Emerging Materials and Processes
Room Tampa Bay Salons 1-2 - Session EM2-TuA

ALD for 2D Materials

Moderators: Hanmei Choi, Samsung Electronics, **Christophe Detavernier**, Ghent University, Belgium

4:00pm **EM2-TuA-11 ALD Synthesis of Transition Metal Phosphides**, ***Raul Zazpe***, *Jhonatan Rodriguez-Pereira, Jaroslav Charvot, Milan Klikar, Filip Bures, Jan Macak,* University of Pardubice, Czechia

The ever-increasing global energy demand together with the environmental issue originated from the use of fossil fuel, has triggered an intense search for sustainable and clean energy alternatives, such us hydrogen energy, biomass and solar energy among others. In this context, a pivotal key to deliver sustainable and superior energy systems lies on the rational design and development of high-quality and cost-effective catalyst offering enhanced stability, activity and selectivity. Consequently, intense efforts have been devoted in the search and synthesis of new catalyst materials to replace the scarce and expensive traditional noble metals (e.g. Pt, Pd, Au and Ru) for energy conversion and energy storage applications.

Among the recently explored novel catalyst materials, metal phosphides (MPs) have emerged in recent years, attracting significant attention thanks to their intriguing properties [1]. In particular, transition metal phosphides (TMPs) exhibit striking properties. The moderately strong M−P bonds lend outstanding mechanical properties, high thermal stability and outstanding chemical resistance to chemical attack and oxidation in acidic and alkaline solutions. Additionally, Co, Ni, Mo-based phosphides demonstrated excellent catalytic and bifunctional properties towards water splitting as both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [2,3].

Herein, we present the synthesis of TMPs by thermal Atomic Layer Deposition (ALD), including cobalt and titanium phosphide [4], based on the use of different transition metal precursors combined with in-house synthesized P precursors. The physical and chemical properties of the resulting TMPs thin films were extensively characterized by different methods, including atomic force microscopy, X-ray photoelectron spectroscopy and X-Ray diffraction. The presentation will introduce and describe the synthesis of the TMPs and the corresponding characterization toward diverse applications.

[1] Z. Pu, T. Liu, I. S. Amiinu, R. Cheng, P. Wang, C. Zhang, P. Ji, W. Hu, J. Liu, S. Mu, *Adv. Funct. Mater.*, **30**, 2004009 (2020).

[2]C.C. Weng, J.T. Ren, Z.Y. Yuan, *ChemSusChem*, **13**, 3357-3375 (2020).

[3] C.-J. Huang, H.-M. Xu, T.-Y. Shuai, Q.-N. Zhan, Z.-J. Zhang, G.-R. Li, *Applied Catalysis B: Environmental*, **325**, 122313 (2023).

[4] R. Zazpe, J. Charvot, J. Rodriguez-Pereira, L. Hromádko,M. Kurka,K. Baishya,H. Sopha, F.Bureš, and J. M. Macak, *Nanoscale*,**17**, 12406-12415, (2025).

4:15pm **EM2-TuA-12 A Novel Chemistry toward the Atomic Layer Deposition of MoS2 thin films for Heterojunction Photocatalysis**, ***Annmary Anto***, *Alexey Ganzhinov, Anjan Deb, Kenichiro Mizohata, Mykhailo Chundak, Mikko Ritala, Matti Putkonen,* University of Helsinki, Finland

Among the transition-metal dichalcogenides (TMDCs), MoS2 is the most extensively studied two-dimensional (2D) material owing to its excellent opto-electronic properties and the semiconducting nature. It is one of the most promising visible-light photocatalytic materials, recognized for potential in electronics to improve device efficiency and enhanced charge retention in energy storage. To harness these applications,researchers have explored a wide range of synthesis techniques,from top-down to bottom-up methods including exfoliation, thermal synthesis, and vapor phase deposition for the development of 2D-MoS2. However, in comparison with any other approach, atomic layer deposition (ALD) offers higher reproducibility and reliability due to its growth insensitivity towards excessive precursors.

