Atomic Scale Processing Mini-Symposium
Room 316 - Session AP+2D+EL+EM+PS+TF-WeA

Atomic Scale Processing to Enable 2D Materials

Moderators: Dr. Robert Bruce, IBM Research, T. J. Watson Research Center, **Prof. Dr. Cristina Satriano**, University of Catania

2:15pm **AP+2D+EL+EM+PS+TF-WeA-1 Chemistry (and Some Physics) of Atomic Layer Deposition of Two-Dimensional Metal Dichalcogenides***, **Miika Mattinen,*** University of Helsinki, Finland **INVITED**

Two-dimensional (2D) materials are of interest for a range of applications from microelectronics to sensing to energy storage and production. One of the most prominent group of 2D materials are metal dichalcogenides, some of which are semiconductors, such as the prototypical MoS_2, while others are (semi)metals such as TiS_2 and TaS_2.[1] Deposition of 2D materials with desired properties on large, often temperature-sensitive, and complexly shaped substrates is a key challenge for practical applications. Atomic layer deposition (ALD) can fulfill these requirements, but unlocking the full potential of ALD requires understanding of precursor chemistry, nucleation, substrates, and film characteristics, among other factors.[1,2]

I will discuss chemistries for deposition of a range of 2D metal dichalcogenides including MoS_2,[3] SnS_2,[4] ReS_2,[5] WS_2,[6] HfS_2 and ZrS_2[7] using thermal ALD. I will cover precursor challenges related to reactivity, thermal stability, and etching reactions. Controlling crystallinity and morphology and continuity at low thicknesses are also key challenges encountered in ALD of 2D materials. To this end, I highlight the role of substrate choice and the use of a two-step SnS_2 process where the deposited amorphous film is crystallized with mild-post deposition annealing.[4,8,9]

Plasma-enhanced ALD (PEALD) can help overcome some of the challenges encountered in thermal ALD, such as limited reactivity of many precursors. For example, few thermal chemistries are available for direct deposition on low-cost plastic substrates for flexible applications (T ≤ 150 °C). To this end, I will discuss PEALD of TMDCs including MoS_2, TiS_2, and WS_2 at record-low temperatures down to 100 °C by controlling plasma chemistry[10] I will also describe advanced ABC type processes with two plasma steps, where both the plasma chemistry (reactive radicals) and physics (low-energy ions) are used to control film growth and properties.[11]

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2:45pm **AP+2D+EL+EM+PS+TF-WeA-3 First-Principles Survey of Molybdenum ALD Precursors for MoS_2 Thin Films***, **Ian Kerby,*** *Ashlee Riedinger, Lan Li,* Boise State University

Transition metal dichalcogenides, such as molybdenum disulfide (MoS_2), are promising candidates for various semiconductor applications. A crucial requirement for these applications is the controlled and conformal deposition of a monolayer film. Chemical vapor deposition (CVD) and atomic layer deposition (ALD) techniques are key to achieving thin films at commercial scale. Towards this end, the reactions of a variety of precursor chemicals with another variety of surfaces need to be understood. A reaction between a surface and a precursor can be difficult to study in-situ and ex-situ, making computational modeling a valuable tool for addressing this challenge. The work presented here is a survey of common and proposed molybdenum precursors for use in atomic layer deposition of MoS_2 films. Our work in modeling nucleation of these precursors includes various surfaces with the primary aim of determining the role of surface morphology and chemistry during deposition. We have conducted thermodynamic surveys using density functional theory (DFT) for spontaneity of proposed reaction pathways for the precursors to interact and nucleate on the surfaces. To generate and account for the inherent variability in the amorphous substrate, we have utilized ab-initio molecular dynamics (AIMD), enabling a more comprehensive exploration of the complex energy landscape. We have also investigated the formation of reaction residues on surfaces. Our studies lay the groundwork for future kinetic analyses. The stable intermediate states identified along the reaction pathways can be used in nudged elastic band (NEB) calculations to determine the associated energy barriers during nucleation. These insights may further help guide and inform experimental efforts.

