Thin Film
Room: Ruidoso - Session TF-ThM

Modeling and Analysis of Thin Films
Moderator: S.B. Sinnott, University of Florida

8:00am **TF-ThM1 Thermodynamics of Clustering and Magnetism in $Ti_{1-x}Al_xN$ and $Ti_{1-x}Cr_xN$ Thin Film Materials from First-Principles**, ***B. Alling***, *I.A. Abrikosov, L. Hultman*, Linköping University, Sweden

Multinary nitride materials are widely used as coatings for wear protection of cutting tools, e.g. TiAlN, as well as in thin film electronic applications. One important aspect of the success of TiAlN is a composition dependent thermodynamically driven age-hardening process through spinodal decomposition into TiN and cubic AlN at cutting tool operational temperatures. To understand this phenomena and to be able to tailor optimal compositions for different applications, we perform a thorough theoretical thermodynamics investigation based on first principles calculations.

By mapping the complete quantum mechanical complexity of the system onto a generalizes Ising Hamiltonian for the configuration of Ti and Al atoms, we are able both to predict thermodynamics using accurate Monte Carlo simulations and achieve a deeper understanding of the interactions governing the system.

One physical property that is difficult to find in nitrides and which disfavors the usage of the materials class in spintronics, is room temperature ferromagnetism. TiCrN is one of the rare nitride systems where strong ferromagnetism is seen. We use our methodological framework to analyze and explain why the magnetic interactions that favor anti-ferromagnetism in pure CrN is changed in the TiCrN solid solution, as well as the intricate dependence of the Curie temperature on the CrN content.

8:20am **TF-ThM2 Electronic Mechanism for Toughness Enhancement in $V_xM_{1-x}N$ Thin Films**, *D.G. Sangiovanni*, ***V. Chirita***, *L. Hultman*, Linköping University, Sweden

We use Density Functional Theory (DFT) calculations in the generalized gradient approximation (GGA) to predict the properties of a number of novel V-M-N thin films in the B1 (NaCl) structure. The new compounds are obtained by alloying VN with Nb, Mo and W, in concentrations of 50 %. We evaluate the elastic moduli and constants of these ternaries and perform a detailed analysis of their electronic structure. These results are compared with the corresponding properties of typical binaries such as TiN and VN. Our calculations show that the new ternaries have hardness comparable with TiN and VN, and significantly, a resolute ductile behavior. This unique combination of hardness/ductility, which is in contrast to the hardness/brittleness relationship typically found in hard coatings, equates to significantly increased toughness, as confirmed by the stress-strain relationship we obtain for all these compounds. The electronic structure results presented herein reveal a layered charge density, consisting in alternating high and low electron density regions, similar to that recently reported for Ti-Mo/W-N thin films [1]. To fully understand the mechanism responsible for this interleaved arrangement of electrons, we carry out crystal orbital overlap population (COOP) and electron localization function (ELF) calculations, and succeed to energetically resolve the bonding/antibonding contributions, of the first and second neighbors, to the chemical bonds in these compounds. Based on the results of this analysis, we find that the electronic mechanism responsible for the observed toughness enhancement in these compounds is rooted in the increased metal-metal (second neighbors) interaction of d-t_{2g} orbitals.

[1] D.G. Sangiovanni, V. Chirita and L. Hultman, Phys. Rev. B **81**, 104107 (2010)

8:40am **TF-ThM3 2010 Gaede-Langmuir Award Lecture- X-ray Absorption Spectroscopy and Many Electron Theory Applied to O-vacancy State Differences between (i) Non-crystalline SiO_2 and (ii) Nano-crystalline HfO_2 Thin Films**, ***G. Lucovsky****, North Carolina State University **INVITED**

Correlated atomic positions of Si-atoms bonded to 2-fold coordinated O-atoms are determined by Si *3d-dervied* T_{2g} states on these atoms [1]. These states constrain dihedral angles contributing to medium range order with *correlation lengths* of ~0.4 and 0.45 nm, and, a *coherence length* of ~1 nm, each obtained from the first sharp diffraction peak in X-ray diffraction [2]. O K edge soft X-ray SiO_2 spectra reveal conduction band edge states with singly degenerate A_1 symmetry, and stronger doubly and triply degenerate E and T_2 *d-state* beginning at energies ~3 eV higher. This difference is smaller in c-Si, ~1 eV. Analysis of O K and $L_{2,3}$ spectra are based on a charge transfer multiplet many electron theory [3]. Energy differences are the same for band edge features obtained from transmission/reflectivity studies in the visible/VUV where the d-state character was not previously recognized [4]. The correspondence derives from O 1s core hole localization, and a coherent process in which 1s core holes are filled by electrons from valence band O 2p p states, accounting for the one-to-one correspondence between sequenced features in the O K edge, and in the Si $L_{2,3}$ spectrum of SiO_2. $L_{2,3}$ spectra, studied by electron energy loss spectroscopy (EELS), have not detected the *weaker* Si A_1 features in the 100 to 104 eV regime of SiO_2, or 98 to 100 eV regime of c-Si. The O K edge X-ray spectra of transition metal elemental and complex oxides are qualitatively different with either doubly or triply degenerate *d-state derived* spectral features at the band edge. This results in significant quantitative differences in (i) the high-spin excited d-states of O-atom vacancy occupied d^2 states, and (ii) the negative ion electronically active d-state traps populated by charge injection. O-vacancy states in SiO_2 are close to mid-gap, and do not contribute to gate stack tunneling processes. This explains the order of magnitude higher interfacial trap densities, d_{it}, and trap-assisted tunneling in HfO_2 gate stacks. It also accounts for significant differences in radiation hardness. XAS spectra are presented for the first time for remote plasma deposited GeO_2. These deposited films display significantly different O K edge spectra than those obtained by oxidation of Ge; more importantly A_1, and E and T_{2g} features *stronger and narrower* than those of SiO_2. Electrical data for deposited GeO_2 dielectrics on Si and Ge substrates are compared for the first time with SiO_2 test devices on the same substrates.

