

Thin Film

Room 104E - Session TF1-ThM

Control and Modeling of Thin Film Growth and Film Characterization

Moderators: Berc Kalanyan, National Institute of Standards and Technology (NIST), Richard Vanfleet, Brigham Young University

8:00am **TF1-ThM1 Adventures in Group IV Ordering: Super-periodicities at the Atomic/Nano/Meso/scale, Jerrold Floro, J. Amartya, C. Duska, C.W. Petz, University of Virginia; D. Yang, J. Levy, University of Pittsburgh**
INVITED

This talk will examine the perils, pitfalls, and possibilities for creating order across different lengthscales and dimensionalities in heteroepitaxial Group IV thin films and nanostructures. I will review our results in three projects: (i) Direct writing of ordered arrays of 3C-SiC quantum dots on Si (001); (ii) Directed self-assembly of 2D and 3D ordered arrays of Ge quantum dots on Si (001); and (iii) chemical ordering in $\text{Si}_{1-x}\text{Ge}_x$ alloys on Si (001). Herein, all the materials are grown by molecular beam epitaxy. Even though Group IV materials are amongst the most heavily studied epitaxial growth systems, in all three cases discussed here there were significant surprises, some “good” and some “bad”. First I will briefly review our goal of using carbonaceous bumps, written on Si (001) by fine-spot electron-beam cracking of hydrocarbons, to direct the self-assembly of Ge quantum dots. We did not observe the latter to occur, but the formation of epitaxial 3C-SiC was itself interesting, and the carbide dots were successfully encapsulated in a Si matrix under optimized overgrowth conditions. We then used Ga focused ion beams (FIB) to create surface morphology that directs the self-assembly of Ge quantum dots. Atomic force microscopy (AFM) showed beautiful long-range order, both in single layers of dots, and in multiple layers of dots. However, cross-section transmission electron microscopy told a rather different story to the AFM, and this ultimately led us to abandon FIB as our patterning method of choice, in favor of electron beam lithography (ongoing). Finally, we recently revisited *chemical* ordering in $\text{Si}_{1-x}\text{Ge}_x$ alloys, which was intensively studied in the 1990's. Our work was driven by predictions that chemical ordering, with large order parameters, could produce observable effects on thermal transport, and likely on electrical transport as well. This could improve the thermoelectric figure of merit. However, despite an extensive survey of growth-parameter space, we never observed order parameters to exceed 0.24. We found it necessary to be very careful in our quantification of the order parameter. More interestingly, our results seem to suggest three mutually inconsistent results with regard to how ordering is affected by step density. Hence there is much more to be understood about the interactions of strain, steps, faceting, and dislocations on chemical ordering. We gratefully acknowledge the support of the Department of Energy Office of Basic Energy Sciences, the II-VI Foundation, and the National Science Foundation Division of Materials Research. Research was performed in part at the NIST Center for Nanoscale Science and Technology.

8:40am **TF1-ThM3 Combinatorial Fabrication of Cu-Fe₂O₃ Composite Nanostructures by Oblique Angle Co-Deposition, S. Larson, W.J. Huang, Yiping Zhao, University of Georgia**

Traditionally, new materials have been explored and discovered via the one by one trial-and-error method. This can require decades of research to identify and optimize a material system for technological application and commercialization. From an experimental point of view, to speed up materials discovery, a large amount of materials need to be synthesized/fabricated and characterized simultaneously. Such a parallel production and characterization process has been traditionally targeted by a so-called high throughput or combinatorial materials science. The adaptation of the combinatorial techniques to nanofabrication has been slow due to the complexity and variety of fabrication techniques. To-date, only few groups have realized combinatory nano-synthesis via multi-well hydrothermal and solvothermal methods. However, based on combinatory thin film deposition technique and shadowing growth mechanism, a new and versatile combinatory nanofabrication technique called the oblique angle co-deposition can be easily facilitated. It can be used to generate a library of nanomaterials with different morphology and structure. In this talk we demonstrate the feasibility of such a nanofabrication technique. Using the Cu-Fe₂O₃ system as an example, by carefully characterizing the vapor plumes of the source materials, a composition map can be generated, which is used to design the locations of all the substrate

holders. The resulting nanostructures at different locations show different thickness, morphology, crystallinity, composition, as well as inhomogeneity in microstructures. In addition, material maps of all these structural parameters are established, which can be used to correlate their properties. By further oxidizing or reducing the composite nanostructures, the properties of the nanostructures such as band gap, photocatalytic performance, and magnetic properties can be easily linked to their composition and other structural parameters. Optimal materials for photocatalytic and magnetic applications are efficiently identified. It is expected that the oblique angle co-deposition and its variations could become the most powerful combinatory nanofabrication technique for nanomaterial survey.

