Tuesday Morning, March 31, 2026

Area Selective Deposition
Room ETEC Atrium - Session ASD2-TuM
ASD of 2D and Al_2O_3

Moderators: Robert Clark, TEL, Gregory Parsons, North Carolina State University

10:45am **ASD2-TuM-10 Selective Heterogeneous Integration of TMDs via Single-Source Spin-on Chemistry*, Zakaria Al Balushi,*** University of California at Berkeley **INVITED**

Two-dimensional (2D) semiconductors offer a compelling pathway beyond the scaling and energy-efficiency limits of silicon nanoelectronics, yet their manufacturable and heterogeneous integration remains a central challenge. Here we report a wafer-scale, conformal growth strategy for continuous mono- to few-layer transition-metal dichalcogenides (TMDs) based on spin-coating single-source dithioacid-derived organosulfur precursors. This chemistry provides an intrinsically high chalcogen-to-metal ratio that enables direct growth and integration without external chalcogen delivery. Upon mild annealing, the precursor undergoes conversion through metastable sulfur-rich intermediates, enabling uniform nucleation, thickness control, and continuous layer formation on both planar substrates and high-aspect-ratio topographies. In situ spectroscopy, molecular dynamics simulations, and density functional theory collectively elucidate the reaction pathway linking precursor chemistry to crystallization kinetics, grain size evolution, and defect formation. The resulting TMD films exhibit optical quality comparable to exfoliated monolayers, as evidenced by strong photoluminescence and well-resolved Raman modes, and enable selective-area growth as well as sub-5 nm high-k dielectric integration without seed layers. Devices fabricated from these films demonstrate robust field-effect transistor performance and vertically integrated memristors exhibiting nanosecond-scale spike-timing-dependent plasticity. By decoupling TMD growth from gas-phase chalcogen chemistry, this intrinsically high-chalcogen single-source approach provides a general and scalable route to the direct heterogeneous integration of layered metal sulfides, establishing a practical foundation for manufacturable 2D electronic and neuromorphic systems.

11:15am **ASD2-TuM-12 Self-Aligned Lateral MoS_2-TiS_2 Heterostructures via Area-Selective ALD of TiS_2 on CVD MoS_2*, Lucas G. Cooper,*** University of Michigan*; Pawan Kumar, Pierre Morin, Benjamin Groven,* IMEC, Belgium*; Ian E. Campbell,* IMEC*; Ageeth A. Bol,* University of Michigan

High contact resistance is one of the main factors holding back the performance of TMD based FETs. One proposed solution to lowering contact resistance is through TMD edge contacts. Edge contacts are theorized to outperform top contacts due to more efficient charge carrier injection, aided by the conductivity anisotropy in TMDs. ALD is an ideal method to deposit these contacts, as it is based on self-limiting surface reactions and has the potential for area selective deposition. Area selectivity would allow for preferential deposition on the edge of the TMD channel rather than the basal plane to form self-aligned lateral heterostructures, allowing for precise contact placement and removing the need for excess lithography steps.

A thermal ALD process for TiS_2 was developed using tetrakis(dimethylamido) titanium(IV) and Ar/H_2S as the reactants. This process is shown to be inherently area selective, as we realize the formation of lateral heterostructures of CVD synthesized MoS_2 and ALD synthesized TiS_2. Beginning with an unclosed monolayer of MoS_2, we are able to selectively deposit on the exposed areas of substrate while avoiding depositions on the basal plane. This selectivity is shown through spectroscopic ellipsometry, AFM, Auger spectroscopy, and SEM.

We also demonstrate the ability to tune the resistivity, stoichiometry, and crystallinity of TiS_2 through altering deposition parameters. At a deposition temperature of 100°C, the material has a stoichiometry of $Ti_{0.96}S_2$ and a resistivity of . When increasing the deposition temperature to 150°C the film becomes more metal rich with a Ti:S ratio of $Ti_{1.07}S_2$. The more Ti-rich film has a resistivity of , lower than that of bulk TiS_2. We also show that the stoichiometry of the films has a direct impact on the crystallinity. By undersaturating the Ti precursor the excess metal can be modulated, resulting in more crystalline material. The impact of oxidation on the resistivity of TiS_2 is also explored. It was found that films with excess Ti maintain a low resistivity after exposure to ambient conditions, while films with little to no excess Ti have large increases in resistivity, showing an alternate mode of conductance based on stoichiometry.

In this research we demonstrate the ability to form lateral heterostructures through an inherently selective ALD process for TiS_2. We are also able to tune the properties of TiS_2 by modifying deposition temperature, and precursor dose time. This provides a clear path for the formation of TMD based FETs with TiS_2 contacts, and the ability to optimize these contacts through altering deposition parameters.

