Nanostructure Synthesis and Fabrication
Room Regency Ballroom A-C - Session NS-MoA

2D Growth

Moderators: Prof. Dr. John Conley, Oregon State University, Prof. Xiangbo Meng, University of Arkansas

4:00pm **NS-MoA-11 A Modified ALD-like Approach to Demonstrate Exceptionally Thin Dielectric Layer Growth on 2D Materials***, **Daire Cott**, S. Sergeant, R. Rennen, G. Benjamin,* IMEC Belgium*; D. Lin,* IMEC, Belgium*; X. Wu,* IMEC Belgium*; Z. Lin,* IMEC Belgium,, Belgium*; T. Schram, Q. Smets, I. Asselberghs, P. Morin,* IMEC Belgium **INVITED**

Uniform deposition of extremely thin dielectrics on 2D materials is sought after to exploit the potential of 2D materials in future nano-electronic devices. To that end, significant challenges must be overcome. The surface of thin layers of pristine 2D materials can be seen as fully passivated where all covalent bonding is located parallel to the plane and layers are bound together by Van der Waals forces. To form an effective interface between the 2D material surface and an oxide covering layer a lowering of the overall surface energy must be achieved. Interestingly, 2D materials already possess an extremely low surface energy (~40 mJ/m^2)[1] indicating that wetting is a significant challenge. Additionally, when considering ALD - the method of choice to form scaled high-k dielectric layers on Si device technology - which relies on the ability to form a uniform covalently bound atomic layer as the starting surface to nucleate subsequent layers. Conversely, to maximize 2D materials electronic potential the pristine nature of the 2D material should be maintained without damaging the in-plane covalent bonding of the system. This excludes many well-established physical deposition techniques such as PVD sputtering or even plasma enhanced ALD techniques where damage to the 2D layer can be created, inducing defects that although will enhance the nucleation of oxides will simultaneously degrade the electrical performance in nanoscale devices.

In this presentation, a method to overcome the inert nature of 2D materials to support oxide formation without inducing defects into the 2D material will be discussed. Insights into the formation mechanism of thin Aluminum oxide based layers on 2D materials will be outlined with particular focus on two types of transition metal dichalcogenides namely, WS_2 and MoS_2. Combining our method with 5nm HfO_2 to form the top oxide in lab based dual gated MOSFETs a low equivalent oxide thickness (EOT) of 2.1nm was demonstrated [2], Additionally, the upscaling of this approach to large area 300mm 2D material covered substrates will be also discussed [3]

[1]: Gaur et al., Nano Lett. 2014, 14, 4314−4321.

[2]: Wu et al., 2021 IEEE International Electron Devices Meeting (IEDM), 7.4. 1-7.4. 4

[3]: Smets et al., 2021 IEEE International Electron Devices Meeting (IEDM). IEDM21-725

4:30pm **NS-MoA-13 Water-free SbO_x-ALD-process for Coating Bi_2Te_3-particles***, **Sebastian Lehmann**, F. Mitzscherling, S. He, J. Yang, M. Hantusch, A. Bahrami, K. Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany

We developed a water-free Atomic Layer Deposition (ALD) process to homogeneously deposit SbO_x using $SbCl_5$ and Sb-Ethoxide as precursors reported for the first time. The coating is applied on Bi_2Te_3 particles which were synthesized via the solvothermal route to enhance the thermoelectric properties (i.e. Seebeck coefficient, thermal and electrical conductivity) via interface engineering. The amorphous character of the coating was shown by the missing reflexes on the XRD diffractograms. A shift from the oxidation state +III to +V of the Sb-species was observed towards increasing SbO_x-coating layer thickness using XPS. Additionally, a peak shift of the Sb $3d_{5/2}$ + O 1s peak indicating increased n-type doping of the material. Electrical measurements of spark plasma sintered bulk samples confirmed the doping effect by a decreased specific resistivity with increasing SbO_x-layer thickness. The Seebeck coefficient was improved for the coated samples compared to the uncoated reference sample while the total thermal conductivity remained almost constant resulting in an enhancement of the Power factor and the zT. The results distinctly show that surface engineering via Powder ALD is an effective tool to improve key properties of thermoelectric materials.

