

## 2D Materials

### Room A216 - Session 2D+AP+EM+MI+NS+PS+TF-MoA

#### 2D Materials Growth and Fabrication

**Moderator:** Sarah Haigh, University of Manchester, UK

2:00pm **2D+AP+EM+MI+NS+PS+TF-MoA2 Synthesis of High Quality Monolayer Transition Metal Dichalcogenides using Direct Liquid Injection, Kathleen M. McCreary, E.D. Cobas, A.T. Hanbicki, M.R. Rosenberger, H.-J. Chuang, B.T. Jonker, U.S. Naval Research Laboratory**

In recent years, interest in monolayer transition metal dichalcogenides (TMDs) has rapidly increased, spurred by the possibility for integration into a variety of technologies such as photodetection, flexible electronics, and chemical sensing. While fundamental investigations can be performed on exfoliated flakes or chemical vapor deposition synthesized isolated islands, the limited size resulting from these techniques poses a significant barrier for implementation of TMDs in technological applications. To overcome these obstacles, new synthesis avenues should be explored. Here, we outline a novel technique that utilizes a commercially available Anneal Sys growth chamber equipped with direct liquid injection (DLI) heads for all precursors. The use of liquid, rather than solid precursors, provides fine control of both metal and chalcogen precursors leading to the synthesis of monolayer MoS<sub>2</sub> across cm<sup>2</sup> areas. Photoluminescence, Raman, XPS, and conductive AFM are used to evaluate DLI grown MoS<sub>2</sub>, and indicate high quality material having low defect density, with metrics comparable to or better than exfoliated and chemical vapor deposition grown MoS<sub>2</sub>.

2:20pm **2D+AP+EM+MI+NS+PS+TF-MoA3 Understanding and Controlling the Growth of 2D Materials with Non-Equilibrium Methods and in situ Diagnostics, David Geohegan, Y-C. Lin, Y. Yu, Oak Ridge National Laboratory; C. Liu, G. Duscher, University of Tennessee Knoxville; A. Strasser, University of Texas at Dallas; A.A. Puretzky, Oak Ridge National Laboratory; K. Wang, Intel Corporation, USA; M. Yoon, C.M. Rouleau, Oak Ridge National Laboratory; S. Canulescu, DTU Nanolab, Technical University of Denmark; P.D. Rack, University of Tennessee Knoxville; L. Liang, W. Zhang, H. Cai, Y. Gu, G. Eres, K. Xiao, Oak Ridge National Laboratory**

#### INVITED

Atomically-thin two-dimensional (2D) materials, including layered 2D transition metal dichalcogenide (TMD) semiconductors and their heterostructures, exhibit remarkable quantum properties that are envisioned for energy-efficient photovoltaics, flexible optoelectronics, catalysis, and quantum information science. However, significant synthesis and processing challenges currently limit the technologic development of these "all-surface" materials, including wafer-scale, bottom-up synthesis of uniform layers of crystalline 2D materials that are comparable in quality to exfoliated flakes of bulk materials. As-synthesized crystals of 2D TMDs display remarkable heterogeneity on both the atomistic level (e.g., vacancies, dopants, and edge terminations) and on the mesoscopic length scale (e.g., misoriented grains, layer orientations, and interactions with substrates and adsorbates) that can strongly influence the structure and electronic properties in 2D materials. This heterogeneity offers a serious challenge for synthesis and processing, yet offers a tremendous opportunity to tailor functionality.

Here we describe several approaches that are being developed for in situ diagnostic analysis and control of synthesis and heterogeneity. In addition to conventional vapor transport techniques, progress in laser-based approaches for 2D synthesis and modification, such as pulsed laser deposition (PLD) and pulsed laser conversion of precursors, are presented that permit control of the growth environment using time-resolved in situ diagnostics. The non-equilibrium advantages of PLD to form alloys and vertical heterojunctions are demonstrated using the tunable kinetic energy and digital nature of the process. Correlated atomic-resolution electron microscopy and atomistic theory are used to understand the size and stoichiometry of the "building blocks" deposited for synthesis and the forces that guide assembly. 2D crystals are grown directly on TEM grids within custom chambers and transmission electron microscopes where the ability to 'see' every atom in these atomically-thin crystals permits a unique opportunity to understand the forces governing their synthesis and functionality. In situ optical spectroscopy techniques are described to characterize the material's evolving structure and properties, offering the opportunity to 'close the loop' between synthesis and optoelectronic functionality of 2D materials and heterostructures.

