

Nanostructure Synthesis and Fabrication Room Plaza ABC - Session NS+EM-SuA

2D Materials (1:30-3:30 pm)/Laminate, Multicomponent, and Emerging Materials (4:00-5:30 pm)

Moderators: Jiyoung Kim, University of Texas at Dallas, Dennis Hausmann, Lam Research, Sumit Agarwal, Colorado School of Mines

1:30pm NS+EM-SuA-1 Plasma-enhanced Atomic Layer Deposition of Large-area MoS₂: From 2-D Monolayers to 3-D Vertical Fins, Akhil Sharma, S Karwal, V Vandalon, M Verheijen, Eindhoven University of Technology, Netherlands; H Knoops, Oxford Instruments Plasma Technology, UK; R Sundaram, Oxford Instruments Plasma Technology; W Kessels, A Bol, Eindhoven University of Technology, Netherlands

Atomic layer deposition (ALD) might prove as a key enabler for tackling the current challenge of large-area growth of 2-D materials with wafer-level uniformity and digital thickness controllability. In this contribution, we have implemented plasma-enhanced ALD to synthesize large-area MoS₂ thin films with tuneable morphologies i.e. in-plane and vertically standing nanoscale architectures on CMOS compatible SiO₂/Si substrates. The large scale 2D in-plane morphology has potential applications in nanoelectronics, while the 3D fin structures could be ideal for catalysis applications such as water splitting.

The ALD process was characterized over a wide temperature range between 150°C - 450°C by using a combination of a metal organic precursor [(*n*TbBu)₂(NMe₂)₂Mo] as Mo source and a H₂S based plasma as the co-reactant. A saturated growth rate of ~0.9 Å/cycle was observed within the parameter space investigated. The number of layers in the MoS₂ film could be controlled down to a mono-layer by tuning the number of ALD cycles. The precise variation in thickness was confirmed by Raman spectroscopy which showed a monotonic decrease in the frequency difference between the two characteristic modes for MoS₂ with decreasing layer thickness down to 21 cm⁻¹ which corresponds to a monolayer. The photoluminescence spectroscopy data was in line with these results, showing a strong peak at ~1.9 eV corresponding to the direct band gap transition for the mono-to-few layered MoS₂. XPS showed that the films were pure and stoichiometric in nature with negligible trace amounts of carbon and oxygen contaminants. The HAADF TEM analysis of the films grown at 450°C showed that during the initial ALD cycles, MoS₂ islands extended in the lateral direction and merged to form a film which continued to grow in a layer-by-layer fashion until a certain thickness. Thereafter, an out-of-plane vertical growth mode started to dominate as shown by cross-sectional TEM analysis. The origin of this transition from in-plane to out-of-plane growth mode might be attributed to the enhanced precursor adsorption on high surface energy locations such as grain boundaries, kinks or ledges. Due to the crowding effects at these favourable adsorption sites, vertical growth of MoS₂ is observed.

These results show that ALD might be instrumental in realizing not only the large area growth of high-quality 2-D materials but can also be applied as a tool to control the morphology of thin films which might yield into interesting structures (including heterostructures) for various optoelectronics and catalysis applications.

1:45pm NS+EM-SuA-2 Low-Temperature Atomic Layer Deposition of MoS₂ Films, Michael Moody, T Jurca, A Henning, J Emery, B Wang, J Tan, T Lohr, T Marks, L Lauhon, Northwestern University

Molybdenum disulfide (MoS₂) is a widely-studied layered semiconductor with interesting fundamental optoelectronic properties and promising applications in the two-dimensional limit. If a suitable metal-organic precursor and reaction chemistry were available, atomic layer deposition (ALD) could extend the impact of fundamental work on this system by enabling growth of consistent, large-area films. Here we report the use of the volatile molybdenum complex, tetrakis(dimethylamido)molybdenum (MoTDMA) and H₂S for direct low-temperature ALD of MoS₂ films. Preliminary wet chemical screening revealed a high reactivity of MoTDMA with H₂S, suggesting suitable chemistry for MoS₂ ALD under mild conditions. Indeed, ALD growth of amorphous MoS₂ was subsequently achieved at temperatures as low as 60°C, a temperature compatible with polymer substrates and photolithographic patterning over multiple length scales. Associated with the high reactivity of this system is robust nucleation, even on layered materials with interlayer van der Waals bonding such as graphene and exfoliated MoS₂. Annealing of amorphous MoS₂ films results in continuous, semiconducting nanocrystalline films, as

characterized by multiple structural techniques including GIXRD and HRTEM. This work provides a route to 2D materials via ALD and post-processing, and exploration of related compounds to further tailor reactivity and ALD window is in progress.

2:00pm NS+EM-SuA-3 Dielectric-MoS₂ Interfaces Grown by Atomic Layer Deposition, Steven Letourneau, Boise State University; A Mane, J Elam, Argonne National Laboratory; E Graungard, Boise State University

Molybdenum disulfide (MoS₂) has become a prototypical transition metal dichalcogenide (TMDC) atomic-layered material because of its unique materials properties. For example, bulk MoS₂ exhibits an indirect band-gap of 1.3 eV, while a single monolayer has a direct band-gap of 1.8 eV. Recently, nanometer scale transistor devices have been made with MoS₂ and graphene, yet much of this work relies on layered materials prepared using chemical vapor deposition (CVD) and mechanically exfoliation. Multiple reports have demonstrated the growth of MoS₂ via CVD, but only a few studies have reported MoS₂ growth using atomic layer deposition (ALD), which offers potential advantages for high volume semiconductor manufacturing. Here, we report the ALD of few-layer MoS₂ films using MoF₆ and H₂S on various ALD-grown dielectric surfaces and the ALD of metal oxides on the ALD MoS₂ films at temperatures between 100-300 °C. In particular, we used in-situ quartz crystal microbalance measurements to investigate the nucleation of MoS₂ ALD on oxide surfaces and vice versa. In general, self-limiting growth of MoS₂ was observed on a wide range of dielectric surfaces including alumina, magnesia, and hafnia. The ALD MoS₂ films were amorphous as-deposited, but crystallized into a layered atomic structure upon annealing at 800 °C. Using in-situ spectroscopy and electrical measurements, growth inhibition of MoS₂ was seen depending on the growth substrate. These studies provide insight into the low-temperature ALD of MoS₂ and provide guidance for the ALD of additional TMDC films.

