

2D Materials Focus Topic

Room 201B - Session 2D+AM+EM+NS-WeM

Dopants, Defects, and Interfaces in 2D Materials

Moderator: Eric Pop, Stanford University

8:00am **2D+AM+EM+NS-WeM1 Carbon Doping of 2D Transition Metal Dichalcogenides by Plasma Enhanced CVD**, *Yanfu Lu, F. Zhang, S. Sinnott, M. Terrones*, The Pennsylvania State University

Doping of 2D transition metal dichalcogenides has been discovered to be an effective way to tune the electronic structure and modify the lattice structure at the surface. The n-type and p-type doping of monolayer MoS₂/WS₂ heterostructures may enable the fabrication of field-effect transistors of ultra-low thickness. Plasma enhanced chemical vapor deposition provides a stable and controllable approach for introducing carbon dopants to monolayer WS₂. Photoluminescence measurement indicates that the band gap of C-doped WS₂ decreases by 0.17 eV.

Corresponding first principles calculations provide the correlation between the position and chemical saturation of the carbon dopants and the electronic structure of the system. To verify covalently bonded dopants, we use Raman spectroscopy, X-ray photoelectron spectroscopy, and scanning transmission electron microscopy to examine the pristine sample and carbon-doped samples. Subsequent I-V characteristics measurements prove p-type doping and the energy band diagram. Finally, the mechanism associated with and, more importantly, the structure-property relationship of chalcogen doping are analyzed. The resulting new insights of transition metal dichalcogenide-based heterostructures and alloys are discussed.

8:20am **2D+AM+EM+NS-WeM2 Methoxy Formation Induced Defects on MoS₂***, *Duy Le*, University of Central Florida; *P. Evans*, University of Nebraska - Lincoln; *Z. Hooshmand*, University of Central Florida; *T.B. Rawal*, Oak Ridge National Laboratory; *L. Bartels*, University of California, Riverside; *P.A. Dowben*, University of Nebraska-Lincoln; *T.S. Rahman*, University of Central Florida

Defects are known to play an important role in determining the chemical properties of otherwise inert MoS₂ basal plane. Here we report our joint experimental and theoretical study of the adsorption and reaction of methanol on the MoS₂ basal plane to determine the factors that control system reactivity. We find that exposure of the MoS₂ basal plane to methanol leads to the formation of adsorbed methoxy and coincides with sulfur vacancy generation and that the methoxy moieties bind to molybdenum, not sulfur, while some adsorbed methanol is readily desorbed near or slightly above room temperature. Our calculations also suggest that the dissociation of methanol via O-H bond scission occurs at the defect site (sulfur vacancy), followed subsequently by formation of a weakly bound H₂S species that promptly desorbs from the surface with creation of a new sulfur vacancy, in great agreement with photoluminescence and scanning tunneling microscopy data that show clear evidence of the sulfur vacancy creation on the MoS₂ surface, after exposure to methanol [1].

[1] P. Evans et al, J. Phys. Chem. C (2018). DOI: 10.1021/acs.jpcc.8b02053

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8:40am **2D+AM+EM+NS-WeM3 Defect Engineering of 2D Materials for Advanced Electronic Devices**, *Gwan-Hyung Lee*, Yonsei University, Republic of Korea

INVITED

Two-dimensional (2D) materials have brought a great deal of excitement to nanoscience community with their attractive and unique properties. Such excellent characteristics have triggered highly active researches on 2D material-based electronic devices. New physics observed only in 2D semiconductors allow for development of new-concept devices. Assembly of 2D blocks for van der Waals heterostructures also provide a big playground for engineers and physicists to investigate unprecedented properties of 2D materials and fabricate multi-functional electronic devices. However, atomically thin 2D materials, such as graphene and transition metal dichalcogenides (TMDs), have only two surfaces at top and bottom without a bulk so that they are very sensitive to environment. In other words, properties of 2D materials can be altered easily by surface modification. In this talk, I will show novel approach to fabricate high performance 2D electronic devices by utilizing various surface treatments, such as fluorination and hydrogenation of graphene and layer-by-layer oxidation of MoS₂. When different types of defects, such as sp³ bonds and vacancies, are induced on the surface of graphene, the electrical properties of graphene can be tuned. With mild plasma treatment, MoS₂ can be oxidized layer-by-layer and monolayer MoS₂ can be fabricated from the

multilayer MoS₂. These surface treatment techniques can be used for fabrication of high performance graphene devices and MoS₂ optoelectronic devices. Defect engineering of 2D materials holds a great promise in engineering the 2D materials and fabricating advanced electronic devices of 2D materials.

9:20am **2D+AM+EM+NS-WeM5 Modeling Defects and Electron-electron Interactions in Low-dimensional Materials**, *Daniel Gunlycke, C.E. Ekuma*, U.S. Naval Research Laboratory

While each nanoscale structure in a low-dimensional material can exhibit a variety of properties, the odds are that it will be (1) sensitive to defects and (2) strongly influenced by electron-electron interactions. The ratio of defect sites to pristine sites naturally increases, as structures become smaller.

