Nanostructure Synthesis and Fabrication
Room Evergreen Ballroom & Foyer - Session NS-TuP

Nanostructures Synthesis and Fabrication Poster Session

NS-TuP-1 Membrane Property Modification for Energy-efficient Membrane Separations via Vapor Phase Infiltration*, **Yuri Choe**, M. Ong, D. Bergsman,* University of Washington

Vapor phase infiltration (VPI) is an emerging method synthesize inorganic materials within polymers using vapor-phase reactants. The incorporation of a secondary molecular species within the polymer via VPI can be used to control the mechanical properties, chemical stability, and thermal resistance of these polymers, making this VPI process applicable to many technologies. For example, VPI has been shown to make commercial membrane filters more stable to organic solvents and high temperatures, potentially enabling their use for emerging separation areas. However, only a handful of VPI process chemistries have been explored. To further expand the properties that can be produced using this technique, more diverse reactants need to be tested. This project focuses on testing organic VPI reactants, such as diethylzinc (DEZ) with ethylene glycol (EG) to synthesize zincones (Zn-organic hybrid material). We expose polyethersulfone (PES) membranes to these reactants, measuring diffusion of reactants and the possible successful reaction of these reactants, along with any changes in the mechanical, thermal, and chemical stability of the resulting hybrid membranes. X-ray photoelectron spectroscopy (XPS) is used to measure any reaction products, while scanning electron microscopy (SEM) along with energy dispersive X-ray (EDX) is used for depth profiling of elemental compositions Ultimately, this project focuses on producing hybrid organic-inorganic membranes with greater stabilities at high temperatures and with various chemicals, in the hope that these membranes could be used to separate materials previously inaccessible to polymer membranes, such as organic solvents.

NS-TuP-2 Stacking 2D Chalcogenides Utilizing ALD*, D. Shin, J. Yang, F. Krahl, **Sebastian Lehmann**, K. Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany

Chalcogenides, especially transition metal dichalcogenides (TDMCs, but also some other chalcogenides like SnS_2 and Sb_2Se_3) have a layered structure similar to graphene, but instead of being a semimetal they offer a wide variety from semiconducting to conducting materials that are interesting for efficient, fast (and possibly flexible) electronics. Their electronic behavior can be strongly influenced by the thickness of the material (e.g. how many sheets are stacked on top of each other) [1].

With atomic layer deposition (ALD) the layer stacking and individual layer thickness can be precisely controlled in the nm scale and several 2D materials have already been deposited with ALD [2], [3]. ALD is also scalable, unlike other methods for the synthesis of 2D materials e.g. exfoliation.

We utilize ALD to deposit superlattice stacks of 2D materials with “spacing” materials in between to examine their electrical properties. An example is our fabrication of a superlattice consisting of SnS_2 and Sb_2S_3 via ALD but results on other systems including TiS_2, PbS and other sulfides will be presented as well.

References

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NS-TuP-3 Stepwise Growth of Crystalline MoS_2 in Atomic Layer Deposition*, A. Cho, S. Ryu, **Seong Keun Kim**,* Korea Institute of Science and Technology, Republic of Korea

Atomic layer deposition (ALD) is considered a promising growth technique for transition metal dichalcogenides (TMDCs) because it ensures uniformity and homogeneity of the TMDC grains. However, the poor crystallinity of ALD-grown TMDCs remains a critical challenge. Although crystallinity depends on the growth mechanism, the growth behavior of crystalline TMDCs in ALD is unclear. We investigated the growth behavior of highly crystallized molybdenum disulfide (MoS_2) by ALD at 650 C with an extra pulse of remote H_2 plasma. Growth at high temperatures using the activated species aided surface diffusion of the adsorbates. The ALD process facilitates repeated growth and saturation of MoS_2, unlike the normal ALD of 3D bulk materials, where the film thickness monotonically increases with the number of ALD cycles. This unique behavior resulted from the evolution of the basal plane without dangling bonds. On the basal plane, MoS_2 lateral growth dominates vertical growth, and prolonged incubation is required for nucleation on the basal plane. The grain size is small (up to two monolayers) because of the limited mobility on SiO_2, and the grains of the third layer grow to a few hundred nanometers. These findings provide insights into the development of ALD technology for application to high-quality TMDCs.

