Nanostructure Synthesis and Fabrication
Room Event Hall - Session NS-MoP

Nanostructure Synthesis and Fabrication Poster Session

NS-MoP-1 Structural Modifications of Porous Templates with Pbte ALD Coatings, *Haifeng Cong*, ***Helmut Baumgart***, Old Dominion University

Porous silicon templates have attracted increasing attention because of their controllable geometry, tunable nanoporous structure, large pore volume/high specific surface area, and versatile surface chemistry. Porous templates show significant advantages and application potential in microfluidics, electro-osmotic pumps, biomedical drug delivery, sensing, photonics, integrated opto-electronics, energy conversion, thermoelectrics, thermo-acoustics, electronics and Lab-on-a-chip technology for biomedical, pharmaceutical and environmental monitoring. For this study we have focused on energy conversion with ALD lead chalcogenide PbTe film coatings since PbTe is a useful narrow band gap thermoelectric material that can operate at comparatively higher temperatures in the range of 600~850 K due to its better chemical stability and high melting point. PbTe thin films have been synthesized inside of porous silicon templates with native oxide by Atomic Layer Deposition (ALD) using lead (II)bis(2,2,6,6-tetramethyl-3,5-heptanedionato) ($Pb(C_{11}H_{19}O_2)_2$), (trimethylsilyl) telluride ($(Me_3Si)_2Te$) as ALD precursors for lead, and tellurium. The Si native oxide surface was functionalized before ALD PbTe thin film deposition to ensure reproducible chemisorption of the ALD precursor compounds. The growth temperature during ALD was varied over a range from 135^{o}C to 170^{o}C. The Lead precursor was volatilized at a temperature of 140 ^{o}C and the Tellurium precursor was heated at 40 ^{o}C. The chamber base pressure was kept at 40 mTorr.Several physical characterization techniques have been employed to determine the ALD PbTe thin film characteristics. The crystal structure and phase purity of samples of PbTe films were analyzed by X-ray diffraction (XRD). The film morphology and structure of the products were determined by field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM). The surface roughness was analyzed by atomic force microscopy (AFM). The analysis of the composition and stoichiometry of the ALD coatings were carried out by Energy dispersive X-ray spectroscopy (EDS). The experimental evidence revealed the ALD growth of lead telluride followed the Vollmer-Weber Island growth model. We found a strong dependence of the nucleation process of the polycrystalline grain distribution on the temperature.We report a systematic study of all ALD parameters required to optimize the coating of the interior walls of porous membranes which open front and backside, straight pores of varying diameter and porosity with dead endings in the substrate and pores with spatially modulated ondulating cross sectional shapes.

NS-MoP-2 Area-Selective Solid-State Synthesis of Nickel Silicide Nanostructures, ***Gabriele Botta***, Nanogune, Italy; *Mato Knez*, nanogune, Croatia

Over the past decade, metal silicides have been re-discovered for their significant potential across various fields of nanotechnology. [1,2,3] However, integrating them into modern devices continues to pose challenges, primarily due to limited control over phase formation during their synthesis. [4] Additionally, since they are typically grown as continuous layers, their structuring often relies on complex top-down patterning techniques, which significantly limit their practical applications. [5] This study addresses these issues by proposing a method for Area-Selective (AS) silicidation (Fig. 1a SD). Our approach ensures that during material synthesis, the resulting silicide nanostructures acquire a predefined morphology and nucleate exclusively in the targeted regions of the substrate.

The AS silicidation process is demonstrated through the formation of $NiSi_2$ structures on Si(100) and Si(111) substrates (Fig. 1b SD), and its broader applicability is further illustrated with the successful AS synthesis of Cu_3Si (Fig. 1c SD). To direct growth, the silicon substrates are patterned using ion beams, which create surface defects that promote silicide nucleation in the desired areas. Unlike conventional Solid State (SS) synthesis, which involves annealing a metal thin film on silicon, our method begins with an ALD deposited metal oxide. Silicidation is performed by annealing in the presence of a reductant (H_2), which reduces the metal oxide to its metallic state. The resulting metal then reacts with the underlying silicon, forming a metal silicide. During this two-step reaction, the material re-arranges along surface defects, which act as templates, guiding both the shape and positioning of the forming silicide crystals.