3:00pm **AP+2D+EL+EM+PS+TF-WeA-4 Thermal and Plasma-Enhanced ALD of MoS_2 using $MoO_2(THD)_2$***, **Ryan Weiland,*** University of Michigan, Ann Arbor*; Ian Campbell,* IMEC*; Pierre Morin, Benjamin Groven,* IMEC Belgium*; Ageeth Bol,* University of Michigan, Ann Arbor

Field effect transistors (FETs) are foundational components of modern electronics. For these applications, scalability is as important as device performance. Two-dimensional MoS_2 exhibits a direct band gap and enables high fidelity electrostatic control due to its reduced dimensionality and the absence of dangling-bonds at the surface. MoS_2 is therefore an ideal channel material for future FETs. Atomic layer deposition (ALD) is a promising technique for scalable, conformal, and back-end-of-line compatible MoS_2 deposition. While promising, the electrical performance of ALD grown 2D MoS_2 does not meet expectations when compared to the electrical properties of mechanically exfoliated MoS_2, due its polycrystalline nature. Polycrystalline MoS_2 contains grain boundaries that act as scattering centers, trap-rich regions, and structural discontinuities, that degrade its desirable electronic properties. In this work, ALD processes were developed using a novel molybdenum precursor, $MoO_2(THD)_2$. $MoO_2(THD)_2$ contains bulky organic ligands, which could impose steric hindrance during surface reactions, thus limiting surface chemisorption density and favoring formation of larger crystal grains.

First, $MoO_2(THD)_2$ volatility and decomposition behavior were studied by thermogravimetric analysis (TGA). TGA showed sublimation beginning at 120°C with 100% mass loss at 300°C. Next, plasma and thermal ALD processes were developed at 400°C. A mixed H_2S/Ar co-reactant was used for both plasma and thermal ALD. The effects of precursor and co-reactant dosing times, co-reactant ratios, as well as purge conditions were systematically investigated using in situ ellipsometry. The growth per ALD cycle (GPC) was measured to be 0.07 Å/cycle for the thermal recipe and 0.15 Å/cycle for the plasma process. The resulting films were characterized by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and atomic force microscopy (AFM). XPS indicates near-stoichiometric MoS_2. Raman spectra confirm MoS_2 vibrational modes and film crystallinity for both processes, while AFM reveals smooth, continuous films without out-of-plane features, with an RMS roughness of ~0.5 nm.

Overall, this work establishes $MoO_2(THD)_2$ -enabled thermal and plasma-enhanced ALD at 400 °C as a scalable route to smooth, continuous, and crystalline MoS_2 thin films. These results lay the groundwork for integrating conformal, large-grain MoS_2 channels into back-end-of-line compatible process flows, with ongoing grain-size quantification and electrical testing expected to link microstructural improvements to device performance.

3:15pm **AP+2D+EL+EM+PS+TF-WeA-5 Low Temperature Magnetized Plasmas for Processing of Two-Dimensional Materials***, **Yevgeny Raitses,*** Princeton Plasma Physics Laboratory*; Stanislav Musikhin, Yerbolat Ussenov,* Princeton University Plasma Physics Lab*; Satya Butler, Saien Xie,* Princeton University*; Nirbhav Chopra,* Princeton University Plasma Physics Lab **INVITED**

Low-temperature magnetized plasmas generated by electron beams or non-thermal electrons offer new opportunities for atomic-scale materials processing relevant to microelectronics and quantum technologies.[1-3] Operating at low pressures (0.1–10 mTorr), the applied magnetic field enables spatial separation between a high-density plasma generation region (~10^{11}–10^{12} cm^{-3}, electron energies >10 eV) and a peripheral processing region characterized by lower plasma density (<10^9 cm^{-3}) and electron temperatures (<1 eV).[4] Substrates placed in this region are primarily exposed to low-energy ion fluxes (≲ a few eV), enabling damageless processing of two-dimensional materials or processing with a controllable defect formation of such materials. However, plasma instabilities can drive anomalous cross-field transport and increase ion fluxes and energies at the surface.[5] We present experimental results on instability mitigation in ExB plasma systems[4] and demonstrate improved low-damage processing of graphene and transition metal dichalcogenides. Quantitative defect characterization in plasma-treated monolayered WS_2 films is presented and benchmarked against conventional RF inductively coupled plasma processing. A focus will also be made on the effect of vacuum conditions in the plasma reactor chamber on the defect formation

(e.g. sulfur vacancies). Applications to hydrogen and nitrogen surface passivation of diamond for quantum devices are also discussed.[2]

References

[1] D. R. Boris et al., ECS J. Solid State Sci. Technol. **4**, N5033 (2015)

[2] C. Pederson et al., Phys. Rev. Mater. **8**, 036201 (2024)

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Acknowledgement

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4:15pm **AP+2D+EL+EM+PS+TF-WeA-9 Impact of Fluorination and Oxygenation Sources on the Thermal Atomic Layer Etching of Crystalline MoS_2, *Spencer Smith,*** *Steven M. Hues, Elton Graugnard,* Boise State University

