## 2D Materials Focus Topic
## Room 103B - Session 2D+MI-MoA
## Dopants, Defects and Interfaces in 2D Materials

**Moderators:** Philip Hofmann, Aarhus University, Denmark, Adina Luican-Mayer, University of Ottawa, Canada

1:40pm **2D+MI-MoA1 High-k Dielectrics on $WSe_2$ by Ozone-based Atomic Layer Deposition: An In-situ XPS Study**, ***Angelica Azcatl***, *R.M. Wallace,* The University of Texas at Dallas

Two-dimensional tungsten diselenide ($WSe_2$) is a layered material that have shown a promising performance when implemented in field effect transistors, exhibiting a hole mobility up to 250 $cm^2/V{\cdot}s$. [1] Furthermore, $WSe_2$ possess hole and electron effective masses smaller than those of $MoS_2$, another widely studied transition metal dichalcogenide, making $WSe_2$ a promising candidate channel material for tunnel field effect transistor applications (TFETs). For the realization of $WSe_2$ based TFETs, a high quality ultra-thin high-k dielectric film is a key requirement. However, the integration of high-k dielectrics by a conventional atomic layer deposition (ALD) process results challenging due to the dearth of nucleation sites at the $WSe_2$ surfaces. Previous studies have shown that the deposition of high-k dielectrics by water-based ALD on $WSe_2$ leads to non-uniform dielectric films. [2]

In this work, we explore the use of an alternative ALD approach to obtain uniform dielectric films on $WSe_2$ through the use of ozone as oxidant precursor. The surface chemistry of $WSe_2$ upon ozone exposure was studied by in-situ X-ray photoelectron spectroscopy to understand the reactivity between ozone and the $WSe_2$ surface. Then, the ozone-based ALD process was studied for the deposition of $Al_2O_3$ and $HfO_2$ on $WSe_2$. It was found that the interfacial chemistry and the nucleation of the dielectric have a dependence on the deposition temperature. Based on these results, a temperature window was identified at which interfacial oxide formation is avoided while a uniform dielectric film is obtained. Furthermore, the differences in reactivity and growth rate between $HfO_2$ and $Al2O_3$ will be discussed. This study helps to elucidate the reaction mechanism of the ozone based ALD process on $WSe_2$ and facilitates the implementation of the ozone based ALD approach to obtain uniform and thin dielectric films on $WSe_2$ for TFETs applications.

This work is supported in part the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation program sponsored by MARCO and DARPA, and by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST.

References

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2:00pm **2D+MI-MoA2 A Two-step Atomic Layer Etching on $MoS_2$ Realized by Remote $O_2$ Plasma**, ***Hui Zhu***, *X. Qin, L. Cheng, A. Azcatl, J. Kim, R.M. Wallace,* University of Texas at Dallas

Molybdenum disulfide ($MoS_2$), a representative layered transition metal dichalcogenide, has obtained considerable research interest in recent years, due to its promising mechanical, electronic, and photonic properties.[1,2] The mechanical exfoliation of $MoS_2$ has led to an intensive research on thin film field-effect transistors made with $MoS_2$ flakes.[3,4] However, the scalable layer engineering of $MoS_2$ flakes is still a challenge for device fabrication. In this work, a novel $MoS_2$ functionalization and layer thinning process is presented by combining the surface oxidation of $MoS_2$ with a remote $O_2$ plasma to form an amorphous $MoO_x$ layer and subsequent annealing to selectively desorb the $MoO_x$ surface layer. Exfoliated $MoS_2$ is shown to chemically oxidize in a layered manner upon exposure to the remote $O_2$ plasma. X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and atomic force microscopy (AFM) are employed to characterize the surface chemistry, structure and topography of the oxidation process, and indicates that the oxidation mainly occurs on the topmost layer without altering the chemical composition of underlying layer. After the desorption of $MoO_x$ by the annealing at 500 °C, a clean, flat and chemically undisturbed $MoS_2$ surface as evidenced from XPS, LEED, AFM and scanning tunneling microscopy (STM) characterization. This work renders promising atomic scale fabrication applications such as surface functionalization, charging engineering and atomic layer etching.