The effectiveness of this multi-step fabrication method, coupled with its adaptability to various metal-silicide systems, underscores its potential to create functional, structured silicides without the need for post-synthesis nanopatterning.

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NS-MoP-3 Atomic Layer Deposition by Pressure-Driven Convective Flow Through 3D Nanocomposite Structures, ***Austin Cendejas***, *Benjamin Greenberg, Kevin Anderson, Boris Feygelson*, US Naval Research Laboratory

Conformal coating of high aspect ratio tortuous 3-dimensional nanostructures has been shown to require careful consideration of dose and purge times to achieve uniform ALD coatings of high quality.[1,2] Specifically, through static-dosing of ALD precursors cycle times for complete surface saturation are often in excess of 10s of minutes for macroscopic substrates.[2] Recently our group has demonstrated an order of magnitude reduction in saturation dose times by forcing precursor flow through the compact via a pressure gradient of 50-100 Torr across the 3D nanocomposite. In this work, diethylzinc (DEZ) and water were pulsed sequentially to deposit conformal films of ZnO completely through the ~2mm thickness of nanocomposite compacts comprised of 200 nm SiO_2 nanoparticles. Due to the nonuniform pressure across the nanocomposite compact, precursors undergo a transition from convective to diffusive transport. Preliminary modeling of the internal pressure gradients of the compacts was utilized to determine the relative contributions of these two transport modes in addition to structural nonuniformities (i.e. cracks, large pores, etc.). It was found that uniformity in the internal pore structure and structural integrity of the initial, uncoated, nanoparticle compact was crucial in achieving uniform coatings on the entire surface. Additionally, the effect of precursor partial pressure during doses on saturation dose times and the extent to which the diffusive transport could be enhanced was studied. Saturation dose times were measured via *in-situ* quadrupole mass spectrometry of the effluent gas and film uniformity and conformality were studied via *ex-situ-* cross-sectional scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDXS), and X-ray diffraction (XRD).

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NS-MoP-4 Atomic Layer Deposition for Novel Nanocomposite Solids with New Functionalities, ***Boris Feygelson***, *Benjamin Greenberg, Kevin Anderson, James Wollmershauser*, U.S. Naval Research Laboratory; *Austin Cendejas*, American Society of Engineering Education, postdoc residing at U.S. Naval Research Lab; *Sarshad Rommel, Mark Aindow*, Department of Materials Science and Engineering, Institute of Materials Science, University of Connecticut

Scaling grains down to nanometer size enhances many properties of polycrystalline solids due to an increase in the grain boundary interfacial volume fraction. Sintering of nanoparticles is the most versatile way to produce nanocrystalline solids of various materials. A crucial prerequisite for achieving advanced, size-dependent properties in these nanocrystalline solids is removing porosity by sintering while preserving nanoscale morphology and grain size. Using our environmentally controlled pressure-assisted sintering (EC-PAS) technique, we have successfully produced fully dense ceramics with grain sizes down to 4 nm [1,2].

By engineering nanoparticle building blocks with designed core/shell structures using particle atomic layer deposition (ALD) [3], we can fabricate novel nanocomposite solids with properties controlled by rationally designed core/shell geometries, constituent properties, and the resultant vast network of interfaces. We refer to such nanocomposites as artificial interfacial solids (AIS). For instance, when the core/shell nanoparticle structure is preserved during EC-PAS, the resulting nanocomposite comprises isolated nanoparticles (cores of initial core/shells) embedded in a host material (a continuous 3D percolated network of shells from adjacent core/shells merged together).

We have further developed the EC-PAS process to produce percolated AIS (PAIS) nanocomposite solids with two separate and interconnected 3D paths for electron and/or heat transport. The process involves creating a porous compact from nanopowder, followed by ALD infiltration and conformal deposition of a second material on all available surfaces within the porous compact [4], and finally, a sintering stage. The nanopowder in the sintered nanocomposite forms the first 3D percolated network, which becomes surrounded by the deposited and merged 3D network of the second material. Both networks are strongly bonded to each other through sintering.