2:15pm NS+EM-SuA-4 Plasma-Enhanced Atomic Layer Deposition of sub-5 nm high- k Dielectrics on 2D Crystals, Katherine Price, F McGuire, A Franklin, Duke University

Recently, 2D crystals have been targeted as the basis for enabling many exciting nanoelectronic and optoelectronic applications. One of the main challenges inhibiting the integration of 2D crystals is uniform deposition of a scalable, high-quality dielectric, which serves as an integral aspect of some devices (as with top-gated field-effect transistors (FETs)) or as a protection from ambient conditions for other devices. This problem arises from the chemically inert surface of 2D crystals, which prevents uniform growth of a dielectric film using atomic layer deposition (ALD). While thick ALD high-k films can be obtained on transition metal dichalcogenides (TMDs) through island growth, ultrathin films (< 5 nm) have not been possible without additional surface modification steps or the addition of a buffer layer. In this work, we show that a plasma-enhanced ALD (PEALD) process, compared to traditional thermal ALD, substantially improves nucleation on TMDs, such as MoS₂ and WSe₂, without hampering their electrical performance, and enables uniform growth of high-k dielectrics to sub-5 nm thicknesses. A custom-designed PEALD system (from Kurt J. Lesker Company) with a remote plasma sustained by Ar carrier gas was used for this study. Ultrathin high-k films, including Al₂O₃ and HfO₂, were successfully grown on mechanically exfoliated 2D crystals. A systematic comparison between PEALD (using O₂ precursor) and ALD (using H₂O precursor) revealed significant improvement in overall surface coverage and rugosity using PEALD. Back-gated FETs were used to study the electrical properties of the TMDs before/after ALD or PEALD. Interestingly, PEALD of HfO₂ resulted in a greater overall improvement in performance based on hysteresis and on-current compared to ALD of HfO₂. Mechanisms for the dramatic nucleation improvement and impact of PEALD on the 2D crystal structure were studied by x-ray photoelectron spectroscopy (XPS). XPS showed no evidence of oxidation that would adversely impact the electrical properties of the TMDs. To demonstrate the utility of the PEALD-enhanced nucleation, HfO₂ films as thin as ~3 nm were realized on MoS₂ and used in the gate stack of top-gated FETs, yielding robust performance for key metrics such as leakage current and gate control. In addition to providing a detailed analysis of the benefits of PEALD vs ALD on 2D crystals, this work reveals a straightforward approach for realizing ultrathin films of device-quality high-k dielectrics on 2D crystals without the use of additional nucleation layers or damage to the electrical performance.

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2:30pm **NS+EM-SuA-5 Novel *in-situ* Electrical Characterization of the Atomic Layer Deposition Process on 2D Transition Metal Dichalcogenides Transistors**, **Antonio Lucero**, J Lee, L Cheng, H Kim, J Lee, S Kim, J Kim, University of Texas at Dallas

Two-dimensional transition metal dichalcogenide (TMD) materials are promising candidates for future, low-power semiconducting applications¹. In spite of their numerous desirable characteristics, there are a number of challenges facing the implementation 2D TMDs into high performance transistors. Key among these problems is the development of a scalable gate dielectric deposition process due to the chemical inertness of the TMD surface². In this report four deposition processes are studied using a novel, *in-situ* electrical characterization system.

Exfoliated MoS₂ backgated devices are loaded into an ultra-high vacuum (UHV) cluster tool which integrates a thermal ALD, a plasma enhanced ALD, and a plasma enhanced chemical vapor deposition with a UHV electrical probe station (Fig. 1). Thermal ALD of Al₂O₃, both alone and combined with nitrogen radical surface functionalization, hollow cathode nitrogen plasma surface functionalization, and ozone surface functionalization are studied. Samples are transferred between deposition and characterization chambers under UHV conditions, allowing "half-cycle" studies to be performed (Fig. 2). Common to all results, as well as *ex-situ* studies, the ALD process results in a reduction of the on-off ratio, an increase in drive current, and a large negative shift in the threshold voltage (V_{th}). The shift in V_{th} can be seen immediately after the functionalization step or from the first ALD pulse if no functionalization is performed. In the case of functionalization, the shift in V_{th} is attributed to the oxidation of the MoS₂ surface, a result of oxygen contamination during radical functionalization. The effect of surface dipoles, precursor adsorption and coverage, and nucleation during the ALD process will be discussed as they relate to the electrical characteristics of the device.

This work was supported by the SWAN Center, a SRC center sponsored by the Nanoelectronics Research Initiative and NIST, and by NRF (No. 2015M3D1A1068061) in Korea. We thank TMEIC for providing the ozone generator and nitrogen radical generator used in this work.

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2. L. Cheng et al., *ACS Appl. Mater. Interfaces*, 6, 11834 (2014)

2:45pm **NS+EM-SuA-6 Deposition of MoS₂ and WS₂ from bis(tert-butylimido)-bis(dialkylamido) Compounds and 1-Propanethiol**, **Berc Kalanyan**, J Maslar, W Kimes, B Sperling, National Institute of Standards and Technology; R Kanjolia, EMD Performance Materials

Layered two dimensional (2D) transition-metal dichalcogenides (TMDs) are finding use in nanoelectronic and optoelectronic applications due to their thickness dependent optical and electrical properties. Scalable fabrication of TMD-based devices requires deposition routes that can produce continuous and uniform films with sub-nanometer thickness control. Atomic layer deposition (ALD) is a highly promising route for the synthesis of 2D TMDs and heterostructures due to digital thickness control achieved by sequential self-limiting chemistry. Another advantage of ALD is that thickness control and the structural development of the films can be decoupled by separating the deposition and crystallization steps. Existing ALD-like chemistries for TMD growth use metal halide and hydrogen sulfide sources. We report on the development of MoS₂ and WS₂ growth processes from metalorganic and thiol precursors, which offer halide-free chemistry and eliminate the safety hazards associated with H₂S.

We deposited thin films using (N^tBu)₂(Nme₂)₂M and 1-propanethiol, where M={Mo,W}, at wafer temperatures of 200°C to 400°C on SiO₂/Si substrates. The amount of precursor injected was directly measured using inline non-dispersive infrared optical flow meters. Precursor saturation conditions were evaluated using optical flow measurements and X-ray photoelectron spectroscopy (XPS). As-deposited and sulfur annealed films were further evaluated using X-ray diffraction (XRD) and Raman spectroscopy. As-grown films were amorphous and included a mixture of a sulfide and a conductive phase, likely a nitride. For the Mo precursor, the onset of sulfur incorporation occurred around 300°C, similar to values reported for Mo₂N produced using ammonia¹. Below 300°C, deposition was limited to a thin surface oxide. Higher temperatures resulted in an increase in growth rate, which also introduced a weak CVD component to the growth. Deposition rates were <0.5 Å/cycle at 350°C. Exposure studies revealed that relatively long saturation times for thiol were required to incorporate sulfur into the film, analogous to the NH₃ reaction for WN₂. As-deposited films were successfully annealed to 2H-MoS₂ under a sulfur atmosphere, which also removed residual ligands, including nitrogen-containing groups. In this

paper, we will also present similar results and process characteristics for the WS₂ route and discuss initial results from MoS₂/WS₂ nanolaminates.

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3:00pm **NS+EM-SuA-7 Direct Growth of Layered Boron Nitride Films on MoS₂ using Atomic Layer Deposition for 2D Based Nano-electronics**, **Jaebeom Lee**, L Cheng, H Zhu, A Ravichandran, A Lucero, M Catalano, M Kim, R Wallace, L Colombo, J Kim, University of Texas at Dallas; Z Che, The University of Texas at Dallas

Hexagonal boron nitride (h-BN), a graphene analogue with strong covalent bonding of boron and nitrogen, is an atomically thin two-dimensional (2D) dielectric material having interesting properties, such as atomic flatness, high stiffness, near lattice matching with graphene, and low surface energy. These unique properties have made h-BN a widely-studied dielectric as a substrate material and a gate dielectric for graphene based device. However, direct integration of h-BN with other 2D semiconductors, such as graphene and MoS₂, remains a major challenge because of their low surface reactivity which leads to poor surface nucleation of h-BN, thus preventing the synthesis of large area films with controllable thickness and grain size.

