Nanostructure Synthesis and Fabrication
Room On Demand - Session NS3

2D Nanomaterials by ALD (including Transition Metal Dichalcogenides)

NS3-1 2D Core-Shell Quantum Dots Grown by ALD, ***Jeff Schulpen***, *M. Verheijen, E. Kessels, V. Vandalon, A. Bol,* Eindhoven University of Technology, Netherlands

Two-dimensional transition metal dichalcogenides (e.g. MoS_2, WS_2) have fascinating optical and electronic properties that make them promising materials for use in next-generation devices. In particular, 2D quantum dots (i.e. nanoparticles of 2D materials) have received great interest in recent years for their effectiveness in catalysis as well as opto-electronic and energy-storage applications [1]. Furthermore, the versatility of 2D materials is greatly enhanced by the fact that they can be assembled with atomically sharp interfaces, resulting in heterostructures that benefit from the combined functionality of multiple 2D materials as well as completely new material properties [2]. Applying heterostructure methods to 2D quantum dots could result in core-shell nanoparticles which combine the useful properties of 2D quantum dots with the versatility of heterostructures. However, little is known about such structures, as most of the literature is aimed at single-material quantum dots.

In this work, we show that 2D monolayer core-shell quantum dots can be grown by atomic layer deposition. Using a supercycle approach, we grow crystalline nano-scale monolayer flakes of MoS2 which are subsequently epitaxially bordered by WS_2. This is achieved by exploiting the reactive edge sites of these materials, by switching from MoS_2 to WS_2 deposition before a closed monolayer is formed. Notably, this method can be extended to the growth of more elaborate structures (e.g. core-shell-shell), whereby the diameter of the core and shell(s) can be straightforwardly and accurately controlled through the number of ALD cycles. In practice, the size control of the grown core-shell structures is limited by the nucleation density of the ALD process, which is linked to the density of reactive sites on the substrate [3,4]. In order to enable the growth of larger and more elaborate structures, we employ strategies to reduce the nucleation density. The growth is investigated in-situ using spectroscopic ellipsometry, and the grown structures are characterized by AFM and TEM, as well as Raman and PL spectroscopy. We expect our technique of growing 2D core-shell quantum dots to extend to other 2D material systems, thereby establishing an important new method of tailoring the properties of 2D quantum dots for applications in catalysis, opto-electronics and energy-storage.

[1] Manikandan, A. et al.Prog. Quantum Electron.68, 100226 (2019)

[2] Novoselov, K. S., Mishchenko, A., Carvalho, A. & Castro Neto, A. H. Science353, aac9439 (2016)

[3] Puurunen, R. L. J. Appl. Phys.97, 121301 (2005)

[4] Groven, B. et al. Chem. Mater.30, 7648–7663 (2018)

NS3-2 2D Molybdenum Dichalcogenides Family by Atomic Layer Deposition, ***Raul Zazpe***, University of Pardubice, Czech Republic*; R. Krumpolec,* Masaryk University, Czech Republic*; J. Charvot, L. Hromadko,* University of Pardubice, Czech Republic*; H. Sopha,* University of Pardubice, Czech Republic , Czechia*; M. Motola, F. Bures, J. Macak,* University of Pardubice, Czech Republic

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 MoS2, 2D selenide and telluride equivalents, MoSe2 and MoTe2, have recently gained considerable interest due to their higher electrical conductivity, wider inter-layer distance and narrower bandgap as compared to MoS2, 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 MoSe2 and MoTe2 by ALD [1-5]. The as-deposited ALD MoSe2 and MoTe2 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 MoSe2 and MoTe2. In parallel, MoSe2 and MoTe2@TiO2 nanotube layers (TNTs) heterostructures were fabricated in a simple and fast fashion to explore and exploit the MoSe2 and MoTe2 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 dichalcogenide family, 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, revision submitted

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

[5] R. Zazpe et al, Appl. Mater. Today 2021, in revision

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

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

NS3-3 Atomic Layer Deposition of Ultrathin Tungsten Oxide Films for 2D WS_2 Synthesis, ***Maxim Kozodaev***, *R. Romanov, A. Markeev,* Moscow Institute of Physics and Technology, Russian Federation

Tungsten oxide attracts great attention as a functional layer of electrochromic [1] or resistive memory devices [2], but also as a source for the synthesis of two-dimensional ultrathin WS_2 nanosheets, which can serve as a channel material in the post-silicon FET technology [3]. In this regard, ALD utilization for the tungsten oxide growth is highly preferable since it allows the best thickness control and reproducibility over other deposition techniques, which is crucial for mass-production. Previously it has been reported that radical-enhanced ALD also allows precise oxygen deficiency control in WO_x films [4].