Atomic layer etching (ALE) has emerged as a transformative technique for atomic-scale processing of two-dimensional (2D) materials, including molybdenum disulfide (MoS_2), a promising semiconductor due to its high carrier mobility in monolayer form. Precise etching of MoS_2 films offers a pathway for tuning electrical and optical properties through controlled thickness. Previous studies have explored alternative fluorination and oxygenation chemistries for thermal ALE of amorphous MoS_2, including oxygen sources such as H_2O and O_3 and fluorine sources including HF/pyridine and MoF_6. In this work, we investigate the application of these alternative chemistries to the thermal ALE of MOCVD-grown and ALD-grown MoS_2 films. Preliminary work on ALE of crystalline MoS_2 indicates that etching occurs at defects and grain boundaries. This study aims to correlate etching behavior with changes in surface topography and defect density. Etching effectiveness will be characterized by atomic force microscopy, Raman spectroscopy, and photoluminescence spectroscopy. This study seeks to further expand the capabilities of ALE for precise processing of 2D materials relevant to next-generation semiconductor devices.

4:30pm **AP+2D+EL+EM+PS+TF-WeA-10 Atomic Layer Etching of Tungsten Disulfide in O2/Ar and BCl3/Ar Remote Plasmas*, Jeremy J. Mettler,*** University of Houston*; Jaehong (Russell) Kwon, David. B. Graves,* Princeton University*; Vincent M. Donnelly,* University of Houston

Transition-metal dichalcogenides (TMDs) are a class of 2D materials consisting of covalently bonded sheets. Multi-layers are held together by cross-plane van der Waals forces. While these materials hold promise in future semiconductor applications, processes for manufacturing using TMDs are in the early stages of development. One challenge is obtaining uniform, monolayer growth of TMD films over large areas. Chemical vapor deposition results in the formation of multilayer islands. Etching of TMD films will also be required, if for no other reason than to thin multilayers to single layers. Atomic layer etching (ALE) is likely to be called upon for etching steps. TMDs are easily damaged by high temperature and energetic species bombardment, making thermal or plasma-assisted etching challenging. We have explored ALE of WS_2, a promising TMD 2D material. A remote plasma supplied reactive radicals. A switchable magnetic field allow low energetic ion bombardment to be turned on or off while having little effect on radical density. ALE of WS_2 was achieved in a two-step process. Vacuum-transfer x-ray photoelectron spectroscopy (XPS) was used to characterize the chemical composition and thickness of the remaining film at various stages in the process. Sulfur-terminated multilayer films of WS_2 were exposed to O atoms downstream of an Ar/O_2 inductively coupled plasma (ICP). Without ion bombardment thermal O atoms removed S from the surface and formed a tungsten oxide layer 1-2 monolayers thick, with a composition of roughly WO_4. These results agree favorably with parallel molecular dynamics simulations. In the presence of low energy ions (~15 eV) at a flux of ~3 x $10^{15}cm^{-2}$, the etching rate increased several-fold and the W-oxide stoichiometry was not changed. The Ar/O_2 plasma was followed by Ar/BCl_3 plasma to selectively etch the tungsten oxide layer relative to the underlying WS_2. This step required low energy ion bombardment to remove the WO_4 film and expose the next WS_2 layer. A detailed analysis of the film at various stages in the ALE process was carried out by using the high-resolution W(4f), S(2p), B(1s) and Cl(2p) in the film as well as the Si(2p) from the underlying substrate and O(1s) in the WS_2 film and underlying interfacial native oxide layer on Si. A complete picture of the stoichiometry of the film during ALE was obtained and will be presented.

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Fusion Energy Sciences and Basic Energy Sciences, as part of the Extreme Lithography & Materials Innovation Center (ELMIC), a Microelectronics Science Research Center (MSRC), under contract No. DEAC02-09CH11466.

4:45pm **AP+2D+EL+EM+PS+TF-WeA-11 Investigation of Layer-by-Layer Etching of MoS_2 by Atomic Oxygen and XeF_2*, Sei-won Chung,*** *Daniel Cho, Jane Chang,* University of California, Los Angeles

As semiconductor devices continuously scale down, the demand for channel materials of field effect transistors (FETs) with high mobility at low dimensions has increased. 2D transition metal dichalcogenides (TMDs) have gained interest due to relatively consistent mobility at 5 nm of body thickness compared to conventional silicon channel. However, non-uniform large area synthesis has been a challenge in integration. To improve device performance, non-uniform adlayers should be removed layer-by-layer to realize a uniform and large-area TMD films.

