

Tuesday Afternoon Poster Sessions, July 23, 2019

Nanostructure Synthesis and Fabrication

Room Evergreen Ballroom & Foyer - Session NS-TuP

Nanostructures Synthesis and Fabrication Poster Session

NS-TuP-1 Molybdenum Disulfides and Diselenides by Atomic Layer Deposition, Raul Zazpe, J Prikryl, M Krbal, J Charvot, F Dvorak, F Bures, J Macak, University of Pardubice, Czech Republic

The discovery and success of graphene paved the way for developing two-dimensional materials with outstanding properties [1]. In particular, monolayers of two-dimensional transition metal dichalcogenides (2D TMDCs) possess a direct band gap [2] that is crucial for optoelectronic applications. Additionally, the direct band gap can be easily tuned by either chemical composition or external stimuli. In parallel to monolayer TMDCs structures, a high surface area layer of TMDCs flakes shows promising properties for hydrogen evolution [3], photodegradation of organic dyes [4] or as electrodes in Li ion batteries [5].

To date, various top-down (e.g. exfoliation) and bottom-up techniques, such as chemical vapor deposition (CVD) and atomic layer deposition (ALD) have been reported for the preparation of 2D-TMDCs [1]. However, ALD is the only technique enabling sub-nanometer thickness control, which is revealed as a crucial factor in the properties of 2D TMDCs materials. In the last years, it has been reported the possibility to employ ALD as a technique to grow MoS₂, which has been extensively studied for many different applications. In these works (CH₃)₂S₂ [6] or H₂S [7, 8] were used as the S precursor and Mo(CO)₆ [6], MoCl₅ [7] or Mo(thd)₃ [8] as the Mo precursors. Further, important efforts have also been devoted to attain the ALD fabrication of MoSe₂, since it possesses higher electrical conductivity than MoS₂ [9, 10]. Recently, we have shown that ALD deposition of MoSe₂ [11] or Mo-O-Se [12] is feasible using (CH₃)₂S₂ as the Se precursor and the MoCl₅ or Mo(CO)₆, respectively, as the Mo precursors.

The presentation will focus on the synthesis of MoS₂ and MoSe₂ by ALD, their characterization and applications in various fields. Experimental details and some recent photocatalytic, battery and hydrogen evolution results will be presented and discussed.

[1] A. V. Kolobov, J. Tominaga, Two-Dimensional Transition-Metal, Dichalcogenides. Springer Series in Materials Science, Springer International Publishing AG, Switzerland 2016

[2] B. Radisavljevic et al, Nat. Nanotechnol. 6 (2011) 147

[3] L. Wang et al, Adv. Mater. Interfaces. 2 (2015) 1500041

[4] Y. Wu et al, Nanoscale. 8 (2016) 440

[5] D. Ilic et al, J.Power Sources. 14 (1985) 223

[6] Z. Jin et al, Nanoscale. 6 (2014) 14453.

[7] L. K. Tan et al, Nanoscale. 6 (2014) 10584

[8] M. Mattinen et al., Adv. Mater. Interfaces 2017, 4, 1700123.

[9] D. Kong, H. et al, Nano Lett. 13 (2013) 1341.

[10] A. Eftekhari, Appl. Mater. Today 2017, 8.

[11] M. Krbal et al., Phys. Stat. Sol. RRL. 12 (2018) 1800023

[12] S. Ng et al., Adv. Mater. Interfaces. (2017) 1701146.

NS-TuP-2 Wafer-scale MoS₂ Thin Film Deposition via H₂S Plasma Sulfurization of ALD-grown MoO₃ at Low Temperature, J Ahn, Jeong-Hun Choi, Korea Maritime and Ocean University, Republic of Korea

Molybdenum disulfide has attracted great interest due to its outstanding mechanical, electrical and optical properties. These unique properties make MoS₂ investigated as a promising candidate material for optoelectronic, sensing and catalysis applications. MoS₂ thin films have been achieved by a variety of methods such as sputtering and chemical vapor deposition. Nevertheless, these methods are limited to controlling the number of layer and uniformity over wafer scale. The most crucial problem of these methods is that they demand high growth temperature or additional heat treatment. High temperature process hinders the application of MoS₂ to a wide range such as flexible and transparent devices. In this work, MoS₂ thin films were deposited by H₂S plasma sulfurization of ALD-grown MoO₃ thin films. While ALD-grown MoO₃ provided precise thickness control and uniformity, H₂S plasma process effectively sulfurized MoO₃ into MoS₂ at low temperature. The sulfurization behavior and physical quality of MoS₂ thin films were investigated under various plasma conditions. The film thickness was measured by

ellipsometry and Raman analysis. X-ray photoelectron spectroscopy was carried out to analyze the chemical composition of MoO₃ and MoS₂ thin films. The crystallization behavior of the films was characterized by X-ray diffraction. Furthermore, the potential of MoS₂ for electric device component was investigated.

