Thursday Morning, November 3, 2011

Thin Film Division
Room: 110 - Session TF2-ThM

Modeling and Analysis of Thin Films

Moderator: P.D. Rack, University of Tennessee Knoxville

8:00am **TF2-ThM1 Aluminum Molecular Model for DSMC Simulations of Thin Film Deposition**, *A. Venkattraman*, ***A. Alexeenko***, Purdue University

The direct simulation Monte Carlo (DSMC) technique has been shown to be able to predict various properties of thin films grown using vacuum deposition methods such as CVD, PVD, EBPVD. Such simulations can also provide information about the energy distribution and orientation of vapor molecules striking the substrate which are critical inputs to the prediction of the grain size, residual stress and other properties of the deposited films. One of the most important inputs to a DSMC simulation is the molecular model that determines the interaction between the simulated particles. The variable hard sphere (VHS) model that is widely used due to its combination of simplicity and accuracy is typically determined by fitting to viscosity data obtained from experiments. In the absence of direct measurements of transport coefficients for metal vapors such as Aluminum, one needs to resort to other techniques to determine a set of accurate molecular model parameters. In this work, we compare DSMC simulations with Aluminum thin film deposition experiments to determine the VHS model parameters. The growth rate of the thin films at the substrate location depends strongly on the transport properties of the metal vapor – viscosity being one of the most important – and hence can be compared with the DSMC simulations to determine a suitable molecular model. In a similar analysis for copper published earlier, we used experimental data available in literature while the experiments for this study are performed in the electron-beam evaporator in the Birck Nanotechnology Center at Purdue University.

8:20am **TF2-ThM2 ISSG Chemistry Modeling to Understand Uniformity Issues in RTP**, ***S. Gupta***, *U. Kelkar*, Applied Materials, Inc.

This paper describes three-dimensional flow/thermal/chemistry modeling efforts to study the silicon oxidation using In-Situ Steam Generation (ISSG). This 3D model incorporates 27 step gas phase reaction mechanism which is responsible for ISSG chemistry. The complex 3D geometry, supersonic flow, detailed chemistry pose major challenges to the model convergence and results in unrealistic results due to H2 and O2 exothermic reaction. Complex 3D geometry causes CFD model mesh size to become more than a million cells. The computational times to include all chemical reactions on a 3D complex flow problem are exorbitant. Thus a simple 2D RTP chamber model was built to examine the validity of gas phase reaction mechanism by comparing in-house simulation results with Professor Robert J. Kee, Colorado School of Mines [1] and to set the solver control parameters for stable solution in 3D. After a working 2D model, simple representative 3D model was built with very good quality structured mesh and the further geometric complexity was added in steps. The oxygen radical distribution predicted from the model matched very well with the oxide growth uniformity over a wide range of chamber pressure, gas flow rate, hydrogen fraction, and gas distributor geometry. At 5 torr, temperature distribution is dominated by wafer temperature as gas phase reaction is weak. At higher pressure exothermic gas phase reaction causes higher temperature above the wafer. There is weak gas phase reaction at 5 torr, resulting in low O atom number density. The O radicals diffuse in the chamber due to higher velocity at 5 torr where they recombine. At higher pressure flame ignites right at the edge of the wafer due to higher residence time resulting in very high O atom number density at the edge. This well calibrated simulation model was used in understanding and expanding process space by optimizing on several hardware and process variables using virtual prototyping before building the hardware.

8:40am **TF2-ThM3 Composition and Finite Size Effects in Thin Magnetic Films for Data Storage Applications: Magnetic and Transport Properties**, ***O.N. Mryasov***, University of Alabama **INVITED**

Scaling of magneto-resistance (MR) and resistance area product (RA) with thickness is one of a critical materials specific properties of hard disk drive sensors. We consider fundamental aspects of MR-RA scaling with two planar FM/NM/FM hetero-structures: (i) Fe/MgO/Fe tunneling junctions and (ii) all Heusler alloy giant-magneto-resistance (GMR) spin valves [1-3]. In both cases we focus on the electronic structure contributions to RA(MR). Third example motivated by rapidly decreasing grain size of data storage media where material specific finite size effects originate from magnetic interactions of 3d-5d(4d) elements [4,5]. First, we show that calculated within the QSGW theory [6] decay constant controlling thickness dependence of RA are consistent with experiment [7]. We also present results of direct spin dependent electronic transport simulations for two types of GMR structures (i) non-magnetic Heusler alloy spacers [1,2] and (ii) Ag spacer [3]. The (110) textured Co_2MnGe (CMG) and Rh_2CuSn (RCS) [1] have been used to build test hard disk drive reader and yielded MR of about 7 % and DRA of about 4.0 mW-mm^2 [2]. The (001) textured FM $Co_2Fe(Ge-Ga)$ with Ag spacer yielded MR values in excess of 45 % and DRA of 9.5 mW-mm^2 [3]. Ab-initio electronic structure methods used to account for composition effects are shown to reproduce experimentally observed trends [1-3]. Finally we investigate finite size effects in the recording media granular films using model of magnetic interactions proposed to explain temperature dependence of magnetic anisotropy energy (MAE) observed in highly order $L1_0$ FePt thin films [4]. We discuss measurements protocol to quantify single vs. two ion contributions to MAE responsible for particular contributions to finite size effects in of 3d-5d(4d) thin films.