To investigate layer-by-layer etching of MoS_2, thermochemical analysis suggests thermodynamic feasibility of using oxygen and fluorine chemistries for MoS_2 etching. Individual and synergistic effects of Ar^+, O radical (produced by a coaxial waveguide microwave source) and XeF_2 (3Torr) were studied in the molecular beam where each species can be independently controlled in flux and energy. The as-received MoS_2 has S/Mo and Si/Mo ratios of 1.6 and 1.0. Neither O nor XeF_2 spontaneously reacted with the as-received MoS_2. Ar^+ ion beam (200V, 0.5mA, 10s) was used to remove surface contamination prior to etching, resulting S/Mo and Si/Mo ratios of 0.94 and 0.18 respectively. Following in-situ Ar^+ ion beam cleaning, O radical was shown to oxidize MoS_2 decreasing S/Mo from 0.94 to 0.46, while XeF_2 removes MoS_2 increasing Si/Mo from 0.18 to 7.1. It showed surface fluorination (~3%), corresponding to formation of $MoOF_x$ and CF_x.

Finally, the sequential process consisting of Ar^+ ion bombardment, O radical introduction, and XeF_2 vapor exposure (0.5T, 10 pulses) was applied which could enable surface activation, self-limiting oxidation and removal of modified layer by forming oxyfluorides. After XeF_2, O atomic composition decreased and S atomic composition increased indicating removal of MoO_3 with surface fluorination (~3%) of MoF_x and $MoOF_x$. Increasing number of pulses to 20 increases S/Mo from 1.1 to 1.4 while reducing the MoO_3 content. This research reveals the individual and combination effects of Ar^+ ion beam, O radicals and XeF_2 on MoS_2 etching and potentially applied to investigating mechanism of layer-by-layer etching of MoS_2.

This research is supported by the U.S. DOE, Office of Science, as part of the ELMIC MSRC through the Plasma-enabled 2D Materials project at PPPL, under contract No. DEAC02-09CH11466.

5:00pm **AP+2D+EL+EM+PS+TF-WeA-12 Width Reduction and Edge Smoothing of 2D MoS_2 Nanoribbons by Lateral Thermal Atomic Layer Etching*, Janine Wyand,*** University of Colorado at Boulder*; Tara Pena, Eric Pop,* Stanford University*; Steven George,* University of Colorado at Boulder

Atomic layer etching (ALE) of 2D MoS_2 nanoribbons is important for the fabrication of MoS_2 channel transistors. E-beam lithography and conventional dry etching processes face problems when etching MoS_2 films. These disadvantages include delamination for nanoribbon widths < 25 nm and inability to control line edge roughness. ALE methods may bypass these limitations and produce narrower width MoS_2 channels with smoother edges that may have better electrostatic control and on/off switching.

Narrowing the width of 2D MoS_2 nanoribbons requires lateral etching in the 2D plane. Our earlier work on the thermal ALE of 2D MoS_2 showed that sequential exposures of O_3 and $SOCl_2$ produced lateral etching by either “outside-in” or “inside-out” mechanisms. In this study, the “outside-in” lateral etching of 2D MoS_2 crystalline nanoribbons was utilized to reduce the widths of 2D MoS_2 nanoribbons. O_3 (ozone) was used for MoS_2 oxidation to MoO_3 and $SOCl_2$ (thionyl chloride) was used for the volatilization of MoO_3 as MoO_2Cl_2. The studies were performed using high quality 2D MoS_2 nanoribbons on silicon coupons. The MoS_2 nanoribbons were prepared from monolayer 2D MoS_2 films using e-beam lithography and dry etching.

The etching of the 2D MoS_2 nanoribbons was examined by atomic force microscopy (AFM) at 150°C. The lateral etching could be quantified by returning to the same nanoribbon after various numbers of etching cycles

and measuring the nanoribbon width using AFM. **Figure 1** shows that the width of the nanoribbons decreases progressively versus number of etching cycles. The AFM images indicate that the etching cycles also smooth the nanoribbon line edge roughness.

The AFM images were consistent with lateral etching at the edges of the 2D MoS_2 nanoribbons. The AFM measurements determined that the 2D lateral etching rate was ~3.9 Å per etching cycle at 150°C as displayed in **Figure 2**. This lateral etch rate represents ~1 MoS_2 units removed per etching cycle at the step edge of the 2D MoS_2 crystalline domains. Additional AFM measurements revealed that nanoribbon widths < 25 nm were possible using this thermal ALE process.

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