4:45pm **NS-MoA-14 2D FeS_X Nanosheets by ALD: Electrocatalytic Properties Towards Hydrogen Evolution Reaction***, **Raul Zazpe**, J. Rodriguez Pereira, S. Thalluri, L. Hromadko,* University of Pardubice, Czechia*; D. Pavliňák, E. Kolíbalová,* Brno University of Technology, Czechia*; H. Sopha, J. Macak,* University of Pardubice, Czechia

In the last years, the search of novel and cost-effective catalysts to replace costly and scarce noble metals drove to explore a wide range of materials, such as transition metal dichalcogenides (TMDCs), phosphides, carbides, nitrides among others.[1] Inspired by the first experimental evidences reported on the catalytic activity of MoS_2 edge sites,[2] an intense researching work has been devoted in exploring the catalytic properties of other 2-dimensional (2D) TMDCs, e.g. WS_2, $MoSe_2$, and $MoTe_2$.[3–6] 2D materials offer unique structural, optical and electronic properties as compared to the bulk counterparts. In addition, they show significant prospects as catalyst mainly due to the flake-like morphology with minimal thickness, high surface-to-volume ratio, and capability of surface functionalization and tuning the catalytically active edges sites.[7] Among the TMDCs materials, the catalytic properties of iron sulfide and its different phases, namely FeS_2, Fe_3S_4 and FeS, have been largely overlooked and barely explored compared to other TMDCs, despite the relative low cost and toxicity and the high natural abundance of iron and sulfur.

Herein, we present 2-dimensional (2D) FeS_x nanosheets of different sizes as an electrocatalyst towards hydrogen evolution reaction (HER) in alkaline media. The 2D FeS_x nanosheets were synthesized by applying different numbers of Atomic Layer Deposition (ALD) cycles on TiO_2 nanotube layers and graphite sheets as active supporting materials. The electrochemical results confirmed the electrocatalytic activity with an excellent long-term stability and an enhanced catalytic activity reflected by a noteworthy drop of the HER overpotential. Using a range of characterization techniques, it was unveiled that the origin of the enhanced catalytic activity was caused by the synergistic interplay between in situ morphological and composition changes experienced by the 2D FeS_x nanosheets during HER. Under the application of a cathodic potential in alkaline media, it was observed that the original 2D FeS_x nanosheets transformed to iron oxyhydroxide-iron oxysulfide core-shell nanoparticles, which exhibited a higher active catalytic surface and newly created Fe-based HER catalytic sites. [8]

[1] P. Yu et al, *Nano Energy***2019**, *58*, 244–276.

[2] T. F. Jaramillo et al *Science (80-.).***2007**, *317*, 100–102.

[3] J. Bonde et al, *Faraday Discuss.***2009**, *140*, 219–231.

[4] J. C. McGlynn et al., *Nat. Commun.***2019**, *10*, 4916.

[5] M. Motola et al., *Nanoscale***2019**, *11*, DOI 10.1039/c9nr08753b.

[6] R. Zazpe et al., *Appl. Mater. Today***2021**, *23*, 101017.

[7] S. H. Noh et al, *J. Mater. Chem. A***2018**, *6*, 20005–20014.

[8] R. Zazpe et al, *submitted*.

5:00pm **NS-MoA-15 300 mm Wafer-Scale and Self-limiting Layer Synthesis of 2D $MoSe_2$ by Atomic Layer Deposition***, A. Zacatzi, M. Miller, R. Kanjolia, **Thong Ngo**,* EMD Electronics

2D Transition metal dichalcogenide (TMD) materials have opened a route to continue the down-scaling trend of semiconductor technology. As part of the TMD materials library, $MoSe_2$ has demonstrated itself to be a very promising candidate as a channel material for transistor devices, achieving field-effect mobilities up to ~ 150 - 200 $cm^2/(V\ s)$. [1]

The synthesis of high quality 2D $MoSe_2$ is required to unlock the potential application of this material in electronic devices. However, to date, there are limited reports on $MoSe_2$ synthesis in comparison to the variety of techniques used to obtain MoS_2 in the literature. A previous approach describes a two-step $MoSe_2$ deposition, where MoO_3 is first deposited by atomic layer deposition (ALD) onto a substrate followed by a selenization process performed at 900°C [2]. While this route produced 2D $MoSe_2$, a single, lower temperature process would be preferred to better meet the high-volume manufacturing demands in the semiconductor industry. In this work, we developed a process to synthesize uniform, 300 mm wafer-scale 2D $MoSe_2$ films using conventional ALD. A detailed study of the $MoSe_2$ ALD process window, from 425 °C - 600 °C, correlated with the composition and structural properties of the $MoSe_2$ film will be presented. The resulting $MoSe_2$ films from the optimized process are stoichiometric and present a 2H phase. Furthermore, this novel optimized ALD process exhibited a self-limiting layer synthesis-like behavior [3], allowing the precise control over the $MoSe_2$ thickness.