Herein, we report a new thermal ALD process to fabricate MoS2 thin films up toa growth rate of 1.5 A°/Cycle at 200–300°C,using Mo(II) acetate dimer and H2S as Mo and S sources, respectively. As-deposited films on Si (100) with native oxide are found to be crystalline in nature, though rough, consisting of flake-like grains, and the X-ray diffraction (XRD) measurements confirmed the presence of (002) plane oriented 2H-MoS2 phase.The ALD-MoS2 films exhibited S/Mo ratio of 2.1–1.3, according to the deposition parameters, with O, C, and H impurities (<10 at.% in total) measured by time-of-flight elastic recoil detection analysis (ToF-ERDA). X-ray photoelectron spectroscopy (XPS) confirmed the formation of chemical bonding from MoS2. The crystalline nature of the films improved with a decline in conductivity along with the temperature. A transformation from in-plane to out-of-plane orientation of the two-dimensional layers as a function of number of cycles was observed.

Optical analysis indicated an energy gap ranging from 2.1 to 1.5 eV for films deposited on soda lime glass, increasing with higher S content. In addition, photocatalytic activity was demonstrated using solar sensitized methylene blue degradation. Further results on the development of heterojunction photocatalyst by integrating the developed MoS2 thin films with suitable oxides will be presented.

4:30pm **EM2-TuA-13 The Role of Plasma Conditions on the Properties of MoS_2 Films Grown by PEALD Using H_2 plasma and Di-tert-butyl Disulfide**, ***Paula Arellano***, University of Michigan, Ann Arbor*; Ian E. Campbell,* IMEC*; Aashi Gupta, Pavlina Metaxa, Vasiliki Nousia, Ray Duffy,* Tyndall National Institute, University College Cork, Ireland*; Ageeth A. Bol,* University of Michigan, Ann Arbor

The presence of plasma species during PEALD enables film growth at temperatures lower than those usually required for thermal ALD and other deposition methods. We recently demonstrated a low-temperature PEALD process for molybdenum disulfide (MoS_2), based on $Mo(tBuN)_2(NMe_2)_2$ and di-tert-butyl disulfide (TBDS) in combination with H_2 plasma as the coreactant. TBDS is a safer and less hazardous alternative to hydrogen sulfide (H_2S) for PEALD of MoS_2 thin films.[1] Raman spectroscopy however showed that MoS_2 films grown using the TBDS process exhibit higher defect densities than those grown using a H_2S PEALD process. In this work, we study the effect of the H_2 plasma conditions on the quality of the resulting MoS_2 films and demonstrate how careful optimization of the plasma conditions (plasma power, plasma feed gas composition, pressure and flow rate) can reduce the plasma-induced damage and improve the crystallinity of the MoS_2.

The use of H_2 plasma during the TBDS process is thought to remove the Mo precursor ligands and reduce chemisorbed Mo^{6+} species to Mo^{4+} before the TBDS exposure. After characterizing the effects of H_2 plasma parameters on PEALD MoS_x, the defects-to-intensity ratio in the Raman spectra ranged from ~2.7 to ~1.0, revealing a substantial decrease in defect density for PEALD recipes with low power, high pressure H_2 plasma exposure. However, the surface roughness (R_q) of 6 nm thick MoS_x films, as measured by AFM, increased under these conditions due to out-of-plane fin growth.

To reduce fin formation in MoS_x films, we incorporated a low flow rate, low power, long duration Ar plasma step in our ALD cycle scheme. As a result, the R_q of ~6 nm thick MoS_x films decreased from 2.09 nm to 0.435 nm, while the defects-to-intensity ratio in the Raman spectra increased from 1.6 to 2.0. Thus, a tradeoff between fin growth and higher structural disorder exists when tuning the parameters of H_2 and Ar plasma exposures.

