Nanostructure Synthesis and Fabrication
Room Hall 3E - Session NS-TuA

2D Nanomaterials by ALD (Including Transition Metal Dichalcogenides)

Moderators: Dr. Jeffrey W. Elam, Argonne National Laboratory, Dr. Chang-Yong Nam, Brookhaven National Laboratory

1:30pm **NS-TuA-1 Combining ALD Infiltration and Pressure-Assisted Sintering for Fabrication of Electrically Conductive Nanocomposites**, ***Benjamin Greenberg***, *K. Anderson, A. Jacobs, A. Cendejas, E. Patterson, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Electrically conductive nanocomposites are critical components of electrocatalytic devices, thermoelectric generators, flexible electronics, and many other existing or envisioned technologies. In a disordered conductor/insulator composite with nanoscale domains, high and stable conductivity is achievable provided that (1) the conductive phase does not oxidize or otherwise degrade, (2) the conductive domains percolate—i.e., form continuous networks that traverse the material, and (3) the conductive channels within the network have sufficient cross-sectional area.

In this work, we explore a nascent nanocomposite fabrication strategy based on ALD infiltration and pressure-assisted sintering of nanoparticle compacts. Specifically, we use ALD with long static precursor doses (>10 min) to deposit Al-doped ZnO inside ~2-mm-thick porous compacts of ceramic (e.g., ZrO_2, SiO_2) nanoparticles with ~100 nm diameter, and then we use environmentally controlled pressure-assisted sintering (EC-PAS)[1] at ~2 GPa and 700**–**1000 °C to remove residual porosity and form fully dense composites. Each ZnO:Al ALD supercycle consists of 15 diethylzinc/water cycles and 1 trimethylaluminum/water cycle, and the deposition temperature is 160 °C except during diethylzinc doses, during which it is lowered to 120 °C to prevent metallic Zn deposition. In principle, this ALD/sintering approach (1) prevents degradation of the ZnO:Al by sealing off the bulk of the composite from the atmosphere, (2) forms percolating ZnO:Al via complete and conformal ALD infiltration, and (3) allows control over the conductive channel cross-sectional area via the number of ALD cycles. In practice, we indeed observe complete infiltration: scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS) of a representative sample reveals Zn throughout the depth of the composite. Electrical resistivity, however, is surprisingly high: despite deposition of enough ZnO:Al to yield channels with ~7 nm thickness—predicted to enable metallic (band-like) conductivity[2]—the composite resistivity is $>10^5$ Ω-cm. Employing SEM-EDS, x-ray diffraction (XRD), electrical measurements, and other characterization techniques, we investigate potential causes of this high resistivity, which include dopant deactivation and disruption of conductive channels during sintering. We also explore several routes toward achieving metallic conductivity, including *in situ* post-ALD ozone cleaning and optimization of sintering parameters to maintain the doping level and continuity of the ZnO:Al.

1. H. Ryou *et al.*, *ACS Nano* **12**, 3083 (2018).
2. T. Chen *et al.*, *Nat. Mater.* **15**, 299 (2016).

1:45pm **NS-TuA-2 ALD on Particulate Materials: A Comprehensive Review of Processes, Support Materials and Applications**, ***Peter M. Piechulla***, *M. Chen,* Delft University of Technology, Netherlands*; R. Puurunen,* Aalto University, Finland*; J. van Ommen, A. Goulas,* Delft University of Technology, Netherlands

Through its course of technology development, atomic layer deposition (ALD) has mostly been applied to flat substrates, typically for applications in the semiconductor industry. Albeit, the inherent processing and coating characteristics of ALD, namely its ability to conformally deposit materials in high aspect ratio geometries with sub-nanometer thickness control, are also attractive for the coating of particulate matter. Application areas requiring substances with large specific surface area, such as heterogeneous catalysis, adsorbents and separations, or highly precise thickness control, such as energy conversion and storage (batteries) or pharmaceuticals are strong drivers for research activities in the realm of ALD on particulate materials. Several scientific review articles on aspects of this field have been published, particularly over the last decade; however, the scope of them is mostly limited to either a processing or an applications point of view.

In this contribution, we present a comprehensive review of the developments in the field of ALD on particles, covering approximately 700 articles in a data-driven rather than anecdotal manner. We target an audience of researchers from the conventional ALD domain who wish to extend their scope of activities to particular media, as well as researchers involved in particle technology who consider ALD as a tool to enhance their technical applications (see supplementary PDF for applications already using ALD on particles). Challenges related to the processibility of powders/particles are addressed by the presentation of an overview of the different reactor engineering approaches implemented. Furthermore, the substrate materials (supports) used are systematically categorized and evaluated with respect to their geometric characteristics (shape and size) but also their surface functionalities. Finally, we cover the range of coating materials attainable and the respective processing conditions; in this way, we also address the similarities and deviations of conventional ALD and ALD on particles in terms of growth characteristics. Through exploring the current state of the art, this review aims to provide both inspiration for new applications of ALD, and a starting point for researchers in particle-based technologies in search of ALD processes for any given application.