This work was supported in part by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, the Center for Low Energy Systems Technology (LEAST), one of the six SRC STARnet Centers, sponsored by MARCO and DARPA, and the US/Ireland R&D Partnership (UNITE) under the NSF award ECCS-1407765.

Reference

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[4] S. Kim, A. Konar, W.-S. Hwang, J.H. Lee, J. Lee, J. Yang, C. Jung, H. Kim, J.-B. Yoo, J.-Y. Choi, Y.W. Jin, S.Y. Lee, D. Jena, W. Choi, and K. Kim, Nat. Commun. **3**, 1011 (2012).

2:20pm **2D+MI-MoA3 Engineering the Atomic Structure of 2D Transition Metal Dichalcogenides using Electron Beam: Experiments and Simulations**, ***Arkady Krasheninnikov***, Helmholtz Zentrum Dresden-Rossendorf, Germany **INVITED**

Following isolation of a single sheet of graphene, many other 2D systems such as hexagonal BN sheets and transition metal dichalcogenides (TMD) were manufactured. Among them, TMD sheets have received particular attention, as these materials exhibit intriguing electronic and optical properties. Moreover, the properties can further be tuned by introduction of defects and impurities. Specifically, as many in-situ transmission electron microscopy experiments indicate, electron beam irradiation can give rise to phase transitions in 2D TMDs (e.g., from H to T phase), development of line defects and domains with mirror symmetry, and other structural transformations. In my talk, I will present the results [1] of our first-principles theoretical studies of the response of 2D TMDs to electron irradiation, and dwell on the characteristics of irradiation-induced defects, their evolution and agglomeration. I will also touch upon beam-mediated phase transitions in 2D TMDs. The theoretical results to be presented were obtained in close collaboration with several experimental groups, so that a detailed comparison of the theoretical data and experimental results will be given. Finally, I will further discuss defect- and impurity-mediated engineering of the electronic structure of 2D TMDs.

[1] Nature Comm. 6 (2015) 6736; ACS Nano 9 (2015) 3274; ACS Nano (2015) ACS Nano 9 (2015) 11249; Phys. Rev. B 91 (2015) 125304; Adv. Mater. 26 (2014) 2857; Phys. Rev. X 4 (2014) 031044; see http://users.aalto.fi/~ark/publist.html for complete list of publications.

3:00pm **2D+MI-MoA5 New Computational Tool for Electron Localization: Application to Low-dimensional Monolayers of h-BN and $MoS_2$**, ***Chinedu Ekuma***, NRC/NRL Postdoctoral Fellow*; V. Dobrosavljevic,* Florida State University*; D. Gunlycke,* Naval Research Laboratory

Low-dimensional monolayer materials such as graphene, MoS2, and hexagonal BN (h-BN) exhibit electronic degrees of freedom that produce exotic properties, which can be fine-tuned to engineer new functionalities for diverse applications. However, the performance of device applications depends strongly on the defect morphology and the quality of the sample. Herein, we explore the role of vacancy and/or Hubbard-type interactions for a spin-1/2 system in monolayer MoS2 and h-BN. We utilize a first-principles many-body typical medium dynamical cluster formalism, which is an effective medium approach with an intrinsic order parameter for characterizing disordered and/or interacting electron systems even in the regime of insulator-metal quantum transition (IMQT). The focus is mainly on the distribution of the local density of states, which is a key fingerprint of the optoelectronic properties of disordered systems. Within our formalism, we predict an IMQT in both systems and show that IMQT in h-BN is due to a combination of electron interactions and defects. A sulfur vacancy concentration as low as 0.01% in MoS2 is shown to lead to an IMQT in agreement with experiments.

