Wednesday Afternoon, October 22, 2008

Thin Film
Room: 302 - Session TF-WeA

Computational and Experimental Studies of Thin Films
Moderator: S. Gupta, The Ohio State University

1:40pm TF-WeA1 Origination and Role of Compressive Stress at Ion Deposition of DLC-film, *V.E. Strel'nitskij*, *A.I. Kalinichenko*, *S.S. Perepelkin*, NSC "Kharkov Institute of Physics and Technology", Ukraine
The known approach to formation of compressive stress in thin films by ion bombardment[1] uses the formalism of the point-like thermal spike (PTS) to describe acceleration of kinetic processes responsible for stress relaxation. But the PTS model does not reflect adequately real thermodynamic conditions in vicinity of the ion path in the target material. It does not take into account the finiteness of the initial volume of the energy release which depends on energy E of the ion and thermal properties of material. As a result the known formula for residual stress σ (E) in thin film under ion bombardment[1] matches with experimental data only by too high values of the activation energy of migration of defects U > 3 eV. Also σ(E) does not depend on the substrate temperature T_0. In this paper the rate of kinetic processes in carbon films at low-energy ion deposition in the model of the nonlocal thermoelastic peak (TEP)[2] of the ion is analyzed. The approximate expressions for temperature T, pressure P and the number of sp^2 to sp^3 transitions in the TEP depending on energy of the ion and substrate temperature T_0 were derived and applied for modification of the expression of σ(E).[1] Unlike the previous expression σ(E) the modified one depends on E in accordance with experimental data when U is closed to 0.3 eV (the typical value for the activation energy of interstitials). Also σ decreases substantially with T_0 in temperature range 300 to 600 K. Calculation of σ and T permitted determining "the initial locations" and "P,T- trajectories" of the ion TEPs on phase P,T- diagram of carbon[2] and investigating possibility of DLC formation depending on E and T_0. As the steady residual stress σ decreases with the substrate temperature increase from 300 to 600 K the initial locations and P,T- trajectories of TEPs shift preferably from the region of diamond stability to that of graphite stability. Such behavior which is pronounced for TEPs with energies E > 100 eV suggests that sp^2 – bound carbon forms preferably in TEPs of low-energy ions C^+ at temperature of deposition T_0 > 600 K. This conclusion agrees qualitatively with experimental data.

[1] C.A. Davis: Thin Solid Films 226 (1993) 30.
[2] A.I. Kalinichenko, S.S. Perepelkin, V.E. Strel'nitskij, Diam. Relat. Mater. 15 (2006) 365.

2:00pm TF-WeA2 Phase Evolution in Sputter Deposited Hafnia-Titania Nanolaminates with Changing Architecture and Thermal Annealing, *M.C. Cisneros-Morales*, *C.R. Aita*, University of Wisconsin-Milwaukee
Thin film HfO_2 is a candidate for a high dielectric constant replacement material for SiO_2 in integrated circuits. The addition of TiO_2 to HfO_2 has shown promise for producing a $Hf_{1-x}Ti_xO_2$ ternary with an even higher dielectric constant than pure HfO_2 while maintaining thermal stability with Si. A convenient way of combining TiO_2 with HfO_2 in thin films is to sequentially sputter deposit them in a nanolaminate structure. In such a structure, interfaces are important in determining phase composition. The bulk pseudobinary HfO_2-TiO_2 temperature-composition phase diagram shows low miscibility between the end-point oxides. In this respect, the HfO_2-TiO_2 system is typical of an oxide nanolaminate in which there is a driving force for the formation of an interfacial mixed cation compound but there is no obvious kinetic path to achieve this structure via the formation of an interfacial crystalline substitutional solid solution. In this paper we examine the moderate temperature annealing behavior of HfO_2-TiO_2 nanolaminates with many different bilayer architectures. Multilayer stacks of HfO_2 and TiO_2 bilayers were grown on unheated fused silica substrates in a rf-excited multiple cathode reactor. The substrates were sequentially positioned under Hf and Ti targets and sputtered in 20 mtorr 80% Ar-20% O_2 discharges to build up the films. Four sequential annealing stages were carried out in laboratory air at the following temperatures: (I) 573 K, (II) 673 K, (III) 773 K, (IV) 973 K for 1 h each. The films were furnace cooled to room temperature and analyzed by double angle x-ray diffraction between annealing stages to obtain crystallographic data. The results show that the as-grown films are nanocrystalline and contain a mixed cation interface. This interface develops upon annealing into an orthorhombic $HfTiO_4$ phase adjacent to a titania layer, followed by an unusual metastable phase, monoclinic $Hf_{1-x}Ti_xO_2$ more remote from the interface. In nanolaminates with thicker HfO_2 layers, a simulaneous development of monoclinic HfO_2 occurs. The lattice parameters of this nanocrystalline intralayer phase, however, are greater than the expected bulk value,

indicating dipole-dipole repulsion at the surface of a HfO_2 nanocrystal might be occurring.