We used atomic layer deposition (ALD) using BCl₃ and NH₃ as precursors in the temperature range of 600~800 °C as shown in figure S1 to grow h-BN thin films. We evaluated the growth of layered BN on different substrates, such as Co, SiO₂, HOPG and MoS₂ and found that the nucleation mechanism depends on substrates. The distinct nucleation mechanisms of layered BN are likely attributed to the unique surface reactivities of the various substrates. Both Co and SiO₂ shows uniform nucleation sites, while growth on HOPG and MoS₂ showed growth mostly at the step edges due to the presence of dangling bonds and the inert nature of the basal plane. In order to increase the nucleation density we used O₃ pretreatment to functionalize the surface of MoS₂. The AFM images revealed enhanced nucleation of BN with an average grain size of ~ 20nm at a growth rate of ~ 0.22 Å/cycle. We also performed XPS measurements of the B 1s and N 1s peaks at 190.66 and 398.07 eV respectively, and the B:N ratio was estimated to be close to 1. The formation of layered BN was also verified further with the identification of satellite features at the higher binding energy shoulders of the XPS peaks, which is in good agreement with the layered BN structure observed in our HR-TEM images that show an interlayer spacing of 0.34nm (Fig S2). The band-gap of ALD grown BN was also estimated to be around 5.1 eV based on the analysis of N 1s XPS loss feature, and the dielectric constant was estimated to be about 3.8 from capacitor measurements. Our results suggest that polycrystalline layered BN can be grown by ALD on Co, SiO₂, HOPG and MoS₂. Further studies will have to be performed to improve the crystalline quality of the films.

We acknowledge partial financial support from the Southwest Academy on Nanoelectronics (SWAN) sponsored by the Nanoelectronic Research Initiative (NRI) and NIST and we thank TMEIC for providing the ozone generator.

Reference

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3:15pm **NS+EM-SuA-8 Fabrication of Functional Complex Nanostructures Based on Novel Atomic Layer Deposition Approach of Boron Nitride**, **Wenjun Hao**, C Marichy, C Journet, A Brioude, Univ Lyon, France **INVITED**

Renewal clean energy and environment are two of the most important concerns for the coming decades. Carbon-based nanostructures are leading nanomaterials due to their outstanding properties. Less investigated, hexagonal BN nanostructures such as nanotubes and nanosheets, which can be seen as the structural analogues to their carbon counterparts^[1], are very attractive materials with various applications such as energy^[2] and environmental domains^[3]. Atomic Layer Deposition (ALD) technique is an effective approach for surface modification and fabrication of complex nanostructured materials.^[4] However, few ALD processes of BN were reported so far and they are mostly based on ammonia and/or halide precursors and no high crystalline quality was yet achieved^[5-8]. Based on Polymer Derived Ceramic (PDC) chemistry^[9], a new low temperature ALD

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process of BN, that permits access to various h-BN complex nano- and hetero-structures, was developed.

In the present communication, we report for the first time the fabrication of h-BN complex nano- and hetero-structures by a two-step ALD approach using trichloroborazine reacting with hexamethyldisilazane. This two-step process consists first of the growth layer by layer of a preceramic BN films at low temperature, and then to its densification into pure h-BN by annealing process. h-BN thin films were successfully deposited onto various substrates/templates, such as carbon nanotubes, SiO₂ nanoparticles, polycarbonate membrane, sapphire, etc. The obtained h-BN materials were characterized by TEM, SEM, EDS, XPS and Raman. The present low deposition temperature ALD approach provides a versatile ammonia free method to fabricate high quality h-BN nano- and hetero-structures.

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4:00pm NS+EM-SuA-11 When There is no Bulk: Growth and Structure of Dielectric and Semiconductor Oxide Nanolaminates, *Angel Yanguas-Gil*, Argonne National Laboratory

INVITED

Nanolaminates represent the first-order generalization of a conventional ALD process, one in which the traditional ABABAB sequence is replaced by a more general (AB)_n(CD)_m combination of two different processes. In this talk I will focus on the growth, properties, and stability of oxide semiconductor and dielectric laminates. These materials are key for a wide range of applications, including photovoltaics, memory, logic, and power electronic devices. However, in addition to their applied interest, nanolaminates constitute a fantastic model system to explore the structure and properties of sub-nm materials whose structure and coordination environment are different from the bulk. Being intrinsically metastable, the stability of these structures also provides us with a way of probing the mobility of atoms at the nanoscale, an important factor in the long-term reliability of nanomaterials.

Through a combination of in-situ characterization, synchrotron characterization techniques, and simulations we have probed the structure and stability of nanolaminate materials as the thickness of its constituents evolve from a bulk like structure down to isolated clusters in a foreign host, focusing primarily on three different subsystems: Al₂O₃/ZnO, In₂O₃/SnO₂, and MO₂/Al₂O₃, where M=Ti, Hf. Changes in microstructure as determined using X-ray absorption spectroscopy correlate with changes in the chemical and electronic properties of the material. This is the case of the Al₂O₃/ZnO system, for which the departure from a wurzite-like coordination environment in ZnO below 10 ALD cycles correlates with an increase in the etching of the ZnO layer by TMA.

I will also focus on how to control the synthesis of doped and nanolaminate materials to tune the microstructure of amorphous materials. I will show how by adding an in-situ surface functionalization step to the conventional AB ALD cycle we can tune the reactivity and the growth per cycle of a wide range of ALD processes. We can leverage this approach to tune the composition of binary and ternary laminate materials, for instance to control the doping efficiency in transparent conductors or the isotropic mixing of components in as-deposited dielectric laminates. In addition to the modification of the structure of the laminate materials, this technique also allows us to probe the precursor-surface interaction during the first CD cycle of a laminate growth by comparing the growth inhibition observed in the laminate and in each of the individual constituents.

4:30pm NS+EM-SuA-13 Perfecting Single-Crystal Ternary Perovskite YAlO₃ Epitaxial Growth on GaAs(111)A Utilizing Atomic Layer Deposited Sub-Nano-Laminated Y₂O₃/Al₂O₃, *Lawrence Boyu Young, C Cheng, K Lin, Y Lin, H Wan*, National Taiwan University, Republic of China; *M Li*, National Nano Device Laboratories, Republic of China; *R Cai, S Lo*, Industrial Technology Research Institute, Republic of China; *C Hsu*, National Synchrotron Radiation Research Center, Republic of China; *J Kwo*, National Tsing Hua University, Republic of China; *M Hong*, National Taiwan University, Republic of China