References:

[1]. T. Ambrose and O. Mryasov, US Patent 6, 876, 522 (April 5. 2005) .

[2]. K. Nikolaev, P. Kolbo, T. Pokhil, X. Peng, Y. Chen, T. Ambrose and O. Mryasov, APL., v.94, p. 222501 (2009).

[3]. Y. K. Takahashi, A. Srinivasan, B. Varaprasad, A. Rajanikanth, N. Hase, T.M. Nakatani, S. Kasaki, T. Furubayashi and K. Hono, Appl. Phys. Lett. **98**, 152501 (2011).

[4]. O. N. Mryasov , U. Nowak, K. Guslienko, R.W. Chantrell , EuroPhysics Letters, v. **69**(5), 805 (2005).

[5]. U. Nowak, O. N. Mryasov, R. Weiser, K. Guslienko, R.W. Chantrell , Phys. Rev. B, v. 72 p.172410, (2005).

[6]. S. Faleev, O. Mryasov and T. Mattsson, Phys. Rev. B., v.81, p. 205436 (2010) and references therein

[7]. S. Yuasa and D.D. Djayaprawira, J. Phys.D: Appl. Phys. v40, R337 (2007).

9:20am **TF2-ThM5 Large Scale TiN Thin Films Growth Simulations via Improved Modified Embedded Atom Parameterization**, *D.G. Sangiovanni*, ***V. Chirita***, *L. Hultman*, Linkoping University, Sweden, *I. Petrov, J.E. Greene*, University of Illinois at Urbana Champaign

Significant advancements within the last decade in the Modified Embedded Atom Method (MEAM) formalism, present the opportunity to perform, previously not possible, realistic large scale simulations of important model material systems such as TiN. The currently limited number of TiN MEAM parameterizations yield reasonable description of general bulk/surface properties of the material. However, to perform Molecular Dynamics (MD) simulations of TiN thin films growth, a number of critical nucleation and diffusion phenomena have to accurately be accounted for in addition to basic properties. Herein, an improved TiN MEAM parameterization is reported, which not only correctly predicts bulk/surface properties, but also reproduces the experimentally observed trends in the diffusion of single species (Ti, N), Ti-N dimers and other complexes, on most representative, (100) and (111), steps/surfaces for TiN growth. The calculated activation energies for diffusion, and the all-important Ehrlich-Schwoebel (ES) step-edge barriers, are in good agreement with ab-initio calculations and experimental observations. To demonstrate the potential of this MEAM parameterization for simulations of TiN thin films growth, illustrative case simulation studies are presented, which successfully reproduce experimentally documented crucial processes in the initial stages of TiN nucleation, known to dramatically affect growth modes, and ultimately, properties of thin films. The implications of these results, and perspectives for large scale simulations of this extremely important material model system, are discussed.

9:40am **TF2-ThM6 Hard, yet Tough, Transition Metal Nitride Thin Films by Alloying and Valence Electron Concentration Tuning**, ***D.G. Sangiovanni***, *V. Chirita, L. Hultman*, Linkoping University, Sweden

