Nanostructure Synthesis and Fabrication
Room Auditorium - Session NS1-WeA

2D Nanomaterials by ALD II

Moderators: Jeffrey W. Elam, Argonne National Laboratory, Hyungjun Kim, Yonsei University, Korea

1:00pm **NS1-WeA-1 Atomistic Simulation of ALD of 2D Transition-Metal Dichalcogenides**, ***Mahdi Shirazi***, *E Kessels, A Bol,* Eindhoven University of Technology, Netherlands **INVITED**

Extensive research has been done during the last decade to unravel the remarkable electronic properties [1], [2] of two dimensional transition-metal dichalcogenides (2D-TMDs) in the monolayer regime. In spite of their astounding electrical properties, these material systems are not ready yet for replacing Si based materials for future nanometer-sized electronic devices. One key challenge is the integration of these materials in bottom-up processes at low temperature (usually < 500 °C) into the semiconductor manufacturing flow. Horizontal growth at wafer scale with a large grain size (typically 1x1 μm^2) is required for nano-electronic devices [3]. The cyclic process of atomic layer deposition (ALD) [4] with tight control over the chemical reactions shows promise as such a bottom-up process. The chemical reactions of ALD are self-limiting and are designed to proceed only at the surface. In this contribution, we have employed density functional theory (DFT) to provide fundamental insight into the reaction mechanisms of the MoS_2 growth. We have studied the deposition of MoS_2 that is initiated by the exposure of metal precursor $Mo(NMe_2)_2(NtBu)_2$ ($C_{12}H_{30}N_4Mo$) to the SiO_2 surface and then followed by exposure of H_2S/H_2 as co-reagent in the second pulse [5]. In this so-called hetero-deposition, the involved chemical reactions during ALD lead to the formation of a buffer layer at the surface of SiO_2 [6]. After formation of this buffer layer, ALD enters into the steady-growth regime (also called homo-deposition). In the steady growth regime, vertically or horizontally aligned MoS_2 structures grow in a layer-by-layer fashion. The calculated reaction energies and activation energies indicate that the reaction kinetics in the hetero-deposition are slower than reaction kinetics in homo-deposition. Artificial intelligence is used to generate an efficient interatomic potential using the calculated energies and forces of configurations obtained by DFT. The generated interatomic potential will be used for larger scale simulations to provide further fundamental insight into the deposition of MoS_2 by ALD.

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1:45pm **NS1-WeA-4 ALD of $MoSe_2$ using New Precursors**, ***Raul Zazpe***, University of Pardubice, Czech Republic; *R Krumpolec,* Brno University of Technology, Czech Republic; *J Charvot, L Hromadko, H Shopa, M Motola, M Krbal, F Bures, J Macak,* University of Pardubice, Czech Republic

2D semiconductor transition metal dichalcogenides (TMDs) have attracted considerable attention due to their layered structure, suitable band gap for visible light absorption, high carrier mobility, electrochemically active unsaturated edges and relatively good stability against photocorrosion [1]. Recently, 2D $MoSe_2$ has been gaining considerable interest due to its higher electrical conductivity as compared to MoS_2, its wider inter-layer distance (~0.65 nm), narrow bandgap (1.33–1.72 eV), high resistance to photo-corrosion, high surface area layer, electrochemically active unsaturated Se-edges and close to zero Gibbs free energy edges for hydrogen adsorption.These properties are promising for different applications of $MoSe_2$ including hydrogen evolution [2], photocatalysis [3] and Li-ion batteries [4]. However, their low light absorption efficiency, recombination issues of the photogenerated electron–hole pairs and slow charge transfer of the intrinsic semiconducting 2H-phase are a handicap. An efficient strategy to surpass those intrinsic limitations are hybrid nanostructures using conducting supporting materials. In this regard, anodic TiO_2 nanotubes (TNTs) are excellent photoactive supporting material providing a high surface area, unique directionality for the charge separation, and highly effective charge collection. [5] Accordingly, we present anodic TiO_2 nanotubes homogenously decorated with $MoSe_2$ nanosheets by atomic layer deposition (ALD). In parallel, we address the current scarcity of convenient ALD Se precursors by the synthesis a set of new selenium precursors - alkysilyl $(R_3Si)_2Se$ and alkytin $(R_3Sn)_2Se$, and cyclic silylselenides compounds. Those Se precursors were extensicely characterized and their reliability as ALD Se precursors explored [6,7]. Several compounds exhibited promising results to be convenient ALD Se precursor as will be presented in the presentation. The synthesis of the $MoSe_2$ nanosheets and their composites with TiO_2 NTs, their physical and electrochemical characterization, and encouraging results in electrochemical characterization, hydrogen evolution reaction (HER) and photocatalysis will be presented and discussed.