11:30am **ASD2-TuM-13 Laser-Activated Area-Selective Atomic and Molecular Layer Deposition on 2D Materials*, Aleksei Emelianov,*** New York University*; Kamila Mentel,* University of Jyväskylä, Finland*; Amr Ghazy, Joona Pekkanen,* Aalto University, Finland*; Yu-Han Wang, Andreas Johansson,* University of Jyväskylä, Finland*; Maarit Karppinen,* Aalto University, Finland*; Mika Pettersson,* University of Jyväskylä, Finland

Developing controlled, defect-free, and spatially selective deposition of molecular and hybrid thin films on two-dimensional (2D) materials remains a key challenge due to their surface inertness and lack of reactive sites for atomic and molecular layer deposition precursors [1]. Here, we demonstrate area-selective atomic/molecular layer deposition (AS-ALD/MLD) of europium-organic (Eu-BDC) thin films on graphene and other 2D materials using direct femtosecond laser two-photon oxidation (TPO).

Ultrafast laser irradiation locally introduces oxygen-containing functional groups on nanomaterials [2,3], enabling selective precursor chemisorption and nucleation in predefined regions. The laser dose defines the density of nucleation sites and allows precise control over Eu-BDC film thickness, uniformity, and selectivity with sub-μm spatial resolution. By optimizing deposition parameters and the graphene transfer process, we achieve over 90% selectivity and high film homogeneity for Eu-organic films up to 11 nm [4]. The choice of transfer polymer strongly affects selectivity. Working with freshly grown 2D materials reduces surface contamination and allows for clean interfaces with deposited thin films.

The resulting graphene/Eu-BDC heterostructures exhibit strong photoluminescence upon 532 nm excitation, including emission features not observed on Si/SiO2 substrates. Photoluminescence quenching and shortened lifetimes indicate efficient energy and charge transfer at the graphene/Eu-organic interface, while electrical measurements reveal a controllable and reversible n-type doping of graphene induced by the Eu-organic layer. Annealing during growth restores graphene close to its initial electronic state.

The same TPO-assisted activation strategy is also demonstrated on other 2D materials, including MoS2 and WS2, where laser-induced oxides and defects act as active nucleation sites. This work establishes a scalable, maskless approach for AS-ALD/MLD on chemically inert 2D surfaces and enables patterned integration of metal-organic thin films with tunable optical and electronic properties.

References:
[1] K. Kim et al., Nat. Commun. 2014, 5, 4781, DOI: 10.1038/ncomms5781
[2] J. Aumanen et al., Nanoscale 2015, 7, 2851-2855, DOI: 10.1039/c4nr05207b
[3] A. Emelianov et al., Adv. Mater. 2024, 36, 2402907, DOI: 10.1002/adma.202402907
[4] A. Emelianov et al. ChemRxiv 2025 (under review), DOI: 10.26434/chemrxiv-2024-81qv0-v2

11:45am **ASD2-TuM-14 Acetic Acid-Modulated Al2O3 Atomic Layer Deposition on Monolayer MoS2 for Controlled Nucleation*, Hwan Oh,*** Brookhaven National Laboratory, Republic of Korea*; Qin Wu,* Brookhaven National Laboratory, China*; Suji Park,* Brookhaven National Laboratory, Republic of Korea*; Kim Kisslinger,* Brookhaven National Laboratory*; Chang-Yong Nam,* Brookhaven National Laboratory, Republic of Korea

Ultrathin dielectric integration on 2D semiconductors is essential for continued device scaling in beyond-Si nanoelectronics. However, the chemical inertness of van der Waals basal planes remains a fundamental obstacle to uniform atomic layer deposition (ALD) nucleation and growth. Here, we present an acetic acid (HAc)-modulated ALD strategy implemented through an ABC-type sequence (HAc/TMA/H_2O) to regulate Al_2O_3 nucleation on monolayer (1L) MoS_2. In situ quartz crystal microbalance (QCM) measurements reveal robust HAc adsorption on Al_2O_3 and suppressed subsequent Al_2O_3 growth on passivated surfaces. Applied to 1L MoS_2, this inhibitory pathway mitigates 3D island coarsening and redirects precursor adsorption toward uncovered basal planes, enabling nearly continuous ultrathin (~1.5 nm) Al_2O_3 films with improved uniformity, as confirmed by atomic force microscopy (AFM) and cross-sectional scanning transmission electron microscopy (STEM) coupled with energy-dispersive X-ray spectroscopy (EDS). Density functional theory calculations further provide atomistic insight, showing the energetic preference of HAc for Al_2O_3 over 1L MoS_2 and attenuated TMA adsorption on HAc-passivated sites. Overall, this small molecule inhibitor-modulated pathway establishes a generalizable route to controlled ALD nucleation for reliable dielectric integration across diverse ALD chemistries and 2D materials, offering opportunities for next-generation nanoelectronics device fabrication.

