Tuesday Afternoon, November 10, 2009

Thin Film
Room: B3 - Session TF1-TuA

Computational Modeling and Analysis of Thin Films

Moderator: M. Creatore, Eindhoven University of Technology, The Netherlands

2:00pm **TF1-TuA1 First Principles Modeling of Hydrogen Diffusion in Thin Films: Crystalline Alloys, Amorphous Alloys, and Metal Hydrides**, ***D. Sholl***, *S. Hao, L. Semidey-Flecha, C. Ling, S.-G. Kang*, Georgia Institute of Technology **INVITED**

The diffusion of hydrogen through thin films is important in a variety of technological applications, including development of membranes for hydrogen purification and control of hydrogen uptake in solid state storage materials. First principles calculations can play an important complementary role to experimental studies of these phenomena. Examples will be discussed of using first principles approaches in combination with cluster expansions and kinetic Monte Carlo to predict hydrogen permeation rates through crystalline and amorphous metal alloys used as membranes. In these materials, hydrogen exists as an uncharged interstitial atom. We will also discuss the diffusion mechanisms of hydrogen in ionic metal hydrides such as magnesiusm hydride and simple borohydrides. Understanding the diffusion mechanisms that exist in these materials has created opportunities for enhancing hydrogen transport rates in this important class of materials.

3:00pm **TF1-TuA4 A Family of High Strength Ternary Titanium and Vanadium Nitride Thin Films**, *D.G. Sangiovanni*, ***V. Chirita***, *L. Hultman*, Linkoping University, Sweden

We use Density Functional Theory (DFT) calculations in the generalized gradient approximation (GGA) to predict the properties of a number of novel Ti-M-N and V-M-N thin films in the B1 (NaCl) structure. The new compounds are obtained by alloying TiN and VN, with Ta, Nb, V, Mo and W, respectively Nb and W, in concentrations of 50 %. We evaluate the elastic moduli and constants for all these ternaries, perform a detailed analysis of their electronic structure, and compare these results with the corresponding properties of TiN and $Ti_{0.5}Al_{0.5}N$. Our calculations show that, in terms of hardness, these ternaries compare with TiN and $Ti_{0.5}Al_{0.5}N$, as we obtain comparable, respectively increased values, for the Young and bulk moduli, in most cases. Significantly, however, these novel compounds exhibit substantially lower values of the C_{44} elastic constant and positive Cauchy pressures, i.e. they are considerably more ductile than TiN and $Ti_{0.5}Al_{0.5}N$. This unique combination of increased hardness and ductility, which is in contrast to the hardness/brittleness relationship typically found in hard coatings, is certainly relevant for applications in which high strength thin films/coatings are desired. In terms of electronic structure, our results reveal a layered charge density for all these ternaries, consisting in alternating high and low electron density regions, similar to that reported for MAX phase materials and other nanolaminates. This combination of metallic and ceramic properties is also evident in the density of states analysis we report. In order to fully understand the mechanism responsible for this interleaved arrangement of electrons, we carry out an improved crystal orbital overlap population (COOP) calculation and succeed in resolving energetically the bonding and antibonding contributions, of the first and second neighbors, to the chemical bonds in these compounds. Herein, we present the results of our COOP analysis, and based on this, we explain the observed trend in hardness and ductility as a result of the interaction between the e_g and t_{2g} sets of *d* orbitals characteristic to these ternaries.

4:00pm **TF1-TuA7 Study on the Influence of Ballistic and Diffusive Deposition Particles on the Evolution of the Surface Morphology of Thin Films**, ***R. Alvarez***, *P. Romero-Gomez, J. Gil-Rostra, A. Palmero, J. Cotrino, F. Yubero, A.R. Gonzalez-Elipe*, CSIC - University of Sevilla, Spain

The influence of ballistic and diffusive particles on the development of the surface morphology of plasma-assisted sputtered thin films is studied. Ballistic particles are sputtered from the cathode and are characterized by their high directionality towards the film surface as well as by typical kinetic energies in the order of 1 eV, whereas thermal diffusive particles follow the Maxwell velocity distribution function, with typical kinetic energies in the order of 0.01 eV. These factors influence the role of non-local surface shadowing and the surface sticking probability of the deposition particles, which, along with other fundamental mechanisms, strongly condition the development of the film morphology. In order to carry out this research, a combined theoretical and experimental approach has been followed: on one hand several thin films have been deposited in different experimental conditions which allow differentiating ballistic and diffusive contributions to the film growth, and, on the other hand, we have developed a basic Monte Carlo model of the depositions process. The comparison between experimental and theoretical results provides fundamental understanding about the influence of ballistic and diffusive particles on the development of the thin film nanostructure.

4:20pm **TF1-TuA8 DSMC Modeling of E-beam Metal Deposition**, *V. Ayyaswamy*, ***A. Alexeenko***, Purdue University

Electron-beam assisted physical vapor deposition (EBPVD) is now used in a wide variety of vacuum material processing applications for generation of thin films of metals and metallic compounds. The thickness uniformity, growth rates, grain size, stoichiometry and other material properties of EBPVD thin films are highly dependent on the specifics of the system such as, for example, the geometric configuration and energy density of electron gun. A general capability to model the metal vapor flows encountered in EBPVD processes can greatly assist in the design and control of such deposition systems and processes. The main goal of this paper is to apply the direct simulation Monte Carlo (DSMC) method for modeling of a typical strip EBPVD system.

