Nanostructure Synthesis and Fabrication
Room Grand Ballroom E-G - Session NS-WeA

2D Nanomaterials by ALD (including Transition Metal Dichalcogenides)

Moderators: Annelies Delabie, IMEC, Harm Knoops, Eindhoven University of Technology

1:30pm **NS-WeA-1 Modified ALD Process to Achieve Crystalline MoS_2Thin Films*, Li Zeng*, *C MacIsaac, J Shi, N Ricky, I Oh, S Bent,* Stanford University

Stimulated by the discovery of two-dimensional (2D) graphene, 2D transition metal chalcogenides (TMDs) are attracting much attention owing to their similar layered structure and graphene-analogous properties. Numerous research efforts are under way to explore their wide ranging potential applications, including but not limited to optoelectronics, electrochemical cells, and energy harvesting devices. However, challenges still remain regarding the development of controllable growth methods for TMDs with large-scale conformality at moderate synthesis temperature. For the past half-decade, there has been an increasing trend toward resolving these issues by employing atomic layer deposition (ALD) due to its inherent growth characteristics. Over a dozen metal sulfide/selenide materials have been explored by ALD and yielded promising results, such as wafer-scale uniformity and compatibility with electrical devices and photochemical cells.

Despite the promise brought by the ALD approach, further effort is needed because the TMD films that are deposited at lower, more desirable temperatures often show non-ideal stoichiometry and require high-temperature post-annealing to improve the film quality. Using the notable molybdenum disulfide (MoS_2) as an example, one of the known processes uses $Mo(CO)_6$ as the Mo ALD precursor and H_2S as the co-reactant with an ALD window of 150 ~ 175 °C. Results from both literature and our laboratory show that the S to Mo ratio is close to 1.5:1—relatively far from the ideal value of 2:1—with the presence of undesired MoO_x species. We performed an investigation into fundamental mechanisms of this ALD process. Based on that understanding, a new methodology was developed that produces higher-quality MoS_2 films from these same precursors. These results were achieved by elevating the growth temperature and shifting the typical ALD process into a pulsed chemical vapor deposition regime. A series of MoS_2 films were synthesized on Si substrates by this modified process, resulting in controllable linear growth behavior, a S-to-Mo ratio of 2-to-1, and strong characteristic MoS_2 Raman peaks. Additional characterization tools, including grazing incident X-ray diffraction (GIXRD), X-ray reflectivity (XRR) and atomic force microscopy (AFM), were also used to examine the film crystallinity, density and surface morphology. By characterizing the material as a function of process conditions, we are able to elucidate fundamental mechanisms and key kinetic factors behind the MoS_2 growth process using $Mo(CO)_6$ and H_2S. This study may help shed some light on future design of ALD processes for 2D TMDs.

1:45pm **NS-WeA-2 Nucleation and Growth of ALD MoS_2 Films on Dielectric Surfaces***, E Graugnard,* Boise State University*; **Steven Letourneau**, A Mane, J Elam,* Argonne National Laboratory

Molybdenum disulfide (MoS_2) is a promising two-dimensional (2D) semiconductor. Similar to graphite, MoS_2 has a layered structure comprising weak van der Waals bonding between layers, and strong covalent bonding within layers. The weak secondary bonding allows for isolation of these 2D materials to a single layer, like graphene. While bulk MoS_2 is an indirect band gap semiconductor with a band gap of ~1.3 eV, monolayer MoS_2 exhibits a direct band gap of ~1.8 eV, making it an attractive candidate for replacing Si in electronic devices. Atomic layer deposition (ALD) has been used previously to grow MoS_2 films using a variety of molybdenum and sulfur precursors. However, many of these precursors are solids at room temperature, require high temperature vapor transport, and have the potential to result in carbon incorporation. Recently, MoS_2 ALD using molybdenum hexafluoride (MoF_6), a high vapor pressure liquid at room temperature, and hydrogen sulfide (H_2S) has been demonstrated. For device applications, the ALD MoS_2 must be integrated with dielectrics. While the nucleation of MoS_2 during chemical vapor deposition (CVD) is understood, the nucleation of MoS_2 ALD using MoF_6 and H_2S on dielectric surfaces has yet to be explored. Unlike films grown by high temperature CVD, ALD MoS_2 is amorphous and must be annealed to crystallize the film. In this study, we utilized *in situ* quartz crystal microbalance (QCM) and Fourier transform infrared (FTIR) spectroscopy measurements to investigate the first few cycles of MoS_2 ALD on Al_2O_3 and HfO_2 surfaces prepared *in situ* by ALD. Self-limiting growth of MoS_2 was observed on a wide range of dielectric surfaces including alumina, and hafnia. The MoS_2 nucleation was found to depend strongly on the substrate. These studies provide insight into the low-temperature ALD of MoS_2 and provide guidance for the integration of MoS_2 and other ALD TMDC films.