Examples of AIS and PAIS nanocomposites for various applications will be presented and discussed, highlighting their potential properties, applications, and versatility.

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NS-MoP-5 Nanostructure and Conductivity of SiO2/ZnO:Al Nanocomposites Fabricated by ALD Infiltration and Pressure-Assisted Sintering*, **Benjamin Greenberg**, Kevin Anderson, Alan Jacobs, Joseph Prestigiacomo, Zoey Warecki, Todd Brintlinger,* U.S. Naval Research Laboratory*; Austin Cendejas,* ASEE Fellow Residing at U.S. Naval Research Laboratory*; Eric Patterson, James Wollmershauser, Boris Feigelson,* U.S. Naval Research Laboratory

Over the past decade, environmentally controlled pressure-assisted sintering (EC-PAS) has been established as a reliable technique for producing dense, nanocrystalline ceramics with exceptional mechanical properties due to their low porosity (less than 1%) and small grain size (as small as 4 nm). Examples include transparent Mg_2AlO_4 with hardness up to 22 GPa[1] and WC with hardness up to 39 GPa[2]. Recently, our group has demonstrated that EC-PAS can also be combined with ALD infiltration to produce nanocomposites with unique combinations of optical, electrical, and thermal properties, which are tunable via the sintering conditions and the number of ALD cycles.

In this work, we examine the nanostructure and electrical properties of SiO_2/ZnO:Al nanocomposites fabricated by this combination of EC-PAS and ALD with the aim of understanding how to maximize electrical conductivity. In an air-free process chain, porous compacts of SiO_2 nanoparticles are infiltrated with ZnO:Al using diethylzinc, trimethylaluminum, and water (15:1 ZnO:Al_2O_3 cycle ratio) prior to sintering at 450 °C and 2 GPa to produce monolithic nanocomposites with ~1 mm thickness and ~100 nm SiO_2 domain size. 16 or 32 ALD cycles yields conductive ZnO:Al channels comprising 16% or 27% of the nanocomposite's volume with nominal channel width of ~6 or ~12 nm and average zincite crystallite size of ~4 or ~6 nm, respectively. Based on theoretical predictions and experimental measurements of the metal-insulator transition criterion for networks of ZnO nanocrystals,[3] these channel widths are expected to be sufficient for metallic/band-like charge transport. Temperature-dependent resistance measurements down to as low as 0.4 K, however, reveal negative temperature coefficients characteristic of non-metallic charge transport. Specifically, for 16 cycles of ZnO:Al ALD, the charge transport mechanism appears to be Efros-Shklovskii variable-range hopping, and for 32 cycles, the temperature dependence is weaker but still clearly negative. To investigate whether this lack of metallic conduction is due to deviations from the ideal ZnO:Al geometry (percolating channels with uniform thickness), we characterize the nanocomposites' micro- and nanostructure via scanning electron microscopy (SEM) and scanning transmission electron microscopy with energy-dispersive x-ray spectroscopy (STEM-EDS). We also compare the nanocomposites' electrical properties to those of ALD ZnO:Al films on SiO_2 wafers and explore the influence of the SiO_2/ZnO:Al interface on conduction.

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NS-MoP-6 Creation of Nanowire-Bundled Grain Boundaries in Bi_2Te_3-Based Thermoelectric Materials via Atomic Layer Deposition*, **Gwang Min Park**, Seunghyeok Lee,* Korea Institute of Science and Technology (KIST), Republic of Korea*; Jinseok Hong, Seokho Nahm,* Hanyang University, Korea*; Seung-Hyub Baek, Jin-Sang Kim,* Korea Institute of Science and Technology (KIST), Republic of Korea*; Seung-Yong Lee,* Hanyang University, Korea*; Seong Keun Kim,* Korea Institute of Science and Technology (KIST), Republic of Korea

