

2D Materials

Room A216 - Session 2D+EM+MI+NS+QS+SS-ThM

Dopants, Defects, and Interfaces in 2D Materials

Moderator: Evan Reed, Stanford University

8:00am 2D+EM+MI+NS+QS+SS-ThM-1 Interfacial Engineering of Chemically Reactive Two-Dimensional Materials, *Mark Hersam*, Northwestern University **INVITED**

Following the success of ambient-stable two-dimensional (2D) materials such as graphene and hexagonal boron nitride, new classes of chemically reactive layered solids are being explored since their unique properties hold promise for improved device performance [1]. For example, chemically reactive 2D semiconductors (e.g., black phosphorus (BP) and indium selenide (InSe)) have shown enhanced field-effect mobilities under controlled conditions that minimize ambient degradation [2]. In addition, 2D boron (i.e., borophene) is an anisotropic metal with a diverse range of theoretically predicted phenomena including confined plasmons, charge density waves, and superconductivity [3], although its high chemical reactivity has limited experimental studies to inert ultrahigh vacuum conditions [4-7]. Therefore, to fully study and exploit the vast majority of 2D materials, methods for mitigating or exploiting their relatively high chemical reactivity are required [8]. In particular, covalent organic functionalization of BP minimizes ambient degradation, provides charge transfer doping, and enhances field-effect mobility [9]. In contrast, noncovalent organic functionalization of borophene leads to the spontaneous formation of electronically abrupt lateral organic-borophene heterostructures [10]. By combining organic and inorganic encapsulation strategies, even highly chemically reactive 2D materials (e.g., InSe) can be studied and utilized in ambient conditions [11].

[1] A. J. Mannix, *et al.*, *Nature Reviews Chemistry*, **1**, 0014 (2017).

[2] D. Jariwala, *et al.*, *Nature Materials*, **16**, 170 (2017).

[3] A. J. Mannix, *et al.*, *Nature Nanotechnology*, **13**, 444 (2018).

[4] A. J. Mannix, *et al.*, *Science*, **350**, 1513 (2015).

[5] G. P. Campbell, *et al.*, *Nano Letters*, **18**, 2816 (2018).

[6] X. Liu, *et al.*, *Nature Materials*, **17**, 783 (2018).

[7] X. Liu, *et al.*, *Nature Communications*, **10**, 1642 (2019).

[8] C. R. Ryder, *et al.*, *ACS Nano*, **10**, 3900 (2016).

[9] C. R. Ryder, *et al.*, *Nature Chemistry*, **8**, 597 (2016).

[10] X. Liu, *et al.*, *Science Advances*, **3**, e1602356 (2017).

[11] S. A. Wells, *et al.*, *Nano Letters*, **18**, 7876 (2018).

8:40am 2D+EM+MI+NS+QS+SS-ThM-3 Effects of Mn Doping on the Surface Electronic Band Structure and Bulk Magnetic Properties of ZnS and CdS Quantum Dot Thin Films, *Thilini K. Ekanayaka*¹, *G Gurusung*, University of Nebraska-Lincoln; *G Rimal*, Rutgers University; *S Horoz*, Siirt University, Turkey; *J Tang*, *T Chien*, University of Wyoming; *T Paudel*, *A Yost*, University of Nebraska-Lincoln

Semiconducting quantum dots (QDs) are desirable for solar cells due to the ability to tune the band gap by changing the QD size without changing the underlying material or synthesis technique. Doping QDs with a transition metal is one way of further tailoring the electronic band structure and magnetic properties of QDs in order to improve overall device performance. Understanding the mechanisms causing the change in the electronic band structure and magnetic properties due to transition metal doping is important to device-by-design schemes. In this study, we measure the effects of Mn dopants on the surface electronic band structure of ZnS and CdS QDs using scanning tunneling microscopy/spectroscopy and photoemission spectroscopy. In both the ZnS and CdS systems, a decrease in band gap upon introduction of Mn is observed. Additionally, a rigid band shift was observed in ZnS upon Mn doping. It is argued, using X-ray photoemission spectroscopy, that the rigid band shift is due to a hole-doping mechanism caused by the formation of Zn vacancies accompanied by a Mn³⁺ oxidation state which leads to the reduction in total S vacancies as compared to the undoped ZnS system. No band shift was observed in CdS upon Mn doping, but a strong sp-d hybridization takes place which results in a significant band gap reduction. Furthermore, induced midgap states originating from the Mn dopant appear in the surface electronic band structure of Mn: CdS. Measurements of the magnetization of Mn doped and undoped ZnS and CdS confirms the