NS-TuP-4 Electrical Properties of ZnO Nanostructures Derived from Sequential Infiltration Synthesis in Self-Assembled Block Copolymer Patterns: Effects of Alumina Priming*, **Won-Il Lee**, A. Subramanian,* Stony Brook University/Brookhaven National Laboratory*; N. Tiwale, K. Kisslinger,* Brookhaven National Laboratory*; C. Nam,* Brookhaven National Laboratory and State University of New York at Stony Brook

Self-assembled block copolymers (BCPs) are promising for the bottom-up, low-cost lithography of functional nanoarchitectures. Especially, BCP thin films can be directly converted into inorganic replicas by sequential infiltration synthesis (SIS), an organic-inorganic hybridization method derived from atomic layer deposition (ALD), which can selectively infiltrate target inorganic materials into one of the polymer blocks in vapor phase. For the high-fidelity infiltration of target materials, alumina is often first infiltrated (“alumina priming”) to overcome weak binding of the precursors of target inorganic materials with BCP templates. However, the effects of priming alumina–an electrical insulator–on the electrical properties of the final inorganic nanostructures have been rarely studied. In this work, we investigate the effects of alumina priming on the structural and electrical properties of ZnO nanowire fingerprint patterns fabricated by SIS using diethylzinc (DEZ) and water vapor on the lamellar pattern of self-assembled poly(styrene-b-methyl methacrylate) (PS-b-PMMA) BCP thin film as a function of the amount of infiltrated AlOx contents controlled by trimethylaluminum (TMA) exposure time during a single alumina priming cycle. We find that the characteristic dimension, chemical composition, and electrical conductivity of synthesized ZnO nanostructures could be fine-tuned by controlling TMA exposure duration. Specifically, increasing TMA exposure time naturally led to improved ZnO infiltration/structural fidelity and increasing feature dimensions (width and height of nanowires), accompanied by elevating Al contents. Counterintuitively, the electrical resistivity of ZnO nanostructure, extracted via transmission line method (TLM) from the two-terminal current-voltage characteristics, was initially decreasing with increasing TMA exposure time, down to 14.3 kΩ·cm, with corresponding Al concentration of 5.3 at.%., while a further increased TMA exposure duration beyond rendered the resistivity up to two orders of magnitude higher. The observed enhancement in ZnO electrical conductivity by alumina priming could be understood from the well-known case of Al-doped ZnO (AZO), where optimal Al doping in a similar concentration range as in the current study maximizes the ZnO conductivity. The results show that the alumina priming condition typically used for SIS in the field would generally improve the conductivity of infiltration-synthesized ZnO nanostructures, along with their infiltration and structural fidelities.

NS-TuP-5 *in-Situ* XPS Analysis for Wo_3 Sulfurization Process*, C. Chang, B. Liu,* Taiwan Instrument Research Institute, NARlabs, Taiwan*; **Yang-Yu Jhang**,* Taiwan Instrument Research Institute, NARLabs, Taiwan

TMDs are layered materials that can exhibit semiconducting, metallic and even superconducting behavior. In the bulk formula, the semiconducting phases have an indirect band gap. Recently, these layered systems have attracted a great deal of attention mainly due to their complementary electronic properties when compared to other 2D materials. However, these bulk properties could be significantly modified when the system becomes monolayer; the indirect band gap becomes direct. Such changes in the band structure when reducing the thickness have important implications for the development of novel applications, such as high photoluminescence (PL) quantum yield, excellent flexibility, and thermal stability.

Previous studies have demonstrated direct sulfurization of the metal precursor as an effective route to produce large-area TMDs. In this paper, we have produced WS_2/SiO_2 by depositing WO_x thin films directly onto Si wafer followed by sulfurization to produce WS_2/SiO_2 heterostructures. However, ALD technique is well known for its thickness controllability, reproducibility, wafer-level thickness uniformity and high conformality. Here, we grew WO_x films by ALD method, and the synthesized WS_2 layer retained the inherent benefits of the ALD process. The overall experiments and measurement were carried out on our homemade 6" cluster systems, which include ALD, RTP, and XPS modules. The sample transfer inside were under 5x10^{-6} torr to avoid air pollution. WO_x films were deposited on Si wafer at ALD moduleat ~230℃. After that, sulfurization process were progressed at RTP module, which connected the sulfurization equipment. This unit heats TAA powder at ~130℃ and results H_2S gas. Lastly, XPS measurements revealed binding energy shift of $W4f_{5/2,\,7/2}$, indicating mostly WO_x converse to WS_2 during the process.