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3:00pm **2D+AP+EM+MI+NS+PS+TF-MoA5 Area-Selective Atomic Layer Deposition of 2D WS<sub>2</sub> Nanolayers, Shashank Balasubramanyam<sup>1</sup>, Eindhoven University of Technology, The Netherlands, Noord Brabant; M.J.M. Merckx, Eindhoven University of Technology, The Netherlands; W.M.M. Kessels, Eindhoven University of Technology, The Netherlands, Netherlands; A.J.M. Mackus, Eindhoven University of Technology, The Netherlands, Nederland; A.A. Bol, Eindhoven University of Technology, The Netherlands, Netherlands**

With continued downscaling of device dimensions, ultra-thin two dimensional (2D) semiconductors like WS<sub>2</sub> are considered as promising materials for future applications in nanoelectronics. At these nanoscale regimes, device fabrication with precise patterning of critical features is challenging using current top-down processing techniques. In this regard, area-selective atomic layer deposition (AS-ALD) has emerged as a promising candidate for bottom-up processing to address the complexities of nanopatterning. Till date, AS-ALD of metals<sup>1</sup> and dielectrics<sup>2</sup> have been successfully demonstrated. However, AS-ALD of 2D materials has remained elusive. In this contribution, we demonstrate area-selective deposition of 2D WS<sub>2</sub> nanolayers by using a three-step (ABC-type) plasma-enhanced ALD process.

AS-ALD of WS<sub>2</sub> was achieved by using acetylacetone (Hacac) inhibitor (A), bis(tertbutylimido)-bis(dimethylamido)-tungsten precursor (B), and H<sub>2</sub>S plasma (C) pulses. This process resulted in immediate growth on SiO<sub>2</sub> while a significant nucleation delay was observed on Al<sub>2</sub>O<sub>3</sub>, as determined from *in-situ* spectroscopic ellipsometry (SE) and *ex-situ* X-ray photoelectron spectroscopy (XPS) measurements. The surface chemistry of this selective process was analysed by *in-situ* Fourier transform infrared spectroscopy (FTIR). The analyses revealed that the inhibitor adsorbed on the Al<sub>2</sub>O<sub>3</sub> surface, blocking precursor adsorption, while little or no inhibitor adsorption was detected on the SiO<sub>2</sub> surface where WS<sub>2</sub> was readily deposited. Furthermore, the area-selective growth was demonstrated on SiO<sub>2</sub> samples with patterned Al<sub>2</sub>O<sub>3</sub> on top. On SiO<sub>2</sub>, WS<sub>2</sub> could be deposited with angstrom-level thickness control.

To improve the crystallinity, the AS-ALD WS<sub>2</sub> films were annealed at temperatures within the thermal budget of industrial semiconductor processing (≤ 450°C). The annealed films exhibited sharp Raman peaks, which is a fingerprint of highly crystalline WS<sub>2</sub>. Furthermore, Raman line scans over the patterns showed very sharp peak intensity transitions at the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> interface which confirmed that annealing had no impact on selectivity.

To summarize, this work pioneered the combination of two key avenues in atomic-scale processing: area-selective growth and ALD of 2D materials. It is expected that the results of this work will lay the foundation for area-selective ALD of other 2D materials.

<sup>1</sup> R. Chen and S.F. Bent, *Adv. Mater.* (2006).

<sup>2</sup> A. Mamelì, M.J.M. Merckx, B. Karasulu, F. Roozeboom, W.M.M. Kessels and A.J.M. Mackus, *ACS Nano* (2017).

3:20pm **2D+AP+EM+MI+NS+PS+TF-MoA6 Growth Behavior of Hexagonal Boron Nitride on Cu-Ni Binary Alloys, Karthik Sridhara, Texas A&M University; J.A. Wollmershauser, U.S. Naval Research Laboratory; L.O. Nyakiti, Texas A&M University; B.N. Feigelson, U.S. Naval Research Laboratory**

Controlled growth of large area n-layered chemical vapor deposited (CVD) hexagonal boron nitride (h-BN) is of great interest as a tunnel dielectric, and substrate for graphene and transition metal dichalcogenides (TMDs). The CVD growth of h-BN has been demonstrated on various transition metal catalytic substrates such as Cu, Ni, Pt and Fe. Of these metal substrates, Cu and Ni are frequently used due to their relative abundance and low cost. However, h-BN growth on Cu leads to monolayer films, and growth on Ni yields thicker, substrate grain-dependent films. Therefore, a cost-effective transition metal substrate is needed that will facilitate controlled n-layered h-BN growth.