2:00pm **NS1-WeA-5 Low Temperature Creation of Layered-MoS_2 Thin Films on Large Area High Aspect Ratio Substrates**, ***Anil Mane***, *D Choudhury, S Letourneau, J Elam,* Argonne National Laboratory

Thin layers of two dimensional (2D) materials mainly transition metal dichalcogenides (TMDs) and more specifically ultra-thin layered-MoS_2 semiconductor possess exceptional properties such as electrical, optical, magnetic, mechanical and chemical properties. This allows the exploration of internal quantum degrees of freedom of electrons and their potential for use in semiconductor microelectronics, optoelectronic, energy, and sensor and detector applications. These exciting results are being achieved mostly by using exfoliation of flecks from bulk MoS_2 crystal. However, the biggest challenge in realizing TMDs full potential has been the lack of scalable material synthesis methods for such films with high uniformity, conformality and interfacing with other materials such as oxides, metals and its process compatibility.

Among the various thin film deposition methods, atomic layer deposition (ALD) offers the best combination of precisely controlled layer-by-layer thin film growth at low temperature with very high conformality on complex substrates. Here we will present the growth of layered-MoS_2 thin films. To grow high quality layered–MoS_2 thin films, we have developed an ALD-based two step processing approach [1]: firstly the growth of well controlled ultra-thin layer of Mo metal using ALD followed by the sulfurization of the ALD Mo layer at various temperatures. This two-steps processing results in high quality layered-MoS_2 thin films on large substrates. For the Mo ALD process we used molybdenum hexafluoride (MoF_6) and Si_2H_6 precursors. We used in-situ QCM measurements to study interfacial and nucleation effects in the formation of continuous ultra-thin metal layer of Mo. The composition of both the ALD Mo and the layered MoS_2 layers was determined by X-ray photoelectron spectroscopy (XPS). Further, cross-sectional transmission electron microscopy (TEM) was performed to confirm the formation of layered MoS_2 on high aspect ratio trenches and Raman analysis to verify the signature of E^1_{2g} blue shift and A_{1g} red shift in the MoS_2 structure. In this presentation we will discuss the details of the two-step thin film growth process for creating layered MoS_2 layers via ALD Mo and subsequent sulfurization as well as the properties of the MoS_2 films.

[1] Anil Mane, Devika Choudhury, Steven Letourneau, Jeffrey Elam, (US patent application submitted 2018)

2:15pm **NS1-WeA-6 Gas Sensing Characteristics of $Mo_xW_{1-x}S_2$ Synthesized by Atomic Layer Deposition**, ***Inkyu Sohn***, *Y Kim, M Lee, J Park, H Kim,* Yonsei University, Republic of Korea

Two-dimensional Transition metal dichalcogenide (2D TMDC) have been attracted great attention as gas sensing materials with high sensitivity in room temperature. [1] Because of this characteristic, 2D TMDC gas sensor could overcome the oxide-based semiconductor which need heating for gas sensing. Therefore, various 2D TMDC gas sensor studies have been ongoing. Recently, it has been shown that the gas sensor property could be improved through the changing the composition in $WS_{2x}Se_{2-2x}$ alloy. [2]

Here we report a synthesis method of $Mo_xW_{1-x}S_2$ alloys for gas sensor by atomic layer deposition. Layer controlled 2D MoS_2 and WS_2 were synthesized with $Mo(CO)_6$, $W(CO)_6$ and H_2S as precursors and reactant. For the first time, we systematically modulate the composition of $Mo_xW_{1-x}S_2$ alloys by changing the configuration of low-temperature ALD super-cycles. AFM and Raman spectroscopy results of $Mo_xW_{1-x}S_2$ alloys demonstrate that the thickness of alloy is accurately controlled by ALD. Also XPS results confirmed that composition of alloy is precisely controlled by ALD super-cycles. Furthermore, gas sensors fabricated by $Mo_xW_{1-x}S_2$ alloys were evaluated for NO_2 gas. It showed response time and recovery characteristics of $Mo_xW_{1-x}S_2$ alloy gas sensor is dramatically enhanced.

References [1] ACS Nano 10, 9287-9296 (2016) [2] ACS Appl. Mater. Interfaces 10, 34163-34171 (2018)

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