9:00am **TF1-ThM4 Structural and Electronic Properties of Titanium Doped Ga₂O₃ Thin Films, Sandeep Manandhar, E. Rubio, C.V. Ramana, The University of Texas at El Paso**

Gallium oxide (Ga₂O₃) has garnered significant interest due numerous applications of this material in gas sensing, optoelectronic devices, transparent electronic devices, and spintronics. From optical applications point of view, Ga₂O₃ finds attractive applications in luminescent phosphors, antireflection coatings, and solar cells. Ga₂O₃ has been recognized as a deep ultraviolet transparent conducting oxide (UV-TCO), which makes the material a potential candidate for transparent electrode applications in UV optoelectronics. However, while the large band gap makes it useful for far UV applications, it is possible to tune the properties and make it suitable for visible or low-UV applications if the band gap and electrical conductivity of Ga₂O₃ thin films are tuned. In this context, we propose and investigate to modify the properties of Ga₂O₃ by selectively doping with titanium (Ti). β -Ga₂O₃ thin films with variable Ti content were deposited by co-sputtering of the Ga-oxide ceramic and Ti metal by varying the sputtering power applied to these targets. The effect of Ti on the crystal structure and optical properties of β -Ga₂O₃ thin films is significant. For low Ti-content, films crystallize in β -phase of Ga₂O₃. However, increased Ti content induces amorphization of the Ga₂O₃ thin films. Band gap values showed a corresponding shift from ~5 eV to lower side indicating that the Ti incorporation induce changes in the electronic structure. A correlation between Ti-chemistry, structure and optical properties of Ga-Ti-O films will be discussed.

9:20am **TF1-ThM5 Characterizing Patterns and Order in Self-Assembled Langmuir Films of Quantum Dots, Zachary Whitfield, J.J. Weimer, University of Alabama in Huntsville**

The goal of this analytical study is to establish methods to quantify the uniformity of self-assembled Langmuir monolayers of quantum dots (QDs) in an efficient and reliable manner. Gradient-core quantum dots (QDs) were selected for creating the thin films because of their growing popularity for use in industries. The QDs were cast as Langmuir films on a water subphase, and the Langmuir films were deposited onto substrates using the Langmuir-Schafer (LS) technique. Images were taken using an iSight digital camera of both the Langmuir and LS films with a black light source. Agglomerations, voids, islands, and ridges were some of the artifacts found when surveying the Langmuir films. These artifacts were seen to template directly to the LS films. Emission spectra of the LS films were mapped using fluorescence spectroscopy. Scanning probe microscopy was also performed to study surface morphology of samples. Image processing software was used to quantify the intensities of the variations at different spatial locations across the films. A direct correlation was made between the spatial variations in image brightness and the intensities of fluorescence spectra at the same given point on the LS films.

9:40am **TF1-ThM6 Radical-Based MBE Growth, Structure, Defects and Transport in High-Mobility Epitaxial La-doped BaSnO₃ Films, A. Prakash, P. Xu, J. Dewey, Bharat Jalan, University of Minnesota**

We will present on the growth of phase-pure, epitaxial BaSnO₃ films using a novel radical-based molecular beam epitaxy (MBE) approach with scalable growth rates [1]. In this approach, we use a metal-organic precursor (hexamethylditin) as a tin source, a solid effusion cell for barium, and an rf plasma source for oxygen. BaSnO₃ films were grown on SrTiO₃ (001), LaAlO₃ (001) and LSAT (001) substrates. The substrate temperature and oxygen pressure were kept fixed at 900° C, and 5x10⁻⁶ Torr respectively whereas Ba/Sn beam equivalent pressure (BEP) ratio was varied to optimize cation stoichiometry. The unstrained lattice parameter determined using high-resolution X-ray diffraction, and the Rutherford backscattering spectroscopy (RBS) were used to optimize cation stoichiometry. Lanthanum was used as n-type dopants.