Hetero-epitaxial growth of functional oxides on commercial semiconductor Si and GaAs wafers enables new technological applications, taking advantages of the advanced CMOS ICs and high-speed opto-electronic devices. Moreover, the hetero-growth between distinctly different chemical bonding and lattice constants is scientifically exciting and technologically challenging. In this work, we have perfected single crystal hexagonal perovskite YAlO₃ on GaAs(111)A using atomic layer deposited (ALD) sub-nano-laminated (snl) Y₂O₃/Al₂O₃ multi-layers (super-cycles) through post-deposition rapid thermal annealing (RTA) with temperatures above 900°C. We have studied the crystallography of single crystal hexagonal perovskite YAlO₃ (YAP) using synchrotron radiation x-ray diffraction (SR-XRD) and scanning transmission electron microscopy (STEM). The epitaxial relationship between YAlO₃ and GaAs is YAlO₃GaAs, as determined from the XRD radial scan along the in-plane direction. Comparing the YAP crystallinity of snl (super-cycles) and nl Y₂O₃/Al₂O₃ multi-layers, the cross-sectional STEM image for the former (Fig. 1(a)) reveals a more ordered atomic image, smoother crystalline YAlO₃/GaAs(111) interface, and continuous crystalline domain over 100-nm along substrate in-plane direction than that for the latter (Fig. 1(b)). Moreover, Pendellösung fringes from the XRD normal scans were observed for the super-cycled samples, much more so than those of nano-laminated samples (Fig. 2),¹ again indicating better crystallinity and smoother interfacial roughness. We have also attained very narrow FWHM of YAlO₃(0004) θ -rocking scan $\sim 0.026^\circ$ from the snl samples, compared favorably with 0.27° from the nl samples (Fig. 3). We have studied the surface morphology of the samples using atomic force microscopy (AFM). The smoother surface root mean square roughness of ~ 0.13 nm was observed in the snl super-cycled sample, which is 6 times smaller than that of our previous nl sample, and was close to the surface roughness of GaAs(111)A substrate ~ 0.13 nm as measured using an in-situ scanning tunneling microscope. Finally, the time-evolutions of surface normal radial scans of snl and nl samples were presented. After the 900°C anneal, the formation of YAlO₃ was much quicker ~ 2 s to reach the saturation thickness than that of our previous sample ~ 60 s, indicating that only 1/30 thermal budget was needed to form YAP by using sub-nano-laminated Y₂O₃/Al₂O₃ super-cycles.

[#]LBY, CKC, and KYL have contributed equally to this work.

^{*}CHH, JK, and MH are the corresponding authors.

¹L. B. Young, et al, J. Vac. Sci. Technol. A 35, 01B123 (2017)

4:45pm NS+EM-SuA-14 Thermal Coefficient of Resistance (TCR) Measurements for Atomic Layer Deposited Metal-Metal Oxide Nanocomposites, *Anil Mane, J Avila, Y Zhang, J Elam*, Argonne National Laboratory

Precisely controlled metal-metal oxide nanocomposite layers prepared by atomic layer deposition (ALD) exhibit material properties that can be tuned over a broad range by adjusting the metal content such as band gap, absorption coefficient, resistivity, and electrochemical corrosion resistance. Consequently, these metal-metal oxide nanocomposites are well suited in a variety of applications including resistive layers in microchannel plates (MCPs), protective coatings for lithium ion battery cathodes, charge drain layers for MEMS devices, and selective absorber coatings for concentrated solar power.

For resistive layers in MCPs, the thermal coefficient of resistance (TCR) is a critical materials property because it dictates the range of allowable operating temperatures for devices (e.g. photon, neutron, or particle detectors) that incorporate the MCP for electron amplification. The ability to control the TCR will enable new applications such as cryogenic detectors or detectors that must endure large temperature changes during operation. To address this need, we have synthesized a variety of ALD metal-metal oxide nanocomposite layers by combining different metals (W, Mo, Ta, and Nb) and metal oxides (Al₂O₃, ZrO₂, TiO₂, Ta₂O₅, Nb₂O₅, and HfO₂). We studied the electrical transport properties of these ALD films and focused on their temperature dependence in order to extract the TCR. In all cases, the TCR is negative, so that the resistance drops with increasing

temperature as expected for a semiconducting material. In addition, the magnitude of the TCR increases with the film resistivity, and depends on both the metal and the metal oxide components of the composite (Fig. 1). This presentation will expound on these findings and explain the implications for MCP detectors.

5:00pm NS+EM-SuA-15 Phase Control of Ga₂O₃ Films Deposited by Atomic Layer Epitaxy, Virginia Wheeler, N Nepal, D Meyer, C Eddy, Jr., U.S. Naval Research Laboratory

Ga₂O₃ has attracted significant interest as a promising ultra-wide bandgap material for next generation high-power, high-temperature electronic and UV detector applications. While there are five polymorphs of Ga₂O₃, the β-Ga₂O₃ (monoclinic) is the most stable and thus the most widely studied to-date. By comparison, the ε-Ga₂O₃ phase is slightly less energetically favorable but has a similar bandgap (4.9 eV) and a hexagonal wurtzite crystal structure that results in a polar phase. The calculated polarization strength of ε-Ga₂O₃ is 10 and 3 times larger than that of GaN and AlN, respectively. Like the III-N system, polarization induced charges can lead to higher charge densities and mobilities in two-dimensional electron gases formed at heterojunctions, which would improve the viability of Ga₂O₃ electronic devices. However, experimental data on attaining the ε-Ga₂O₃ phase is extremely limited and homo- or heteroepitaxial films currently demonstrated are of very poor quality. In this work, we use atomic layer epitaxy (ALE) to produce high-quality heteroepitaxial Ga₂O₃ films and demonstrate phase selectivity with a variation in growth temperature, plasma gas chemistry and plasma pressure.

ALE Ga₂O₃ films were deposited on c-plane sapphire substrates in an Ultratech Fiji 200 reactor equipped with a load lock and turbo pump. All films were produced using trimethylgallium and O₂ plasma precursors with pulse/purge times of 0.015s/10s and 10s/10s, respectively. The growth temperature, plasma gas flow, and pressure were varied to determine their impact on resulting film crystallinity and phase composition. Independent of growth conditions, all films were crystalline, high resistivity films with Ga/O ratios between 0.68-0.70 and no indication of C contamination by XPS.

Decreasing chamber pressure an order of magnitude drastically effected the resulting phase, yielding pure β-Ga₂O₃ at high pressure and pure ε-Ga₂O₃ at low pressures. Additionally, at low pressures, as the growth temperature was increased from 300 to 500°C, subsequent films went from mixed phase, to purely ε-Ga₂O₃ at 350°C, to purely β-Ga₂O₃ at 500°C. Alternatively, at 350°C and low pressure, the phase could be altered by a change in O₂ plasma flow. High-quality β-Ga₂O₃ films were produced at 5sccm O₂ that had an RMS roughness of 0.38nm and XRD FWHM of 268 arcsec for a 30nm film. At 40sccm, high-quality ε-Ga₂O₃ films were obtained with an RMS roughness of 0.15nm and XRD FWHM of 250 arcsec for a 30nm film. Thus, using ALE high-quality, phase selective films can be achieved to satisfy application requirements.

5:15pm NS+EM-SuA-16 High Quality SiN and SiO₂ Films Produced by PEALD with Microwave ECR Plasma Below 200 °C, Jesse Kalliomaki, V Kilpi, Picosun Oy, Finland; T Maline, Picosun Oy; H Enami, N Mise, Hitachi High-Technologies Corp., Japan; H Hamamura, T Usui, Hitachi R&D Group

Due to continuous feature size scaling down and change to the 3D structures, currently new process innovations are required more strongly than the previous. Conformal film formation of Si compounds like SiO₂ and SiN is the key technologies and is widely used for double patterning, spacer and liner applications. PEALD at low temperature is one of the suitable solutions for these applications. We reported the superiority of low pressure microwave ECR(M-ECR) plasma for Si substrate nitridation at low temperature [1].