Improving thermoelectric material performance is essential for energy harvesting and solid-state cooling applications. This study demonstrated a novel structure of Bi_2Te_3-based thermoelectric materials with ZnO nanowire-bundled grain boundaries, realized via atomic layer deposition (ALD) and subsequent spark plasma sintering (SPS). The ZnO nanowires formed at the interfaces due to the rearrangement of the ALD-grown ZnO ultrathin layer over $Bi_{0.4}Sb_{1.6}Te_3$ powder, driven by localized heating during the SPS process and the anisotropic nature of ZnO. The nanowire-bundled interfaces enhanced phonon scattering, thereby reducing lattice thermal conductivity while maintaining excellent electronic transport. This structural innovation achieved a high figure-of-merit, $zT_{max} = 1.69 \pm 0.09$ at 373 K and an average zT of 1.55 over the range of 300–473 K. A thermoelectric module fabricated with 127 p–n pairs achieved a record-high conversion efficiency of 6.57% at a temperature difference of 163 K. These findings highlight the potential of nanowire-bundled interfaces to enhance the thermoelectric material performance and pave the way for scalable next-generation energy conversion technologies.

NS-MoP-7 Surface Engineered Polymeric Membranes for Improved Fouling Resistance and Superior Oil-Water Separation*, Bratin Sengupta, Yining Liu, Seth Darling, **Jeffrey Elam**,* Argonne National Laboratory

Fouling is a grand challenge which severely degrades membrane system performance, especially for applications in water treatment. Polyvinylidene fluoride (PVDF) is widely used for membrane fabrication due to its inertness and stability. However, PVDF is extremely susceptible to fouling due to its inherent hydrophobicity. Post-synthetic functionalization of PVDF membranes can increase the membrane-foulant interaction energy and reduce fouling. In this regard, vapor phase functionalization is particularly promising since it can produce ultrathin films (<5 nm) which do not alter the membrane pore structure and morphology. For example, thin metal oxide layers impart hydrophilicity and are often positively charged at the pH of the wastewater, realizing high membrane – foulant interaction energy. Atomic layer deposition (ALD) can produce ultrathin metal oxide layers on polymers, but the inert PVDF surface inhibits nucleation necessitating a prohibitively large number of ALD cycles to impart fouling resistance. In this presentation, I describe a novel pretreatment step that dramatically accelerates the nucleation of metal oxide ALD on PVDF. Using this pretreatment, we create highly effective anti-fouling surfaces using one ALD cycle compared to >150 ALD cycles on the pristine PVDF membranes. This strategy is effective for a range of ALD metal oxides including Al_2O_3, TiO_2, and ZnO. We employ a suite of in situ and ex situ analytical techniques to elucidate the surface chemical mechanism for the enhanced nucleation. We perform extensive characterization and testing of the surface-engineered PVDF to quantify the benefits for water filtration and demonstrate >99% flux recovery with only ~1% irreversible flux loss during operation. We also demonstrate the efficacy of our surface engineered PVDF membranes for oil-water separation. Efforts are underway to perform this surface treatment using our roll-to-roll, atmospheric pressure spatial ALD system.

NS-MoP-8 Interface Engineering of 2D MoS_2 Devices through ALD Oxidant Selection*, Si Eun Yu, Thi Thu Huong Chu, Minjong Lee, Dushyant M. Narayan, **Doo San Kim**, Dan N. Le,* University of Texas at Dallas*; Rino Choi,* Inha University, Republic of Korea*; Jiyoung Kim,* University of Texas at Dallas

Two-dimensional transition metal dichalcogenides (2D TMDCs) have emerged as promising semiconductor materials for next-generation electronic devices due to their high mobility within atomic-scale thickness. To preserve the superior performance of 2D semiconductors in field-effect-transistor (FET) applications, gate dielectrics should be deposited via physisorption to prevent chemical reactions between the atomic-scaled 2D surface and ALD precursors.[1] A straightforward approach to achieving this is reducing the deposition temperature; however, this is often accompanied by the formation of lower-quality gate dielectrics. It is thus essential to establish alternative strategies for gate dielectric deposition, such as exploring precursors and/or employing advanced ALD techniques.

