

# Tuesday Afternoon, October 30, 2012

## Thin Film

Room: 10 - Session TF+AS-TuA

## Modeling and Analysis of Thin Films

Moderator: D. Irving, North Carolina State University

2:00pm **TF+AS-TuA1 Nanoconfined Fluids: Fundamentals and Application to Ionic-Liquid-Based Supercapacitors**, G. Feng, S. Li, P.T. Cummings, Vanderbilt University **INVITED**

Phase transitions in nanoconfined fluids have been contentious for two decades. In the 1980s and early 1990s a large number of surface force apparatus (SFA) experiments on a variety of ultrathin nonpolar liquid films (e.g., such as dodecane, cyclohexane and octamethylcyclotetrasiloxane (OMCTS)), reached a common conclusion: When their confinement between molecularly smooth mica sheets reached the order of several molecular diameters (approximately 3 or less, depending on the fluid being studied) they exhibited behavior typical of the stick-slip response of a crystalline solid structure.

In contrast to the solid-like behavior under extreme nanoconfinement, when the mica surface separation is sufficiently large, the confined fluid exhibits bulk-like liquid behavior. Thus, a phase transition as a function of separation must exist. In this talk, we review the two-decade-old debate on the nature of this phase transition (first order vs continuous), and its effective resolution using very high fidelity molecular dynamics simulations. In particular, the origin of the phase transition from fluid to solid-like behavior is, unexpectedly, driven by electrostatic interactions between ions in mica and partial charges on the atoms in the nonpolar organic molecules.

More recently, our interest in nanoconfined fluids has focused on novel energy storage devices: electrical double layer (EDL) capacitors, also called supercapacitors. Supercapacitors have attracted considerable attention, owing to their desirable properties, such as high power density, high capacitance, and excellent durability. As emerging electrolytes for these supercapacitors, room-temperature ionic liquids (RTILs) have attracted considerable attention due to their wide electrochemical windows, excellent thermal stability, non-volatility, relatively inert nature, and high ionic conductivity. With high specific surface area and electrical conductivity, nanoporous carbon-based materials are the most widely used electrodes for supercapacitors, including activated carbons, templated and carbide-derived carbons (CDC). Using molecular simulations, model porous carbon electrodes (e.g., CDC), supercapacitors composed of slit-shaped micropores ranging in size from 0.67 nm to 1.8 nm in an IL were studied to investigate the dependence of capacitance on pore size. The capacitance was found to show an oscillatory behavior with pore size. In good agreement with experiment, we find that, as the pore shrinks from 1.0 nm to 0.7 nm, the capacitance of the micropore increases anomalously. The persistence of oscillations in capacitance beyond 1.0 nm is a new theoretical prediction currently being probed experimentally.

2:40pm **TF+AS-TuA3 XPS Analysis of Monomolecular Films Prepared by Self-Assembly and Langmuir-Blodgett Techniques**, G.G. Jernigan, F.K. Perkins, M.G. Ancona, A.W. Snow, Naval Research Laboratory

Characterization of self-assembled monolayers (SAMs) using x-ray photoelectron spectroscopy (XPS) measurements of the gold (4f) attenuation from increasing molecular length alkane thiols were pioneered by Bain and Whitesides[1]. Since then, the gold attenuation has been used by many others as a method for determining the length/thickness of molecular films formed as SAMs on gold. We have done similarly with carboxylic acid (COOH) terminated alkane thiols SAMs deposited on gold with the aid of additives[2], and we obtained similar results. We discovered, however, that the attenuation of the sulfur (2p) signal did not correspond with the gold attenuation. Additionally, neither the gold or sulfur attenuation could correctly account for the observed carbon (1s) signal in the XPS measurements. This fact was originally noted, but not addressed, by Bain and Whitesides.

In conjunction with experiments, we will present our successful solution to the modeling of XPS measurements of molecular films prepared by self-assembly and by the Langmuir-Blodgett (LB) technique. In a classic alkanethiol SAM, one third of the surface gold atoms, typically, are bound to a thiol-terminated molecule, due to the steric effect of a radial shell created by the molecule. Thus, the gold signal is only partially attenuated by the molecule. Use of the attenuation of the sulfur signal associated with the

S-Au bond (obtained by fitting the XPS signal), we find that we are able to correctly determine the electron escape depth ( $\lambda$ ) for sulfur and carbon through the molecular film. Using a poly(thiomethyl methacrylate) thin film as a carbon and sulfur XPS standard combined with the correct  $\lambda$ , we developed a model for the packing density and molecular orientation of COOH terminated alkane thiols that is consistent with gold, sulfur, and carbon XPS measurements as a function of molecule length. We have expanded our model to include SAMs formed of sterically crowded tertiary thiols, where fewer molecules per gold atom can attach to the surface, and to LB films formed from carboxylic acid terminated alkanes on gold surfaces, where no sulfur linkage is made. The consistent interpretation provided by our model will be presented at the talk.

[1] C.D. Bain and G.M. Whitesides, *J. Phys.Chem.* **93**, 1670 (1989).

