Thin Films Division
Room A216 - Session TF-FrM
Theory and Characterization of Thin Film Properties

Moderators: Angel Yanguas-Gil, Argonne National Laboratory, Gerben van Straaten, Eindhoven University of Technology, The Netherlands

8:20am **TF-FrM1 Incorporation Mechanisms and Electronic Properties of Impurities in Wide-Band-Gap Semiconductors**, ***John (Jack) Lyons***, *S.C. Erwin,* U.S. Naval Research Laboratory **INVITED**

The management of unwanted impurities as well as the controlled introduction of dopant species continue to be challenges in wide-band-gap (WBG) semiconductors such as AlN and Ga_2O_3. In these materials, contaminants such as carbon often incorporate during growth and subsequently act as trapping centers, which can have a detrimental impact on device performance. Moreover, establishing hole conductivity through the introduction of acceptor impurities has proven to be especially difficult in these compounds. In this talk, I will discuss the use of first-principles calculations to understand the incorporation and electronic properties of impurities in WBG semiconductors.

In many growth techniques carbon-containing precursors, such as trimethylaluminum (TMA) for AlN, are often employed. These precursors are thought to be a major source of carbon contamination during growth. Focusing on atomic-layer deposition, we have developed a model to elucidate the decomposition of TMA at the AlN surface, and subsequent incorporation of carbon into the AlN film during growth. We find that the use of H-containing plasma is crucial for scrubbing methyl species from the surface. However, the plasma also leads to atomic carbon, which opens a channel for trapping carbon impurities into the film. In light of this dual role, we propose a solution for minimizing carbon contamination into AlN.

Quantitative determination of the electrical role of particular impurity species present within WBG semiconductors has long been a challenge for theoretical calculations. However, using hybrid density functional theory we are now able to accurately predict the role of impurities such as carbon. We find that carbon acts predominantly as a deep acceptor trap in AlN, as it does for GaN. In contrast, carbon is found to act as a donor species in WBG oxides such as Ga_2O_3. Other potential acceptor dopants, such as magnesium, are also found to act as deep acceptors, due to their propensity to trap localized holes. In fact, no acceptors are found to be effective *p*-type dopants in either Ga_2O_3 or AlN. However, acceptor dopants are still found to be useful for producing semi-insulating material.

9:00am **TF-FrM3 Review and Demonstration of Feature Scale Simulations**, ***Paul Moroz,*** TEL Technology Center, America, LLC

Feature-scale simulations (FSS) represent an important tool for modeling of etching, deposition, and implantation processes routinely applied during semiconductor materials processing and device fabrication. Traditionally, FSS uses a combination of Monte Carlo methods with special algorithms for modeling gaseous and solid (in volume and at the surface) species, as well as algorithms for advancing feature profiles and materials composition as a result of reactive interactions of incoming species with solid materials. The mentioned FSS approach, at least at present time, seems to be the only feasible approach to simulate materials processing at the feature-scale level ranging from tens of nanometers to tens of micrometers, while applications of such advanced methods as quantum chemistry or molecular dynamics are still too expensive computationally in spite of highly efficient code parallelization to run on multi-processor computers. Phenomenological description of reactions (chemical and physical) represents a weakness of FSS, as it is very difficult to implement proper sets of reactions valid at different conditions. Here, we discuss an approach used in the FPS3D code [1-5], for simulation of etching, deposition, and implantation with the present focus given to simulation of ALD/CVD processes. Examples include such difficult topics as HAR etching, as well as CVD and ALD. For ALD examples we consider silicon nitride deposition [5] for different chemistries, some of them allowing deposition of a single monolayer per cycle, while others allowing only a fraction of a monolayer to be deposited per cycle.

References:

[1] P. Moroz, IEEE Trans. on Plasma Science, 39 2804 (2011).

[2] P. Moroz, D. J. Moroz, ECS Transactions, 50 61 (2013).

[3] P. Moroz, D. J. Moroz, J. Physics: CS 550 012030 (2014).

[4] P. Moroz, 15th Int. Conf. on Atomic Layer Deposition, Portland, OR (2015).

[5] P. Moroz, D. J. Moroz, Japan. J. Appl. Phys. **56**, 06HE07 (2017).