Thursday Morning, November 10, 2016

Stoichiometric composition yielded an unstrained lattice parameter value of $4.116 \pm 0.001 \text{ \AA}$, which is identical to that of bulk BaSnO_3 . This value was found to increase for Ba-rich films whereas Sn-rich films resulted into secondary phase formation. A range of Ba/Sn flux ratio was identified where films cation stoichiometry was self-regulating indicating the presence of a "MBE growth window". Time-dependent reflection high-energy electron diffraction (RHEED) intensity oscillations were observed during film growth indicating films grew in a layer-by-layer fashion. Atomic force microscopy confirmed smooth surface morphology for stoichiometric films. Non-stoichiometry films showed surface nanocrystallites, which correlated with the film stoichiometry. Most remarkably, phase-pure BaSnO_3 could also be grown with the molecular oxygen (i.e. without any rf plasma) suggesting an important role of reactive radical chemistry during film growth. We will discuss these results in the context of highly reactive Sn radicals growth mechanism that assist with the reaction and compound formation.

Finally, we will present a comprehensive electrical characterization of La-doped BaSnO_3 and will discuss how electrical transport is influenced by the presence of structural defects such as dislocations, non-stoichiometry, and dopant concentration. We will also present different scattering mechanisms in La-doped BaSnO_3 that limits the room temperature electron mobility. We will present pathways to suppress these scattering rates - a step closer towards defect-managed high mobility oxide thin films and heterostructure.

Work supported by the NSF, and the AFOSR YIP Program.

[1] A. Prakash, J. Dewey, H. Yun, J.S. Jeong, K.A. Mkhoyan, and B. Jalan, "Hybrid molecular beam epitaxy for growth of stoichiometric BaSnO_3 ", *J. Vac. Sci. Technol. A*, **33**, 060608 (2015).

11:00am TF1-ThM10 Reduction of Extended Defects in SiC Epilayers Grown on 2° Offcut Substrates, Rachael Myers-Ward, N. Mahadik, R. Stahlbush, P. Klein, K.M. Daniels, A. Boyd, K. Gaskill, Naval Research Laboratory

Silicon carbide is a material of interest for high-voltage and high-power switching device applications. Basal plane dislocations (BPDs) are a major concern for SiC bipolar devices as they source Shockley-type stacking faults in the presence of an electron-hole plasma and reduce minority carrier lifetimes. Many researchers have investigated methods to reduce the BPD density by experimenting with pre-growth treatments, substrate orientation, growth parameters and growth interrupts. This work investigates extended defects, morphology and lifetime in 4H-SiC epilayers grown on substrates offcut 2° toward the [11-20].

Epilayers were grown on 2° offcut substrates in a horizontal hot-wall reactor using the standard chemistry of silane (2% in H_2) and propane. Epilayers were grown at various growth rates, C/Si ratios, and growth temperatures. The pressure was maintained at 100 mbar for all growths. Some samples were grown with a 5 μm highly doped n^+ buffer layer using ultra high purity nitrogen prior to the low doped epilayers. Ultraviolet photoluminescence (UVPL) imaging was used to identify BPDs in the low doped epilayers. Time resolved photoluminescence measurements were performed to determine the minority carrier lifetime of the layers and Raman spectroscopy was used to analyze polytype inclusions. Electron trap concentrations were determined using deep level transient spectroscopy (DLTS). Surface roughness was measured by atomic force microscopy and the morphology was also characterized using Nomarski microscopy.

When a 15 μm epilayer was grown without a buffer layer, step bunching was observed and the surface roughness was 6.0 nm RMS. For comparison, a standard 4° offcut sample typically has 3.0 nm RMS for a 20 μm epilayer. Using UVPL, it was found that after 4 μm of epi, 90% of the BPDs had converted in the low doped layer as compared to 70% in a 4° offcut sample, indicating the conversion is faster in the lower offcut material. 3C-SiC inclusions were present in the epilayers as verified using Raman spectroscopy for both unintentionally doped (UID) and N^+ epilayers. These inclusions were reduced by increasing the growth temperature and lowering the C/Si ratio for N^+ epilayers, but increasing C/Si ratios for UID films. Changing these growth parameters resulted in specular film morphology and resulted in minority carrier lifetimes on the order of 1 μs .