Finally, the electrical properties of MoS_x films with varying crystallinity and morphology will be compared. This work shows that the incorporation and optimization of plasma steps during PEALD of MoS_2 can further improve the quality of the resulting MoS_2, enabling the use of safer sulfur chemistry while achieving scalable, damage-controlled thin-film growth.

(1) Campbell, I. E.; et al. *Chem. Mater.* **2025**, *37* (4), 1478–1490.

4:45pm **EM2-TuA-14 ALD-Induced Doping Effect in 2D MoS_2 FETs: Roles of Oxidant Chemistry and MoS_2 Quality**, ***Minjong Lee***, *Thi Thu Huong Chu, Inhong Hwang, Doo San Kim, Dushyant Narayan, Dan Le, Soham Shirodkar, Jiyoung Kim,* University of Texas at Dallas

As scaling pushes device platforms toward three-dimensional (3D) integration, ultrathin gate dielectrics must be deposited directly on two-dimensional (2D) channels [1]. Atomic layer deposition (ALD) is a leading method for enabling such gate-stack integration. However, the surface chemistry required for nucleation can also unintentionally modulate carrier density in the 2D channel [2]. In MoS_2 field-effect transistors (FETs), this deposition-induced “atomic-layer doping (ALDo)” can alter key device metrics in ways that are often difficult to separate from nucleation-driven interfacial reactions and trap generation.

This work presents an *in-situ*/*ex-situ* characterization framework to track MoS_2 device evolution throughout the ALD gate-dielectric process. *In-situ*, we monitor electrical changes associated with individual ALD half-cycles to capture the initial deposition-induced shifts. *Ex-situ*, we quantify net performance evolution after dielectrics growth to few-nanometer thicknesses. Across ALD cycles, the most pronounced performance changes

occur in the initial-growth regime, indicating that interfacial reactions dominate the ALDo response. MoS_2 film quality further sets the baseline sensitivity to ALDo. Exfoliated single-crystal MoS_2 exhibits minimal performance perturbation following few-nanometer gate-dielectric formation, whereas chemical vapor deposition (CVD)-grown MoS_2 shows clear degradation, implicating stronger interfacial reactions. Oxidant chemistry further modulates device behavior: O_3 tends to induce more severe surface perturbation, while H_2O_2 can promote S-O bond formation and yield qualitatively improved electrical characteristics.

Building on these insights, we outline practical routes toward quasi-single-crystal-like behavior in CVD-grown MoS_2 films by scaling channel length to confine transport within a single grain with suppressing excessive oxidation in the defect states. This study demonstrates a device-level diagnostic that accelerates mechanism-guided optimization of ALD gate stacks on 2D channels. The presentation will cover the measurement methodology, integration strategies, and prototype workflows for engineering ALDo, with implications for reliable 2D-FET operation toward future 3D-integrated electronics.

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[1] K. S. Kim et al. Nat. Nanotechnol. 19, 895–906 (2024).

[2] S.-E. Yu et al. ALD/ALE Conference (2025).

5:00pm **EM2-TuA-15 Processing MoS_2 and WS_2 using ALD and Patterning on 8-Inch Wafers**, ***Nils Boysen***, *Leon Doman, Rahel-Manuela Maas, Anjana Devi,* Fraunhofer IMS, Germany

Processing 2D materials using various deposition and patterning methods on larger wafer scales is a major challenge in developing next-generation devices, such as ultra-sensitive sensors for photo-, gas-, and biosensing. In particular, ultra-thin films of layered 2D materials such as MoS_2 and WS_2 exhibit promising properties for sensing applications due to their semiconducting nature, high surface-to-volume ratio, and intrinsic selectivity for different analytes. One of the main challenges to date is the deposition and subsequent patterning of such delicate layers on larger areas, such as 8" silicon wafers. Because of their high sensitivity to oxidation and delamination, standard patterning routes cannot be readily adopted. Typically, MoS_2 and WS_2 are exfoliated and transferred to the target substrates. However, this top-down route adds a significant number of processing steps and is not easily scalable to larger scales. Furthermore, the layers must be on the uppermost layers of the device stack to be accessible for sensing applications, which rules out thick protective capping layers typically used in such stacks.