In this work, we prepare isomorphous Cu-Ni binary alloys from 10-90 wt.% Ni by creating Ni-rich (Ni-Cu) and Cu-rich (Cu-Ni) alloys using electroplating of Cu on Ni foils and Ni on Cu foils, respectively. The electroplated foils are then annealed at ~1030° C for >5 hours to create Ni-Cu and Cu-Ni alloys. The alloys are subsequently polished mechanically to create a planarized

<sup>1</sup> TFD James Harper Award Finalist

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surface suitable for h-BN growth. The surface morphology before and after polishing is assessed using a scanning electron microscope (SEM). Energy dispersive spectroscopy (EDS) characterization of the alloys confirms a designed stoichiometry at every weight percent. h-BN is grown on the alloys using atmospheric pressure chemical vapor deposition (APCVD) at 1030° C, with ammonia borane as the precursor, and H<sub>2</sub>/N<sub>2</sub> as the carrier gas flowing at ~200 sccm. Cu and Ni foils are used as control samples for this study. Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS) is used to confirm and characterize h-BN growth directly on Cu, Ni and alloy substrates. SEM is performed to evaluate the h-BN film and crystal morphology. The results indicate that the h-BN growth behavior on Ni-Cu is different than on Cu-Ni alloys. A trend of decreasing h-BN amount with reducing Ni concentration is observed on Ni-Cu alloys while no such trend is observed on Cu-Ni alloys. Additionally, there are large (~20 μm) multilayer and monolayer single crystals of h-BN on Ni-Cu alloys, and predominantly monolayer crystals and films of h-BN on Cu-Ni alloys. The difference in growth behavior is studied using x-ray photoelectron spectroscopy (XPS) and electron backscattering diffraction (EBSD), which reveal that the alloy surface composition determines the h-BN growth. This work demonstrates how Cu-Ni alloy substrate of different compositions, along with CVD growth conditions, can be used to control h-BN growth.

**4:20pm 2D+AP+EM+MI+NS+PS+TF-MoA9 Controlled Growth of Transition Metal Dichalcogenide Monolayers for Applications in Nanoelectronic and Nanophotonic Devices**, A. George, C. Neumann, D. Kaiser, R. Mupparapu, Friedrich Schiller University Jena, Germany; U. Hübner, Leibniz Institute of Photonic Technology, Jena, Germany; Z. Tang, A. Winter, I. Staude, **Andrey Turchanin**, Friedrich Schiller University Jena, Germany

Controlling the flow rate of precursors is highly essential for the growth of high quality monolayer crystals of transition metal dichalcogenides (TMDs) by chemical vapor deposition. Thus, introduction of an excess quantity of precursors affects the reproducibility of the growth process and results in the multilayer growth. Here, we demonstrate the use of Knudsen-type effusion cells for controlled delivery of sulfur precursor for the large area, high density, size-controlled and highly reproducible growth of monolayer TMD crystals [1]. The size of the grown crystals can be tuned between 10 - 200 μm. We grow MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub> and WSe<sub>2</sub> monolayer crystals as well as MoSe<sub>2</sub>-WSe<sub>2</sub> lateral heterostructures and characterize them by optical microscopy, atomic force microscopy, Raman spectroscopy, photoluminescence spectroscopy and electrical transport measurements. It has been found that they possess a high crystalline, optical and electrical quality based on their single crystalline nature. We demonstrate their implementation in novel field-effect and nanophotonic devices and discuss an influence of the point defect density on their functional characteristics [2-3]. Moreover, we present a novel synthetic route for the integration of TMDs into lateral heterostructures with other 2D materials [4].

[1] A. George et al., *J. Phys.: Mater.* 2 (2019) 016001.

[2] T. Bucher et al., *ACS Photonics* 6 (2019) 1002.

[3] R. Meyer et al., *ACS Photonics* 6 (2019) DOI: 10.1021/acsp Photonics.8b01716

[4] A. Winter et al., *Carbon* 128 (2018)106.