The proposed ALD approach presented in this work contributes to the efforts in developing high-quality 2D materials for the realization of atomically thin channel materials.

[1] N. R. Pradhan, D. Rhodes, Y. Xin, S. *et al*., ACS Nano, 8, 8, 7923–7929 (2014).

[2] T.-J. Dai, X.-D. Fan, Y.-X. Ren, *et al*. Mater. Sci. 53, 8436–8444, (2018).

[3]Y. Kim, JG. Song, Y. Park, *et al*. Sci Rep 6, 18754 (2016).

5:15pm **NS-MoA-16 Wafer-Scale Controlled Growth of Two-Dimensional Metal Dichalcogenides Through Atomic Layer Deposition and Top-Bottom Epitaxy**, ***Chanyoung Yoo**, W. Choi, J. Jeon, B. Park, G. Jeon, S. Jeon, C. Hwang,* Department of Materials Science and Engineering and Inter-University Semiconductor Research Center, Seoul National University, Republic of Korea

Two-dimensional (2D) metal dichalcogenides (MDCs) are a class of MX_2 compounds that exhibit unique electrical, optical, and mechanical properties due to their 2D van der Waals (vdW) structures[1]. Among them, Sb_2Te_3 is a p-type semiconductor with a narrow direct bandgap that has the potential for applications in a topological insulator[2], thermoelectric[3], and optoelectronic. Sb_2Te_3 is also utilized in phase-change memories, where the pseudobinary GeTe-Sb_2Te_3 tie line compositions are the primary materials[4]. To utilize the unique properties of Sb_2Te_3 and for other 2D MDCs, continuous films with ultrathin thicknesses (<< ~10 nm) must be formed on substrates. However, depositing 2D MDCs such as Sb_2Te_3 with ultrathin thickness is challenging due to their tendency to grow in an island-type non-uniform manner, exhibiting prominent plate-shaped morphologies.

In this study, a novel atomic layer deposition (ALD) method utilizing amorphous (a-) GeTe as a buffer layer was developed to change the island-type growth of Sb_2Te_3 film to layer-by-layer growth, enabling precise control of film thickness with high uniformity, as shown in Figure 1. The Ge atoms in the buffer layer act as anchoring sites where the Sb-precursors can adhere uniformly. After forming a uniform Sb_2Te_3 layer, the growth was self-terminated by the inert vdW surface (Figure 2a), and the substitutional reaction of Ge atoms with the Sb-precursors dominated the growth. The replacement of Sb atoms formed crystalline (c-) GeSbTe and further Sb_2Te_3 cycles transformed the c-GeSbTe layer into a pure Sb_2Te_3 film (Figure 2b). The self-terminated thickness of the Sb_2Te_3 film was determined by the thickness of the a-GeTe buffer layer (Figure 2c). This new ALD method, referred to as top-to-bottom epitaxial growth, involved depositing the Sb_2Te_3 film through the displacement and diffusion of Sb atoms from the surface to the substrate (see the overall illustrations in Figure 2d). This approach resulted in conformal c-axis-oriented Sb_2Te_3 films with ideal layer-by-layer growth. Furthermore, layer-by-layer growth was maintained on contact hole structures (compare Figure 3a-c and 3d-f), exhibiting c-axis orientation along the curvature without any protruding plates, as evidenced by the characteristic vdW gaps of Sb_2Te_3 parallel to the curved corner. This new ALD method utilizing an amorphous buffer layer holds great potential for application to other 2D MDCs and provides a versatile and scalable platform for their growth.

References

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2 H. Zhang et al., Nat Phys, 2009.
3 L. M. Goncalves et al., Thin Solid Films, 2011.
4 H. S. P. Wong et al., Proceedings of the IEEE, 2010.

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