Janus crystals derived from MoS_2 and $MoSe_2$ was also fundamentally different. In the course of conversion of $MoSe_2$ to MoSeS pre-existing tensile strain in MoSe2 was complemented by additional tensile strain resulting from the replacement of the selenium atoms with sulfur which led to physical breakage of the crystals. TERS imaging demonstrated that the gaps between the domains in MoSeS monolayers seen in topography and the surface potential images were physical cracks.

Conversely, compressive strain appearing in MoSSe Janus crystals converted from MoS_2 results in the formation of wrinkles that after the transfer to gold or silver looked like cracks in MoSeS, but in reality there was no physical breakage in these crystals. Interestingly, by varying the substrate on which the precursor crystals are grown, nice wrinkle- and crack-free Janus monolayers can be produced.

Finally, we'll briefly discuss the TERS spectral peculiarities with 785 nm and 473 nm excitation.

11:00am **2D-ThM-13 Oxidation Stability of SnSe Under Atmospheric Conditions**, ***Jonathan Chin**, B. Gardner, M. Frye,* Georgia Institute of Technology*; D. Liu,* Applied Materials*; S. Marini,* Cornell University*; J. Shallenberger,* The Pennsylvania State University*; M. McDowell,* Georgia Institute of Technology*; M. Hilse, S. Law,* The Pennsylvania State University*; L. Garten,* Georgia Institute of Technology

Tin selenide (SnSe) is predicted to exhibit a d_{11} piezoelectric response of 250 pm/V when scaled down to the monolayer limit [1], but as the film thickness is decreased surface interactions can have a greater impact on performance. For example, in 2D transition metal dichalcogenides (TMDs), oxides form not only on the surface but also propagate between layers, degrading the thin film [2]. Oxide layers have been shown to form at the surface of bulk SnSe above 200 °C [3], but the impact of oxygen on the surface and layer stability at room temperature has yet to be fully explored. Therefore, it is critical to understand the stability of the surface and interlayer structure in SnSe under standard operating condition.

This talk describes the chemical and structural stability of SnSe thin films to atmospheric exposure. The structure and composition of thin films of SnSe grown by molecular beam epitaxy is compared immediately upon growth and after a two-year exposure to ambient atmosphere. X-ray diffraction (XRD) taken before and after atmospheric exposure shows no measurable change in the crystallographic phase, orientation, or layer spacing. Similarly, the characteristic Raman vibrational modes of SnSe are unchanged with exposure, and there are no indications of modes corresponding to $SnSe_2$, SnO or SnO_2. These measurements show that the bulk of the SnSe thin film is not degrading over time as incorporating oxygen between layers would have changed the peak spacing in XRD and Raman spectroscopy. The chemical stability of the bulk phase is further supported by x-ray photoelectron spectroscopy (XPS) measurements that show that the film maintains a 1:1 Sn:Se stoichiometry. XPS cross-sections show indications of SnO_2 but only at the surface of the SnSe film. The oxide layer was limited to the surface within approximately 3.5 nm, as confirmed via x-ray reflectivity (XRR) measurements of the layer thicknesses. Resistivity measurements show an electrical response dominated by SnSe, not SnO_2. These XPS, Raman, XRR, and resistivity results suggest that exposure to atmosphere creates a passivated layer of SnO_2 on the surface of SnSe but does not impact the bulk. Overall, SnSe demonstrates long-term chemical stability under atmospheric conditions, rendering it a suitable option for device applications that employ the protective metal oxide layer found in SnSe and possibly other layered chalcogenide structures.

1. R. Fei, W. Li, J. Li, L. Yang, *Appl. Phys. Lett.* **107**, 173104 (2015).
2. Y. Guo, S. Zhou, J. Zhao, *ChemNanoMat* **6**, 838–849 (2020).
3. *Sci.* **21**, 3333–3338 (1986).

11:15am **2D-ThM-14 Enhanced Chemical Sensing with Ag-Functionalized WS2 Vertical Nanoflakes Grown by PLD for SERS Applications***, **Arvind Kaushik**, J. Singh,* IIT Delhi, India

Two-dimensional transition materials dichalcogenides (TMDCs) have a distinct advantage as a surface-enhanced Raman scattering (SERS) substrate because of their exceptional optical features, which facilitate efficient charge transfer with probe molecules and improve chemical enhancement. In this work, vertically oriented WS_2 flakes are synthesized on a Silicon (Si) substrate using the pulsed laser deposition (PLD) technique. WS_2 flakes are then used as SERS substrate for detecting low concentrations (up to 10^{-9} M) of Rhodamine B (RhB) and Methyl orange (MO) organic dyes with promising enhancement factors of nearly ~ 10^7 using 532 nm excitation laser. Using a thermal evaporation process, Ag nanoparticles (NPs) were decorated to further improve the plasmonic activity of vertical WS_2 flakes. WS_2-Ag nanocomposite substrate demonstrates superior detection capabilities when compared to pristine WS_2 flakes, achieving impressive sensitivity at ultralow concentrations of 10^{-16} M for RhB and MO dyes and an enhancement factor of the order of 10^8. The 633 nm laser was utilized to examine the SERS performance of WS_2-Ag substrate for Methylene blue (MB) dye. The MB dye was effectively detected down to an ultra-low concentration of 10^{-13} M. In addition to Ag NPs involvement, a charge transfer mechanism between WS_2 and RhB dye molecules is proposed to explain the nanocomposite SERS substrate's excellent detection capabilities and huge enhancement in SERS signal.

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