Improved toughness in hard and superhard thin films is a primary requirement for present day ceramic hard coatings, known to be prone to brittle failure during ***in-use*** conditions, in modern applications. Based on the successful approach and results obtained for TiN- and VN-based ternary thin films [1,2], we expand our Density Functional Theory (DFT) investigations to TiAlN-based quarternary thin films. (TiAl)1-xMxN thin films in the B1 structure, with $0.06 \leq x \leq 0.75$, are obtained by alloying with M = V, Nb, Ta, Mo and W, and results show significant ductility enhancements, hence increased toughness, in these compounds. Importantly, these thin films are also predicted to be hard/superhard, with similar and/or increased hardness values, compared to TiAlN. For (TiAl)1-

xWxN these results have experimentally been confirmed recently [3]. As previously demonstrated [1], the ductility increase originates in the enhanced occupancy of d-t2g metallic states, induced by the valence electrons of substitutional elements (V, Nb, Ta, Mo, W). This effect is more pronounced with increasing valence electron concentration (VEC), and, upon shearing, leads to the formation of a layered electronic structure, consisting of alternating layers of high and low charge density in the metallic sublattice. This, in turn, allows a selective response to tetragonal and trigonal deformation: if compressive/tensile stresses are applied, the structure responds in a "hard" manner by resisting deformation, while upon the application of shear stresses, the layered electronic arrangement is formed, bonding is changed accordingly, and the structure responds in a "ductile/tough" manner as dislocation glide along the {110}<1-10> slip system becomes energetically favored [2].

[1] D. G. Sangiovanni et. al. Phys. Rev. B 81 (2010) 104107.

[2] D. G. Sangiovanni et. al. Acta Mater. 59 (2011) 2121.

[3] T. Reeswinkel et. al. Surf. Coat. Technol. (2011) in press.

10:40am **TF2-ThM9 Using Crystallographic Space Group-Subgroup Relations to Analyze Phase Selection and Transition in HfO_2 and Hf-based Ternary Oxide Films**, ***C.R. Aita***, University of Wisconsin-Milwaukee

HfO_2 and Hf-based ternary oxides are important candidates for ultrathin high permittivity dielectric applications. However, technological aspects of their use in actual devices far outstrips our knowledge of the fundamental science that governs phase selection and transition in these materials. The latter is important for predicting both initial device performance and long term stability. One big issue is that pure HfO_2 readily forms nanocrystallites in thin films. These crystallites exhibit finite size effects on two different length scales: (1) *Two* metastable phases initially form in crystallites < ~ 7nm in size [1] and transform to monoclinic (m) HfO_2, the standard state, as crystallites grow. (2) Upon transformation from the metastables, m-HfO_2 nanocrystallites whose size is <~ 11 nm exhibit a lattice expansion concurrent with surface dipole repulsion [2]. A second issue involves the stability of Hf-based ternaries that are either intentionally grown or inadvertently form as a result of cation mixing during thermal processing or heating upon device use. These questions are being addressed from an experimental viewpoint through controlled isochronal and isothermal annealing studies. In this paper, we use crystallographic space group-subgroup analysis to examine phase selection and transition in three sputter deposited nanolaminates, HfO_2-Al_2O_3, HfO_2-TiO_2, and HfO_2-ZrO_2. The goal is demonstrate how this tool connects phase transitions between seemingly unrelated structures by symmetry considerations. We show that several important transitions observed in these materials are 2nd order and can be described by a simple relation between a parent group of higher symmetry and a daughter group of lower symmetry. Using the suite of programs in the Bilbao Crystallographic Server [3], first, conjugacy classes associated with the parent → daughter transition are identified, and then using the operations within each class, the general atom positions of the parent are decomposed into cosets of symmetry elements expressed the daughter's basis. Symmetry elements that are "lost" in the decomposition are used to identify a twin domain structure in the daughter resulting from the transition. Using these formalisms, we discuss metastable phase→m-HfO_2 transition in pure HfO_2, the robustness of an entropy-stabilized HfAl-oxide phase, and the initiation $HfTiO_4$demixing.

Support from UWM Foundation Catalyst Grant / Rockwell Automation Charitable Trust.

[1] E.E. Hoppe et al. APL 91, 203105 (2007); APL 92, 109903 (2008).

[2] M.C. Cisneros-Morales et al., APL 96, 191904 (2010).

[3] M.I. Aroyo et al., Z. Kristallogr. 221, 15 (2006); M. Nespolo, Acta Crystall. A64, 96 (2008).

11:00am **TF2-ThM10 Experimental and Theoretical Investigations Using SiO_2 Nanotemplates to Relieve Stress Caused by Thermal Expansion Coefficient Mismatch in Epitaxial Germanium Grown on Silicon**, ***S. Ghosh**, D. Leonhardt, S.M. Han*, University of New Mexico