11:20am TF1-ThM11 Modeling the Structure and Medium Range order of ALD Amorphous Oxide Thin Films, Angel Yanguas-Gil, J.W. Elam, Argonne National Laboratory

The evolution of microstructure during the early stages of growth is crucial for the chemical and electronic properties of oxide materials at the core of a wide range of applications, from gate dielectrics for conventional and

power electronics to energy storage and catalysis. Through a combination of synchrotron studies and atomistic models we have studied the evolution of the structure for a variety of oxide materials including ZnO , In_2O_3 , TiO_2 , and HfO_2 .

We have leveraged ALD's unique ability to grow conformally on high surface area materials to characterize the evolution of the coordination environment and medium range order using EXAFS, XANES, and PDF. We have compared these results with atomistic simulations, which have allowed us to calculate the pair correlation function and the EXAFS of the simulated material as a function of thickness and temperature.

We have combined these molecular dynamic calculations with simple Monte Carlo simulations to understand the evolution of microstructure during the early stages of growth. Our results are consistent with local structural relaxation mechanisms having a key role in allowing the transition from isolated cluster to bulk-like coordination and medium range. In particular, using the REAXFF potential we were able to look at the impact that hydroxyl groups have on delaying the formation of crystalline phases for low temperature ALD ZnO .

11:40am TF1-ThM12 From Nano-porosity to Macro-scale Defects: Ellipsometric Porosimetry and Electrochemical Impedance Spectroscopy Characterization of Thin Inorganic Films, Alberto Perrotta*, W.M.M. Kessels, M. Creatore, Eindhoven University of Technology, Netherlands

Nano-porosity is an intrinsic property of thin films, and it is identified in inorganic layers by the size of rings (e.g., $-\text{SiOSi}-$) and ring termination units (e.g., Si-OH). Porosity control is the key to several technological applications and selected examples are separation membranes, low- k dielectrics, and permeation barrier layers.

In moisture permeation barriers, H_2O permeation is known to occur through nano-porosity and the so-called macro-scale defects (from few nm to hundreds of μm). Therefore, the development of methodologies able to follow both permeation paths and predict the quality of a barrier layer are needed.

In this study, an in-depth analysis of nano-porosity in thin films and its impact on their moisture barrier performance are presented.¹ Several inorganic layers (SiO_2 , Al_2O_3 , SiN_x) deposited by plasma enhanced-chemical vapor deposition (PE-CVD) and (plasma assisted-) atomic layer deposition (ALD) have been considered. Ellipsometric porosimetry (EP) and electrochemical impedance spectroscopy (EIS) have been adopted as complementary techniques for the analysis of nano-porosity ranging from H_2O kinetic diameter (0.27 nm) up to 1 nm. The role of the specific nano-pore range in controlling the *intrinsic* barrier properties has been disclosed. In detail, absence of porosity with diameter above 0.27 nm led the transition from mediocre ($10^{-4} \text{ gm}^{-2}\text{day}^{-2}$) to excellent ($10^{-6} \text{ gm}^{-2}\text{day}^{-1}$) H_2O barrier properties. Moreover, PA-ALD Al_2O_3 and SiN_x (10-40 nm) layers showed no porosity in the 0.27-1 nm range, and therefore excellent *intrinsic* barrier properties.

Also, next to nano-porosity, macro-scale defect detection is shown possible by both EIS and EP. Specifically, EIS was shown able to directly detect such defects for barriers deposited on c-Si. With EP, the permeation of probe molecules through barriers deposited on polymers can be followed in time. It is thereby possible to discern diverse events, i.e., filling of nano-porosity in the barrier layer and swelling of the polymer.² The rate of permeation through the polymer and its swelling has been found to decrease of one order of magnitude upon deposition of porous barriers. The application of a denser layer, impermeable to the probe molecule, showed a further decrease in permeation rate and limited uptake in the polymer. This allowed the isolation of the permeation through macro-scale defects and, thus, their detection.

This research forms part of the research program of the Dutch Polymer Institute (DPI), project #752.

¹ Perrotta *et al.*, *Microp. Mesop. Mat.* 188 (2014) 163; *Appl. Mater. Interfaces*, 7 (2015) 15968; *Plasma Processes Polym.* 12 (2015) 968.

² Perrotta *et al.*, to be submitted.