Electron localization can furthermore dramatically magnify the role of defects. In low-dimensional materials, dielectric screening is generally less effective, reducing the tendency for electronic interactions to become uniform across the sites in the materials. Despite the importance of both defects and electron-electron interactions, the properties of low-dimensional materials are often investigated in the absence of one or the other. This not only creates uncertainty over the predictions but could entirely miss certain physical phenomena, including insulator-to-metal transitions. In this presentation, we will discuss a general first-principles-based approach to explore realistic low-dimensional structures that explicitly accounts for both defects and electron-electron interactions [1]. It is based around a generalized Anderson Hamiltonian and applies density functional theory, as well as dynamical mean-field theory. We will also present electronic and optical properties of two-dimensional materials obtained using our method and discuss the potential for using defect engineering for improved solar cell performance.

[1] C. E. Ekuma, V. Dobrosavljevic, and D. Gunlycke, *Physical Review Letters* **118**, 106404 (2017)

This work was supported by the Office of Naval Research, directly and through the U.S. Naval Research Laboratory.

9:40am **2D+AM+EM+NS-WeM6 Post-Synthesis Modifications of Two-Dimensional MoSe₂ or MoTe₂ by Incorporation of Excess Metal Atoms into the Crystal Structure**, *Paula Mariel Coelho*, University of South Florida; *H. Komsa*, Aalto University, Finland; *H. Coy Diaz*, Y. Ma, University of South Florida; *A.V. Krasheninnikov*, Institute of Ion Beam Physics and Materials Research, Germany; *M. Batzill*, University of South Florida

Modifications of MoSe₂ and MoTe₂ with metallic mirror twin grain boundaries (MTB) in films grown by molecular beam epitaxy have been previously reported [1,2]. The goal of the study presented here has been to understand the formation-mechanism of MTB networks and apply this gained knowledge for controlled modifications of these 2D materials. In a combined scanning tunneling microscopy and density functional theory approach we demonstrate that excess Mo can easily diffuse into the pristine MoSe₂ or MoTe₂ (but not into MoS₂) layer and cause crystal modifications into Mo-rich twin grain boundaries. Vapor deposited Mo atoms are first incorporated by diffusing into interstitial (or split-interstitial) sites. Then, further Mo-atoms incorporate into the crystal structure to form triangular, Mo-rich grain boundary loops. Only after a critical density of MTBs is reached, Mo is no-longer absorbed by the 2D-crystal sheet and Mo-clusters start to form at the surface. The energetics and barriers for Mo-incorporation is calculated by DFT and shows that the formation of twin grain boundaries in the presence of excess Mo is favorable for MoTe₂ and MoSe₂, but not for MoS₂ - in agreement with the experiment. The achievable dense networks of MTBs constitute a new Mo-rich metallic phase that may be used for controlled electric contacts or creation of active sites in electro-catalysis [4] and thus adding new functionalities into transition metal dichalcogenide-based materials and devices. Moreover, DFT simulations suggest that this mechanism for incorporation of transition metals is not limited to Mo. This enables modification of the materials properties by heteroatom dopants and initial experimental work demonstrates the incorporation of both Ti and V. V-interstitials in MoTe₂ are predicted to have a magnetic moment and magnetic hysteresis curves indicate the induction of ferromagnetism in MoTe₂ by doping the material with less than 1% of V interstitials.

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- [1] Ma Y, et al. (2017) Metallic Twin Grain Boundaries Embedded in MoSe₂ Monolayers Grown by Molecular Beam Epitaxy. *ACS Nano* **11**, 5130-5139.
- [2] Coy Diaz H, Ma Y, Chaghi R, Batzill M. (2016) High Density of (Pseudo) Periodic Twin-Grain Boundaries in Molecular Beam Epitaxy-Grown van der Waals Heterostructure: MoTe₂/MoS₂. *Appl. Phys. Lett.* **108**, 191606.

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[3] Ma Y. et al. (2017) Angle resolved photoemission spectroscopy reveals spin charge separation in metallic MoSe₂ grain boundary. *Nat. Commun.* 8, 14231.

[4] Tomasz Kosmala et al. (2018) Metallic Twin Boundaries Boost the Hydrogen Evolution Reaction on the Basal Plane of Molybdenum Selenotellurides. *Adv. Energy Mater.* 2018, 1800031.

11:00am **2D+AM+EM+NS-WeM10 Dry Cleaning and Doping of MX₂ for Contact Engineering**, *Daniil Marinov*, IMEC, Belgium; *J. Ludwig*, IMEC & KU Leuven, Belgium; *D. Chiappe*, IMEC, Belgium; *E. Voronina*, *T. Rakhimova*, Skobel'syn Institute of Nuclear Physics, Lomonosov Moscow State University; *J.-F. de Marneffe*, *I. Asselberghs*, IMEC, Belgium; *S. De Gendt*, IMEC, KU Leuven, Belgium

Two-dimensional transition metal dichalcogenides (e.g. MoS₂, WS₂) are promising materials for a number of electronic and optoelectronic applications. Wafer-scale integration of these materials into sophisticated devices requires atomic-scale control of the processing steps such as deposition, etch, clean and doping. Reduction of the contact resistance is a major roadblock towards demonstration of high-performance devices. Significant Schottky barrier at the metal-MX₂ interface as well as surface contamination (e.g. by polymer residues) are the main factors contributing to the high contact resistance in fabricated MX₂ devices. In this study, a fully dry cleaning and doping technique is developed with a particular focus on contact engineering.