[1] Whitten J, et al., J. Vac. Sci. Technol. B 20, 1710 (2002).

[2] Lucovsky G, et al. physica status solidi (a) 207, 631 (2010).

[3] de Grott F, Kotani A. Core level spectroscopy of solids (Boca Raton, CRC, 2008).

[4] Laughlin RB, Phys. Rev. B 22, 3021 (1980).

9:20am **TF-ThM5 New Parameterization of the Modified Embedded Atom Potential for Large Scale Simulations of TiN Thin Films Growth**, ***D.G. Sangiovanni***, *V. Chirita, L. Hultman*, Linköping University, Sweden

Classical Molecular Dynamics (MD) has become an indispensable tool in thin films modeling, as it allows the study of systems and phenomena reaching far beyond the inherent limitations of ab-initio and/or Density Functional Theory (DFT) methods. Generally, the range of systems to which the method can be applied has typically been limited to materials characterized by single-type bonding, such as ionic, covalent or metallic. This situation has been considerably improved in the last decade within the formalism of the Modified Embedded Atom Method (MEAM), which allows the treatment of mixed-type bonding materials, and in recent years, a number of studies have been devoted to MD simulations of important model systems such as TiN. Nevertheless, the very few MEAM parameterizations for TiN reported thus far are able to reasonably reproduce bulk, as well as some surface properties of this material. However, if meaningful MD simulations of TiN thin films growth are to be performed, a number of critical nucleation and diffusion phenomena have to be accounted for besides basic bulk/surface properties. Herein, we propose a new parameterization of the MEAM interaction potential for TiN, which in addition to correctly predicting bulk and surface properties, reproduces the experimentally observed trends in the diffusion of single species (Ti, N) and Ti-N dimers, on the most representative steps/surfaces for TiN growth, the (100) and (111) respectively. Our estimations of activation energies for diffusion and Ehrlich-Schwoebel (ES) step-edge barriers are in good agreement with previous ab-initio calculations and experimental observations. Consequently, this new MEAM parameterization has the potential to adequately account for most essential processes during the initial stages of TiN nucleation, which, as it is well known, dramatically affect the growth mode and properties of thin films in laboratory and computer experiments.

9:40am **TF-ThM6 DSMC Modeling of Metal Vapor Flow in Vacuum in Application to Thin-Film Depositions**, ***V. Ayyaswamy***, *A. Alexeenko*, Purdue University

Electron beam assisted physical vapor deposition (EBPVD) is widely used in a number of vacuum material processing applications for deposition of thin films of metals. The properties of these thin films including thickness uniformity, growth rates and other material properties are dependent, to a great extent, on the geometric configuration of the deposition source and electron gun power. A complete understanding of the deposition process

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requires the ability to accurately simulate the vapor flow that varies from highly collisional in regions near the source to being free-molecular near the substrate location. The direct simulation Monte Carlo technique, which is by far the most powerful technique to simulate such flows rapidly expanding into vacuum, requires an accurate molecular model for the interaction between the metal vapor atoms. A molecular model has been formulated [1] for the interaction of Cu atoms and validated with experimental data for electron-beam deposition of copper. The main goal of this work is to formulate molecular models for common metal vapors including Gold, Titanium, Nickel, and Aluminium and validate them with experimental data[2,3] for thin-film growth rates at various evaporation rates. The ability to accurately model deposition processes of thin films of metals would greatly assist in the design and control of such vacuum deposition systems and processes.

References

[1] A. Venkattraman and A.A. Alexeenko, "DSMC Modeling of E-beam Metal Deposition", J. Vac. Sci. & Tech. A, July 2010 (*accepted*).

[2] D. Chaleix, P. Choquet, A. Bessaudou, L. Frugier, and J. Machet, "A spatial distribution study of a beam vapour emitted by electron-beam-heated evaporation sources", J. Phys. D: Appl. Phys. 29(1996) 218-224.

[3] K.B. Thakur and G.K.Sahu, "Spatial distribution of copper vapour flux during strip electron beam vaporation", J. Phys. D: Appl. Phys. 35(2002) 1812-1820.

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