2:00pm **NS-TuA-3 Tuning $MoCl_5$ Self-Etching Effect for Deposition of 2D MoS_2 on 300mm Wafer by Thermal ALD**, ***Angelica Azcatl-Zacatzi***, *N. Vu, D. Lee, T. Ngo, R. Kanjolia,* Merck KGaA, Darmstadt, Germany

Crystalline 2D MoS_2 is a semiconductor material with potential application in the next generation of logic and memory devices. The adoption of MoS_2 for future high-volume manufacturing requires the synthesis of high quality and large area 2D material on substrates of interest. The control of MoS_2 film properties such as film uniformity, thickness, and crystallinity are critical for this objective. In the literature, reports of large area deposition of 2D materials include deposition techniques such as chemical vapor deposition (CVD) and atomic layer deposition (ALD). [1] Among the proposed chemical systems for ALD, the $MoCl_5$-based process has produced crystalline 2D MoS_2 [2,3].

In this work, we investigate the $MoCl_5$ and H_2S system to deposit MoS_2 by thermal ALD. The effect of the $MoCl_5$ etch component will be discussed. It was found that self-etching of $MoCl_5$ can be tuned by process parameters such as precursor pulse time and deposition temperature. The deposition window for 300mm SiO_2/Si wafer substrates will be presented. X-ray fluorescence, Raman spectroscopy, atomic force microscopy, X-ray photoelectron spectroscopy, and transmission electron microscopy were used to characterize the ALD-grown MoS_2. The resulting 2D MoS_2 films exhibit low surface roughness, high uniformity across the wafer, and high level of crystallinity [Fig. 1]. The demonstration of large area and high quality 2D MoS_2 produced by the $MoCl_5$-based process provides a path toward the implementation of ALD processes for deposition of large area 2D MoS_2.

[1] Y. Liu and F. Gu, *Nanoscale Adv.*, 2021, 3, 2117.

[2] Y. Huang, et al., *Thin Solid Films*, 2017, 624, 101–105.

[3] Kim, Y., Song, JG., Park, Y. et al., *Scientific Reports*, Vol. 6, 2016, 18754.

2:15pm **NS-TuA-4 Low-Temperature ALD of SbO_x/Sb_2Te_3 Multilayers with Boosted Thermoelectric Performance**, *J. Yang,* IFW Dresden, Germany*; S. Mukherjee,* Jio Institute, India*;* ***Sebastian Lehmann***, *K. Nielsch,* IFW Dresden, Germany

Nanoscale superlattice (SL) structures have proven to be effective in enhancing the thermoelectric (TE) properties of thin films. Herein, the main phase of antimony telluride (Sb_2Te_3) thin film with sub-nanometer layers of antimony oxide (SbO_x) is synthesized via atomic layer deposition (ALD) at a low temperature of 80 °C. The SL structure is tailored by varying the cycle numbers of Sb_2Te_3 and SbO_x. A remarkable power factor of 520.8 μW m^{-1} K^{-2} is attained at room temperature when the cycle ratio of SbO_x and Sb_2Te_3 is set at 1:1000 (i.e., SO:ST = 1:1000), corresponding to the highest electrical conductivity of 339.8 S cm^{-1}. The results indicate that at the largest thickness, corresponding to ten ALD cycles, the SbOx layers act as a potential barrier that filters out the low-energy charge carriers from contributing to the overall electrical conductivity. In addition to enhancing the scattering of the mid-to-long-wavelength at the SbO_x/Sb_2Te_3 interface, the presence of the SbO_x sub-layer induces the confinement effect and strain forces in the Sb_2Te_3 thin film, thereby effectively enhancing the Seebeck coefficient and reducing the thermal conductivity. These findings provide a new perspective on the design of SL-structured TE materials and devices.

2:30pm **NS-TuA-5 Enhancing Electrical Properties of 2D WS_2 Grown by ABC PE-ALD with Ion Energy Dose Control**, ***Cindy Lam***, *E. Kessels, B. Macco,* Eindhoven University of Technology, Netherlands

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) are currently on the roadmap of major semiconductor companies as beyond-Si channel material in field-effect transistors (FETs).[1] While 2D TMDCs are typically grown by chemical vapor deposition (CVD), the addition of post-processing steps such as the transfer to specific substrates limits and complicates the overall fabrication process. Accordingly, atomic layer deposition (ALD) is considered a promising method for the direct growth of TMDCs on planar substrates and 3D structures at low temperatures suitable for back-end-of-line (BEOL) processes and its potential for area-selective deposition.[2] However, the mobility of ALD-grown 2D TMDCs substantially falls behind that of CVD-grown 2D TMDCs often due to smaller grain sizes.