9:20am **TF-FrM4 Process Optimization in Atomic Layer Deposition Using Machine Learning**, *A. Yanguas-Gil, S. Letourneau, A.U. Mane,* ***Noah Paulson****, A.N. Lancaster, J.W. Elam,* Argonne National Laboratory

Process development and process optimization are ubiquitous, resource-intensive tasks in thin film research and development. The goal of these activities is to find the set of process parameters (e.g. temperature, pressure, and flow) that maximize film quality at minimal cost. Typically, this is accomplished by coating a substrate (e.g. a silicon wafer) under a given set of conditions, measuring the film properties ex situ, and adjusting the conditions to improve the film quality. This activity can consume significant time and resources, especially if an additional goal is to achieve uniform films across a large substrate. Process development can be accelerated and economized using in situ measurements. For instance, quartz crystal microbalance (QCM) measurements can be employed to monitor film thickness in real time as the deposition conditions are varied. However, this still requires the careful attention of a skilled operator to make informed choices based on experience and intuition. An alternative strategy is to use machine learning (ML) to analyze the QCM data and adjust the growth conditions based on an algorithm. To explore this possibility, we used ML to optimize the atomic layer deposition (ALD) of Al_2O_3 with trimethyl aluminum (TMA) and H_2O in a viscous-flow tubular reactor using in situ QCM measurements. We initially developed the ML code using simulated QCM data generated by a 1-D model of ALD transport and reaction. This allowed us to tailor the algorithm to ensure saturation of the TMA and H_2O ALD reactions and to converge efficiently on the optimal dose and purge times. An additional benefit of these simulations was that we could explore the effects of non-ideal behavior such as a CVD component to the surface reactions and strong interaction between the reaction products and the surface. Next, we interfaced the ML code to our ALD system and allowed the algorithm to optimize the TMA and H_2O timings. We observed rapid convergence, as predicted by our simulations, and found that the ML algorithm was capable of adapting to large variations in the initial conditions such as the precursor partial pressures and the carrier gas flow rate. We are now building an array of QCM sensors to measure the thickness simultaneously at 10 locations along our flow tube, and we hope to report on ML opimization of thickness and uniformity using this array.

9:40am **TF-FrM5 Electroless Deposition of Cobalt Metal on a Palladium Layer on an Amine-modified Surface**, *A. Ng,* ***Anthony Muscat,*** University of Arizona

Solution-deposited palladium on amine-terminated self-assembled monolayers (SAMs) is a well-characterized catalyst and adhesion layer combination for solution-based electroless metallization of dielectric films. A reducing agent is typically added to the deposition bath or a sensitizer such as tin is co-deposited producing relatively thick Pd layers. Thinner Pd deposits would enable barrier seed layers for filling < 10 nm wide gaps in patterned dielectric films with metal. In this work, we eliminated the reducing agent from the deposition bath and worked at pH < 2 to deposit monomeric Pd(2+) species and show that the amine groups terminating the SAM reduce Pd(2+) to Pd(0). The amount of Pd deposited depended on the coverage of the two types of amines on the SAM. The adsorption of $PdCl_4^{2-}$ ions in solution on protonated amine groups ($-NH_3^+$) is well known. Our data suggest that the nonprotonated amine groups ($-NH_2$), which coexist with $-NH_3^+$, chemically reduce the Pd(2+) ion to Pd metal by oxidizing to the amine radical cation ($-NH_2^{\bullet+}$). Pd bonds to and covers the $-NH_2^{\bullet+}$groups in the process depositing around a monolayer of Pd from solution on the SAM-covered silicon oxide surface. The Pd layer served as a catalyst for solution deposition of cobalt films on the surface using a reducing agent under oxygen-free conditions. The cobalt deposited initially as islands that grew together into a closed film with good adhesion.