NS-TuP-3 ALD-based Synthesis of Few-layer Transition Metal Disulfides with Wafer-scale Uniformity for Device Integration, Tao Chen, Y Wang, H Zhu, L Chen, Q Sun, D Zhang, Fudan University, China

Different transition metal disulfides (TMDs) ultra-thin films with wafer-scale uniformity have been successfully synthesized by ALD-based process. Two growth routes have been developed: sulfurizing transition metal oxides deposited by ALD, and annealing amorphous TMD films deposited by ALD. Molybdenum hexacarbonyl and ozone were used as precursors to deposit MoO₃ film by plasma enhanced ALD followed by sulfurization in a tube furnace to form MoS₂ TMD films. Tungsten hexachloride and hexamethyldisilathiane (HMDST) were used as ALD precursors to deposit WS₂ films which were further annealed at high temperature to improve crystallinity. Both approaches can produce high-quality and thickness-controllable TMD films with wafer-scale uniformity, which have been confirmed by AFM, XPS, Raman and TEM characterizations. Field-effect transistor (FET) device arrays have been further fabricated based on both films showing excellent homogeneous and reproducible electrical performance. The FET on/off ratio was about ~10⁴ with decent mobility over 10 cm²V⁻¹s⁻¹. These experimental results demonstrated attractive and promising potentials of the novel two-dimensional TMD films in future micro-/nanoelectronics device integrations and applications by using ALD-based techniques.

NS-TuP-4 Overcoming Agglomeration and Adhesion in Particle ALD, Benjamin Greenberg, J Wollmershauser, B Feigelson, U.S. Naval Research Laboratory

The fundamental challenge of particle ALD (pALD) is that small particles are sticky. Nanoparticles (NPs) in particular are highly susceptible to van der Waals, dipole-dipole, electrostatic, and chemical forces. When NPs are fluidized or agitated to expose their surfaces to ALD precursors, these forces can cause persistent agglomeration and adhesion to reactor surfaces, preventing conformal coating and reducing core-shell NP yield. To understand and overcome these obstacles, we examine NPs coated in a reactor with two agitation modes, rotation and vibration. We analyze high-speed videos of NP motion while varying agitation parameters (velocity, frequency, timing) as well as NP material and size. After pALD, we weigh the coated powders and study core-shell NP composition and morphology via TEM and N₂ adsorption measurements.

NS-TuP-5 Density Function Theory for Nucleation of MoF₆ with Oxide Surfaces in Atomic Layer Deposition of MoS₂, Matthew Lawson, Boise State University

Several two-dimensional (2D) atomic-layered transition metal dichalcogenides (TMDs) are of great interest for electronic and optoelectronic applications due to their wide direct band gaps for few layer materials. Beyond mechanical or liquid exfoliation of bulk materials, high quality 2D TMDs have been grown via chemical vapor deposition (CVD) but growth is typically performed at high temperatures. Several studies have reported atomic layer deposition (ALD) of thin TMD films at lower temperatures, but as-deposited films are typically amorphous or nanocrystalline. Complementary to *in-situ* experimental studies of the growth and nucleation of nanoscale films, we have employed density functional theory (DFT) to understand the nuanced interactions during precursor nucleation. Hydroxyl groups are commonly found on metal oxide surfaces and play an important role during many ALD processes. To develop a deeper understanding of the ALD of MoS₂ from MoF₆ and H₂S, we studied the reactivity of MoF₆ with three substrates: Al₂O₃, MgO, and HfO₂ without hydroxyls and fully saturated with hydroxyls using DFT. We calculated the electronic distribution of the surfaces, how the electronic structures changed with single MoF₆ precursors, and calculated the valence electron transfer. Our calculations support the important role of hydroxyls in the nucleation of MoF₆ with oxide surface and provide insight into the formation of precursor bonds at the surface.

