Thin Films Division
Room: 21 - Session TF+MI+NS-ThA

ALD and Nanostructures
Moderators: Christophe Vallee, LTM, Univ. Grenoble Alpes, CEA-LETI, France, Richard Vanfleet, Brigham Young University

2:20pm **TF+MI+NS-ThA1 Coating and Infilling 3D Geometries by Low-T CVD : HfB_2 throughout 0.5 mm Thick CNT Forests**, ***John Abelson***, University of Illinois at Urbana-Champaign **INVITED**

We describe the use of extremely conformal chemical vapor deposition to coat carbon nanotube forests throughout their depth with a film of HfB_2, a mechanically hard, electrically conductive and highly refractory alloy. CVD uses the precursor $Hf(BH_4)_4$ at partial pressures ≤ 15 Torr at substrate temperatures ≤ 200°C. The CNT forests are up to 500 µm thick and can be shaped by pre-depositing patterns of seed metal on the underlying substrate prior to their synthesis.

Coating CNT forests affords a new class of composite foams with adjustable mechanical properties : the HfB_2 coating both stiffens individual tubes and "welds" them together wherever they touch, whereas in the uncoated forest the tubes can slide relative to one another. We fabricate cylindrical pillar structures with HfB_2 thicknesses from 3-50 nm. As measured by nanoindentation using a flat punch, the Young's modulus varies over three orders of magnitude as $E \sim \rho^{1.7}$, where the mass density ρ is dominated by the HfB_2 coating. The maximum stiffness and strength are 56 and 1.9 GPa, respectively.

A major question is how CVD can achieve a nearly uniform coating in such a deep structure. The challenge is inherent in the diffusion-reaction kinetics : the transport of reactants occurs by molecular diffusion, which is slow in narrow cross-sections; while at the same time the reaction (consumption) rate must be high enough to be useful. In combination, these factors imply that the partial pressure (flux) of reactants must diminish with depth; if the film growth rate varies monotonically with flux, then the coating thickness must decline with depth in the structure.

The solution is to (i) employ a precursor that exhibits a hard saturation in the growth rate vs. partial pressure, (ii) use a high partial pressure above the sample, and (iii) grow at low temperature to limit the reaction rate. Under these conditions, even though the partial pressure of precursor drops considerably from the top to the bottom of the sample, the growth rate remains almost constant. To achieve the high precursor pressure, we employ a static (unpumped) reaction tube apparatus. We previously derived a master relationship [1] that predicts the precursor pressure (*p*) necessary to achieve a desired step coverage (*SC*) and growth rate (*GR*) in a given aspect ratio (*AR*) given knowledge of the atomic density (r), growth rate coefficient (*K*) and molecular diffusivity (D_0): $p = (GR\ AR) * ((c\ r\ kT) / (2\ D\ K) * (1 - SC))$^0.5

We will discuss extension of this method to other thin film systems and substrate geometries.

1. A. Yanguas-Gil, Y. Yang, N. Kumar, and J. R. Abelson, JVST A **27,** 1235 (2009) [DOI: 10.1116/1.3207745]

3:00pm **TF+MI+NS-ThA3 Varying Penetration Depths in ALD on High Aspect Ratio Carbon Nanotube Forests**, ***David Kane***, *RC. Kane, R.R. Vanfleet*, Brigham Young University

We have observed steps in the penetration depth in atomic layer deposition on tall vertically aligned multiwall carbon nanotube (MWCNT) forests. The deposition thickness at the top of the forest is greater than that at the bottom and varies in distinct steps. The MWCNT forests used were 200 µm tall with an aspect ratio of about 2000. In the thermal TMA/water process on MWCNTs, precursor pulse times ranged from 0.5s to 2s. We propose a model for banding where Al2O3 nuclei grow in each cycle, thus the number of TMA adsorption sites increases. Due to the confined geometry, Knudsen diffusion and adsorption site density determine the relationship between precursor penetration depth and exposure time. The penetration depth is inversely proportional to the square root of the precursor adsorption site density and proportional to the square root of the exposure time. We have measured the penetration depth for different bands and a good fit to our model is shown.

3:20pm **TF+MI+NS-ThA4 NiOx Decorated Platinum Nanoparticles Via Atomic Layer Deposition for Enhanced Sintering Resistance**, ***Jiaming Cai***, *K. Cao, M. Gong, B. Shan, R. Chen*, Huazhong University of Science and Technology, PR China

Platinum nanoparticles (NPs) play an important role in the catalytic applications such as conversion of automotive exhaust, fuel cells, nano sensing and so on. For most catalytic applications, sintering of Pt NPs is undesired since the coalescence decreases the number of active sites of the catalyst. Herein we report the utilization of active oxide layers to encapsulate Pt NPs to enhance sintering resistance at high working temperature. The active oxide coated catalysts have additional metal-oxide interfaces which may further improve the catalytic activity besides good sintering resistance. Nickel oxide coating layer is prepared via atomic layer deposition (ALD) method. The effect of layer thickness towards catalytic properties and thermal stability for CO oxidation are investigated. The thickness of nickel oxide coating layer was controlled accurately by varying the ALD cycles. Characterizations including TEM, XPS, FTIR and XAFS were undertaken to explore the origin of the CO oxidation catalytic activity enhancement. *In-situ* AFM test is carried out to explore the mechanism of nanoparticles migration and sintering phenomenon in different environment by controlling the calcination temperature and oxygen partial pressure. Nickel oxide anchors Pt NPs with a strong metal oxide interaction, and coating structure around Pt NPs provide physical blocking that suppresses NP particle migration and coalescence. The catalysts show both enhanced CO conversion activity and improved sintering resistance up to 700 °C under oxidative atmospheric conditions.