High-quality Ge-on-Si (GoS) heterostructures are pursued for many applications, including near-infrared photodetectors, high-mobility devices with Si-based integrated circuits, and virtual substrates for III-V multijunction solar cells. Growing low-dislocation-density GoS and subsequently integrating III-V layers present two significant engineering challenges: lattice mismatch and thermal expansion coefficient mismatch. The materials engineering solutions to circumvent the lattice mismatch include metamorphic growth, graded buffer layers, selective epitaxial overgrowth, aspect ratio trapping (ART), and a variety of defect filtering strategies. The ART technique, in particular, utilizes high-aspect-ratio holes or trenches etched through dielectric films to trap dislocations, greatly reducing the dislocation density. However, one shortcoming of ART is that it has been demonstrated to be effective only for small holes or narrow strips with dimensions less than 1 μm. In this study, we demonstrate that a combination of ART with selective epitaxial growth can produce large areas of high-quality GoS. We focus on the use of SiO_2-based templates with nanoscale windows placed on GoS to relieve the thermal stress. We observe that voids form around the top and sidewalls of SiO_2 template deposited by chemical vapor deposition, further relieving the thermal stress. The same templates also filter threading dislocations propagating from the underlying Ge-Si interface. The Ge layer grown and coalesced over the template is analyzed by transmission electron microscopy and etch pit density measurements. When the template is used, the threading dislocation density near the Ge film surface is approximately $<10^7$ cm^{-2}, while the twin defect density is approximately $<5x10^7$ cm^{-2}. Finite element modeling based on a commercial software package COMSOL is used to calculate the thermal stress occurring in the epitaxial Ge due to differences in thermal expansion coefficients among Ge, Si, and SiO_2. The simulation results, comparing Ge grown on Si with and without SiO_2 templates, show that the nanoscale templates can effectively reduce the thermal stress. The resulting stress results obtained using the simulation model corroborate the experimental observations. In summary, the simulation results suggest that the SiO_2 nanotemplates can reduce the stress caused by the thermal expansion coefficient mismatch, while simultaneously reducing the lattice-mismatch-induced dislocations in Ge grown on Si.

11:20am **TF2-ThM11 Controlling Heteroepitaxy through Surfactant-Enabled Growth: An *Ab Initio* Thermodynamics Study**, *B.E. Gaddy, E.A. Paisley, M.D. Losego, J.S. Tweedie*, North Carolina State University, *R. Collazo*, North Carolina State Univeristy, *Z. Sitar*, ***D.L. Irving***, *J.-P. Maria*, North Carolina State University

We demonstrate that surfactant-assisted epitaxy is a useful method for stabilizing the growth of {111} CaO films on (0001) GaN. Surface free energies, calculated by ab initio thermodynamics, for configurations of CaO surfaces with varying surfactant coverage will be presented. These results explain the recent experimental observation that incorporating water vapor during CaO deposition produces a hydroxylated surface. Hydroxylation changes the preferred habit of CaO from (001) to (111), which enables layer-by-layer growth of (111) CaO on (0001) GaN. Together with experiment, these results demonstrate a new approach, applicable to numerous materials systems, where chemical boundary conditions are engineered to regulate the growth mode. Unique opportunities to integrate highly heterogeneous materials of dissimilar structure and symmetry are consequently available.

11:40am **TF2-ThM12 Deposition and Modeling of Nanoscale Organic Porous Polymeric Layers and their Characterization with Visual and Electrical Methods**, *G. Franz*, ***F. Schamberger***, Munich University of Applied Sciences, Germany

To act as long-term antibacterial coating on the interior of hollow implants like artificial bladders or flexible pipes which can act as urethrae, silver layers have to be partly protected against aggressive solutions of the human body, e.g. urine or gall. One of these organic polymers is poly-p-xylylene, commonly known as polyparylene. In order to control this process of dissolution from metallic silver to silver ions which is responsible for the toxic impact, the layers should exhibit an adjustable hole density. This requires the growth control of very thin layers between zero and about 250 nm. By application of the conventional Gorham method, only thicknesses beyond 2 microns are accessible. We present a completely new method to control the growth of these very thin layers with defined porousity for which exact knowledge of vapor pressure and evaporation rate is required which have been measured and modeled using statistical rate theory (SRT) [1]. Applying a digital evaluation procedure of the micrographs gained with AFM, the hole density is correlated with the breakdown voltage and the capacitance which can both easily applied to the samples. Whereas the coating of open surfaces is controlled by flow, this mechanism is not applicable for coating of narrow holes which takes place as a diffusive process with losses due to deposition. In a series of experiments, the growth behavior in thin, narrow pipes with an aspect ratio between 10 and 30 has been obtained, and a theoretical model is presented which reflects the crossover of these two transport mechanisms as function of chamber pressure and temperature. [1] C.A. Ward, and G. Fang, Phys. Rev. E59, 429 (1999)

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