2D Materials Technical Group
Room 303 - Session 2D+AS+SS-MoA

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

Moderators: Chih-Kang (Ken) Shih, University of Texas at Austin, **Young-Woo Son**, Korea Institute for Advanced Study, Republic of Korea

2:20pm **2D+AS+SS-MoA-3 Effect of Defects in 2D Materials on the Dielectric Breakdown***, **Abdulrahman H. Basher**, M. Lanza, U. Schwingenschlogl,* King Abdullah University of Science and Technology (KAUST), Saudi Arabia

Two-dimensional (2D) materials are one of today's hot topics in the semiconductor industry due to the fact that they can be used to fabricate nanodevices with attractive properties [1, 2]. However, they may lose their features in the presence of defects. For instance, 2D hexagonal boron nitride (hBN) is an excellent insulator but defects lower its breakdown voltage in the experiment [3]. Therefore, the aim of this study is to understand the mechanism of the dielectric breakdown in hBN as compared to amorphous boron nitride (aBN), using first-principles calculations based on density functional theory. The CP2K quantum chemistry and solid-state physics software package is used (quickstep algorithm based on the Gaussian and plane waves method) [4, 5]. The generalized gradient approximation of Perdew-Burke-Ernzerhof [6] is employed, and Grimme's dispersion correction [7, 8] with Becke-Johnson damping [9] is used as the van der Waals forces play a significant role in 2D materials. The obtained densities of states show that the size of the band gap decreases for increasing defect density, confirming that 2D materials are sensitive to defects. We explain the experimental observation that the breakdown voltage decreases from hBN (crystalline) to aBN (amorphous).

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2:40pm **2D+AS+SS-MoA-4 Palladium Nucleation and Alloying at the WTe_2(001) Surface***, **Prescott E. Evans**, P. Sushko, Z. Dohnálek,* Physical and Computational Sciences Directorate and Institute for Interfacial Catalysis, Pacific Northwest National Laboratory

A deeper understanding of atomic-scale functionalization of transition metal dichalcogenides, especially topologically interesting variants such as WTe_2, is critical in developing deployable structures in quantum information science. Discerning the role of intrinsic surface defects as adsorption and functionalization sites is a key step towards device realization. In this study, scanning tunneling microscopy (STM), X-ray photoemission spectroscopy (XPS), and density functional theory (DFT) were utilized to examine the initial nucleation and growth of palladium on the WTe_2(001) surface as both a function of coverage and temperature. XPS measurements of the WTe_2(001) surface after palladium deposition at room temperature show significant interaction between Pd and surface tellurium reminiscent of $PdTe_2$ in electronic structure with an absence of interaction between Pd and tungsten. Using STM, we found palladium deposited at room temperature, where Pd clusters outnumber surface defects more than 10:1, produced no change in surface defect density. This indicates a lack of interactions between deposited Pd clusters with intrinsic surface defects. The annealing temperature-dependent STM studies further show that palladium clusters are stable to about 475 K. Palladium deposition at an elevated temperature of 425 K was performed to determine that the lack of nucleation on defects is, in fact, not a result of diffusion limitations during the growth. Complementary theoretical studies predict that palladium atoms interact strongly with Te adatoms and Te vacancies, while only binding weakly on pristine WTe_2(001). Based on these results, we conclude that the nucleation of Pd clusters is initiated by mobile Te adatoms that likely significantly outnumber other surface defects. Our high-temperature Pd deposition studies further support this assertion. Atomically resolved images of large Pd nanoparticles annealed above 475 K exhibit a superstructure on the top terrace indicating alloying with tellurium. Atomically precise, tailored heterostructures with tunable electronic, and topological properties are necessary for the growing need for quantum devices. A full account of the surfaces of these quantum materials, as in with WTe_2(001) where excess chalcogenide complicate interactions at the surface, is vital in directing both accurate predictive theory and material synthesis efforts.