Thursday Morning, November 10, 2016

12:00pm **TF1-ThM13 Thermal Conductivity and Mechanical Properties of AlN-based Thin Films**, *Vincent Moraes*, *H. Riedl*, Technische Universität Wien, Austria; *H. Bolvardi*, Oerlikon Balzers, Liechtenstein; *S. Kolozsvári*, Plansee Composite Materials GmbH, Germany; *M. Ikeda*, *L. Prochaska*, *S. Paschen*, *P.H. Mayrhofer*, Technische Universität Wien, Austria

While many research activities concentrate on mechanical properties and thermal stabilities of protective thin films, only little is known about their thermal properties being essential for the thermal management in various industrial applications. Based on the 3ω -method, we show the influence of Al and Cr on the temperature dependent thermal conductivity of single-phase cubic structured TiN and single-phase wurtzite structured AlN thin films, respectively, and compare them with the results obtained for CrN thin films.

The dc sputtered AlN thin films revealed a highly c-axis oriented growth for deposition temperatures of 250 to 700 °C. Their thermal conductivity was found to increase strongly with the film thickness, indicating progressing crystallization of the interface near amorphous regions during the sputtering process. For the 940 nm AlN film, we found a lower boundary for the thermal conductivity of $55.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. By the substitution of only 10 at.% Al with Cr, κ significantly reduces to $\sim 5.0 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, although the single-phase wurtzite structure is maintained. The single-phase face centered cubic TiN and $\text{Ti}_{0.36}\text{Al}_{0.64}\text{N}$ thin films exhibit at room temperatures κ values of $3.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and $2.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, respectively. Hence, also here, the substitutional alloying reduces the thermal conductivity, although at a significantly lower level. Single-phase face centered cubic CrN thin films show κ values of $3.6 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.

For all nitride based thin films investigated, the thermal conductivity slightly increases with increasing temperature between 200 and 330 K. This rather unusual behavior is based on the high defect density (especially point defects) within the films prepared by physical vapor deposition.

PACS numbers: 68.60.Dv; 68.55.J;

Keywords: Thermal conductivity; Nitride based thin films; Alloying effects; 3ω -method;

Author Index

Bold page numbers indicate presenter

— A —

Amatya, J.: TF1-ThM1, **1**

— B —

Bolvardi, H.: TF1-ThM13, **3**

Boyd, A.: TF1-ThM10, **2**

— C —

Creatore, M.: TF1-ThM12, **2**

— D —

Daniels, K.M.: TF1-ThM10, **2**

Dewey, J.: TF1-ThM6, **1**

Duska, C.: TF1-ThM1, **1**

— E —

Elam, J.W.: TF1-ThM11, **2**

— F —

Floro, J.A.: TF1-ThM1, **1**

— G —

Gaskill, K.: TF1-ThM10, **2**

— H —

Huang, W.J.: TF1-ThM3, **1**

— I —

Ikeda, M.: TF1-ThM13, **3**

— J —

Jalan, B.: TF1-ThM6, **1**

— K —

Kessels, W.M.M.: TF1-ThM12, **2**

Klein, P.: TF1-ThM10, **2**

Kolozsvári, S.: TF1-ThM13, **3**

— L —

Larson, S.: TF1-ThM3, **1**

Levy, J.: TF1-ThM1, **1**

— M —

Mahadik, N.: TF1-ThM10, **2**

Manandhar, S.: TF1-ThM4, **1**

Mayrhofer, P.H.: TF1-ThM13, **3**

Moraes, V.: TF1-ThM13, **3**

Myers-Ward, R.L.: TF1-ThM10, **2**

— P —

Paschen, S.: TF1-ThM13, **3**

Perrotta, A.: TF1-ThM12, **2**

Petz, C.W.: TF1-ThM1, **1**

Prakash, A.: TF1-ThM6, **1**

Prochaska, L.: TF1-ThM13, **3**

— R —

Ramana, C.V.: TF1-ThM4, **1**

Riedl, H.: TF1-ThM13, **3**

Rubio, E.: TF1-ThM4, **1**

— S —

Stahlbush, R.: TF1-ThM10, **2**

— W —

Weimer, J.J.: TF1-ThM5, **1**

Whitfield, Z.: TF1-ThM5, **1**

— X —

Xu, P.: TF1-ThM6, **1**

— Y —

Yang, D.: TF1-ThM1, **1**

Yanguas-Gil, A.: TF1-ThM11, **2**

— Z —

Zhao, Y.P.: TF1-ThM3, **1**