NS-TuP-7 Reversible Electronic Phase Transition in VO_2 Thin Films and Nanostructures*, **Jun Peng**, D. Hensel,* Center for Hybrid Nanostructures, Universität Hamburg, Germany*; L. Maragno, N. James,* Integrated Materials Systems Group, Institute of Advanced Ceramics, Hamburg University of Technology, Germany*; C. Heyn,* Center for Hybrid Nanostructures, Universität Hamburg, Germany*; K. Furlan,* Integrated Materials Systems Group, Institute of Advanced Ceramics, Hamburg University of Technology, Germany*; R. Blick, R. Zierold,* Center for Hybrid Nanostructures, Universität Hamburg, Germany

High-quality vanadium dioxide (VO_2) reveals a phase transition from a dielectric to a metallic state at around 340 K. Despite ongoing discussions regarding the underlying cause of this transition. It has been demonstrated that the complex coupling among lattice, charge, spin, and orbital results in an electronic transition that alters the sample's electrical, thermal, and optical properties at the phase transition. This unique property has led to its utilization exploration in various electronic and optoelectronic applications, including high-temperature thermoelectric materials, thin-film resistors, and optical modulators.

We will present the synthesis and characterization of tailor-made VO_2 thin films (2D), nanotubes (1D), and inverse opals (3D) prepared through a combination of thermal atomic layer deposition (ALD, from TDMAV plus water in a custom-built reactor) and subsequent thermal annealing. Temperature-dependent electrical measurements, Raman spectroscopy, and UV-Vis-NIR characterization comprehensively evaluate the electronic phase transition. First, the report will discuss the impact of various parameters during preparation on the thin film quality and the insulator-to-metal transition (IMT), including substrates, ALD parameters, and annealing conditions. Afterward, the fabrication of VO_2 nanostructured electrical devices will be highlighted, based on the optimized recipe for synthesizing VO_2 thin films with a phase transition temperature of around 335 K, a hysteresis width of approximately 10 K, and a remarkable resistance change of about three orders of magnitude. Specifically, the phase transition in electrically contacted, individual core-shell (Si-VO_2) nanowires is shown. Moreover, we show that the applied voltage can trigger the IMT in such an ALD-based one-dimensional VO_2 device. Finally, we will outline the preparation route for switchable photonic crystals based on inverse VO_2 opals.

Based on the reported results, it can be concluded that ALD of VO_2 holds significant promise for the development of functional, switchable materials in 1D (elongated structures), 2D (thin films), and 3D (inverse opals or bulk-like samples) laying a solid basis for future large-scale applications. Exemplarily, energy-efficient, next-generation nanostructured smart windows are conceivable that can dynamically alter their transmission properties in response to external stimuli, such as temperature, voltage, and current.

NS-TuP-8 Fabrication of 2D-SnS_2 Film Using Atomic Layer Deposition and Hydrogen Sulfide Gas Annealing*, **Yeonsik Choi**, S. Song, J. Kim, D. Lee, J. Bae, Y. Lee, H. Jeon,* Hanyang University, Korea