This study will present a promising approach utilizing H_2O_2 as an oxidant source for gate dielectric deposition, along with a strategy to achieve uniform deposition without damaging 2D materials. Comparative studies were conducted using H_2O, O_3, and H_2O_2 for high-k HfO_2 growth on 2D MoS_2. Each oxidant exhibited distinct growth behaviors. While O_3 facilitated uniform HfO_2 deposition, its strong oxidation effect led to Mo-S bond conversion into Mo-O bonds, inducing damage to the MoS_2 surface. The resulting surface damage led to degraded FET device performance, indicating that O_3 cannot be a viable candidate for high-k dielectric deposition on 2D semiconductors. For H_2O and H_2O_2, achieving fully conformal coverage remains a significant challenge. To address this limitation, stop-valve techniques were employed to extend oxidant exposure time and dosage, effectively enhancing dielectric coverage while maintaining interface integrity. The interface properties were further analyzed using a top-gate FET structure,[2] providing insights into the interface trap density associated with different oxidants.

This presentation will cover material characterization, ALD techniques, and electrical performance, offering a comprehensive evaluation of oxidant effects on 2D semiconductor integration.

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NS-MoP-9 Facile Synthesis of Copper Germanium Oxide with Carbon Shell for Lithium Ion Battery Anode Applications

Deug Hyun Nam, Chan Woong Na, ***Yoon Myung****,* Korea Institute of Industrial Technology, Republic of Korea

Metal germanates such as Zn_2GeO_4, Fe_2GeO_4, and Co_2GeO_4 have been widely studied for various applications, including catalysts, sensors, lasers, and batteries. Cu_2GeO_4 has recently emerged as a promising candidate for lithium-ion battery anodes and sensor technologies, owing to its high mechanical strength, structural stability, and potential for enhanced electrochemical performance. However, traditional synthesis methods for Cu_2GeO_4 despite its promising properties, the synthesis of Cu_2GeO_4 remains challenging, with traditional methods often requiring high temperatures or complex multi-step processes. In this study, we introduce a simple and effective hydrothermal method for synthesizing carbon coated Cu_2GeO_4 nanoparticles. The size distribution of $CuGe_2O_4$ nanoparticles were in the range of 20 to 50 nm, as observed through scanning electron microscopy (SEM), and their structure was confirmed as tetragonal by X-ray diffraction (XRD) (JCPDS 83-1872). Raman spectroscopy indicated the presence of crystalline Ge, supporting the material's structural integrity. These Carbon coated Cu_2GeO_4 nanoparticles show significant potential for lithium-ion battery anodes where their enhanced chemical and mechanical stability, and electrochemical performance offer significant advantages over conventional materials.

NS-MoP-10 Amorphous Boron Nitride Deposited on MoS_2 Monolayers by Thermal Atomic Layer Deposition for High-Performance Two-Dimensional Electronics

Yu-Chuan Lin, National Yang Ming Chiao Tung University (NYCU), Taiwan

We report a wafer-scale, low-temperature process using thermal atomic layer deposition (ALD) with sequential flows of BCl_3 and NH_3 for the synthesis of uniform, conformal amorphous boron nitride (aBN) thin films on Si and 2D semiconductors. The deposition temperatures of aBN between 125 and 250 °C lead to stoichiometric BN films with high stability against oxidation and yield a dielectric strength of 8 MV/cm. The impact of ALD processing parameters on the resulting morphology, atomic compositions, and structural properties of aBN on Si was evaluated. Furthermore, we present the ALD of ultrathin (2–20 nm) aBN as a scalable and non-water-based process for dielectric integration with 2D semiconductors. The lack of nucleation sites on van der Waals surfaces to form thin, uniform dielectric layers could lead to interfacial defects that degrade the device performance. Therefore, by utilizing two-step approach including *in situ* seeding at lower temperature and carrying out ALD back at regular temperatures, we were able to form uniform aBN dielectric layers on 2D surfaces and fabricate few-layer quantum well structures made of aBN/MoS_2 building blocks and aBN-encapsulated double-gated monolayer MoS_2 field-effect transistors to investigate the impact of aBN dielectric on MoS_2 properties. Our work in scalable aBN dielectric integration provides a means for improving the performance of 2D materials for next-generation electronics.

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