presence of d⁰ ferromagnetism. The magnetization is reduced and the coercive field is increased post Mn doping which suggests the anti-ferromagnetic alignment of Mn dopant atoms. Density Functional Theory calculations support the Mn anti-ferromagnetic alignment hypothesis and a ground state with Mn in the 3⁺ valence. This study provides important information on the role of dopants and vacancies in dilute magnetic semiconductor quantum dot materials for applications in photovoltaics and spintronics.

9:00am 2D+EM+MI+NS+QS+SS-ThM-4 Interaction of Molecular O₂ with Organolead Halide Nanorods by Single-Particle Fluorescence Microscopy, *Juvinch Vicente*, *J Chen*, Ohio University

The photoluminescence (PL) of organolead halide perovskites (OHPs) is sensitive to its surface conditions, especially surface defect states, making the PL of small OHP crystals an effective way to report their surface states. At the ensemble level, when averaging a lot of nanocrystals, the photoexcitation of OHP nanorods under inert nitrogen (N₂) atmosphere leads to PL decline, while subsequent exposure to oxygen (O₂) results to reversible PL recovery. At the single-particle level, individual OHP nanorods photoblinks, whose probability is dependent on both the excitation intensity and the O₂ concentration. Combining the two sets of information, we are able to quantitatively evaluate the interaction between a single surface defect and a single O₂ molecule using a kinetic model. This model provides fundamental insights that could help reconcile the contradicting views on the interactions of molecular O₂ with OHP materials and help design a suitable OHP interface for a variety of applications in photovoltaics and optoelectronics.

9:20am 2D+EM+MI+NS+QS+SS-ThM-5 Complementary Growth of 2D Transition Metal Dichalcogenide Semiconductors on Metal Oxide Interfaces, *T Wickramasinghe*, *Gregory Jensen*, *R Thorat*, Nanoscale and Quantum Phenomena Institute; *S Aleithan*, Nanoscale and Quantum Phenomena Institute, Saudi Arabia; *S Khadka*, *E Stinaff*, Nanoscale and Quantum Phenomena Institute

A chemical vapor deposition (CVD) growth model will be presented for a technique resulting in naturally formed 2D transition metal dichalcogenide (TMD) based metal-oxide-semiconductor structures. The process is based on a standard CVD reaction involving a chalcogen and transition metal oxide-based precursor. Here however, a thin metal oxide layer, formed on lithographically defined regions of a pure bulk transition metal, serves as the precursor. X-ray diffraction and cross-sectional SEM studies show insight into the type and thickness of the metal oxide created during optimal growth conditions. The chalcogen reacts with the metal oxide, forming TMD material which migrates outward along the substrate, leading to lateral growth of highly-crystalline, mono-to-few layer, films. In addition to displaying strong luminescence, monolayer Raman signatures, and relatively large crystal domains, the material grows deterministically and selectively over large regions and remains connected to the bulk metallic patterns, offering a scalable path for producing as-grown two-dimensional materials-based devices.

