

2D Materials Focus Topic

Room: 212C - Session

2D+EM+MG+NS+SE+SM+SS+TF-ThM

Emergent 2D Materials

Moderator: Paul Sheehan, Naval Research Laboratory

8:00am **2D+EM+MG+NS+SE+SM+SS+TF-ThM1 CVD Growth and Characterization of 2D MoS₂, MoSe₂, MoTe₂, WS₂, WSe₂, and MoS₂-_xSe_{2x} Alloys**, David Barroso, T. Empante, A. Nguyen, V. Klee, I. Lu, E. Preciado, C. Lee, C. Huang, W. Coley, S. Naghibi, G. von Son, A. Brooks, J. Kim, L. Bartels, University of California, Riverside

Transition Metal Dichalcogenides (TMDs) have been of increasing interest over the past years due to their exciting semiconducting properties. In the bulk, TMDs possess a native indirect bandgap and transition to a direct bandgap as they approach the monolayer limit. The bandgaps range from 1.15 eV to 1.95 eV depending on composition. Using organic liquids and/or inorganic powders as precursors, CVD growth techniques have been realized for MX₂ TMDs (M = Mo, W; X = S, Se, Te) and their alloys at tunable compositions. We achieved consistent synthesis of these TMDs materials. The films can either be made homogeneous in bandgap or exhibiting a linear bandgap gradient. Characterization of the films include Raman and photoluminescence spectroscopy, as well as AFM. Device fabrication allows for transport measurements. Depending on the composition, the materials show n- or p-doping in a consistent fashion.

8:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM2 Investigation of Manganese Dioxide Nanosheets by STM and AFM**, Loranne Vernisse, S. Afsari, S.L. Shumlas, A.C. Thenuwara, D.R. Strongin, E. Borguet, Temple University

Interest in ultrathin two-dimensional nanosheets has grown exponentially thanks to their unique and diverse electronic properties. As they possess atomic or molecular thickness and infinite planar dimension, they are expected to have different properties than the bulk of the material from which they originate. This offers opportunities for the development of devices in various areas, ranging from catalysis to electronics. Using the exfoliation approach, it is possible to investigate 2D nanosheets of different materials in search of new phenomena and applications. Bearing this mind, we focused on manganese dioxide (MnO₂), and more specifically δ-MnO₂ (Birnessite). This mineral has the advantage to present a low surface enthalpy [1], which results in weak water binding. Moreover, the presence of defects, e.g., oxygen vacancies has a dopant effect on water oxidation. These properties make MnO₂ a perfect candidate as a catalytic surface for water splitting and pave the way to the design of clean and renewable energy system. Furthermore, MnO₂ can be easily exfoliated into ultrathin nanosheets owing to the layered structure of the manganese oxide precursors.

Our goal is to investigate the catalytic activity of ultrathin MnO₂ nanosheets using scanning probe microscopy techniques, especially atomic force microscopy (tapping mode) and scanning tunneling microscopy (ambient and electrochemical conditions). In this perspective, we have first improved the deposition processes and find the imaging conditions to observe MnO₂ nanosheets with an average thickness of one or two layers. We have also showed that MnO₂ single layer nanosheets exhibit an expected hexagonal atomic pattern and present some defects. We will now resolve and identify the different defects and investigate the evolution of the conductivity as a function of the defect concentration and the number of layers.

This work was supported as part of the Center for the Computational Design of Functional Layered Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0012575.

[1] M. M. Najafpour, E. Amini, M. Khatamian, R. Carpentier, S. I. Allakhverdiev, Journal of Photochemistry and Photobiology B: Biology (2014), 133, 124.

8:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM3 Two-Dimensional Early Transition Metal Carbides and Carbonitrides "MXenes": Synthesis, Properties and Applications**, Michael Naguib, Oak Ridge National Laboratory

INVITED

Ternary layered carbides and nitrides with formula of M_{n+1}AX_n (M stands for early transition metal, A for group A element, X is carbon or nitrogen, and n=1, 2, or 3), so called MAX phases, are known for their unique combinations properties of ceramics and metals. It was found recently that etching atomically thin layers of aluminum from the MAX phases results in

forming weakly bonded stacks of two-dimensional (2D) layers of early transition, coined as MXenes. The etching was carried out in fluoride contained aqueous systems. Thus MXenes surfaces are terminated with a mixture of groups including OH, O, and F. Sonicating MXenes in water results in delaminating few layers of MXenes from each other. However, to achieve a large-scale delamination, intercalation of a large compound between the layers prior to delamination is needed. MXenes were found to be a very interesting family of 2D materials since they are electrically conductors and hydrophilic. They also showed an excellent performance as electrodes for electrochemical super capacitors and Li-ion batteries. Here the recent progress in MXenes research from the synthesis to properties and applications will be covered, and in more details, large-scale delamination of MXenes will be discussed. Also, light will be shed on the performance of MXenes as electrode materials for electrochemical energy storage systems.

9:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM5 Molecular Beam Epitaxy of Large area HfSe₂(ZrSe₂)/MoSe₂ van der Waals Heterostructures on AlN(0001)/Si substrates**, Athanasios Dimoulas, P. Tsipas, E. Xenogiannopoulou, D. Tsoutsou, K.E. Aretouli, J. Marquez-Velasco, S.A. Giamini, N. Kelaidis, NCSR DEMOKRITOS, Greece

Two dimensional (2D) semiconductor van der Waals heterostructures (HS) made of group IVB (Zr, Hf) and group VIB (Mo, W) metal dichalcogenides are predicted [1] to have type II or type III band alignments mainly because of a large difference in their workfunctions and band gaps, which makes them candidates for novel 2D staggered, or broken gap tunneling field effect transistors (TFET). We use molecular beam epitaxy (MBE) to grow high quality large area HfSe₂ [2,3], ZrSe₂ [4] and MoSe₂ [5] films directly on AlN(0001)/Si(111) substrates. We confirm by RHEED and HRTEM that atomically thin layers (1-6 ML) are grown in single crystal form with a well-defined in-plane orientation on AlN. The films are continuous with smooth surface morphology (0.6 nm RMS roughness) and abrupt interfaces with no detectable reaction as verified by in-situ XPS and HRTEM. Micro Raman mapping for all layers confirms their structural integrity down to one monolayer and reveals very good uniformity on a cm-scale wafer and excellent stability of MoSe₂ over a period of at least two weeks in air. Strong room temperature PL signal of 1 ML MoSe₂ indicate high quality direct gap semiconductor in agreement with valence band structure details imaged by our in-situ ARPES [3, 5]. In a second step, MoSe₂/HfSe₂ [3] and MoSe₂/ZrSe₂ [4] HS were grown. Despite the large lattice mismatch, all layers are grown epitaxially as evidenced by RHEED with no detectable defects at the interfaces as confirmed by HRTEM suggesting good quality vdW epitaxy [6]. Using UPS the workfunctions (WF) were estimated to be 5.2, 5.5 and 5.4 eV for MoSe₂, HfSe₂ and ZrSe₂ respectively [3,4]. The last two differ substantially from theoretical values (~ 6 eV). Based on our STM and DFT calculations [3], we conclude that this difference is due to an ordered Se adlayer which lowers the HfSe₂ and ZrSe₂ WF bridging the WF gap between them and MoSe₂. As a result, small valence band offsets of 0.13 and 0.58 eV were found for the HfSe₂/MoSe₂ and ZrSe₂/MoSe₂ HS, respectively leading to type II band alignments. The availability of low cost wide-gap-AlN/Si wafers in 300 mm wafer sizes defines a manufacturable route for single crystal 2D semiconductor technology.

We acknowledge financial support from ERC Advanced Grant SMARTGATE-291260. We thank IMEC for providing the AlN/Si substrates.

[1] C. Gong et al., *APL*, **103**, 053513 (2013)

[2] R. Yue et al., *ACS Nano*, **9**, 474 (2014)

[3] K. E. Aretouli et al., *APL*, **106**, 143105 (2015)

[4] P. Tsipas et al., *Microelectron. Eng.* (2015), <http://dx.doi.org/10.1016/j.mee.2015.04.113>

[5] E. Xenogiannopoulou et al., *Nanoscale* **7**, 7896 (2015)

[6] F.S. Ohuchi et al., *JAP*, **68**, 2168 (1990)

9:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM6 Surface Investigation of WSe₂ Atomically Thin Film and Bulk Crystal Surfaces**, Rafik Addou, H. Zhu, University of Texas at Dallas, Y.-C. Lin, S.M. Eichfeld, J.A. Robinson, Penn State University, R.M. Wallace, University of Texas at Dallas

Heterogeneous fabrication of semiconducting two-dimensional layered materials presents a promising opportunity to develop highly tunable electronic and optoelectronic materials. (1-2) An example of crystalline monolayer of WSe₂ grown by chemical vapor deposition on epitaxial graphene (EG) grown from silicon carbide had been investigated at nanoscale level. The WSe₂ surface was characterized using atomic force microscopy (AFM) scanning tunneling microscopy/spectroscopy (STM/STS) and X-ray photoelectron spectroscopy (XPS). (3,4) AFM and

large STM images show high-quality WSe₂ monolayers. The sharpness of the W 4f and Se 3d core levels confirms the absence of any measurable reaction at the interface and oxide formation. The photoemission measurements of WSe₂-Graphene interface suggest p-type doping due to charge transfer (EG withdraws electrons from WSe₂) at the interface and formation of Schottky-type contact,(5) suggesting possible applications of such heterostructures as diodes and photodetectors. High-resolution STM images reveal atomic-size imperfections induced by Se vacancies and impurities. Additionally, the investigation of bulk WSe₂(0001) surface shows spatial variation attributed to the presence of two components in W 4f_{7/2} core level attributed to the presence of both n- and p-type behavior. STM images exhibit also various types of defect induced by vacancies and dopants. The STS spectra reveal two main characteristics i) expected p-type conductivity where the Fermi level located at the valence band edge, and ii) zero conductivity at negative bias explained by defect-induced band bending as reported on geological MoS₂ crystal surfaces.(4) In conclusion, the spatial variation (topography and electronic structure) is more noticeable in bulk WSe₂ grown by chemical vapor transport than in CVD thin films.

This work was supported in part by the Southwest Academy on Nanoelectronics sponsored by the Nanoelectronic Research Initiative and NIST and the Center for Low Energy Systems Technology, one of six centers supported by the STARnet phase of the Focus Center Research Program, a Semiconductor Research Corporation program sponsored by MARCO and DARPA.

- (1) Yu-Chuan Lin et al., Nano Lett., **14** (2014) 6936-6941.
- (2) Yu-Chuan Lin et al., Nature Comm. arXiv:1503.05592v1.
- (3) Robert M. Wallace, *ECS Trans.* **64** (2014) 109-116.
- (4) Rafik Addou, Luigi Colombo, and Robert M. Wallace, ACS Appl. Mater. Interfaces (Accepted, 2015).
- (5) Horacio Coy Diaz, Rafik Addou, and Matthias Batzill, *Nanoscale* **6** (2014) 1071-1078.

11:00am **2D+EM+MG+NS+SE+SM+SS+TF-ThM10 A Kinetic Study on the Adsorption of Polar (Water) and Non-Polar (Benzene) Molecules on CVD Graphene, Nilushni Sivapragasam, U. Burghaus, North Dakota State University**

The adsorption kinetics of water and benzene at ultrahigh vacuum conditions were studied. Two different chemical vapor deposited graphene samples (graphene/SiO₂ and graphene/Cu) were utilized. Different surface analytical techniques (Auger electron spectroscopy, X-ray photoelectron spectroscopy, and Raman spectroscopy) were used to characterize the surface. Subsequently, a kinetics study - to understand the adsorption of water and benzene- using thermal desorption spectroscopy (TDS) was conducted. The TDS results revealed the hydrophobicity of water on graphene. However, the adsorption kinetics of water on graphene did not mimic the bare substrate, i.e., graphene is non-transparent for water adsorption. In contrast, graphene was transparent for benzene adsorption. Furthermore, the adsorption kinetics of both, water and benzene were substrate dependent.