In this study, SiN and SiO₂ film properties were evaluated for demonstrating the advantage of the newly combined tool with the M-ECR plasma and the leading ALD system from Picosun. BDEAS (Bis(Diethylamino)Silane) was used as Si precursor. N₂ and O₂ gas were introduced into M-ECR plasma to form SiN and SiO₂, respectively. Process pressure was set lower than 1Pa. Film density and WER (wet etching rate) were measured by XRR and DHF (0.5%), respectively. Composition of film was analyzed by XPS with Ar sputter.

SiN film density obtained in this study was investigated as a function of deposition temperature and compared with that of the conventional PEALD SiN [2,3] as shown in Fig. 1. The film density slightly increases with rise in deposition temperature and the value is about 2.9 g/cm³ at low temperature below 200 °C. This value is much higher than that of the conventional PEALD SiN and nearly equal to that of LPCVD SiN at 850 °C. WER obtained in this study is extremely low compared to that of the

conventional PEALD SiN as shown in Fig. 2. This low WER is advantageous for device fabrication. XPS analyses reveal that residual C in the film is less than 3 %. Longer exposure time of N₂ plasma could reduce the C content and WER. Efficient generation of the radicals and ions by M-ECR plasma at low pressure [4] is supposed to improve the film properties.

SiO₂ film properties deposited at 150 °C were also investigated. Film density is 2.2 g/cm³, this value is nearly equal to that of thermal SiO₂. WER is 4.5 nm/min and this value is smaller than that of the conventional LPCVD SiO₂ formed at 750 °C (6.0 nm/min). O/Si ratio of the film is 2.1 and residual C is less than 1 %.

From these results, PEALD with M-ECR plasma can be one of the most advantageous solutions for next-generation leading edge devices and other novel devices.

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5:30pm NS+EM-SuA-17 Tertiary Butyl Hydrazine as a Reducing Agent for Low-Temperature Atomic Layer Deposition of Low-Resistivity Copper Thin Films, Katja Väyrynen, K Mizohata, J Räsänen, University of Helsinki, Finland; D Peeters, A Devi, Ruhr-University Bochum, Germany; M Ritala, M Leskelä, University of Helsinki, Finland

Copper plays an important role in the development of microelectronics as it is the primary interconnect material. The manufacturing procedure of the Cu interconnects is typically two-fold: first, a Cu seed layer is deposited by PVD followed by a Cu fill process carried out by electrochemical deposition. In order to reduce component sizes, and thus increase device efficiency, thin yet continuous Cu films are desired. This can be accomplished by replacing the existing course of action, or at least the PVD step, with more accurate deposition methods such as ALD. The Cu ALD processes known to date, however, exhibit limited applicability due to issues ranging from agglomeration caused by high temperatures to Zn incorporation and strong substrate sensitivity.

Tertiary butyl hydrazine (TBH) was recently introduced as an ALD reactant for the reduction of silver thin films.¹ Otherwise, the use of hydrazine or its alkyl derivatives in metal ALD has been scarce.^{2,3} In this work, Cu thin films were deposited via reduction of Cu(dmap)₂ (dmap = dimethylamino-2-propoxide) by TBH. The process was investigated between temperatures of 80 and 140 °C. A saturating growth mechanism was observed with respect to both precursors at 120°C. Both the growth characteristics and the film properties were found to vary depending on the substrate, but deposition was not limited only on certain starting surfaces. The films were identified as crystalline cubic Cu with a minor preference towards (111) orientation. The films were relatively smooth and showed uniform thickness across the 5 x 5 cm² substrates. At the lowest, a resistivity of 1.9 μΩcm was measured from a 54 nm film exhibiting a Cu content of 97.2 at.%. Oxygen was identified as the main impurity (1.7 at.%) but it was limited almost entirely to the film surface indicating oxidation upon exposure to air (Figure 1).

The films were deposited in a hot-wall flow-type F-120 ALD reactor (ASM Microchemistry). Thorough film characterization was carried out by energy-dispersive X-ray spectrometry, scanning electron microscopy, X-ray diffraction, four-point probe, and time-of-flight elastic recoil detection analysis.

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Nanostructure Synthesis and Fabrication Room Plaza Exhibit - Session NS-SuP

Nanostructures Synthesis and Fabrication Poster Session

NS-SuP-1 Refractive Index and Bandgap Variation in Al₂O₃-ZnO Ultrathin Multilayers Prepared by Atomic Layer Deposition, Javier López Medina, CONACYT - Centro de Nanociencias y Nanotecnología - UNAM, Mexico; E Solorio, H Borbón, F Castillon, R Machorro, Centro de Nanociencias y Nanotecnología - Universidad Nacional Autónoma de Mexico, Mexico; N Nedev, Universidad Autónoma de Baja California, Mexico; M Farias, H Tiznado, Centro de Nanociencias y Nanotecnología - Universidad Nacional Autónoma de Mexico, Mexico

This research focuses on the study of the refractive index and bandgap behavior in ultrathin multilayer films of Al₂O₃-ZnO bilayers grown via atomic layer deposition (ALD) technique on Si(100) substrates. The multilayer configuration stack consists in alternate layers of constant thickness Al₂O₃ (2 nm) and varying thickness ZnO films in order to obtain a total thickness of ~100 nm. A set of 10 samples based on bilayers with various 2:X thickness ratios were prepared, where X refers to the ZnO layer thickness. X is proportional to the number of cycles (N) of the ZnO precursor, varying from 1 to 100. The sample morphology was studied via Atomic Force Microscopy and the results show that the surface roughness of the multilayers varies from 0.2 to 1.2 nm, as the ZnO layer thickness increases. In all cases, the roughness values remain below 2% of the total thickness of the multilayer. The refractive index $n(\lambda)$ and optical bandgap, E_g , of each multilayer sample were studied via spectroscopic ellipsometry (SE). A General Oscillator optical model was utilized to fit the experimental data in order to obtain the total thickness, refractive index and absorption coefficient. Cross-sectional mode scanning electron microscope images verified the multilayer total thickness and corroborated the accuracy of the optical model. The refractive index varies significantly from values close to the Al₂O₃ refractive index when the bilayer thickness is small, up to values corresponding closely to ZnO for thicker bilayers. The refractive index, as a function of bilayer thickness, varies between 1.63 and 2.3, for $\lambda \approx 370$ nm (UV region), showing high sensitivity. In addition, the optical bandgap energy, E_g , determined using the Tauc model, decreases when the bilayer thickness increases, with a maximum variation of $\Delta E_g \sim 1.6$ eV. These results reveal that the refractive index and optical bandgap of Al₂O₃-ZnO material can be modulated systematically as a function of the bilayer thickness. Such behavior is of great importance for optoelectronics applications, in particular for the development of devices with response in the UV spectral range.

Acknowledgments

This work was partially supported by Direccion General de Asuntos del Personal Academico (DGAPA-UNAM) through PAPIIT research projects IN105114, IN107715 and IN106715.

J. Lopez kindly thanks DGAPA-UNAM for a 2-year postdoctoral fellowship.

The authors also would like to thank valuable technical support and the collaboration of David Dominguez, Eduardo Murillo, Jose Juan Gervacio, Noemi Abundiz, David Mateos, Israel Gradilla, Francisco Ruiz, Jaime Mendoza, Jose Luis Cervantes and Eric Flores.