4:00pm **TF+MI+NS-ThA6 Atomic Layer Deposition of HfO_2/Al_2O_3 Nanolaminates on Single-crystal GaN and Ga_2O_3: Investigation of Device Degradation in Power Semiconductor Devices**, ***David Mandia***, *A. Yanguas-Gil, J.A. Libera, J.W. Elam*, Argonne National Laboratory

The search for adequate binary metal oxide dielectric nanolaminates (NLs) to prevent degradation of power semiconductor devices is ongoing and involves the atomic layer deposition (ALD)-growth of a variety of binary metal oxide combinations. In the present work, we explore the ALD growth of amorphous $(x)HfO_2/(y)Al_2O_3$ NLs on Si (with native SiO_2 layer) substrates and then on both GaN and Ga_2O_3 single crystals. A variety of samples ranging from their homogeneous mixtures to HfO_2 or Al_2O_3-rich NLs are assessed before and after a thermal annealing by spectroscopic ellipsometry (SE), X-ray reflectometry (XRR), X-ray photoelectron spectroscopy (XPS) and 4-point probe resistivity measurements in order to elucidate the structural evolution of the NL at the GaN (or Ga_2O_3)-NL interface. By quantifying the HfO_2 incorporation throughout the Al_2O_3 layer and using the programmable nature of ALD to alternate layers of the HfO_2 and Al_2O_3 in an $(AB)_x$-$(CD)_y$ fashion, the influence of HfO_2 mobility within Al_2O_3 layer on the NL dielectric constant can be verified unequivocally. Moreover, combined X-ray absorption near-edge (XANES) and X-ray absorption fine structure (XAFS) spectroscopy data obtained at the Advanced Photon Source will confirm the local coordination environment of the Ga at the GaN (or Ga_2O_3)-HfO_2 interface and, at low super-cycle numbers (sub-nm scale), the ultimate stability of the NLs can be probed and optimized such that the bulk material properties are retained.

4:20pm **TF+MI+NS-ThA7 Atomic Layer Deposition Enabled Synthesis of Multiferroic Composite Nanostructures**, ***Jeffrey Chang****, University of California at Los Angeles, *A. Rosenberg*, Stanford University, *A. Buditama*, University of California at Los Angeles, *E. Jin, L. Kornblum, C. Ahn*, Yale University, *S.H. Tolbert*, University of California at Los Angeles, *K.A. Moler*, Stanford University, *J.P. Chang*, University of California at Los Angeles

Multiferroic materials, which exhibit the coexistence and coupling between ferroelectricity and magnetism, are of great interest due to their potential for enabling next-generation memories. To overcome the scarcity and weak responses of single-phase multiferroics, composite strategies were proposed for a robust multiferroic behavior by coupling the functional properties through the interface. By interfacing magnetostrictive and piezoelectric materials, the strain-mediated coupling strategy holds great promise, while both the interfacial-area-per-volume and the quality of interfaces play important roles in attainable functional properties. To obtain applicable magnetoelectric (ME) coupling under such scheme, lead-free multiferroic $BiFeO_3$ (BFO) and ferrimagnetic $CoFe_2O_4$ (CFO) were used in this study due to their robust functionality.

With the aim of enhancing the coupling by nanostructuring, atomic layer deposition (ALD), with its high quality and conformal film growth, was

* **TFD James Harper Award Finalist**

employed to achieve BFO/CFO composites with closely coupled interfaces and industrial scalability. BFO and CFO with were synthesized by radical enhanced ALD on $SrTiO_3$ (001) substrates using tmhd-based organometallic precursors(tmhd=2,2,6,6-tetramethylheptane-3,5 dione). The use of oxygen radicals as the oxidant provides a low temperature processing capability at 200°C. Post-deposition thermal treatments promotes the crystallization of both the BFO and CFO films and thus comparable functional properties were obtained. 2D-2D BFO/CFO composites were then synthesized by combining the ALD processes, with an optimized functionality obtained by nanolayering. ME behaviors comparable to previously studied multiferroic composites were observed, and the scaling of materials leads to an enhancement in the coupling coefficient (≈64 Oe cm/kV). The change in magnetic domains upon electrical poling was characterized using scanning SQUID. The 2D-2D BFO/CFO on $SrTiO_3$-buffered Si substrates exhibited comparable ME behaviors to the case on $SrTiO_3$, illustrating a path to integrate multiferroic materials into current industrial processes by ALD.