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 Knoop, Eindhoven University of Technology

1:30pm NS-WeA-1 Modified ALD Process to Achieve Crystalline MoS₂ Thin Films, Li Zeng, C Maclsaac, 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 (MoS₂) as an example, one of the known processes uses Mo(CO)₆ as the Mo ALD precursor and H₂S 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 MoS₂ 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 MoS₂ 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 MoS₂ 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 MoS₂ growth process using Mo(CO)₆ and H₂S. 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 MoS₂ Films on Dielectric Surfaces, E Graugnard, Boise State University; Steven Letourneau, A Mane, J Elam, Argonne National Laboratory

Molybdenum disulfide (MoS₂) is a promising two-dimensional (2D) semiconductor. Similar to graphite, MoS₂ 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 MoS₂ is an indirect band gap semiconductor with a band gap of ~1.3 eV, monolayer MoS₂ 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 MoS₂ 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, MoS₂ ALD using molybdenum hexafluoride (MoF₆), a high vapor pressure liquid at room temperature, and hydrogen sulfide (H₂S) has been demonstrated. For device applications, the ALD MoS₂ must be integrated with dielectrics. While the nucleation of MoS₂ during chemical vapor deposition (CVD) is understood, the nucleation of MoS₂ ALD using MoF₆ and H₂S on dielectric surfaces has yet to be explored. Unlike films grown by high temperature CVD, ALD MoS₂ 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 MoS₂ ALD on Al₂O₃ and HfO₂ surfaces prepared *in situ* by ALD. Self-limiting growth of MoS₂ was observed on a wide range of dielectric surfaces including alumina, and hafnia. The MoS₂ nucleation was found to depend strongly on the substrate. These studies provide insight into the low-temperature ALD of MoS₂ and provide guidance for the integration of MoS₂ and other ALD TMD 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 (H₂/H₂S ratio) in the co-reactant step. This has a direct influence on the number a catalytic edge sites in WS₂ 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 H₂ 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 HfS₂ and ZrS₂, 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 MoS₂. Semiconducting 2D materials, in particular, are promising for electronics applications including field-effect transistors (FETs), photodetectors, and sensors. HfS₂ and ZrS₂, members of the transition metal dichalcogenide (TMDC) group, are indirect band gap semiconductors that have recently emerged as potential alternatives to MoS₂ and other 2D semiconductors.[1] They have an indirect band gap suitable for many semiconductor applications, 1.7–1.8 (ZrS₂) or 1.8–2.1 eV (HfS₂) in bulk.[2] A notable benefit of HfS₂ and ZrS₂ is that their native oxides, HfO₂ and ZrO₂, are well-known high-k oxides, a situation analogous to Si and SiO₂. [3]

We present the first ALD processes for HfS₂ and ZrS₂ using simple, thermally stable and industrially applied halide precursors HfCl₄ and ZrCl₄ with H₂S. Crystalline, continuous, high-quality 2D HfS₂ and ZrS₂ 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 HfS₂ and ZrS₂ films can be grown on a variety of substrates, including oxides, metals, and sulfides. Single-crystalline

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substrates, such as sapphire and muscovite mica, enable tailoring the morphology and texture of films and even epitaxial growth. Due to the sensitivity of HfS₂ and ZrS₂ 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 HfS₂ and ZrS₂ 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- (MX₂) and Tri- (MX₃) Sulfides, Saravana Balaji Basuvalingam, M Verheijen, E Kessels, A Bol, Eindhoven University of Technology, Netherlands

The synthesis of two-dimensional transition metal dichalcogenides (TMDCs, MX₂) 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-electronics¹. There is also another class of two-dimensional materials involving similar elements as in TMDCs, which are known as transition metal trichalcogenides (TMTCs, MX₃). Contrary to TMDCs, TMTCs have quasi-1D properties which give added freedom for applications as they have strong anisotropy in both electrical and optical properties². 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 synthesizing 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 (TiS₃ and NbS₃) by ALD using metalorganic precursors and H₂S 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 (TiS₃ and NbS₃) can be synthesized using plasma-enhanced ALD using H₂S plasma as co-reactant at low temperatures, while TMDCs (TiS₂ and NbS₂) 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., *Environ. Science Nano.*, 4, (2017), 2311.

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

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