2:00pm **NS-WeA-3 Plasma-Enhanced Atomic Layer Deposition of Transition Metal Dichalcogenides: From 2D Monolayers to 3D Vertical Nanofins***, **Ageeth Bol**,* Eindhoven University of Technology, Netherlands **INVITED**

2D materials have been the focus of intense research in the last decade due to their unique physical and chemical properties. The synthesis of crystalline transition metal dichalcogenide nanolayers (TMDs) using atomic layer deposition (ALD) has attracted a lot of interest lately as ALD offers monolayer thickness control, scalability and low temperature growth (T ≤450°C). However, ALD grown films have been reported in literature to exhibit a high density of out-of-plane 3D structures in addition to 2D horizontal layers[1, 2]. The presence of such 3D structures are a benefit for catalysis, as it increases the density of active edge sites. However, these structures can hinder charge transport and consequently raise film resistivity, which hampers both electrocatalysis and nanoelectronic applications. Hence it is essential to understand and control 3D structure formation during atomic layer deposition of TMDs.

In this presentation I will first focus on the formation mechanism of 3D structures. Extensive high resolution transmission electron microscopy studies in our lab have shown that grain boundaries and the grain orientation of adjacent 2D crystals play an important role in 3D structure formation.

Then I will demonstrate that we can control both the shape and density of the 3D structures during plasma-enhanced ALD. The shape of the 3D structures can be varied by modulating the plasma gas composition (H_2/H_2S ratio) in the co-reactant step. This has a direct influence on the number a catalytic edge sites in WS_2 films. The density of 3D structures can be suppressed by introducing a novel three step (ABC) ALD process, which involves the addition of an extra Ar and/or H_2 plasma step (step C) to the conventional AB-type ALD process. This reduces the 3D structure density and consequently reduces the resistivity of the TMD film by an order of magnitude.

Our work showcases the versatility of plasma-enhanced ALD for the controlled synthesis of transition metal dichalcogenide nanolayers, which can enable applications in both the nanoelectronics and catalysis field.

[1] A. Sharma *et al*, *Nanoscale* **10,** 8615–8627 (2018).

[2] T.A. Ho *et al*, *Chem. Mater.* **29**, 7604-7614 (2017).

2:30pm **NS-WeA-5 Atomic Layer Deposition of Emerging 2D Semiconductors HfS_2 and ZrS_2***, **Miika Mattinen**, G Popov, M Vehkamäki, P King, K Mizohata, P Jalkanen, J Räisänen, M Leskelä, M Ritala,* University of Helsinki, Finland

Two-dimensional (2D) materials are being studied intensively due to their unique electronic, optical, and catalytic properties and the wide range of potential applications arising from their layered crystal structures. However, the majority of studies focus on only a few of the large group 2D materials, such as the semimetallic graphene, insulating h-BN, and semiconducting MoS_2. Semiconducting 2D materials, in particular, are promising for electronics applications including field-effect transistors (FETs), photodetectors, and sensors. HfS_2 and ZrS_2, members of the transition metal dichalcogenide (TMDC) group, are indirect band gap semiconductors that have recently emerged as potential alternatives to MoS_2 and other 2D semiconductors.[1] They have an indirect band gap suitable for many semiconductor applications, 1.7–1.8 (ZrS_2) or 1.8–2.1 eV (HfS_2) in bulk.[2] A notable benefit of HfS_2 and ZrS_2 is that their native oxides, HfO_2 and ZrO_2, are well-known high-k oxides, a situation analogous to Si and SiO_2.[3]