[2] A.W. Snow, G.G. Jernigan, and M.G. Ancona, *Analyst* **136**, 4935 (2011).

3:00pm **TF+AS-TuA4 The Dynamics of Atomic-Scale Transport on the Anisotropic Compound Surface TiN(001)**, D.G. Sangiovanni, V. Chirita, L. Hultman, Linköping University, Sweden, I. Petrov, J.E. Greene, University of Illinois at Urbana Champaign

We use classical molecular dynamics (MD) and the modified embedded atom method (MEAM) formalism to investigate the dynamics of atomic-scale transport on a low index anisotropic model compound, TiN(001). Our simulations, totaling 0.25 ms for each case study, follow the pathways and migration kinetics of Ti and N adatoms, as well as TiN<sub>x</sub> complexes with x = 1, 2 and 3, all of which are known to contribute to the growth of TiN thin films by reactive deposition from Ti, N<sub>2</sub>, and N precursors. The simulations are carried out at 1000 K, a reasonable temperature for TiN(001) epitaxial growth. We find Ti adatoms to be the highest mobility species on TiN(001), with the primary migration path involving jumps of one nearest-neighbor distance d<sub>NN</sub> between four-fold hollow sites along in-plane <100> channels. Long jumps, 2d<sub>NN</sub>, are also observed, but at much lower frequency. N adatoms exhibit much lower migration rates than Ti, diffuse only along in-plane <110> directions, and are unstable to associative formation of N<sub>2</sub> molecules which desorb at kinetic rates. As expected, TiN and TiN<sub>3</sub> complexes migrate at even lower rates with complex diffusion pathways involving rotations, translations, and roto-translations. TiN<sub>2</sub> trimers, however, are shown to have surprisingly high diffusion rates, comparable to that of Ti adatoms, due to, as revealed in our density functional theory (DFT) investigations, the significantly more symmetric charge transfer between trimer and terrace atoms, as compared with the charge distributions observed for dimers and tetramers.

4:00pm **TF+AS-TuA7 Multi-Method Calculations of the Thermodynamics of Film Deposition on Fuel Rods in Light Water Reactors**, D.W. Brenner, A.D. Dongare, C.J. O'Brien, North Carolina State University **INVITED**

Corrosion products in light water reactors are driven to deposit on the fuel rods, which reduces their efficiency and lifetime. The thermodynamics and kinetics that lead to this deposition are notoriously difficult to characterize *in situ* experimentally due to the extreme conditions of temperature and radiation within the reactor, and the relationship of deposits studied *ex situ* to processes under reactor conditions is unclear. It is thought that deposition is related to bubbles that form at the surface of the fuel rods due to sub-cooled boiling, but further details are lacking. We have been using first principles methods combined with molecular modeling to understand the thermodynamic driving force for this deposition, including how pH, pressure, temperature, and aqueous versus semi-aqueous "bubble" environments affects this driving force. The results of these calculations, which include studies of solvated ions, clusters and solid surfaces containing Ni, Fe, O, B, C and H will be presented along with ideas for suppressing deposition based on these results. The broader implications of our calculations for understanding and controlling film deposition in various types of aqueous environments will also be discussed.

This research is supported by the Department of Energy

4:40pm **TF+AS-TuA9 Toughness Enhancement in Transition Metal Nitride Thin Films by Alloying and Valence Electron Concentration Tuning**, D.G. Sangiovanni, V. Chirita, L. Hultman, Linköping University, Sweden

Enhanced 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 quaternary thin films. (TiAl)<sub>1-x</sub>M<sub>x</sub>N 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 [3]. Importantly, these thin films are also predicted to be hard/superhard, with hardness values comparable to TiAlN. For (TiAl)<sub>1-x</sub>W<sub>x</sub>N these results have been experimentally confirmed [4]. The general, electronic mechanism responsible for the ductility increase is rooted in the enhanced occupancy of d-t<sub>2g</sub> 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 unique electronic structure 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]. The findings presented herein open new avenues for the synthesis of hard, yet tough, ceramic coatings, by tuning the VEC of alloying elements to optimize the hardness/toughness ratio in relevant applications.

- [1] D. G. Sangiovanni et. al. Phys. Rev. B **81** (2010) 104107.
- [2] D. G. Sangiovanni et. al. Acta Mater. **59** (2011) 2121.
- [3] D.G Sangiovanni et. al. Thin Solid Films **520** (2012) 4080.
- [4] T. Reeswinkel et. al. Surf. Coat. Technol. **205** (2011) 4821.

5:00pm **TF+AS-TuA10 Non-Destructive Element Specific Density Depth Profiling by Resonant Soft X-ray Reflectometry**, *S. Macke*, Max Planck - UBC Centre for Quantum Materials, Canada, *A. Radi*, University of British Columbia, Canada, *R. Sutarto*, Canadian Light Source, Canada, *G. Christiani*, *G. Logvenov*, Max-Planck-Institute for Solid State Research, Germany, *G. Sawatzky*, University of British Columbia, Canada, *B. Keimer*, Max-Planck-Institute for Solid State Research, Germany, *V. Hinkov*, Max Planck - UBC Centre for Quantum Materials, Canada

X-ray resonant reflectometry (XRR) is the ideal tool to study the depth resolved and element-specific electronic structure of multilayer films. Besides the structural parameters of thin films like thicknesses and roughnesses one is sensitive to the dielectric tensor of the film which allows to retrieve depth profiles of the magnetic, orbital[1] and valence configuration.