NS-SuP-2 Controlled and Selective Etches for Gate All-Around Device Fabrication, Subhadeep Kal, J Smith, N Mahanty, Y Su, C Pereira, A Masden, P Biolsi, T Hurd, Tokyo Electron

In scaling beyond the 5nm technology node there is an impetus for gate all-around (GAA) device architecture. A basic requirement for GAA is the formation of silicon-germanium (SiGe) and silicon (Si) nanowires (NW). Fabricating either Si or SiGe NW (also known as NW release) requires an extremely selective, isotropic and precise SiGe (shown in Fig.1, step 1) and Si etch, respectively. After the Si NW release (or SiGe etch), the SiN gate spacer is formed around the Si NW, making a continuous and sealed gate spacer (Fig.1, step 2). In the case of a partial NW release (Fig.1), the SiGe etch must be controlled with an accuracy of >5Å since this recess will effectively define the gate spacer thickness in the area above and below the Si NW after spacer etch (SE)/liner etch (step 3, Fig.1). Here we highlight why a precise etch control is essential: (1) if the SiGe recess is too small, the reformed gate spacer thickness will be under specification and will result in capacitance problems between gate and adjacent source/drain bar metals. (2) If the SiGe recess is too much, the reformed gate spacer will penetrate into the replacement gate and will decrease the amount of gate

metal wrapping around the nanowire and will impact gate functionality. Once only the silicon wire is protruding through the seamless gate spacer (Fig.1, step 3), SiGe:B can be grown from the ends of the silicon wires protruding through the gate spacer (Fig.1, step 4). In addition to the above requirements, etch selectivity towards to the gate and low K material around the gate (not shown in Fig 1) is also preferable. Therefore, a process flow enabled with extremely high selective etches, where the selectivity is a function of film properties and/or etch chemistry is a quintessential advantage. In this article, we demonstrate the significance of such selective etches for Si NW formation step (Fig.1, step 1) and corresponding SiGe NW fabrication.

Fig.1 (step 1), shows the process performance of a selective gas phase SiGe etch for Si NW (SiGe etch) formation. Research is ongoing to explore further how these techniques can be optimized together to obtain a straight SiGe and Si etch front. Similar etch techniques has also proved to be essential for full NW release, where the requirements are selective, isotropic and complete etch of Si or SiGe stacks. In addition we will also show an alternate selective etch technique to fabricate corresponding SiGe NW (Si etch) formation.

NS-SuP-3 Wafer-Scale Synthesis of High-Quality and Few-Layer WS₂ Films on Si/SiO₂ Substrates, Yung-Ching Chu, National Chiao Tung University, Republic of China; C Jong, NARLabs, Republic of China; Y Ho, National Chiao Tung University, Republic of China; P Lu, UCLA; C Zhang, National Chiao Tung University, Republic of China; H Hsu, ITRI, Republic of China; Y Tu, National Chiao Tung University, Republic of China; J Woo, UCLA; E Chang, National Chiao Tung University, Republic of China

Due to their attractive properties for next-generation electronic and optoelectronic devices, two-dimensional (2D) layered transition metal dichalcogenides (TMDs) materials such as MoS₂, WSe₂ and WS₂ have attracted a great deal of attention recently. Among these 2D TMDs materials, few-layer tungsten disulfide (WS₂) is particularly attractive for electronic applications due to its potential high hole mobility. The theoretically predicted room temperature mobility of WS₂ is 1,103 cm²·V⁻¹·s⁻¹, much higher than that for MoS₂ (304 cm²·V⁻¹·s⁻¹) and WSe₂ (705 cm²·V⁻¹·s⁻¹) [1]. In addition, few-layer WS₂ with a direct band-gap about 2.0 eV is suitable for electronic and optoelectronic devices. While remarkable methods for other TMDs large area preparation have been reported, large area synthesis of WS₂ remains a challenge.

In this study, a novel scalable method of realizing wafer-scale well controlled WS₂ films is proposed and demonstrated. The synthesis of WS₂ films start by depositing tungsten trioxide (WO₃) films on 4-inch heavily doped silicon substrate with 80-nm SiO₂ cap layer by e-gun evaporation. These films were then converted into few-layer WS₂ via sulfurization with hydrogen sulfide (H₂S) at elevated temperatures. Figure 1(a) shows that a uniform WS₂ film is achieved, fully covering the 4-inch substrate wafer. The WS₂ film thickness can be controlled by adjusting the e-gun evaporated tungsten oxide film thickness, which was confirmed by cross-sectional transmission electron microscopy (TEM). Figure 1(b) shows the cross-section TEM image for 1 nm WO₃ film converted to a continue WS₂ film. The inset is a high resolution TEM showing 2~3 layers of WS₂. Both Raman and photoluminescence (PL) spectra of the samples were acquired using a Raman microscope system with a laser excitation wavelength of 532 nm. Raman spectrum (Figure 1(c)) indicates that the as-synthesized WS₂ thin films have two characteristic peaks of the in-plane vibrational mode, E_{2g}, at about 353 cm⁻¹ and the out-of-plane vibrational mode, A_{1g}, at about 418 cm⁻¹. PL spectrum of as-synthesized WS₂ (Figure 1(d)) shows the major PL peak (A) at approximately 1.98 eV associated with the direct band-gap transition at K point. The weak PL peak (I) associated with the indirect band-gap transition.

In conclusion, a promising method for the synthesis of wafer-scale high quality WS₂ on insulating substrates that could enable batch fabrication of 2D electronic and optoelectronic devices were proposed. TEM, Raman and PL were performed on these samples to demonstrate their excellent material qualities.

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NS-SuP-4 Towards Producing Bulk Monolithic Core/Shell Nanocomposites, Boris Feigelson, J Wollmershauser, K Manandhar, U.S. Naval Research Laboratory

With designed bulk nanostructured solids, one could potentially combine properties that are mutually exclusive in a single bulk material, and, as a result, dramatically improve the desired performance. However, a major

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research challenge and roadblock is how to produce 3D nanostructured materials consistently with the required phases arranged in designated spatial order that are at the same time fully dense without porosity and detrimental phases. Known state-of-the-art techniques for producing bulk nanostructures cannot simultaneously meet all these requirements. As a result, the inherent properties of such bulk monolithic nanostructured materials are greatly unknown and unexplored.

We developed an Enhanced High Pressure Sintering (EHPS) process to consolidate oxide, metal, and semiconductor nanoparticles into 3-dimensional monolithic nanostructured materials. EHPS incorporates stringent environmental control and utilizes high pressures to break agglomerates while simultaneously exploiting the increased pristine surface potential of nanoparticles for surface-energy-driven densification without microstructural changes. Using this approach, monolithic nanocrystalline transparent ceramics with grain size below 30 nm are demonstrated. Such ceramics exhibit a 30% increase in hardness over a corresponding order of magnitude reduction in grain size and suggest that Hall-Petch type (strengthening via grain size reduction) relations exist in ceramics at least down to 25nm [1].

Core/shell nanoparticles offer fundamentally new means for nanostructured solids design and tailoring basic properties of these artificial materials. To provide flexibility in core/shell nanoparticles design, a particle atomic layer deposition (pALD) reactor was incorporated in the EHPS facility. The new setup allows to controlling environment during all stages of the nanoparticles processing, atomic layer deposition and sintering. Spinel/alumina core/shell nanoparticles were the first material system tested for producing the first core/shell ceramic nanocomposite. Alumina shell was grown on spinel nanoparticles, and then core/shell nanoparticles sintered under pressure without exposing to atmospheric air. The developed nanocomposite ceramics demonstrated better hardness and fracture toughness than pure nanocrystalline spinel.