10:00am **TF-FrM6 The Origins of Condensation-Driven Degradation of Hydrophobic Thin Films**, ***Jingcheng Ma****, N.M. Miljkovic,* University of Illinois at Urbana-Champaign

Dropwise condensation of steam on metallic surfaces coated with thin (~ 1μm) functional hydrophobic films has the potential to achieve remarkable heat transfer coefficients approaching ~100 kW/m^{2}K. However, the long-term durability of these thin films has limited the application of functional coatings for the past century. Although degradation due to steam condensation has been qualitatively described as 'blistering', no satisfactory insight exists capable of answering two key questions: what is

the mechanism of water vapor mass transfer, and what is the driving force for film delamination. Hence, scientists have been forced to abandon rational thin film development in favor of ad-hoc trial-and-error approaches. Here, we demonstrate that pinholes on hydrophobic coatings are the source of blisters so commonly seen during degradation. By creating shape-controlled pinhole-blister structures in thin deposited films, we show that blisters form in a spatially-controlled order during water vapor condensation from the ambient. The shape, initiation, and growth of the blisters was systematically investigated. Our experiments demonstrate that water vapor is mainly transferred to the blister through spatially-random pinholes which exist in the film after deposition, and the driving force for film delamination is capillary force. Based on the new insights developed here, we propose a non-dimensional pressure to determine the threshold when blistering will be initiated by a pinhole, or when discrete droplets grow up and above pinholes. To the best of our knowledge, our work represents the first quantitative description of blistering initiation. The techniques and insights presented here will inform future work on polymeric thin films to enable their rational and durable design for a variety of applications.

10:20am **TF-FrM7 Structural and Electrical Properties of Sputtered HEA Thin Films of CrFeCoNiCu and their Oxidation Studies***, **Jeyanthinath Mayandi**,* SMN, Department of Physics,University of Oslo, Norway*; M. Stange, E. Sagvolden, M.F. Sunding, Ø. Dahl,* SINTEF Materials and Chemistry, Norway*; M. Schrade,* SINTEF, Materials and Chemistry, Norway*; J. Deuermeier, E.Fortunato. Fortunato,* Universidade Nova de Lisboa, Portugal*; O.M.Løvvik. Løvvik, S. Diplas,* SINTEF Materials and Chemistry, Norway and University of Oslo, Norway*; P.A. Carvalho,* SINTEF Materials and Chemistry, Norway and Universidade de Lisboa, Portugal*; T.G. Finstad,* SMN, Department of Physics, University of Oslo, Norway

High-entropy alloys (HEAs) represent a class of materials that is intensively investigated for a range of possible applications. They generally show a high degree of phase stability by the high entropy while the structure is a random atom position disorder unlike other alloys which can influence physical properties differently than regular alloys. In general, there are few studies on oxidation of HEA and studies on adding oxygen during the fabrication of HEA. In this study we have sputtered thin films of CrFeCoNiCu onto insulating and optically transparent substrates in order to measure structural, electrical and optical functional properties. We have varied the oxygen pressure in the sputtering environment as well as oxidizing the samples at elevated temperatures after deposition. Optical and electrical characterization was performed on films sputter deposited on fused quartz wafers. The films were characterized by TEM, XRD and XPS. The films with no intentional oxygen had an FCC structure with a texture showing strong (111) preferred orientation as seen by XRD. TEM analysis showed columnar morphology with twins parallel to (111) planes. Samples sputtered under high oxygen content showed a simple NaCl structure(FeO). The samples were annealed in air and O_2 ambient in the temperature range of 300 to 500 °C. This caused an oxide layer growing on top of the FCC structure. XPS was utilized to find the atomic compositions and chemical stated of the elements. Hall measurements and Seebeck measurements were performed on the as prepared and oxidized films from 10 K to 600K. For the FCC structure the resistivity was a factor 10^4 higher than the elemental metals while can be satisfactory described by electron phonon scattering by the Bloch-Grüneisen description and the low temperature negative temperature effect by the Kondo effect. The sign of the Hall coefficient was positive while the Seebeck coefficient was negative, indicating the Fermi surface containing pockets of electrons and holes and an energy dependent scattering time. A detailed comparison of the as prepared and the oxidized thin films will be discussed in terms of the structural chemical and electrical properties of the grown films. In addition the electric properties will be discussed in terms of a model considering electronic structure and scattering.