9:40am 2D+EM+MI+NS+QS+SS-ThM-6 Kagome-type Lattice Instability and Insulator-metal Transition in an Alkali-doped Mott Insulator on Si(111), *Tyler Smith*, *H Weitering*, University of Tennessee Knoxville

The 1/3 ML monolayer (ML) 'alpha phase' of Sn on Si(111) is a remarkable platform for the study of strong correlations in a spin 1/2 triangular adatom lattice. In this work, we employ an adatom doping scheme by depositing potassium onto the triangular Sn lattice. The K-atoms destabilize the parent Mott insulating phase and produce a charge-ordered insulator, revealing a rare Kagome lattice at the surface. Scanning Tunneling Microscopy and Spectroscopy reveal a phase transition from an insulating kagome lattice to a metallic triangular lattice at about 200 K. DFT band structure calculations for this kagome system [J. Ortega et al., unpublished] reveal the presence of a flat-band just below the Fermi level, making this novel system a compelling platform for hole-doping studies of magnetic and/or superconducting instabilities.

11:00am 2D+EM+MI+NS+QS+SS-ThM-10 Chemical Migration and Dipole Formation at TMD/TI Interfaces, *Brenton Noesges*, *T Zhu*, The Ohio State University; *D O'Hara*, University of California, Riverside; *R Kawakami*, *L Brillson*, The Ohio State University

Proximity effects at the interface between two materials can induce physical properties not present in either material alone. Topological insulators (TIs) such as Bi₂Se₃ with non-trivial surface states are sensitive to interface proximity effects where overlayers and adsorbates can act as a dopant source, chemically interact with the TI surface, or couple across the

¹ National Student Award Finalist

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Tl surface states leading to novel quantum phases. Transition metal dichalcogenides (TMDs), a class of 2D van der Waals materials, are a promising candidate to control this interface given the shared general hexagonal symmetry and wide range of TMD properties. However, the interface between TMDs and Bi_2Se_3 can be more complex than the ideal van der Waals interface. Chemical species exchange like metal cation exchange and selenium migration from substrate to growing film can impact the structure and properties of either layer. Self-assembly mechanisms have also been observed where complete metal monolayers form inside the Bi_2Se_3 quintuple layer [1]. We used x-ray photoelectron spectroscopy (XPS) connected in vacuo via UHV suitcase to a molecular beam epitaxy (MBE) system to investigate chemical interaction at the interface between selenide TMDs and Bi_2Se_3 . Air-free transferring is crucial to minimize contamination at the interface and prevent oxidation in the air-sensitive TMDs. We compare the effects of ultrathin pure Mn metal overlayers and monolayer MnSe_x on Bi_2Se_3 to pristine Bi_2Se_3 . In the case of pure Mn metal on Bi_2Se_3 , Bi core levels exhibit a 1.7 eV shift toward lower binding energies while the Mn core levels also show signs of Mn-Se bonding. These core level changes indicate that, in the absence of excess Se during growth, Mn pulls Se from the substrate leaving behind Bi_2 bilayers near the surface. Depositing a monolayer of MnSe_x produces very different results than the pure metal case. Bi_2Se_3 core levels measured below the monolayer MnSe_x film exhibit a rigid 0.8 eV chemical shift toward higher binding energies indicative of surface/interface dipole formation. The presence of this dipole is likely due to growth of primarily α -MnSe instead of the 1T-MnSe₂ 2D phase [2]. Scanning tunneling microscopy (STM) height maps and spectroscopy data provide further evidence of majority α -MnSe formation. XPS core level analysis combined with controlled depositions, air-free transfers and surface analysis can provide a consistent explanation of chemical diffusion and dipole formation at a TMD/Tl interface. This work is supported by NSF MRSEC under award number DMR-1420451.

[1] J. A. Hagmann et al., *New J. Phys.* 19, 085002 (2017).

[2] D.J. O'Hara et al. *Nano Lett.*, 18(5), 3125-3131 (2018).