In this work, we modify the previously reported $WH_2(Cp)_2$-based ALD process by the oxygen source exchange to ozone. This process showed a clear saturation behavior on both reactants, good deposition uniformity, and higher oxygen deficiency level, which was monitored by in-situ X-Ray photoelectron spectroscopy to exclude film degradation under ambient conditions. The V_o presence was concluded from the visible electronic states formation in the bandgap, an increase in the concentrations of tungsten in the W5+ state and oxygen in the non-lattice state. An increase in the V_o concentration was accompanied by a significant film resistivity decrease and an abrupt change in the crystalline structure, which was revealed by XRD analysis. The early stages of the suggested WO_x ALD process were studied by angle-resolved XPS and the moment of film continuity was determined. The subsequent sulfurization allowed its' effective conversion to WS_2 nanosheets with the terrace-terminated structure. Recently it was shown that preliminary seed WO_x film hydrogen treatment allowed to significantly change WS_2 morphology and improve its' electrical quality [5]. Noteworthy, exactly ultrathin WS_2 layers are of particular interest, therefore, the seed WO_x thickness influence on the resulting WS_2 morphology was also investigated. In particular, such a technique allowed us to obtain the continuous WS_2 nanosheets with a thickness down to 3-4 monolayers. The obtained results expand the opportunities horizon of the 2D materials by the possibility of a fab-oriented production technique.

1. S. Balaji et al., Chem. Mater. 2009, 21, 7, pp. 1381-1389
2. F.-M. Lee et al., DOI: 10.1109/IEDM.2013.6724672
3. T. Schram et al., 2017 Silicon Nanoelectronics Workshop (SNW), 17436971
4. R. I. Romanov et al., J. Phys. Chem. C 2020, 124, pp. 18156-18164
5. M. G. Kozodaev et al., J. Phys. Chem. C 2020, 124, pp. 28169-28177

NS3-6 Wafer-Scale Synthesis of Transition Metal Dichalcogenide Thin Films by ALD-Based Technique Towards Nanoelectronics and Optoelectronics Applications, ***Hao Zhu**, Z. Gu, T. Zhang, H. Liu, L. Chen, L. Ji, Q. Sun,* Fudan University, China

Two-dimensional (2D) transition metal dichalcogenides (TMDs) are attracting growing interests in recent years due to their unique electronic properties even with thickness at atomic scale. Though tremendous progress has been made in the understanding and implementation of the physical properties of TMDs in advanced micro-/nanoelectronic devices through conventional fabrication methods like mechanical exfoliation or chemical vapor deposition (CVD), the large-scale device integration for system-level applications have been severely bottlenecked by the lack of effective synthesis approaches to achieve wafer-scale, uniform, crystalline and stoichiometric TMD films.

Atomic layer deposition (ALD) is a surface-controlled film fabrication and can provide a promising route towards the synthesis of high-quality TMD thin films since the ALD approach follows the layer-by-layer deposition mechanism. As compared to other synthetic methods like CVD, ALD can enable precise thickness control on atomic scale and excellent film uniformity as well as good stoichiometry and crystallinity with proper annealing steps. Here, we have developed ALD-based synthesis approaches to prepare wafer-scale MoS_2 and WS_2 TMD thin films. Non-toxic $MoCl_5$, WCl_5 and hexamethyldisilathiane (HMDST) are used as precursors. Film characterizations have confirmed the wafer-level uniformity and good crystallinity by annealing in sulfur atmosphere. The field-effect transistor (FET) device arrays fabricated on the wafer-scale TMD film have shown excellent homogeneity in electrical performance, which provides good platform for further integration. In our work, we have fabricated optoelectronic device arrays as well as inverter, NAND, NOR, AND, and OR logic gates which have shown robust and repeatable logic functions. This has paves solid basis for the system and circuit-level applications.

It should also be noted that we have been designing and optimizing a high-temperature ALD process to grow crystalline TMD thin films eliminating the high-temperature annealing step in the previous flow. Preliminary experimental results have been achieved demonstrating satisfactory film quality, and the FET devices fabricated on it can exhibit repeatable switching performance with on/off ratio over 10^3. We believe that this can be a more encouraging synthetic method to prepare wafer-scale TMD thin films for practical electronic applications.

Author Index

Bold page numbers indicate presenter