3:00pm **2D+AS+SS-MoA-5 Advanced Doping Schemes for 2D Nb:WS_2 for Catalysis and Electronics***, **Jeff Schulpen**, C. Lam, W. Kessels, M. Verheijen,* Eindhoven University of Technology, The Netherlands*; A. Bol,* University of Michigan, Ann Arbor

Two-dimensional semiconductors such as WS_2 are promising materials for use in next-generation nanoelectronics due to their high mobility and scalability allowing for ultra-short gates. Doping is required to make the p-type FETs needed for CMOS logic and doping can also reduce the contact resistance, which is another important challenge to overcome for transistors based on 2D materials.[1] Separately, doped 2D materials are receiving interest as affordable catalysts, as the dopants enhance the catalytic activity of the basal plane in addition to the already high activity of the edge sites.[2]

Essential for both electronic and catalytic applications is the precise control over the amount and distribution of dopants in the film. The synthesis method of atomic layer deposition (ALD) allows excellent control over these parameters such that e.g. graded doping profiles and edge decorations can be achieved.[3]

In this work we synthesize Nb-doped WS_2 by plasma-ALD and characterize the electronic and catalytic performance of the films.Conventional supercycles of type $(AC)_m(BC)_n$ were used to achieve excellent composition control from W-rich to Nb-rich films. Optimal hydrogen evolution reaction (HER) activity was found for Nb-rich films (~85% Nb). Beyond composition tuning, we investigate the effect of different edge terminations on the HER activity by modifying the cycle order in the ALD process. For electronic applications where low dopant concentrations are relevant, we use a modified $(AC)_m(ABC)_n$ scheme, where adsorbed W precursor largely inhibits adsorption of the Nb precursor. This allows for better dopant distribution than conventional supercycles, thereby improving the resistivity and Hall mobility of the films by a factor of two. Further characterization of devices based on the grown films is presented.

These results confirm that ALD-grown Nb-doped WS_2 is a promising material for both electronics and catalysis, and that the use of advanced doping schemes can further improve the performance of these films. This also serves as a demonstration of inhibition-assisted doping using ALD, which could be of interest for other material systems.

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4:00pm **2D+AS+SS-MoA-8 Atomic Imaging of Dynamic Behaviour at 2D Material Solid-Solid and Solid-Liquid Interfaces***, **Sarah Haigh**,* University of Manchester, UK **INVITED**

Transmission electron microscopy (TEM) is used for understanding the local structure of nanomaterials. Although, we are frequently concerned about understanding behaviour during chemical reactions or while undergoing physical processes, most TEM is performed with the sample exposed to high vacuum, which can change the atomic structure of surfaces and interfaces. Unfortunately, commercial in-situ liquid, gas or electrochemical cell TEM imaging holders often severely limit atomic resolution imaging and chemical analysis.

For investigating the chemical reactivity and degradation of 2D materials without exposing them to the TEM vacuum, an effective approach is to encapsulate the sample between two inert and impermeable few-layer 2D sheets (such as graphene or hexagonal boron nitride). This also enables transfer of air sensitive specimens from an inert vacuum or glove

environment to the TEM without exposing the material to atmospheric conditions. We have applied this approach to study air sensitive 2D materials, including local point defects, doping and edge structures in a wide range of structures (e.g. CrBr3, GaSe, black phosphorus) (Fig. 1c)[1,2]. We also find that encapsulation with inert 2D materials is an effective route to preserve the delicate surface structure of hydrated 2D materials, enabling the visualization of exchangeable surface cations on few layer clays and micas [3] and a route to understand the changes in atom/ion motion at interfaces where the 2D materials are twisted with respect to each other (Fig. 1d).[3,4]

This 2D heterostructure approach can also be used to investigate solid-liquid interfaces. Building on nanochannel technology developed by the group of Andre Geim (Fig. 1b)[5] we have developed in-situ liquid phase TEM imaging using 2D heterostructure nanochannels. The in-situ 2D heterostructure liquid cell approach provides atomic resolution imaging and analysis and makes it possible to study the earliest stage of chemical synthesis [6]. It also reveals the large differences in adatom adsorption sites on 2D surfaces in vacuum compared to hydrated environments and allows study of dynamic adatom motion at solid liquid interfaces [7]; something that was not previously possible by any technique (Fig. 1a).

