Nanostructure Synthesis and Fabrication
Room Auditorium - Session NS-WeM2

2D Materials I

Moderators: Gregory N. Parsons, North Carolina State University, Henrik Pedersen, Linköping University, Sweden

10:45am **NS-WeM2-1 Atomic Layer Deposition of Layered Chalcogenides*,* *Suzanne Mohney*, *J. Carter, I. Campbell, A. Agyapong,* Penn State University **INVITED**

Layered chalcogenide materials with van der Waals bonding between layers are fascinating materials. Some are semiconductors with bandgaps suitable for transistors or have been used in atomically thin memory devices, while others are thermoelectrics or topological insulators that are interesting for quantum devices. Antimony(III) telluride has a layered structure with van der Waals bonds between Te atoms in adjacent quintuple layers. We have performed ALD of Sb_2Te_3 using bis(trimethylsilyl)tellurium and antimony(III) ethoxide, which is a pair of previously reported precursors,[1] expanding the set of studied substrates and employing various surface treatments prior to deposition. Growth of a continuous layer is highly dependent on the starting surface through at least the first 500 cycles. Growth on the van der Waals surface of epitaxial monolayers of MoS_2 was difficult, as has been the case for other thermal ALD processes on transition metal dichalcogenides.[2] On SiO_2, we observed incompletely coalesced islands by SEM. Conversely, on amorphous GeTe, single-crystal Bi_2Te_3, or polycrystalline TiN substrates subjected *in situ* toa remote Ar plasma, we grew continuous Sb_2Te_3. On amorphous GeTe and TiN, we measured a pronounced drop in sheet resistance after 500 cycles. X-ray photoelectron spectroscopy confirms the presence of Sb and Te with $3d_{5/2}$ core levels near 527 eV and 572 eV, respectively. Compared to reference spectra, the ratio of intensities matches the expected stoichiometry. Bi_2Te_3 crystals are interesting because they have the same structure as Sb_2Te_3. In our prior study of plasma enhanced ALD on MoS_2, we observed that growth on single-crystal GaN, which has nearly the same lattice parameter in the basal plane, led to much less out-of-plane growth than on other substrates.[3]In reports on ALD of Sb_2Te_3 with the same Te precursor but antimony trichloride instead of antimony(III) ethoxide,[4] or growth of Sb with analogous chloride and alkylsilyl precursors,[5] engineering the hydroxyl groups on the substrate seems to play an important role in promoting in-plane nucleation and rapid coalescence. However, our experiments with bis(triethylsilyl)tellurium and antimony(III) ethoxide did not show an analogous advantage. We will further consider atomic layer epitaxy of van der Waals solids in this presentation. We thank ONR N0014-18-12511 for support and the NSF 2DCC DMR-1539916 for epitaxial substrates.

1. Eom et al., Chem. Mater. 24, 2099, 2012
2. Walter *et al.*, Appl. Surf. Sci. 480, 43, 2019
3. Mughal *et al.*, J. Vac. Sci. Technol. A 37, 010907, 2019
4. Nminibapiel *et al.*, ECS J Solid State Sci Technol 3P95, 2014
5. Mohney *et al.*, ALD2016

11:15am **NS-WeM2-3 2D Alloys of WS_2 and NbS_2 by PEALD*,* *Jeff Schulpen*, *C. Lam,* Eindhoven University of Technology, The Netherlands*; E. Coleman, F. Gity,* Tyndall National Institute, University College Cork, Ireland*; M. Mattinen, M. Verheijen, E. Kessels,* Eindhoven University of Technology, The Netherlands*; R. Duffy,* Tyndall National Institute, University College Cork, Ireland*; A. Bol,* Eindhoven University of Technology, The Netherlands

2D transition metal dichalcogenides (TMDs) have many unique properties such as high electronic mobilities and a large surface-to-volume ratio, making them promising materials for various applications such as nanoelectronics and electrocatalysis. In particular, *alloys* of 2D TMDs hold great potential due to their composition-controlled properties, making them more versatile than pure TMDs. Atomic layer deposition can be used to synthesize thin films of such TMD alloys with sub-monolayer growth control, making this method particularly relevant for the aforementioned applications. In this work we employ plasma-enhanced atomic layer deposition (PEALD) to synthesize alloys of the 2D TMDs NbS_2 and WS_2, i.e. $Nb_xW_{1-x}S_2$ using $W(NtBu)_2(NMe_2)_2$ and $Nb(NtBu)(NEt_2)_3$ as precursors and H_2S plasma as coreactant. We present a thorough characterization of the alloy growth, showing excellent composition control ranging from nanocrystalline WS_2 to amorphous NbS_2 based on ellipsometry, XPS, SEM, Raman spectroscopy and TEM. The morphology of the films depends strongly on the composition, as the alloy films have a significantly enhanced occurrence of out-of-plane oriented crystallites.