0D-3D BFO/CFO was realized by incorporating ALD-grown $BiFeO_3$ and mesoporous CFO substrates. Composite functionality as well as ME coupling were studied as a function of residual porosity after ALD filling. Higher BFO incorporation increases the overall ferroelectricity but limits the strain interaction due to a decreased mechanical flexibility. The strain interaction was verified by the change in lattice parameters observed using high-resolution XRD measurements. The results showed that the residual porosity is the key for ME coupling in a strain-mediated scheme.

4:40pm **TF+MI+NS-ThA8 Recent Developments in the Analysis of ALD/CVD Thin Film Conformality**, ***Riikka Puurunen***, Aalto University, School of Chemical Engineering, Finland **INVITED**

The downscaling of future semiconductor devices with increasing 3D character has lead to increasing demand of highly conformal thin films. Atomic layer deposition (ALD), based on the use of repeated, self-terminating reactions of typically at least two compatible reactants on a solid substrate, is often the only technique that can meet the conformality specifications. Conformal films made by ALD are also needed in other fields with intrinsic three-dimensionality requirements such as microelectromechanical systems (MEMS) and porous particle based applications (e.g., catalysis).

This work overviews recent progress in thin film conformality analysis made with the microscopic lateral high-aspect-ratio (LHAR), especially the "PillarHall" structures developed at VTT. Significant progress has taken place during the past year in the design and fabrication of the structures, conformality testing by academic and industrial partners, as well as modelling. The key feature of VTT's PillarHall structures is the existence in silicon of a lateral gap of controlled height, typically 500 nm (can be varied from wafer to wafer, 100 to 2000 nm demonstrated), and controlled length up to 5 mm (several variations inside one chip, starting from 1 µm). Test structures with aspect ratio (AR) up to 50 000 : 1 ("hole-equivalent AR (EAR)" up to 25 000 : 1) have been fabricated this way. Growth of thin film inside the controlled 3-D gap and analysis of the film thereafter, often after removing the top part of the test structure by applying an adhesive, reveals the film thickness and composition profile. As compared to conventional vertical trenches etched into silicon, with VTT's lateral PillarHall test structures, one can in a significantly shorter time obtain more detailed information on the conformality, which can be used for optimising processes, designing new processes, and investigating the fundamental mechanisms behind the deposition processes. Three scientific publications [1-3] report on the use of PillarHall 1st generation prototypes. At the time of writing this abstract, we work with 3rd generation prototypes and design the 4th generation.

Acknowledgements: Funding for the development of the conformality test structures has come from the Academy of Finland's Finnish Centre of Excellence in Atomic Layer Deposition and the Tekes PillarHall project.

[1] Gao et al., J. Vac. Sci. Technol. A, 33 (2015) 010601 (5 pages). http://dx.doi.org/10.1116/1.4903941

[2] Mattinen et al., Langmuir 32 (2016) 10559-10569. http://dx.doi.org/10.1021/acs.langmuir.6b03007

[3] Puurunen & Gao, IEEE Xplore 2017, http://ieeexplore.ieee.org/document/7886526/

5:20pm **TF+MI+NS-ThA10 Spatial Atomic Layer Deposition Reactor Design for Nano-laminates**, *X.L. Wang,* ***Yun Li****, J.L. Lin, J.M. Cai, R. Chen*, Huazhong University of Science and Technology, PR China

Atomic layer deposition (ALD) is commonly a vacuum based technique for ultrathin film fabrication with precise control of film thickness, uniformity and conformity. In contrast to conventional temporal ALD (T-ALD) that precursors and purging gases are introduced into reactor sequentially, the separation mode of spatially-separately ALD (S-ALD) between reactive precursors is in space instead of in time, thus the process is continuous. In S-ALD process, the inert gas serves as a flow gas barrier to separate the precursors' zones, which prevents the cross contamination and atmosphere perturbation. With the alternating arrangements of oxidizer gas channels, metal source channels, and gas barriers of inert gas, the deposition rate of S-ALD could reach 1-3 order of magnitude higher than T-ALD. Moreover, the atmospheric pressure in S-ALD system enables this technique in a continuous form without vacuum. As the continuing development of S-ALD, it has found many potential high through-put and large scale applications. Here we present an S-ALD system design for fabricating binary oxides and their nano-laminates. The design of S-ALD reactor is based on motion structure of linear track and injector with a multiple slit gas source channel. By optimizing the structure of precursor channel based on the flow field simulation, a tree-branch-like gas feed structure is obtained, and the uniformity of the precursor distribution is enhanced significantly. The T-curve motion profile is replaced by the S-curve t o control the movement of substrate which can avoid abrupt change of acceleration and jerk in the acceleration and deceleration process, stabilizing the distance between injector and substrate precisely. The growth of thin film at different moving speeds has good linearity and uniformity. By integrating different reaction units, nano-laminates with tunable optical and electrical properties can be obtained.

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