We demonstrate that a remote H₂ plasma is efficient for removal of organic residues from MX₂ surfaces. However, sulfur can be also stripped from the topmost layer by reactive H atoms. The main challenge is thus to precisely control the sulfur loss while maintaining the cleaning efficiency. At high substrate temperature, a 200 nm PMMA layer can be fully removed selectively to a single layer of WS₂ without damaging the 2D material (as confirmed by photoluminescence measurements). At low substrate temperatures significant S-vacancy formation was observed. Surface temperature is therefore the key parameter for controlling the reactivity of H atoms on WS₂.

Controllable formation of sulfur vacancies opens routes for substitutional doping. After H₂ plasma strip, WS₂ and MoS₂ samples were exposed to a flow of molecular gases (Cl₂, CO, OCS) without igniting the plasma. It is shown that Cl₂ and OCS can react with H₂ plasma treated MX₂ forming stable surface groups. Ex-situ conductive AFM measurements confirm that molecular doping prevents the loss of conductivity (that is observed after H₂ plasma alone). Moreover, OCS and Cl₂ exposure enhances electrical current injection in the material through grain boundaries and edges. The latter effect is beneficial for contact resistance reduction on MX₂.

To gain a deeper insight in the observed surface phenomena, DFT simulation of the interaction of atomic (H, Cl, F) and molecular (OCS, Cl₂) species with MX₂ surface was performed. S-vacancy creation by atomic hydrogen via formation of gas phase H₂S was observed in simulations, in qualitative agreement with the experiments. Moreover, dissociative adsorption of Cl₂ and OCS in S-vacancy sites is predicted by the DFT model.

Dr D. Marinov has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 752164.

11:20am **2D+AM+EM+NS-WeM11 Deep Learning for Atomically-Resolved Scanning Transmission Electron Microscopy Experiments on 2D Materials**, *Maxim Ziatdinov*, *S.V. Kalinin*, Oak Ridge National Laboratory

Understanding fundamental atomic-scale mechanisms behind solid state reactions and phase transformations is critical for optimizing functional properties of technologically relevant materials. Recent advances in scanning transmission electron microscopy (STEM) have allowed to visualize dynamic processes in solid state systems, induced by thermal or chemical stimuli or electron beam, on the level of individual atoms and single atomic defects. However, while there have been multiple STEM studies on materials structure evolution, the materials-specific knowledge on the kinetics and thermodynamics of these processes and atomic potentials is almost non-existent, which is mainly due to the inherent limitations of the current (semi-)manual image analysis techniques. Here we demonstrate an approach based on deep convolutional neural networks for automated analysis of dynamic STEM data from 2-dimensional materials, such as monolayer WS₂, under e-beam irradiation. Our approach allows to create a library of atomic defects, explore subtle atomic distortions around the defects of interest and map chemical transformation pathways on the atomic level. We specifically show how the developed framework can be used for extracting diffusion parameters

of sulfur vacancies in WS₂ and for studying transformation pathways for Mo-S complexes, including detailed transition probabilities.

11:40am **2D+AM+EM+NS-WeM12 Magnetic Doping in 2D MBE-grown MoSe₂/graphene Heterostructures Studied by Photoelectron Spectroscopy and Band Structure Imaging**, *Maxime Gay*, *O.J. Renault*, CEA-LETI, France; *MT. Dau*, *C. Vergnaud*, *M. Jamet*, CEA-INAC-SPINTEC, France

2D TMDCs present a unique combination of electronic and mechanical properties such as a direct bandgap, strong spin-orbit coupling and K-valley inequivalence, with an atomic-scale thickness [1]. Introducing magnetic phases into these materials opens exciting perspectives towards spin control in magnetic tunnel junctions. To date, magnetism in 2D systems was mostly studied by theoretical calculations. Within the diluted magnetic semiconductors model, transition metal atoms from the monolayer are substituted by a few Mn, Fe or Co atoms [2-4].

Our study focuses on Mn-doped-MoSe₂ monolayers, grown by molecular beam epitaxy on graphene, and characterized by photoemission techniques (XPS, kPEEM) coupled with observations at different scales (DRX, TEM). Before doping, we found that the in-plane lattices of graphene and MoSe₂ are aligned with each other and that a bandgap opens in the graphene around the Fermi level [5-6]. After Mn doping, the obtained Mn insertion is measured up to 15% by XPS. The influence of Mn doping on the band structure of MoSe₂/graphene heterostructure will be presented and discussed.

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