The suitability of $Nb_xW_{1-x}S_2$ as a channel material for transistors is evaluated by Hall measurements and FET device characterization. We find that the incorporation of only 10% Nb reduces the resistivity of the WS_2 film by 4 orders of magnitude at a mobility of 0.3 cm^2/Vs. Furthermore, improving the Nb distribution in the film through consecutive precursor dosing (ABC-type cycles) further increases the mobility by a factor of 2.5. At the same time we observe that the formation of out-of-plane oriented crystallites is strongly suppressed when using this process type, which is critical for applications in nano-electronics. Fabrication and characterization of FETs based on the alloy films are currently ongoing. Secondly, we assess the efficacy of the $Nb_xW_{1-x}S_2$ films as electrocatalysts for the hydrogen evolution reaction (HER). The alloys were found to outperform the pure NbS_2 and WS_2 films deposited by PEALD, having lower Tafel slopes and overpotentials. The alloy with a composition x = 0.84 performed best with a Tafel slope of 131 mV/dec and an overpotential of 470 mV.

Our results show that the $Nb_xW_{1-x}S_2$ alloys improve on the electrical and electrocatalytic performance of pure WS_2 and NbS_2. Furthermore, the various supercycle schemes provide a valuable platform for fundamental insight into the surface reactions and growth mechanics during the PEALD process and for further fine-tuning of the alloy functionalities.

11:30am **NS-WeM2-4 2D Molybdenum Dichalcogenides by Atomic Layer Deposition*,* *Raul Zazpe*, *J. Charvot, L. Hromadko, H. Sopha, J. Rodriguez Pereira , F. Bures, J. Macak,* University of Pardubice, Czechia

2D semiconductor transition metal dichalcogenides have attracted considerable attention due to their layered structure, suitable band gap, electrochemically active unsaturated edges and relatively good stability against photocorrosion. These properties result promising for different applications including, Li-ion batteries, photocatalysis and hydrogen evolution reaction (HER). Apart from the widely studied 2D MoS_2, 2D selenide and telluride equivalents, $MoSe_2$ and $MoTe_2$,have recently gained considerable interest due to their higher electrical conductivity, wider inter-layer distance and narrower bandgap as compared to MoS_2, high surface area and close to zero Gibbs free energy edges for hydrogen adsorption.

Unlike sulfide dichalcogenides, the lack of Se and Te precursors have prevented the synthesis of selenide and telluride dichalcogenides by ALD. In order to surpass such impediment, we present a set of novel in-house synthesized Se and Te compounds, which were successfully combined with commercial Mo precursor to synthesize $MoSe_2$ and $MoTe_2$ by ALD [1-5]. The as-deposited ALD $MoSe_2$ and $MoTe_2$ on substrates of different nature were extensively characterized by different techniques, which confirmed the chemical composition and revealed the growth of 2D flaky nano-crystalline $MoSe_2$ and $MoTe_2$. In parallel, $MoSe_2$ and $MoTe_2$@TiO_2 nanotube layers (TNTs) heterostructures were fabricated in a simple and fast fashion to explore and exploit the $MoSe_2$ and $MoTe_2$ photo- and electrocatalytic properties. TNTs act as excellent photoactive supporting material providing a high surface area, unique directionality for charge separation, and highly effective charge collection.

The presentation will introduce and describe the synthesis of the 2D Mo dichalcogenides, the corresponding physical and electrochemical characterization and encouraging results obtained in HER [4,5], photocatalysis [4-6] and Li-ion batteries [7].

[1] R. Zazpe et al, FlatChem (2020) 21 100166

[2] J. Charvot et al, Chempluschem (2020) 85 576

[3] J. Charvot et al, RSC Adv. (2021) 11 22140

[4] R. Zazpe et al, ACS Appl. Nano Mater. (2021) 3 12 12034

[5] R. Zazpe et al, Appl. Mater. Today (2021) 23 101017

[6] M. Motola et al, Nanoscale (2019) 11 23126

[7] H. Sopha et al FlatChem (2019) 17 100130

11:45am **NS-WeM2-5 Plasma-enhanced Atomic Layer Deposition of Crystalline MoS_2 Thin Films Using a Novel Precursor*,* *Jeong-Hun Choi*, *M. Ha, D. Kim, J. Ahn,* Hanyang University, Korea (Republic of)

Layered two-dimensional molybdenum sulfide (MoS_2) has attracted great interest for a promising candidate material for opto-electronics and photo sensors applications due to its unique characteristics such as tunable bandgap, high electron mobility and high current on/off ratio. In order to apply MoS_2 to the industrial field, significant efforts have been placed in obtaining a wafer-scale uniform MoS_2. Plasma-enhanced atomic layer deposition (PEALD) is a promising approach for depositing a 2D MoS_2 because of its excellent thickness control. However, the low growth temperature of PEALD makes it difficult to guarantee the quality of the MoS_2 thin films.

In the present study, to overcome this limitation, Cp based molybdenum precursor was used for the PEALD of MoS_2 thin films. This novel precursor with high thermal stability resulted in MoS_2 films with high crystallinity without post thermal treatment.The composition and crystallinity of MoS_2 thin films depends on the PEALD process conditions were investigated by X-ray photoelectron spectroscopy and transmission electron microscopy. Furthermore, through fabricating the field-effect transistors, the potential of MoS_2 for electric device component was investigated.

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