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NS-SuP-5 Nanolaminate Copper Barriers of Ru/TaN_x Thin Films by Inductively Coupled Plasma Enhanced Atomic Layer Deposition, Bo-Heng Liu, W Cho, C Kei, National Applied Research Laboratories, Republic of China

Ru/TaN nanolaminate barriers and Cu interconnect were sequential directly grown on dual damascene nano-porous dielectrics by inductively coupled plasma enhanced atomic layer deposition (PEALD). Ru/TaN thin films were successfully deposited by home-built PEALD using [Ru(EtCp)₂] and Ta(NC₂H₆)₅ as precursor with high energy reductive Ar/H₂ and Ar/O₂ plasma. The substrate temperature of Ru/TaN thin films were 300 and 250 °C with 500 cycles to PEALD process. The N₂ purge time and plasma power were held on 5 s and 400 W. Ru/TaN thin films were analyzed by X-ray photoelectron spectroscopy (XPS: Perkin Elmer PHI 670) and HRTEM (JEOL JEM-2100F). The resistivity was measured by using Hall effect measurement system (Accent/HL 5500PC). Fig. 1 shows the XPS of Ru 3d spectra deposited by PEALD. The energy states of 3d_{5/2} (at 280.2 eV) and 3d_{3/2} (at 284.3 eV) indicated metallic Ru. However, the lower intensity peaks at 281.2 eV and 285.9 eV are from RuO₂. Growth rate of Ru the films was increased significant from 0.01 to 0.1 nm/cycle by using dc biased PEALD. The resistivity of Ru thin films prepared by PEALD was 40 μΩ cm. The growth rate of TaN thin films was 0.05 nm/cycle as the PDMAT pulse time is more than 2 s. Cross-section HRTEM image in Fig. 2 shows that the Ru/TaN nanolaminate barriers were formed. In summary, Ru/TaN nanolaminate barriers were prepared by using Ru(EtCp)₂ and Ta(NC₂H₆)₅ precursor with the aid of the high energy reductive Ar/O₂ and Ar/H₂ plasma in ITRC PEALD system.

NS-SuP-6 On the Possibility of the Development of Vicinal Superlattices in Quantum Wires on Semiconductor Low - Index Surfaces, Victor Petrov, Russian Academy of Science, Russian Federation

As is well known, vicinal superlattices (VSLs) are realized in 2D electron systems on semiconductor high-index Miller surfaces. The existence of SL effects in VSLs is due to the appearance in these systems of a new crystallographic translation period in the plane of quantum wells $A \gg a_0$ (a_0 is the lattice constant). A new translation period A produces minigaps (MGs) in the energetic spectrum of the particles in these systems and, as a result, different SL effects. At the present time, all these VSLs are developed only in 2D systems. At the same time, it is known that

superlattice effects should be maximal in quantum wires (QWR) when the SL period A appears along the axis of the QWR.

In this work we suggest a new method of development of VSL in QWR on semiconductor low-index surfaces. For this purpose we suggest to orient the axis of the QWR at the necessary angles to the basic translation vectors on a low-index surface. In this case in the QWR the new basic translation period along the axis of the QWR $A \gg a_0$. Thus, the period A along the surface in the one-dimensional VSL is selected by the orientation of the QWR on the low-index surface. If the QWR is realized in the MOS system with the use of a narrow gate then the orientation of the wire will be determined simply by the appropriate orientation of the gate. The analytic expressions of the new periods A were obtained as a function of the angles which determine orientation of the QWR for the different low-index surfaces GaAs and Si. The positions of MGs in the one-dimensional k-space were determined. It is should be noted that in the region of the particle wave function localization in the QWR there are many crystallographic planes which form a SL energetic spectrum of the particle. Illustrative estimates of the magnitude of the MGs for the QWR of the rectangular cross-section made in the weak coupling approximation demonstrate their dependence on the geometric parameters of the cross-section, on the period A as well as on the crystal potential.

NS-SuP-7 Rational Design of Hyperbranched Nanowire Systems for Tunable Superomniphobic Surfaces Enabled by Atomic Layer Deposition, Ashley Bielinski, M Boban, University of Michigan, USA; *Y He*, University of Pittsburgh; *E Kazyak, D Lee*, University of Michigan, USA; *C Wang*, Pacific Northwestern National Laboratory; *A Tuteja, N Dasgupta*, University of Michigan, USA

The hierarchical assembly of semiconductor nanostructures to form heterogeneous material systems has the potential to advance a range of technologies including electronics, optics, sensors, mechanical resonators, and energy conversion. Semiconductor nanowire (NW) arrays have already been successfully applied in these fields, but challenges such as lack of deterministic control of feature size, shape, and position limits the development of more complex geometries. One example, hyperbranched NWs, have been synthesized for a variety of applications, but the ability to tune the morphology along a spectrum at each level of hierarchy requires further development. Here we demonstrate surface and interface modification via atomic layer deposition (ALD) to control the fabrication and bottom-up solution growth of ordered hyperbranched NW systems.

Existing techniques for the assembly of complex nanostructures generally rely on either nanoscale patterning, or solution based processes. The patterning techniques while slow and costly on planar substrates, often become impossible on high aspect ratio surface geometries. The solution-based approaches offer scalability and lower cost, but the results are often disordered and difficult to tune. ALD is an enabling technique for the control of low-cost, scalable hydrothermal NW synthesis. This process relies on atomic-scale precision of conformal films deposited on nanowire arrays, for which ALD is an ideal process.

We start by demonstrating the control of ZnO NW array properties such as density and orientation by tuning the crystallographic orientation, roughness, and surface stress of ALD films used to seed the NW nucleation.[1] We then show how ALD can be used to overcome the challenges that arise when transitioning from simple NW arrays to complex branched structures. Sub-monolayer deposition of inert blocking layers were used to reduce NW density independent of orientation in order to make room for subsequent branched NW growth. ALD interlayers were then used to prevent epitaxial ALD growth of subsequent seedlayers on the single crystalline NWs. These techniques were all combined to fabricate hyperbranched NW arrays. The array properties were controlled with ALD at each level of hierarchy to produce superomniphobic (repellent to high and low surface tension liquids) with tunable contact angles for different liquids.[2]

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NS-SuP-8 Designing Low Density Foams by ALD Templating, Monika Biener, Lawrence Livermore National Laboratory

Low density foams with precisely controlled architectures, compositions and densities have many promising applications in the fields of energy storage, catalysis, biomaterials, and high energy density physics. Here, atomic layer deposition offers a unique opportunity for rapid on-demand

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development of functional nanoporous bulk materials by applying the principle of templating to material systems for which robust synthesis strategies have already been developed. I will summarize recent progress made in synthesis and characterization of ALD-derived ultralow density target materials that are important for inertial confinement fusion (ICF) experiments. As porous substrates we use Polystyrene beads deposited by electrophoretic deposition, additively manufactured 3D micro lattices and nanoporous gold. Nanometer-thick metal oxide ALD coatings (ZnO, Ta₂O₅, Al₂O₃) provide the desired functionality and often dramatically improve the mechanical properties of the porous substrate. Even only nanometer thick coatings can be mechanically so robust that the substrate can be removed without collapse of the structure. The resulting materials can have air-like densities which, for example, enable the realization of brighter X-ray sources and promise to improve the performance of ICF targets.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