3:20pm **2D+MI-MoA6 Effects of helium-ion beam irradiation on opto-electrical properties of multi-layers WSe2**, ***Anna Hoffman***, *P.R. Pudasaini, M.G. Stanford, P.D. Rack, D.G. Mandrus, N. Cross, J.H. Noh, M. Koehler, G. Duscher,* The University of Tennessee Knoxville*; A. Belianinov, A.J. Rondinone,* Oak Ridge National Laboratory*; I. Ivanov, T.Z. Ward,* Oak Ridge National Lab

Transition metal dichalcogenides (TMD) possess interesting properties that render them attractive for opto-electronic applications. Tuning optical and electrical properties of mono and few layer TMDs, such as tungsten diselenide ($WSe_2$), by inducing defects is an intriguing opportunity to

fabricate the next generation opto-electronic devices. Here we report the effects of helium ion beam irradiation on optical and electrical properties of few layer $WSe_2$. By controlling the ion dose irradiation**,** we can tune the concentration of point defects present on few layer $WSe_2$, thereby locally tuning the electrical resistivity of the material. Semiconductor-insulator-metal like transitions have been observed with exposure to increasing helium ion beam dose, resulting in more than a seven order change in electrical resistivity. Furthermore, by selectively exposing the ion beams at the metal-$WSe_2$ contact area, we demonstrate reduced contact resistance of the described device, thereby reducing the Schottky barrier height. This could be particularly interesting for single layer TMD devices as the Schottky contacts, formed at metal/semiconductor interfaces, have a huge influence on the TMD device's performance.

4:00pm **2D+MI-MoA8 $CO_2$ Adsorption Kinetics on Nitrogen Doped Graphene and Graphite***, **Takahiro Kondo**, R. Shibuya, D. Guo, J. Nakamura,* University of Tsukuba, Japan

Nitrogen doped carbon materials are known to have $CO_2$ adsorption property at room temperature under atmospheric pressure. Recently, we have clarified that the $CO_2$ adsorption property is created by the one of the specific type of nitrogen dopants, pyridinic-N, which has two N-C bonds based on the temperature programmed desorption (TPD) measurements of $CO_2$ from nitrogen-doped graphene nanosheets (N-GNS) and nitrogen-doped model graphite (N-HOPG) catalysts [1]. According to our scanning tunneling microscopy and spectroscopy (STM/STS) measurements of N-HOPG, the $CO_2$ adsorption sites are suggested as the carbon atoms next to the pyridinic-N, where the distinct localized states are formed at near the Fermi level in the occupied region as non-bonding $p_z$ orbital of carbon which plays a role of Lewis base site [2]. Furthermore, based on the X-ray photoelectron/absorption spectroscopy, we found that the adsorbed $CO_2$ is lying flat on the N-HOPG surface [3]. In this work, we reports the kinetics of $CO_2$ adsorption on both N-GNS and N-HOPG. From the measurements of $CO_2$-TPD, the desorption temperatures of $CO_2$ have been found to be 373 K in both N-GNS and N-HOPG, indicating that the same Lewis base sites are formed on N-GNS and N-HOPG. The adsorption energy can be roughly estimated as 100 kJ/mol from the desorption temperature. The relatively small adsorption energy can be attributed to the larger activation barrier and/or small pre-exponential (frequency) factor for $CO_2$ adsorption. The adsorption probability of $CO_2$ at 300 K has been estimated to be as 1/100 for N-HOPG. The detail kinetics as well as the selectivity for the $CO_2$ adsorption among many type of mixture gas will be presented.

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[3] H. Kiuchi, R. Shibuya, T. Kondo, J. Nakamura,et al.,Nano. Res. Lett. 11 (2016) 127.

4:20pm **2D+MI-MoA9 Electronic Structure of Metallic Twin Grain Boundaries in Monolayer $MoSe_2$***, **Matthias Batzill**,* University of South Florida

Monolayers of $MoSe_2$ grown by molecular beam epitaxy on van der Waals substrates (HOPG or $MoS_2$), may exhibit twin grain boundaries. These Se-deficient line defects have been predicted by DFT to be metallic with dispersing bands. We examine their structural and electronic properties by scanning tunneling microscopy (STM) and angle resolved photoemission spectroscopy (ARPES). A dispersing parabolic band is observed that intersects the Fermi-level indicating the metallic property of this defect. Below 235 K the line defect undergoes a Peierls, or charge density wave (CDW), transition. STM indicates a periodicity of 3 lattice constants of the CDW consistent with the Fermi-wavevector determined in ARPES. In addition, we determine that the defect behaves like an ideal one-dimensional metal. More specifically we show evidence of Tomonaga Luttinger liquid suppression of the density of states at the Fermi-level and the splitting of the band in a 'spinon' and 'holon' band, also known as spin-charge separation.

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