10:40am **TF-FrM8 Observation of Topological Hall and Curie Temperature above Room Temperature in Strain-engineered FeGe Thin Films***, **Adam Hauser**, S. Budhathoki, K. Law, S. Ranjit, A. Sapkota,* The University of Alabama*; A. Thind, R. Mishra,* Washington University in St. Louis*; D. Heiman,* Northeastern University*; M.E. Jamer,* United States Naval Acadamy*; A. Borisevich,* Oak Ridge National Laboratory*; T. Mewes,* The University of Alabama*; J. Gallagher,* U.S. Naval Research Laboratory

The need to control and manipulate magnetic spin in nonvolatile memory applications drives exploration of new magnetic materials with non-uniformly ordered magnetic phases. Of particular interest are materials with inversion asymmetry, most commonly found in non-centrosymmetric space groups. Our group has successfully grown epitaxial B20 FeGe films with 4% tensile strain on a Ge(111) substrate by Sputter Beam Epitaxy, an off-axis magnetron sputtering technique in which beam-shaping, shutter control, and QCM-guided flux control of off-axis, direct-current (DC) magnetron sputter sources are employed upon high-purity elemental Fe and Ge targets in ultra-high vacuum. QCM control is modified to relative atomic ratios, and film compositions are confirmed by energy dispersive x-ray spectroscopy (EDS) and Rutherford Backscattering (RBS). X-ray diffractometry has confirmed that the films are single-crystal and phase pure, with near-substrate-limited rocking curve (FWHM 0.07º) and strong Keissig fringes in x-ray reflectometry. We find no evidence of strain relaxation up to 110nm, and off-axis XRD and HAADF STEM confirm the B20 phase necessary for the Skyrmionic phase. A strain-enhanced T_C = 350K by SQUID magnetometry and a clear Topological Hall effect (THE) signature observed at 330K suggest potential for Skyrmionic behavior at or above room temperature in a single layer thin film. Direct observation is required for confirmation of a Skyrmion lattice phase.

11:00am **TF-FrM9 Infrared Absorption Oscillator Strength Factors in SiNx Thin Films***, **Sara DiGregorio**, S. Habermehl,* Sandia National Laboratories

The oscillator strength factor of the Si-N asymmetric stretch mode of SiN films was studied for films of varying composition and thickness. Thin films were deposited by low pressure chemical vapor deposition at 850°C from mixtures of dichlorosilane and ammonia. The oscillator strength factor for each film was determined from Fourier Transform infrared spectroscopy and ellipsometric measurements. We found that the oscillator strength factor systematically decreases with increasing silicon volume fraction from2.10x10 cm to 1.44x10 cm for compositions ranging from 0% to 25% volume fraction amorphous silicon. We believe this trend is related to charge transfer induced structural changes in the basal SiN_x tetrahedron as the volume fraction of amorphous silicon increases. For stoichiometric silicon nitride the oscillator strength factor was found to be 2.01×10^{19} ± 7.25×10^{17} cm^{-2}, which is consistent with a reported value of 2.07×10^{19} cm^{-2} and a theoretical value of 1.99×10^{19} cm^{-2}. Additionally, in the composition range investigated, we found that the oscillator strength values agree favorably with trends observed in films deposited by plasma enhanced chemical vapor deposition. This work was selected as the best graduate student presentation at the 2019 NMAVS symposium (Albuquerque-June2019).

11:20am **TF-FrM10 Computer Aided Molecular Design of novel precursor materials for Atomic Layer Deposition***, **Mina Shahmohammadi**,* University of Illinois at Chicago*; R. Mukherjee,* Vishwamitra Research Institute*; C.G. Takoudis,* University of Illinois at Chicago*; U.M. Diwekar,* Vishwamitra Research Institute

Atomic Layer Deposition (ALD) is a vapor phase technique to deposit thin films of various metals and metal oxides on a substrate. Due to sequential and self-limiting reactions, conformal and pinhole-free thin films can be produced which have widespread applications. In this process, a precursor, which is often a metal surrounded by organic functional groups, chemisorbs on the substrate and part of the molecule subsequently desorbs from the surface after completion of the reaction. Precursor chemisorption on the substrate leads to a self-limiting process and it eventually results in films with desired thickness at the Ångström length scale. To design and conduct an ALD experiment, the precursor(s) should be chosen based on the ALD conditions (i.e., bubbler and reactor temperatures, pressure, gas flow, etc.) and likely applications of the final film. It is practically impossible to carry out a huge number of ALD experiments using numerous precursors and deposition conditions in order to find the optimum one depending on the applications of interest. In addition, only existing precursors can be tested experimentally. This study focuses on developing a computational tool for the design of novel precursor materials with enhanced properties for the ALD of metal oxides and metals.