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4:40pm **2D+AS+SS-MoA-10 Electrodeposition of Nanofiberous H-Type MnO_2 Birnessite on Epitaxial Graphene Silicon Carbide Heterostructures, and transformation to Alkali Birnessites (Na, Li, K) via Simple Intercalation**, ***Michael Pedowitz***, *D. Lewis, K. Daniels,* University of Maryland, College Park

Mixed valence manganese oxides (MnO_x) have attracted significant research interest in recent years due to the reversible low energy redox reactions between manganese oxidation states (Mn^{+2}, Mn^{+3}, and Mn^{+4})[1], which has enabled its use in catalysis[2], energy storage[3], and gas sensing[4]. Of these manganese oxide compounds, manganese dioxide (MnO_2) has been of particular interest due to its wide variety of synthesized structural polymorphs (α (1x2 tunnel), β (1x1 tunnel), γ (spinel), and δ (layered))[5] which allow for significant control over the active surface area and reactive properties MnO_2. In particular, the Mn^{+3} defect density, which has been found to increase the reactivity of the MnO_2 film[6], is highly variable between polymorphs, with the δ phase exhibiting the highest defect density. Water stabilized δ-MnO_2 (H-δ-MnO_2) in particular contains the highest number of Mn^{+3} defects due to the presence of $Mn^{+2/+3}$ in the interlayer, which neutralize the layer charge from lattice defects[7]. However, the production of H-δ-MnO_2 has proven challenging in the literature. In this work, we present the synthesis of H-δ-MnO_2 on epitaxial graphene silicon carbide via electrodeposition. The electrodeposition was carried out in a 3 electrode electrochemical cell in a 3-step process with a duration of 1.25 seconds. The resulting films were then characterized using a combination of Raman spectroscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM) to confirm the formation of H-δ-MnO_2 and probe its surface morphology. The Raman spectra indicated the successful formation of H-δ-MnO_2, while the AFM and SEM indicated the surface has a nanofibrous character, increases the active surface area of the thin film. We then demonstrated that the material can be converted to Alkali type (Li, Na, K) δ-MnO_2 via intercalation without damaging the EG substrate. After the process, the material was characterized again with Raman, AFM, and SEM, which confirmed the transformation from H-type to Alkali-Type. As the interlayer spacing of δ-MnO_2 and its applications are related to the intercalated ions, this demonstrates the tunability of this heterostructure and its potential to be a platform for a variety of applications, including energy storage and gas sensing.

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5:00pm **2D+AS+SS-MoA-11 Signature of Coexistence of Ferroelectricity and Ferromagnetism in a Quantum Material**, ***I-Hsuan Kao***, *S. Yuan, J. Katoch, S. Singh,* Carnegie Mellon University

Electric field-controlled magnetism by combining van der Waals (vdW) based semiconducting ferromagnets and Weyl semimetal is appealing because of the gate tunability and efficient charge-spin transduction[1], which can be exploited for modular memory and logic devices. Ferroelectric switching has been previously demonstrated in bilayer and trilayer WTe_2[2-4], where the polarity can be controlled by electric gating. VdW based semiconducting FMs, such as $Cr_2Ge_2Te_6$ (CGT), provide the opportunity to study tunable magnetic phenomena and to build superlattices with other quantum materials[5]. By coupling a semiconducting ferromagnet to a Weyl semimetal, magnetization can be induced at the interface by magnetic proximity effect. We have fabricated WTe_2/CGT devices and observed anomalous Hall effect, which is a signature of magnetic proximity effect. In the same device, we are able to perform ferroelectric switching of WTe_2 by applying an electric field. Furthermore, the presence of the anomalous Hall effect can be enhanced (suppressed) by negative (positive) electric gating. We will present detailed measurements, which are required to understand this novel platform where ferroelectricity and ferromagnetism coexist.

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