To overcome these challenges, we introduce a feasible approach to deposit MoS_2 and WS_2 via bottom-up ALD as the uppermost layer on pre-structured metallization layers. Subsequently, we enable patterning of MoS_2 and WS_2 via lithography and ion-beam etching, using in situ ALD Al_2O_3 capping layers that can be later porosified for sensing applications. Accordingly, we developed an ALD process at low deposition temperatures of 100 °C for MoS_2, and at higher deposition temperatures of 350 °C for WS_2 using $[Mo(NMe_2)_4]$, $[W(NtBu)_2(NMe_2)_2]$, and H_2S as precursors (Fig. 1). This resulted in ultra-thin layers that were amorphous for MoS_2 and crystalline with a 2D layered structure for WS_2. Subsequent patterning of the MoS_2 and WS_2 by photolithography and ion-beam etching (IBE) with the help of in-situ deposited Al_2O_3 capping layers prevented delamination and severe oxidation of the amorphous and crystalline layers, as proven by Raman spectroscopy and transmission electron microscopy (TEM) (Fig. 2) of the resulting structures. The integrity of the layers was preserved after porosifying the Al_2O_3 capping layer in boiling water, enabling sensing applications (Fig 3). In the case of patterned MoS_2, selective gas-sensing of relevant gases such as NO_2, NH_3, and H_2S could thus be achieved.

In summary, the new and promising developments in bottom-up 2D material processing via ALD have enabled us to realize sensing structures at a larger wafer scale and will facilitate the adoption of these materials for other device applications.

5:15pm **EM2-TuA-16 Exploiting Atomic Layer Deposition for Contacts to Semiconductors**, ***Suzanne Mohney***, *Chan-Wen Chiu, M. Saifur Rahman, Ryan Wang, Sree Palaniappan,* Pennsylvania State University

Electrical contacts to semiconductors in transistors and other electronic devices are typically formed by physical vapor deposition techniques such as sputtering or evaporation. Atomic layer deposition (ALD), however, offers unique opportunities for engineering electrical contacts across a wide range of semiconductor families. For example, we previously used an ultrathin ALD-grown dielectric to reduce the metal/semiconductor Schottky barrier height and achieve low-resistance ohmic contacts to silicon [1]. We also compared thermal ALD [2] and remote–plasma ALD [3] processes for depositing conductive films on gallium nitride, producing high-quality Schottky diodes. Most recently, we employed ALD for hole injection in source-drain contacts to the two–dimensional (2D) semiconductor WSe_2, motivated by the promise of 2D semiconductors for device scaling and integration with silicon platforms. Achieving low contact resistance for *p*–channel 2D field effect transistors is often challenging, but we obtained a contact resistance of 10 kΩ·μm [4] using semimetallic TiS_x contacts with MoO_x capping. The TiS_x was grown by thermal ALD from tetrakis(dimethylamido)titanium and hydrogen sulfide at 100 °C. Because contact yield was impacted by nonuniform coverage of TiS_x on WSe_2, we are investigating remote-plasma ALD processes to improve nucleation of TiS_2 on WSe_2 and are examining the interplay between deposition parameters and device performance. The presentation will conclude with an analysis of the outlook for using ALD for contacts to semiconductors across technologies. The authors acknowledge support from the National Science Foundation (NSF) through ECCS 2227346. WSe_2 epilayers were provided by the Penn State 2D Crystal Consortium–Materials Innovation Platform (2DCC-MIP) under NSF DMR 2039351.Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

[1] Agrawal et al., Applied Physics Letters 104, 112101 (2014)

[2] Clark et al., Journal of Vacuum Science & Technology A 43, 032402 (2025)

[3] Molina et al., Applied Physics Letters 119, 102102 (2021)

[4] Rahman et al., RSC Advances 15, 45417 (2026)

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