12:00pm **ASD2-TuM-15 Aluminum Precursor Impact on Selectivity for Dielectric on Metal Selective Deposition***, **Florian Preischel,*** Leibniz Institute for Solid State and Materials Research, Germany*; Jiyeon Kim, Dennis Hausmann, Alexander Fox,* LAM Research*; Harish Parala, Anjana Devi,* Leibniz Institute for Solid State and Materials Research, Germany

Selective deposition of a dielectric film, such as aluminum oxide (Al_2O_3) or hafnium oxide (HfO_2), on metal or metal-oxide surfaces (also known as DoM), without growth on silicon dielectric surfaces, has numerous applications in semiconductor manufacturing. These include the selective deposition of hard masks to enhance dry etch performance. Typical growth surfaces include W, Mo, and Co, with or without their native oxides, whereas inhibited surfaces are usually doped (C, N)- silicon oxides.Typically, this is achieved using small-molecule inhibitors (SMI), such as dimethylaminotrimethylsilane (DMATMS), which selectively chemisorb onto silicon oxide surfaces but not onto metal/metal oxide surfaces. The DMATMS-modified SiO_2 surface exhibits a significant (~2 nm) nucleation delay relative to the uninhibited surface from AlO_x deposition from DMAI/H_2O. The goal of this work is to evaluate alternate aluminum precursors and determine their impact on selectivity. Methods for assessing the selectivity failure modes are also examined in the context of screening alternative precursors.

Evaluation of selectivity performance is primarily conducted using microscopy techniques such as TEM and SEM, spectroscopic methods such as FTIR and ellipsometry, and physical techniques such as water contact angle (WCA) measurement. These methods typically do not provide information about the surface state of the inhibited surface prior to continuous film formation. We use vapor-phase decomposition mass spectrometry (VPD-MS), which can determine effective film thicknesses of <0.0001 nm. Compared with conventional methods, which require>0.1 nm of continuous film for detection, VPD-MS enables the determination and quantification of events during the initial nucleation period. The selectivity and nucleation behavior of several aluminum precursors are evaluated using ellipsometry, WCA, and VPD-MS, in comparison to the baseline process with DMAI/H_2O. In addition, the failure mode mechanisms revealed by this metrology are presented.

12:15pm **ASD2-TuM-16 Area-Selective Atomic Layer Deposition of Al_2O_3 Film Using Bulky Al Precursor $AlMe_2$(iPr-AMD)***, **Akihiro Nishida**, Atsushi Yamashita, Takuya Takahashi, Masaki Enzu, Ryota Fukushima, Tomoharu Yoshino,* ADEKA CORPORATION, Japan

Trimethylaluminum (TMA) loses its selectivity within a short time, which is problematic because it exhibits excessively high reactivity toward H2O and surface sites, an extremely small molecular size, and low thermal stability even if a passivation layer is used. To achieve high selectivity, precise control of the reaction between the precursor and the substrate surface and minimization of unwanted reactivity are essential. Therefore, to achieve excellent area-selective atomic layer deposition (AS-ALD), we thoroughly investigated novel precursors and found that AlMe2(iPr-AMD) is an outstanding candidate that exhibits good thermal properties and high volatility. We carried out AS-ALD of an Al2O3 film on Cu and native oxide Si substrates using AlMe2(iPr-AMD) with H2O as a coreactant. For the dielectric-on-dielectric selective growth process, 1-dodecanethiol (DDT) was used as a self-assembled monolayer (SAM) passivant on the Cu surface. The Al2O3 film growth was inhibited on the Cu surface as a result of passivation by the SAM during deposition of a >100 Å-thick Al2O3 film onto the native oxide layer of a Si surface at 150 °C using AlMe2(iPr-AMD). This result substantially exceed thtat achieved with Dimethylaluminum isopropoxide (DMAI) under identical conditions. For the dielectric-on-metal selective growth process, n-octadecyltrichlorosilane (ODTS) was used as a SAM passivant on the dielectric surface. In contrast to the DDT SAM, the ODTS SAM showed restrained Al2O3 film growth on the Si surface and achieved Al2O3 film growth only on the Cu surface. These results indicate that the AlMe2(iPr-AMD) precursor adsorption is strongly inhibited by SAM passivation as a result of its bulky structure, reduced Lewis acidity, and lower level of reactivity compared to TMA. In addition, results from AS-ALD processes employing not only DDT and ODTS but also additional passivation molecules will also be discussed.

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