11:20am **2D+EM+MI+NS+QS+SS-ThM-11 Atomically Resolved Electronic Properties of Defects in the in-plane Anisotropic Lattice of ReS_2** , *Adina Luican-Mayer*, University of Ottawa, Canada

Among the layered transition metal dichalcogenides, the compounds that exhibit in-plane anisotropy are of particular interest as they offer an additional tuning knob for their novel properties. In this talk, we present experimental evidence of the lattice structure and properties of semiconducting ReS_2 by using scanning tunneling microscopy and spectroscopy (STM/STS). We demonstrate that rhenium atoms form diamond-shaped clusters, organized in disjointed chains and characterize the semiconducting electronic band gap by STS. When imaging the surface of ReS_2 , we encounter "bright" or "dark" regions indicating the presence of charged defects that will electrostatically interact with their environment. By spatially mapping the local density of states around these defects, we explore their origin and electrostatic nature. Experimental results are compared with ab-initio theory.

11:40am **2D+EM+MI+NS+QS+SS-ThM-12 Charge Diminishing at the Si-SiO₂ System and its Influence on the Interface Properties**, *Daniel Kropman, V Seeman*, Tartu University, Estonia; *A Medvids, P Onufrievs*, Riga Technical University, Latvia

The fact that a positive charge formation occurs in SiO_2 film during the process of Si thermal oxidation is already known, with the formation being dependent upon the oxidation conditions which involve temperature, time, and ambient conditions. This is connected by oxygen vacancies in the SiO_2 film and unsaturated Si^{3+} bonds at the interface. Until now this process has not been studied in depth at an atomic level. The purpose of the present work is to investigate the charge formation in the Si-SiO₂ system and its diminishing by means of the appropriate choice of oxidation conditions via EPR spectroscopy, IR spectroscopy, CV curves, TEM, and deflection measurements. Laser irradiation and ultrasonic treatment were used for the modification of interface properties. It has been established that, at an oxidation temperature that is within the range of 1125°C-1130°C in SiO_2 film with a thickness of 0.2-0.3 μm at the interface, there appears a low positive or negative charge which is connected with negatively charged acceptors that are formed by Si vacancies, and the positive charge in the SiO_2 is compensated. The results that were obtained coincide with the point defects generation kinetic model in the Si-SiO₂ system which was proposed in [1] and was confirmed experimentally [2]. Integral circuit technology conditions that allow the interface charge to diminish were introduced by the semiconductor plant, ALFA (Riga, Latvia) [3]. We

supposed that these results, which were obtained during long term collaboration between Estonia and Latvia, constituted a discovery that had been achieved by Si-SiO₂ system investigation no less than thirty years ago: the discovery of the quantum Hall effect on the Si-SiO₂ structure [4].

References

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3. D Kropman, E Mellikov, T Kärner, Ü Ugaste, T Laas, I Heinmaa, A Medvids, *Material Science and Engineering B* 134 (2006) 222-226.
4. K von Klitzing. Private communication (2018).

12:00pm **2D+EM+MI+NS+QS+SS-ThM-13 Size-independent "Squeezed" Shape of Metal Clusters Embedded Beneath Layered Materials**, *A Lii-Rosales*, Ames Laboratory and Iowa State University; *S Julien, K Wan*, Northeastern University; *Y Han*, Ames Laboratory and Iowa State University; *K Lai*, Iowa State University; *M Tringides, J Evans, Patricia A. Thiel*, Ames Laboratory and Iowa State University

We have developed a continuum elasticity model for metals embedded beneath the surfaces of layered materials. The model predicts that the equilibrated cluster shape is invariant with size, manifest both by constant side slope and by constant aspect ratio (width:height ratio). This prediction is rationalized by dimensional analysis of the relevant energetic contributions. The model is consistent with experimental data for Cu and Fe clusters embedded in graphite, especially in the limit of large clusters. For comparison, we have performed a Winterbottom analysis of the equilibrium shape of an uncovered Cu cluster supported on top of graphite. The aspect ratio of the embedded cluster is about an order of magnitude higher than that of the supported cluster. Analysis of key energetics indicates that this is due to the strain energy (resistance to deformation) of the top graphene membrane, which effectively squeezes the metal cluster and forces it to adopt a relatively low, flattened shape. These insights may be useful for developing components such as metallic heat sinks or electrodes in electronic devices that use two-dimensional or layered materials.

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