11:20am **2D+EM+MG+NS+SE+SM+SS+TF-ThM11 Epitaxial Ultrathin MoSe₂ Layers Grown by Molecular Beam Epitaxy, Ming-Wei Chen, M.B. Whitwick, O. Lopez-Sanchez, D. Dumcenco, A. Kis, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland**

Two-dimensional transition metal dichalcogenides (TMDs) have attracted widespread attention recently, and the focus is specifically on ultrathin layers due to the strong spin-orbit coupling and direct band-gap transition of single-layers. The unique properties of various TMDs also enable the possibilities for future optoelectronic applications. However, the synthesis of TMDs with uniform large-area and high-quality still remains challenging. While chemical vapour deposition has been demonstrated as a promising technique, the complexity of chemical precursors and the lacking of *in-situ* observation technique strongly hinder the progress.

Here, We propose to use ultra-high vacuum molecular beam epitaxy (MBE) to grow MoSe₂ ultrathin layers, down to single-layer in a controllable way. Epitaxial MoSe₂ layers were successfully grown on different crystalline substrates via van der Waals epitaxy mechanism, benefited from the weak interlayer interaction and the lacking of dangling bonds. Reflection high energy electron diffraction (RHEED) was used to *in-situ* monitor the initial growth stage and revealed a clear transition of the streaks, demonstrating the formation of MoSe₂ layer. Sharp streaks were obtained in the growth end, with the streak spacing corresponding to MoSe₂ lattice constant, and no significant strain effect was observed. In order to demonstrate the validity of van der Waals epitaxy, different crystalline substrates with lattice mismatch up to 30 % have been tested. The epitaxial layers showed a smooth and uniform surface in atomic force microscopy, and the quality was further confirmed in Raman spectrum and transmission electron

microscopy. Furthermore, photoluminescence of the single-layer MoSe₂ showing a sharp peak of ~1.58 eV at room temperature demonstrates the direct band-gap feature and indicates the potentials of photovoltaic applications. In the end, the growth of two-dimensional van der Waals heterostructures has also been addressed and the results pave way for heterostructure studies.

In summary, molecular beam epitaxy has been proved to be a reliable route to grow large-area and high-crystalline transition metal chalcogenides, and is promising to facilitate the integration of other two-dimensional materials in the future.

11:40am **2D+EM+MG+NS+SE+SM+SS+TF-ThM12 A Two-Dimensional Oxide Quasicrystal, Stefan Förster, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany, J.I. Flege, Institute of Physics, University of Bremen, Germany, K. Meinel, R. Hammer, M. Trautmann, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany, J. Falta, Institute of Solid State Physics, University of Bremen, Germany, T. Greber, Physik-Institut, University of Zürich, Switzerland, W. Widdra, Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Germany** **INVITED**

With the recent discovery of the first oxide quasicrystal (QC) aperiodicity is entering the field of two-dimensional materials [1]. Aperiodicity means that the system exhibits long-range order as expressed by sharp diffraction spots but since the ordering follows an aperiodic function the system is lacking translational symmetry. We report here on the complex growth process of the oxide QC involving a high-temperature wetting process and periodic approximant structures.

The QC is derived from BaTiO₃ thin films on a hexagonal Pt(111) substrate and exhibits a sharp twelve-fold diffraction pattern [1]. Based on scanning tunneling microscopy the aperiodic atomic structure had been resolved [1]. It is formed by surface atoms arranged in forms of squares, triangles, and rhombi with a next-neighbour distance of 0.69 nm. In addition to this dodecagonal atomic arrangement, building blocks of squares, triangles, and rhombi are also found on (2+√3) and (2+√3)² larger scales indicating the characteristic self-similarity of an ordered QC [1]. The high-resolution STM measurements allow furthermore to identify atomic flips in the structure indicating lattice excitations in the quasicrystal called phasons. Using low-energy electron microscopy (LEEM) the preparation and the growth of the QC films on top of the hexagonal Pt(111) is monitored in all details from room temperature up to about 1200 K. LEEM shows that upon high-temperature annealing large 3DBaTiO₃ islands are formed with bare Pt(111)-(1x1) in between. At temperatures above 1020 K a wetting layer spreads on the free Pt area. This wetting process can be reversed by annealing in an oxygen atmosphere. In-situ LEEM measurements show that under these conditions the QC decays into small BaTiO₃ islands. The observed interface-driven formation of a 2D QC from a perovskite oxide in contact with a hexagonal substrate is expected to be a general phenomenon.

1. S. Förster, K. Meinel, R. Hammer, M. Trautmann, and W. Widdra, *Nature* **502**, (2013) 215.

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