Computer-Aided Molecular Design (CAMD) is a methodology where materials with optimal desired properties are generated from the combination of functional groups. This approach is the reverse of Group Contribution Method (GCM) in which the thermodynamic properties of a compound are estimated from the structural and functional groups comprising the molecule. For CAMD, we need the properties of the functional groups. In our previous work, we have redeveloped a new GCM for ALD effectively to predict the growth rate curve using Adsorbate Solid Solution Theory (ASST). In this work, novel precursor molecules for ALD are generated using properties of the functional groups. In order to do that, we will be using a combinatorial optimization method called Efficient Ant Colony Optimization (EACO). This is the first time CAMD is being applied to

design precursor materials for ALD. In the future, novel designed precursors will be synthesized and their properties will be tested experimentally using a Kurt J. Lesker ALD150LE™ system. Characterization of the deposited films with designed precursors will validate the proposed simulation technique and help us to optimize materials in the best possible way.

11:40am **TF-FrM11 The Use of Molecular Oxygen for a Low Cost and Low Temperature ALD of Amorphous Titania**, ***Harshdeep S. Bhatia***, *C.G. Takoudis,* University of Illinois at Chicago

The interest in Titania films has been increasing in the past few decades. This interest can be attributed to the various applications of ultrathin films of Titanium dioxide. The thin film deposition of amorphous titania can be done at a low temperature using tetrakis(dimethylamido) titanium (TDMAT) along with ozone and oxygen; growth rates have only been reported at temperatures greater than 150 °C. For titania use with organic substrates, it is important that the reaction is performed at low temperatures to prevent denaturation and degradation. The use of Ozone has also been reported to cause degradation in some elastomeric polymers. Along with the high cost of manufacturing a high concentration of ozone, Oxygen could be considered as a replacement for Ozone. In this study, growth temperatures at or below 150 °C were used to uniformly deposit amorphous titania using TDMAT and oxygen using a highly sophisticated pulse gas source (c/o Kurt J Lesker Co.) ensuring a constant pressure of gas is pulsed into the reactor which is believed to be the contributing factor in the success of this reaction. The as-deposited films were characterized using Spectroscopic Ellipsometry (SE) and X-ray Photoelectron Spectroscopy (XPS). Applications of this reaction could lead to low temperature deposition of titanium oxide on organic substrates for the use in biomedical implants, as a protective coating, and as a seed layer to deposit other conductive metals on organic substrates. One of the interesting phenomena observed using SE was the appearance of a very small but non-zero extinction coefficient in the visible range. This extinction coefficient was similar to the urbach tail absorption usually observed in the UV range. This could also point towards slight absorption of visible light by the deposited Titania films which opens new avenues for research in photocatalytic activity of Titania films within the visible light spectrum.

12:00pm **TF-FrM12 Ultra-High Purity Process Capability for High-Performance Atomic layer Deposition**, ***Noel O'Toole***, *G.B. Rayner, Jr.,* Kurt J. Lesker Company; *N.A. Strnad,* General Technical Services, LLC; *D.M. Potrepka,* U.S. Army Research Laboratory

Ultra-high purity (UHP) process capability is motivated by the need to produce superior, high-quality thin films and interfaces by atomic layer deposition (ALD) techniques. In particular, UHP equipment design reduces background impurity levels, including oxygen, to limit incorporation during film growth. Creating and maintaining a UHP process environment are also essential for ALD process reproducibility. This presentation will address the potential sources of background contamination, as well as system design requirements to obtain a controlled UHP process environment. Results will be presented that demonstrate the effectiveness of this technology to obtain high-quality titanium nitride thin films by plasma-enhanced ALD (PEALD) techniques.

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