In this work, we present that tuning our developed plasma-enhanced ALD (PE-ALD) process which utilizes an inductively coupled Ar plasma (ICP) as an additional C step (AB → ABC) [3],[4] can modify the material properties of WS_2 during film growth. The comparison between WS_2 films grown using the conventional AB and ABC process showcases a significant decrease of the resistivity by four orders of magnitude from ~10^8 to ~10^4 μΩ-cm due to the improvement of the grain morphology (Fig. 1, SI). While the AB WS_2 film was too resistive for Hall analysis, the ABC WS_2 film exhibited a strong *p*-type character with a Hall mobility μ_H of 0.78 cm^2/Vs, which is only one order of magnitude lower than CVD-grown TMDCs. Our results demonstrate effectively improving the electrical properties of WS_2 using the ABC PE-ALD process. Finally, preliminary results on the ion energy $E_{i,flux,}$ and ion flux Γ_i as function of various plasma processing conditions such as the Ar plasma pressure *p* and plasma exposure time t_p during PE-ALD (Fig. 2 and 3, SI) provide insight into how the material properties can be affected and further tailor them to our specific needs by the use of plasma.

[1] Chung, C.C. *et al*. International Electron Devices Meeting, IEDM, *3451–3454*. (2022)
[2] Balasubramanyam, S. *et al*. *ACS Materials, 2***(5)**, *511-518.* (2020)
[3] Balasubramanyam, S. *et al. ACS Appl. Mater. and Interfaces, 12***(3),** 3873-3885. (2020)
[4] Mattinen, M. *et al. ACS Appl. Mater. and Interfaces, 15, 35565-35579.* (2023)

2:45pm **NS-TuA-6 Impact of ALD Precursor Choice on Nucleation and Growth of Dielectrics on 2D Materials**, *A. Shearer, J. Ko, K. Saraswat, E. Pop,* ***Stacey Bent***, Stanford University

2D semiconducting materials have received attention for their potential to facilitate further downscaling of microelectronic devices by overcoming the physical shortcomings of silicon. Due to their inherent atomic thinness and lack of surface dangling bonds, 2D materials can be well-controlled by a gate while preserving the carrier mobility, leading to excellent current switching characteristics, even at the scaling limit. However, the lack of dangling bonds and reactive sites on the surface makes it difficult to deposit a gate oxide by ALD, often leading to sparse nucleation and the growth of films that are low density, defective, rough, and filled with pinholes.

In this work, we employ physisorption-assisted ALD processes and study the nucleation and quality of the deposited dielectrics. We deposit Al_2O_3 on monolayer MoS_2 using a series of ALD precursors in order to investigate the impact of the ALD precursor on nucleation. The precursors utilized in this study are dimethyl aluminum isopropoxide (DMAI), trimethylaluminum (TMA), triethylaluminum (TEA), and a novel Al_2O_3 precursor, triisobutylaluminum (TIBA). Using scanning electron microscopy (SEM), we study film nucleation and continuity as a function of ALD precursor, cycle number, and temperature. The results show that the precursor used in the ALD process dramatically impacts coverage and growth. With the best performing precursor, we observe full coverage of MoS_2 after just 3 nm of material is deposited. After optimizing the temperature and purge time of each process to maximize nucleation, we fabricate transistor devices in which the deposited Al_2O_3 serves as a seed layer for high-k HfO_2 deposition to create the gate stack. Using x-ray photoelectron spectroscopy (XPS) and electrical testing, we investigate the character of the dielectric/MoS_2 interface. While all three alkyl precursors lead to seed layers and dielectrics that produce functioning devices, the devices with the best performance are obtained by the precursor that achieves a more uniform, smoother, and denser film, which we attribute to improved nucleation and growth properties. This improved deposition also permits the most thinning of the seed layer. The devices fabricated using the best precursor and improved dielectric show excellent performance such as good on/off ratios (10^6), small device-to-device variation (ΔV_T < 1 V), and low effective oxide thickness (~1 nm).This work provides useful insights into how ALD precursors can be designed to improve the quality of dielectrics on 2D materials, potentially improving the viability of 2D materials for wide ranging applications.