Due to the complex physics of reflectometry this measurement method needs sophisticated tools to analyze the results quantitatively [2]. The issues arising with this method are addressed and discussed.

By changing angle, energy and polarization of the incoming beam complete reflectivity maps can be measured leading in principle to an accurate picture of the depth resolved electronic states of thin films. The standard model used in reflectometry is based on compound layers with a defined thickness, roughness and dielectric tensor. But such a simple model is usually not capable to reproduce a full measured reflectivity map. The main reasons are especially contaminations, additional oxide layers and interdiffusion between layers.

However, introducing a layer system based on the element specific atomic density and scattering factors instead of dielectrics tensors allows more degrees of freedom for the system and allows to reproduce the reflectivity maps. Thereby the advanced model is capable to retrieve the element specific density profiles of thin films.

The method is introduced by analyzing a simple film of PrNiO<sub>3</sub> grown on an LSAT substrate. The reflectivity map is measured from 500eV to 1100eV.

- [1] E. Benckiser et. al., Nature Materials **10**, 189 (2011)
- [2] ReMagX, [www.simulationcorner.net/ReMagX/](http://www.simulationcorner.net/ReMagX/)

5:20pm **TF+AS-TuA11 Monte Carlo Radiation Model for Heat Transfer of Lamp for Advanced Thermal Annealing Process**, *K. Bera*, *J. Ranish*, *U. Kelkar*, Applied Materials, Inc.

Advanced thermal annealing process of semiconductor wafer uses lamp heating, specially for rapid thermal oxidation, silicidation, ion-implant anneal and spike anneal. As the technology node shrinks and the wafer size increases, wafer temperature uniformity becomes significant. The thermal modeling challenge includes complexity of the lamp filament and chamber configuration, and complex optical properties of semitransparent media. In order to analyze lamp heating, two-dimensional Monte-Carlo based

radiation, and thermal conduction model for a single lamp is built using CFD-ACE+. The Tungsten lamp filament is immersed in Nitrogen. The single lamp is enclosed by a reflector, and protected at the top by a quartz plate. For the single lamp thermal model, effective surface area and volume of the coil are considered. The irradiance profile of the lamp at a distance of a few cm from the quartz plate compared well with the experimental data. The single lamp model is simplified using a cylindrical filament structure that matches the irradiance profile. The cylindrical filament structure is used in 3D chamber model that considers thermal convection in addition to radiation and conduction. In both single lamp and chamber models, for semi-transparent non-gray media, wavelength dependent real and imaginary parts of refractive indices are used in optical database to calculate thermal absorption. For gray material, surface emissivity of the material is defined. For reflective material, the degree of specularly on the surface is defined as well. For gas conduction, temperature dependent thermal properties are used. The single lamp power is varied by several hundreds of Watts. The irradiance profile shows a peak at the center that decays substantially as we move radially outwards. The effect of quartz plate thickness on irradiance profile is evaluated. The chamber model is used to determine wafer temperature distribution and transient thermal response for a range of lamp assembly power.

5:40pm **TF+AS-TuA12 First Principles Studies of Oxygen Transfer at Buried Metal/Metal Oxide Interfaces**, *C. Goldstein*, *E. Mily*, *J.-P. Maria*, *D.W. Brenner*, *D. Irving*, North Carolina State University

Heterogeneous material interfaces between metals and metal-oxides provide a unique opportunity to create active functional materials. The functionality of these heterostructures can hinge either on limiting or enabling oxygen transfer across the interface. For example, there has been recent research on how to use thin film metal/metal-oxide super-structures to control the power output generated by the exothermic exchange of oxygen across the as-deposited interface. In all of these heterogeneous systems, it is imperative to fundamentally understand the mechanisms that facilitate oxygen exchange, as the dynamics are not currently well understood. In the work presented here, chemically accurate Density Functional Theory calculations have been used to predictively determine likely reaction pathways for oxygen transport in energetic nanocomposite materials and to characterize the stability of novel heterogeneous material interfaces. Our ultimate goal is to tune power output through an understanding of the mechanisms of oxygen transport across heterogeneous interfaces and within the super-structure. Several systems have been investigated, including more traditional thermite materials such as Al and Ti paired with Cu<sub>2</sub>O. In these systems, the energy release is large, but there is also a high degree of strain when ideal systems are modeled. Other model systems were chosen based on structural similarity, minimal lattice mismatch, and the degree of exothermicity associated with oxygen transfer. Results on these systems will also be presented. Preliminary calculations simulate systems at various early stages to isolate factors that could influence the reaction, such as strain or initial barrier height. The results presented here show qualitative agreement between calculations and experimental observations. This project has been supported by the Army Research Office through grant # W911NF-10-1-0069 and the NSF Graduate Research Fellowship Grant # DGE0750733.

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