We present the first ALD processes for HfS_2 and ZrS_2 using simple, thermally stable and industrially applied halide precursors $HfCl_4$ and $ZrCl_4$ with H_2S. Crystalline, continuous, high-quality 2D HfS_2 and ZrS_2 films with thicknesses from a few to tens of monolayers (monolayer = 0.58 nm) are deposited at 400 °C once care is taken to minimize the presence of impurities such as water in the ALD reactor. Good ALD characteristics, including rapid saturation and linear growth rate at approximately 0.1 Å/cycle are achieved. The HfS_2 and ZrS_2 films can be grown on a variety of substrates, including oxides, metals, and sulfides. Single-crystalline

substrates, such as sapphire and muscovite mica, enable tailoring the morphology and texture of films and even epitaxial growth. Due to the sensitivity of HfS_2 and ZrS_2 towards oxidation, we demonstrate encapsulation of the sulfide films "in situ" with an ALD-grown oxide layer using an oxidant-free process. We are currently studying the use of HfS_2 and ZrS_2 films as photodetectors to highlight the potential of the films for electronic applications.

[1] Yan et al., *Adv. Funct. Mater.*, **2018**, 28, 1803305

[2] Abdulsalam and Joubert, *Phys. Status Solidi B*, **2016**, 253, 705–711

[3] Mleczko et al., *Sci. Adv.*, **2017**, 3, e1700481

2:45pm **NS-WeA-6 Low Temperature ALD for Phase-controlled Synthesis of 2D Transition Metal (M=Ti, Nb) *di-* (MX_2) and *Tri-* (MX_3) Sulfides***,* ***Saravana Balaji Basuvalingam****, M Verheijen, E Kessels, A Bol,* Eindhoven University of Technology, Netherlands

The synthesis of two-dimensional transition metal dichalcogenides (TMDCs, MX_2) by atomic layer deposition (ALD) has gained a lot of attention lately due to the need for precise thickness control over a large area at low temperatures for future applications in opto-electronics[1]. There is also another class of two-dimensional materials involving similar elements as in TMDCs, which are known as transition metal trichalcogenides (TMTCs, MX_3). Contrary to TMDCs, TMTCs have quasi-1D properties which give added freedom for applications as they have strong anisotropy in both electrical and optical properties[2]. The present study is the first exploration of the synthesis and characterization of TMTCs using ALD.

The most commonly used technique for synthesizing TMTCs is chemical vapour transport (CVT), which is a non-scalable, high temperature and time consuming technique that grows crystals having dimensions of the order of a few cm. Therefore there is a need for synthesising TMTCs on a large scale at low temperature with a good control over the phase and thickness.

In this work, we report the first results on the controlled synthesis of TMTCs (TiS_3 and NbS_3) by ALD using metalorganic precursors and H_2S at low temperatures (100°C – 300°C). We demonstrate that by controlling deposition conditions one can tailor the phase (di- or trichalcogenide) of the material. In order to gain control over the phase of the materials we studied the effect of the deposition temperature, co-reactant (thermal ALD versus plasma-enhanced ALD) as well as co-reactant gas composition on the materials phase (Figure 1). The phase of the materials as a function of deposition parameters was studied by X-ray photoemission spectroscopy (XPS) and Raman spectroscopy (Figure 2). The quality and the composition of the films were studied using Rutherford back scattering (RBS). It was observed that TMTCs (TiS_3 and NbS_3) can be synthesized using plasma-enhanced ALD using H_2S plasma as co-reactant at low temperatures, while TMDCs (TiS_2 and NbS_2) were synthesized by both plasma-enhanced ALD (at high temperatures) and thermal ALD. The morphology and crystallinity of the synthesized films were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which revealed the two-dimensional and nano/poly-crystalline nature of the films. Our experiments show that ALD enables the controlled synthesis of both TMDCs and TMTCs at low temperatures over large scales, which opens up new avenues to include both TMDCs and TMTCs in nano- or optoelectronic applications.