3:00pm **NS-TuA-7 Noble Metal Nanoparticles Functionalized 2D Transition Metal Dichalcogenides by Atomic Layer Deposition for Enhanced Sensing Properties Toward Amino Acids**, ***Jisang Yoo***, *S. Lee, J. Kim, I. Sohn, S. Jung, H. Kim,* Yonsei University, Korea

Due to their large surface-to-volume ratio and stability in aqueous environments, two-dimensional (2D) transition metal dichalcogenides (TMDCs) have recently emerged as promising candidates for biosensing materials.[1] Among various biomolecules, amino acids (AAs) have been proposed as one of key biomarkers of human body status and diseases.[2] The changes in the physiological levels of AAs in biological fluids (e.g., blood, urine) can be used to determine not only nutritional status, but also specific diseases including cancer and diabetes. Therefore, monitoring and detection of AA profile can be of significant importance in potential early diagnostics. Recently, the possibility of detecting AA molecules through direct charge transfer after adsorption on the TMDC surface has been theoretically investigated. Particularly, noble metal (NM) nanoparticles (NPs), such as Au and Pt, functionalization has been proposed to improve the adsorption of biomolecules including AAs, thereby significantly enhancing the sensing properties.[3,4] However, experimental demonstration of NM NP-functionalized 2D TMDCs for AA sensing is still lacking.

In this study, we aim to develop a biomolecular sensor to detect AAs using Pt NP-functionalized monolayer (ML) WS_2 (Pt-WS_2) channel. Using chemical vapor deposition process, we synthesized grain boundary(GB)-rich ML WS_2, where GBs can serve as active sites for surface functionalization. By facilitating atomic layer deposition (ALD), Pt NPs were selectively functionalized on GBs of WS_2. By optimizing the process parameters such as precursor flux, purge time and cycle number, the size and distribution of Pt NPs were controlled precisely. Following the interaction with AA molecules, n-type charge transfer from AA to Pt-WS_2 was confirmed by Raman spectroscopy, photoluminescence and X-ray photoelectron spectroscopy. For measuring the sensing properties, Pt-WS_2 based biosensors were fabricated through lithography process. Enhanced sensitivity and a lower limit of detection compared to pristine WS---$_2$ were observed. Additionally, concentration-dependent linearity curve was established. Finally, enhanced selectivity towards other interfering biomolecules (e.g. dopamine and uric acid) was demonstrated through comparative measurements. This study could be contributed to both basic and expanded research on early disease diagnosis through biomarker monitoring.

Reference

[1] *Materials Science and Engineering: C* 70 (2017): 1095-1106.

[2] *Amino Acids* 48 (2016): 1339-1345.

[3] *Computational and Theoretical Chemistry* 1118 (2017): 115-122.

[4] *ACS Applied Electronic Materials* (2023).

3:15pm **NS-TuA-8 Surface Modification of Polyolefin Nonwoven Fabric Through Atomic Layer Deposition (ALD) and Molecular Layer Deposition (MLD)**, ***Jae Seok Lee***, *S. Song, B. Choi,* Korea University, Republic of Korea

Polyolefins, renowned for their exceptional mechanical and chemical properties and low density, find extensive applications across diverse fields such as architecture, biomedicine, manufacturing, and environmental sectors. Efforts to supplant conventional metal and ceramic materials with polyolefins are underway by fabricating three-dimensional structural configurations. Nonetheless, the inherent hydrophobicity of polyolefins poses constraints on their applications. Surface modification strategies emerge as viable solutions to address these limitations. While plasma treatment is the conventional approach for surface modification, its propensity to induce polymer damage and its transient effects warrant exploring alternative methodologies.

Surface modification of polyolefin fibers via Atomic Layer Deposition (ALD) and Molecular Layer Deposition (MLD) at low temperatures offers a non-destructive means to achieve targeted surface properties. This method enables the deposition of conformal thin films onto intricate three-dimensional structures without compromising the integrity of the fibers. Additionally, the surface modification persists until degradation or delamination of the thin film occurs. Depending on the nature of the deposited thin film, the production of specialized polyolefin fiber materials becomes feasible.

This investigation examines surface property alterations of polyolefin nonwoven fabric by applying Al_2O_3 and polyurea films. Trimethylaluminum (TMA) and H_2O serve as precursors for Al_2O_3 deposition, while 1,4-phenylene diisocyanate (PDIC) and ethylenediamine (ED) are utilized for polyurea formation. The study involves a comparative analysis between intrinsic nonwoven fiber surfaces and those coated with three distinct types of thin films: Al_2O_3, polyurea, and a layer-by-layer (LBL) configuration employing Al_2O_3 and polyurea layers. The wettability of each fiber is quantified through measurement of the water contact angle (WCA). Furthermore, for polyurea, the adjustability of wettability is explored by varying the terminating groups between isocyanate and amine through alteration of the final precursor. Additionally, the differences in roughness among the fibers, as measured by atomic force microscopy (AFM), provide insights into adjusting surface properties through thin film composition.

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