NS-SuP-9 Fully CMOS-Compatible Synthesis and Photodetector-Integration of Ultrathin, Parallel-Aligned ZnO Nanowire Arrays by Infiltration Synthesis, *Chang-Yong Nam, A Stein*, Brookhaven National Laboratory

Semiconductor nanowires with reduced diameters enable high-performance chemical sensors and photodetectors owing to their large surface-to-volume ratios and enhanced surface band bending. Synthesis of nanowires and their device integration by CMOS (complementary metal-oxide-semiconductor)-process-compatible methodologies can be extremely powerful for various technological applications of nanowires. Here we report fully CMOS-compatible synthesis and ultraviolet (UV)-photodetector-integration of ultrathin (~30 nm diameter), parallel-aligned, polycrystalline ZnO nanowire arrays by infiltration synthesis, a type of inorganic-organic hybridization technique derived from atomic layer deposition. The ultrathin ZnO nanowire array was generated by infiltrating diethylzinc (DEZ) and water vapors into lithographically patterned polymer nanowire template made of a negative-tone resist SU-8. The integrated ZnO nanowire array photodetectors featured ultralow dark currents <20 fA unchanging with the number of nanowires, photocurrent on-off ratios over 10⁶ leading to >120 dB linear dynamic range, and super-linear photocurrents causing unusually increasing photodetector performance parameters for a higher incident light power. Considering the temperature-dependent field-effect transistor characteristics of the ZnO nanowire arrays, we explained the observed super-linear photoconductivity by the new type of photo-thermionic emission mechanism involving the reaction of chemisorbed oxygen and photo-generated holes at grain boundaries. The developed rationale provides guidelines for utilizing polycrystalline semiconductor nanostructures for photodetectors and other sensors. The demonstrated synthesis and fabrication methods based on the infiltration synthesis have potentials for CMOS-integration of nanowire sensor devices and circuitries.

NS-SuP-10 Monodispersed, Highly Interactive Facet Oriented Pd Nanograins Grown by ALD onto Electrospun Polymeric Nanofibers, *Kugalur Ranjith, A Celebioglu*, Bilkent University, Turkey; *H Eren*, Delft University of Technology, Netherlands; *N Biyikli*, Utah State University; *T Uyar*, Bilkent University, Turkey

We present a membrane form of templates for the growth of Pd nanograins through the atomic layer deposition (ALD) on the electrospun polymeric nanofibers such as Nylon 6,6, PAN and Polysulfone. Under the selective atmosphere, the stable flexible polymeric nanofibers were utilized as a template and the Pd nano grains were made to interact with the polymer surface and decorated on it. Utilizing the template avoided the aggregation of the nanograins during growth and initiated mono dispersive nature of the Pd nanostructures immobilized with the size of 2 nm. Template form of Pd decorated nanofiber network exhibited an effectualness towards the reduction of 4-nitrophenol into 4-aminophenol through hydrogenation process. Even under low loading capacity of Pd nanoparticle, effective catalytic performance was exhibited which was ascribable to the exposure of single crystalline highly interactive (111) planes with high surface area on the nanofiber surface. With the aid of Pd nanograins decorated polymeric fibers, the catalytic reduction can be finished within 35 mins, even when the content of Pd ions was as low as 2 wt%. Pd nanograins exhibited thermal stability and structural integrity even after 3 consecutive reactions. Improvisation of the catalytic performance on Pd loading in different polymeric fibers was evidently a resultant of the higher surface area of the nanofibers with higher surface interaction. The

method opens up possibilities for synthesizing decorative metal nanostructures on functional polymeric fibers based membranes for multifunctional applications.

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Li, M: NS+EM-SuA-13, 3
Lin, K: NS+EM-SuA-13, 3
Lin, Y: NS+EM-SuA-13, 3
Liu, B: NS-SuP-5, 6
Lo, S: NS+EM-SuA-13, 3
Lohr, T: NS+EM-SuA-2, 1
López Medina, J: NS-SuP-1, 5
Lu, P: NS-SuP-3, 5
Lucero, A: NS+EM-SuA-5, 2; NS+EM-SuA-7, 2
— M —
Machorro, R: NS-SuP-1, 5
Maline, T: NS+EM-SuA-16, 4
Manandhar, K: NS-SuP-4, 5
Mane, A: NS+EM-SuA-14, 3; NS+EM-SuA-3, 1
Marichy, C: NS+EM-SuA-8, 2
Marks, T: NS+EM-SuA-2, 1
Maslar, J: NS+EM-SuA-6, 2
McGuire, F: NS+EM-SuA-4, 1
Meyer, D: NS+EM-SuA-15, 4
Mise, N: NS+EM-SuA-16, 4
Mizohata, K: NS+EM-SuA-17, 4
Mohanty, N: NS-SuP-2, 5
Moody, M: NS+EM-SuA-2, 1
Mosden, A: NS-SuP-2, 5
— N —
Nam, C: NS-SuP-9, 7
Nedev, N: NS-SuP-1, 5
Nepal, N: NS+EM-SuA-15, 4
— P —
Peeters, D: NS+EM-SuA-17, 4
Pereira, C: NS-SuP-2, 5
Petrov, V: NS-SuP-6, 6
Price, K: NS+EM-SuA-4, 1
— R —
Räsänen, J: NS+EM-SuA-17, 4
Ranjith, K: NS-SuP-10, 7
Ravichandran, A: NS+EM-SuA-7, 2
Ritala, M: NS+EM-SuA-17, 4
— S —
Sharma, A: NS+EM-SuA-1, 1
Smith, J: NS-SuP-2, 5
Solorio, E: NS-SuP-1, 5
Sperling, B: NS+EM-SuA-6, 2
Stein, A: NS-SuP-9, 7
Su, Y: NS-SuP-2, 5
Sundaram, R: NS+EM-SuA-1, 1
— T —
Tan, J: NS+EM-SuA-2, 1
Tiznado, H: NS-SuP-1, 5
Tu, Y: NS-SuP-3, 5
Tuteja, A: NS-SuP-7, 6
— U —
Usui, T: NS+EM-SuA-16, 4
Uyar, T: NS-SuP-10, 7
— V —
Vandalon, V: NS+EM-SuA-1, 1
Väyrynen, K: NS+EM-SuA-17, 4
Verheijen, M: NS+EM-SuA-1, 1
— W —
Wallace, R: NS+EM-SuA-7, 2
Wan, H: NS+EM-SuA-13, 3
Wang, B: NS+EM-SuA-2, 1
Wang, C: NS-SuP-7, 6
Wheeler, V: NS+EM-SuA-15, 4
Wollmershauser, J: NS-SuP-4, 5
Woo, J: NS-SuP-3, 5
— Y —
Yanguas-Gil, A: NS+EM-SuA-11, 3
Young, L: NS+EM-SuA-13, 3
— Z —
Zhang, Y: NS+EM-SuA-14, 3
Zhong, C: NS-SuP-3, 5
Zhu, H: NS+EM-SuA-7, 2