**4:40pm 2D+AP+EM+MI+NS+PS+TF-MoA10 Atomic Layer Deposition of BN as a Novel Capping Barrier for B<sub>2</sub>O<sub>3</sub>**, **Aparna Pilli**, J. Jones, J.A. Kelber, University of North Texas; A. LaVoie, F. Pasquale, Lam Research Corporation

The deposition of boron oxide (B<sub>2</sub>O<sub>3</sub>) films on Si and SiO<sub>2</sub> substrates by atomic layer deposition (ALD) is of growing interest in microelectronics for shallow doping of high aspect ratio transistor structures. B<sub>2</sub>O<sub>3</sub>, however, forms volatile boric acid (H<sub>3</sub>BO<sub>3</sub>) upon ambient exposure, requiring a passivation barrier, for which BN was investigated as a possible candidate. Here, we demonstrate, deposition of BN by sequential BCl/NH reactions at 600 K on two different oxidized boron substrates: (a) B O deposited using BCl/H O ALD on Si at 300 K ("B O/Si"); and (b) a boron-silicon oxide formed by sequential BCl/O reactions at 650 K on SiO followed by annealing to 1000 K ("B-Si-oxide"). X-ray photoelectron spectroscopy (XPS) data demonstrate layer-by-layer growth of BN on B<sub>2</sub>O<sub>3</sub>/Si with an average growth rate of ~1.4 Å/cycle, accompanied by some B<sub>2</sub>O<sub>3</sub> removal during the first BN cycle. In contrast, continuous BN growth was observed on B-Si-oxide without any reaction with the substrate. XPS data also indicate that the oxide/nitride heterostructures are stable upon annealing in ultrahigh vacuum to >1000 K. XPS data, after the exposure of these heterostructures to ambient, indicate a small amount of BN oxidation at the surface NH species, with no observable hydroxylation of the underlying oxide films.

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These results demonstrate that BN films, as thin as 13 Å, are potential candidates for passivating boron oxide films prepared for shallow doping applications.

**5:00pm 2D+AP+EM+MI+NS+PS+TF-MoA11 Atomic Layer Deposition of SiO<sub>2</sub> on Group VIII Metals: Towards Formation of a 2D Dielectric**, T. Suh, R. Yalisove, **James Engstrom**, Cornell University

The atomic layer deposition (ALD) of many metals, particularly Group VIII (now known as Groups 8, 9 and 10), on SiO<sub>2</sub> has been an active area of research in many fields, which include microelectronics and heterogeneous catalysis. There have been many fewer studies of the inverse—the deposition of SiO<sub>2</sub> on many of these same metals. One possible reason to explore the ALD growth of SiO<sub>2</sub> on transition metals is that it might provide a route to an atomically thick SiO<sub>2</sub> dielectric, *silicatene*. Silicatene is a 2D material that consists of a bilayer of Si<sub>2</sub>O<sub>3</sub> linked to each other by bridging oxygen atoms (giving SiO<sub>2</sub>), where there are no dangling bonds or covalent bonds to the underlying substrate on which it is grown. For example, an established route to form silicatene involves deposition of elemental Si in UHV and subsequent high-temperature annealing on various single-crystalline metal surfaces including, but not limited to, Ru(0001), Pt(111), and Pd(100). Such a process, unfortunately, is likely not compatible with high-volume manufacturing. With this motivation we embarked on a study of the plasma-assisted ALD of SiO<sub>2</sub> on e-beam deposited polycrystalline thin films of Ru, Pt and Pd using a commercial ALD reactor. We analyzed both the thin films and the starting substrates using a combination of techniques including contact angle, spectroscopic ellipsometry (SE) and X-ray photoelectron spectroscopy. Thin films of SiO<sub>2</sub> were deposited using tris(dimethylamido)silane and an oxygen plasma at a substrate temperature of 200 °C, and we examined growth for 5, 10, 20, 50 and 100 cycles. Contact angle measurements showed immediate evidence for SiO<sub>2</sub> deposition on all metal surfaces, and the contact angle decreased and remained constant and < 10° from 5 to 100 cycles of ALD. From SE we found little evidence of an incubation period, and growth was linear for the range of sample examined and the thickness deposited per cycle was remarkably constant at a value of 0.76-0.78 Å-cycle<sup>-1</sup>. Analysis of these films using angle-resolved XPS was consistent with the formation of a thin film of SiO<sub>2</sub> with uniform thickness. Having characterized the thin film thickness-ALD cycle relationship we subjected SiO<sub>2</sub> thin films with thickness of ~7-15 Å to post-deposition high-temperature anneals in oxygen furnace. Initial attempts to form silicatene with an anneal at 800 °C, produced a structure suggesting possible interfacial reaction between the SiO<sub>2</sub> and Ru, perhaps involving silicide formation. We will end our presentation with a discussion of recent work involving a more extensive examination of the post-deposition annealing step, and deposition on patterned wafers.

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