Under the conditions of high energy electron-beam deposition in ultra-high vacuum, the flow of metal vapor in EBPVD systems varies from high-density collisional flow in the proximity of the source to free-molecular flow at the deposition site. The application of the DSMC method for such flows requires a model for metal atom and cluster collisions. In this work, a model for copper-copper collisions is formulated and validated by comparison with experimentally measured deposition data reported by Sahu and Thakur (2006). The proposed molecular model can be used in DSMC simulations for the prediction of growth rates in thin film depositions of copper thereby leading to a more efficient designs of such deposition systems.

4:40pm **TF1-TuA9 Electrochemical Capacitance in Cerium Oxide Thin Films and Its Relations to Anionic & Electronic Defects**, ***W. Chueh***, *S. Haile*, California Institute of Technology

The electronic properties of thin film oxides are relevant in a broad range of phenomena and devices. In many instances, these properties are strongly influenced by the extent of deviation of the material stoichiometry away from that of the perfect crystal. Specifically, nonstoichiometry in oxides due to the formation of point defects can substantially impact electrical, electrochemical, and optical properties of thin films. However, the small sample mass and the constraints of a substrate hinder precise measurements, particularly with respect to the determination of oxygen nonstoichiometry, and, effectively, electronic carrier concentration. Even a relatively straightforward Hall effect measurement is precluded in the case of low mobility materials (typical of solid electrolytes). Thus, a reliable and highly accurate method for determining nonstoichiometry and carrier concentration in thin film oxides may be useful for a number of fields.

In this work, we show that it is possible to accurately determine oxygen nonstoichiometry and electronic carrier concentration in epitaxial nonstoichiometric samarium doped ceria thin films from an analysis of the capacitance measured by electrochemical impedance in a cross-plane configuration. For sufficiently thick bulk samples, it has been shown that a "chemical capacitance" arises from the change in the oxygen nonstochiometry in response to the change in the oxygen chemical potential, analogous to the change in the polarization of a dielectric in response to the change in electric potential in an electrostatic capacitor. We extend this method to thin films and show that both interfacial and chemical capacitances contribute strongly to the observed capacitance and successfully decouple the two. The thin film oxygen nonstoichiometry and electronic defect concentration determined using chemical capacitance corresponds closely to bulk values in literature.

5:00pm **TF1-TuA10 Virtual Sputter Chamber - Multiphysics Simulation of Magnetron Sputter & Deposition**, ***C. Walton***, *G. Gilmer, M. McNenly*, Lawrence Livermore National Laboratory, *J. Verboncoeur*, University of California, *S. Wilks, L. Zepeda-Ruiz, T.W. Barbee*, Lawrence Livermore National Laboratory

Lack of detailed process conditions knowledge remains a key challenge in magnetron sputtering, both for chamber design and for process development. Fundamental information such as the pressure and temperature distribution of the sputter gas, and the energies and arrival angles of the sputtered atoms and other energetic species is often missing, or is only estimated from general formulas. However, open-source or low-cost tools are available for modeling all the physics of the sputter process,

which can give more accurate data from desktop computations than traditional empirical approaches.

To get a better understanding of magnetron sputtering, we have collected existing models for the 4 main physics steps: 1) dynamics of the plasma using Particle In Cell-Monte Carlo Collision (PIC-MCC), 2) impact of ions on the target using molecular dynamics (MD), 3) transport of sputtered atoms to the substrate using Direct Simulation Monte Carlo (DSMC), and 4) growth of the film using hybrid Kinetic Monte Carlo (KMC) and MD methods. All the models have been tested against experimental measurements. The spatial distribution and electron temperature T_e of the plasma have been reproduced within ~25% for a scaled model of an example magnetron system. The rarefaction of the neutral gas in front of a magnetron observed by Rossnagel and others has been reproduced, and it is associated with a local pressure increase of ~50% which may strongly influence film properties such as stress and film density. Results on energies and arrival angles of sputtered atoms and reflected gas neutrals are applied to the Kinetic Monte Carlo simulation of film growth. Model results and applications to growth of Cu, Zr and Be films will be presented. Work underway on increasing computation speed with parallelization will also be discussed.

5:20pm **TF1-TuA11 Tuning Knobs for the Morphology and Dewetting of a Bimodal Molecular System**, ***J. Topple***, McGill University, Canada, *S. Burke*, UC Berkeley, *S. Fostner*, *P. Grutter*, McGill University, Canada

The interesting optical and electronic properties of certain organic molecules have led to their use in a range of organic electronic and optoelectronic applications. The morphology of thin films critically determines application relevant properties, and can be controlled during growth to some degree by experimental parameters. However, post-growth dynamics may change the film structure and resulting properties. We explore methods of tuning film morphology and the rate of dewetting through coverage, surface templating and temperature control. Non-contact atomic force microscopy (NC-AFM) is a non-destructive, high resolution scanning probe technique that can be applied to non-conductive surfaces. Perylene derivatives have been studied as prototypal organic semiconductors for use in electronic applications. Deposition of sub-monolayer coverages of 3,4,9,10-perylenetetracarboxylic diimide onto NaCl (001) at room temperature results in the bimodal growth of coexisting square and needle shaped islands. The epitaxy of each island type was determined from molecular and atomic resolution NC-AFM images. Post-deposition, the stable needle islands grow while the metastable square islands disappear completely within days. This is characterized as a dewetting transition, the dynamics of which have been described and empirically fit to the monomolecular growth model. The resultant island distribution, size, and rate of dewetting may be tuned by templating the NaCl substrate with single atomic layer deep pits, depositing gold nanoclusters, or a combination of the two to modify island nucleation. The diffusion lengths may be altered by varying the substrate temperature. This characterization is an important step in controlling the structure of thin organic films for nanoscale devices which are sensitive to the nanoscale film structure.

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