[1] W. Hao et. al, 2D Mater. **6**, 012001 (2018).

[2] J.O. Island et. al, 2D Mater. **4**, 022003 (2017).

3:00pm **NS-WeA-7 ALD Boron Nitride Coated and Infiltrated Carbon Materials for Environmental Applications***, W Hao, C Journet, A Brioude,* Université Lyon, France*; H Okuno,* Université Grenoble-Alpes, France*;* ***Catherine Marichy****,* Université Lyon, France

Atomic Layer Deposition (ALD) has proven to be an effective approach for surface modification and fabrication of carbon based heterostructures [1]. Nevertheless, ALD BN coating of carbon material has been poorly studied up to date. Our group recently reported a two-step ammonia-free ALD approach for BN allowing the coating of various substrates such as inorganic and polymeric nanostructures [2,3]. While successful deposition of BN layers on carbon nanomaterial has been realized, it has been observed that some BN precursor diffuses into some polymers [4].

Herein various carbon nanostructures (nanoparticles, nanotubes, nanofibers) coated with ALD are discussed. The inertness of highly graphitic carbon inhibiting the initiation of ALD growth, the influence of the crystalline nature of the substrate on the BN coating is investigated in term of growth and structure, using different graphitized/amorphous carbon supports. Nucleation delay and impact on the crystalline quality (amorphous, turbostratic, hexagonal phase) of BN films are observed as a function of the degree of graphitization. Furthermore, obtained from vapor infiltration of polymers, BN-carbon hybrid structures are briefly introduced. The obtained materials are characterized by advanced electron microscopy and related techniques. Finally, the potential of such a coating to improve the oxidation resistance of carbonaceous material is demonstrated.

[1] C. Marichy, N. Pinna, Coordination Chemistry Reviews, (2013), 257, 3232.

[2] W. Hao, Marichy C., Brioude A., ChemNanoMat., 3, (2017), 656.

[3] Hao W. Marichy C., Journet C., Brioude A., Enviro. Science Nano., 4, (2017), 2311.

[4] Hao W. PhD thesis, (2017)

Author Index

Bold page numbers indicate presenter

— B —
Basuvalingam, S: NS-WeA-6, **2**
Bent, S: NS-WeA-1, 1
Bol, A: NS-WeA-3, **1**; NS-WeA-6, 2
Brioude, A: NS-WeA-7, 2
— E —
Elam, J: NS-WeA-2, 1
— G —
Graugnard, E: NS-WeA-2, 1
— H —
Hao, W: NS-WeA-7, 2
— J —
Jalkanen, P: NS-WeA-5, 1
Journet, C: NS-WeA-7, 2
— K —
Kessels, E: NS-WeA-6, 2
King, P: NS-WeA-5, 1
— L —
Leskelä, M: NS-WeA-5, 1
Letourneau, S: NS-WeA-2, **1**
— M —
MacIsaac, C: NS-WeA-1, 1
Mane, A: NS-WeA-2, 1
Marichy, C: NS-WeA-7, **2**
Mattinen, M: NS-WeA-5, **1**
Mizohata, K: NS-WeA-5, 1
— O —
Oh, I: NS-WeA-1, 1
Okuno, H: NS-WeA-7, 2
— P —
Popov, G: NS-WeA-5, 1
— R —
Räisänen, J: NS-WeA-5, 1
Ricky, N: NS-WeA-1, 1
Ritala, M: NS-WeA-5, 1
— S —
Shi, J: NS-WeA-1, 1
— V —
Vehkamäki, M: NS-WeA-5, 1
Verheijen, M: NS-WeA-6, 2
— Z —
Zeng, L: NS-WeA-1, **1**