2D-tin disulfide (SnS_2) is a material with unique physical, optical, and electrical characteristics that can be used in various optoelectronic devices. In addition, it is possible to fabricate a 2D-SnS_2 material forming a two-dimensional layered structure with precise thickness control using atomic layer deposition (ALD). Since 2D-SnS_2 deposited through ALD is based on a low-temperature process, it has the advantage of being applicable not only to silicon substrates but also to flexible substrates such as polyimide (PI) and polyethylene terephthalate (PET). However, since the process is performed at a low temperature, the crystallinity of the material is low and the film quality is relatively poor compared to other processing methods. Therefore, various post-annealing processes that improve the crystallinity of SnS_2 material have been studied, and various aspects such as the crystallinity improvement or the phase transitions were shown depending on the post-annealing atmospheres and temperatures. In this work, we analyzed the crystallinity and grain sizes of 2D-SnS_2 deposited by ALD according to the concentration of hydrogen sulfide (H_2S) in a H_2S gas atmosphere at 4.00 and 99.99% and the high crystallinity was shown at 350℃ with a high concentration of 99.99% H_2S gas. Carrier concentration was also measured and more than 10^{18} cm^{-3} was measured at 350℃ in the 99.99% concentration of H_2S atmosphere. Comparing to 4.00% concentration of H_2S, pure tetravalent positive states of Sn (Sn^{4+}) were confirmed through binding energy analysis in the post-annealing in the H_2S atmosphere of 99.99% concentration. In addition, as a result of the post-annealing process after deposition on a 4-inch large-area substrate, a high film uniformity and high step coverage (> 98%) on a trench structure wafer were achieved confirming the possibility of future application to the semiconductor industry.

NS-TuP-11 Phase Control of Two-Dimensional Tin Sulfide Compounds Deposited by Atomic Layer Deposition*, **Dong Geun Kim**, J. Lee, J. Choi, J. Ahn,* Hanyang University, Korea

Two-dimensional (2D) metal chalcogenides have received great attention because of their unique properties, which are different from bulk materials. Among 2D metal chalcogenides, tin sulfide compounds (SnS_x) including tin monosulfide (SnS) and tin disulfide (SnS_2) have excellent optoelectronic properties, low melting point, thermal stability, and hydrolytic stability compared to the other representative 2D materials such as MoS_2 and WS_2. Because the electrical property of SnS_x is highly dependent on its phase, phase-selective deposition has been required. It has been reported that high-quality SnS_x flakes can be synthesized for chemical vapor deposition (CVD) and sulfurization of metals or metal oxides. However, there is a limitation of applying for next-generation semiconductor devices because of a high process temperature and poor uniformity. Meanwhile, the ALD method based on the self-limiting reaction enables large-area uniformity and conformality over complex-shaped substrates with low growth temperatures. In addition, since the properties of 2D materials are strongly affected by their thickness, the ALD with atomic level thickness control is a suitable deposition technique for 2D materials. In this study, we investigated the phase transition tendency of SnS_x thin films according to deposition temperature and post-annealing atmosphere. SnS_2 phases were dominated at H_2S ambient annealing of relatively low annealing temperature regardless of deposition temperature, according to the increased annealing temperature, the phase transition for SnS_2 to SnS occurred. These phase transitions from SnS_2 to SnS phase were observed at forming ambient gas annealing. In addition, as the annealing pressure decreased regardless of ambient gas, the phase transitions occurred at a lower temperature. Finally, the electrical properties were evaluated by fabricating thin film transistors (TFTs) using optimized conditions of SnS_2 and SnS thin films.

NS-TuP-12 Area-Selective Deposition of 2D-MoS_2 using Self-Assembled Monolayer*, **Jeong-hun Choi**, D. Kim, S. Lee, J. Ahn,* Hanyang University, Korea

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. Significant efforts have been placed to apply MoS_2 in industrial fields, leading to significant progress in the deposition method of MoS_2. [1],[2] However, patterning technology for MoS_2 remains a challenge. In particular, 2D materials like MoS_2 have extremely thin and weak interlayer bonding due to the absence of dangling bonds, making it difficult to apply traditional top-down patterning approach. Therefore, we demonstrated a new area-selective deposition method for MoS_2 using self-assembled monolayer (SAM). To prevent the degradation of SAM, the deposition of MoS_2 was carried out using a pulsed metal-organic chemical vapor deposition (MOCVD) method, which allowed for the synthesis of high-quality MoS_2 at a low temperature. The growth of MoS_2 was effectively prevented by the SAM patterned using photolithography processes. The selectivity for MoS_2 according to the length of the SAM backbone was investigated using X-ray Fluorescence spectroscopy and Raman measurement. Additionally, the influence of the SAM coating process on the crystallinity and impurity concentration of the MoS_2 film was confirmed using X-ray diffraction and X-ray photoelectron spectroscopy. Furthermore, the potential of area-selective deposition of MoS_2 using SAM was demonstrated by fabricating a MoS_2 gas sensor.

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