2:20pm TF-WeA3 Rapid Diffusion of Magic-Size Islands by Combined Glide and Vacancy Mechanism, *O.U. Uche*, *J.C. Hamilton*, Sandia National Laboratories
Monolayers of Ag on Cu(001) are well known to reconstruct forming a (10x2) reconstruction with Ag atoms packed hexagonally on the four-fold Cu(001) surface.[1] We have investigated the surface diffusion of hexagonally-packed Ag monolayer islands of various sizes on Cu(001) using computer simulation techniques. Our examination reveals a novel cooperative diffusion mechanism consisting of core glide coupled with the migration of edge vacancies. It should be noted that island diffusion is completely one-dimensional with the orientation determined by the (10x2) reconstruction of the diffusing island. In other words, rows of the hexagonal Ag lattice move along the hollow and bridge sites of the Cu substrate in the {110} type direction. In addition, we have observed magic-sized islands for which diffusion occurs much more rapidly as a result of their reduced diffusion barrier. In particular for a 169-atom hexagonal island, the activation energy for diffusion is smaller than the barrier for a single Ag atom hop. For this island size, diffusion occurs rapidly at temperatures as low as 200K. Molecular dynamics simulations suggest that the surface diffusion process displays non-Arrhenius behavior possibly resulting from the temperature-dependent lattice mismatch. Our findings should provide insight to future experimental research on the size distribution and shapes observed during the growth of thin films in similar systems.

[1] P.W. Palmberg and T.N. Rhodin, J. Chem. Phys. 49, 134 (1968).

2:40pm TF-WeA4 The Influence of Oxygen Impurities on the Formation of Self-Assembled Nanostructures in Al/Al(110) Homoepitaxy, *Y. Tiwary*, *K.A. Fichthorn*, The Pennsylvania State University
Recent experimental studies of Al/Al(110) homoepitaxy show that self-assembled nano-structures can form due to an interplay between the kinetics of diffusion and deposition.[1] These "nanohuts" are characterized by smooth {111} and {100} facets. At temperatures between 330 and 500 K and for a deposition rate of 1 ML/min, the nanohuts emerge after about 10 ML have been deposited. Upon further deposition, these huts grow and self-organize, reaching average heights of 50 nm after 30 ML has been deposited. Understanding the formation of these features and developing the capability to control them in this and similar systems is both scientifically and technologically significant. To predict the formation and self-organization of these features, we employ first-principles calculations based on density-functional theory to study diffusion and atomic interactions on Al surfaces. We quantify many-body interactions between Al adatoms,[2] as well as the interactions between Al adatoms and isolated O impurities on Al(110). The interactions between Al and O atoms are expected to be especially important in the initial stages of growth, as oxygen is a common impurity on Al surfaces, even in ultra-high vacuum environments. We show that O impurities can significantly influence island nucleation and lead to entirely different growth modes than those observed in pure Al/Al(110) homoepitaxy. Using kinetic Monte Carlo, we simulate multi-layer growth under various conditions to predict the growth morphologies and understand the implications of surface impurities for self-assembled nanostructures.

[1] F. Buatier de Mongeot, W. Zhu, A. Molle, R. Buzio, C. Boragno, U. Valbusa, E. Wang, and Z. Zhang, Phys. Rev. Lett. 91, 016102 (2003).
[2] Y. Tiwary and K. A. Fichthorn, Phys. Rev. B 75, 235451 (2007).

3:00pm TF-WeA5 A Formula for Increased Hardness and/or Ductility in TiN-based Thin Films and γ-TiAl Compounds, *D.G. Sangiovanni*, *V. Chirita*, *L. Hultman*, Linköping University, Sweden
TiN-based thin films, such as $Ti_{1-x}Al_xN$ and their alloys, are known to have excellent mechanical and thermal properties. In this paper we report the initial results of our ab-initio investigations of two novel ternary compounds, $Ti_{1-x}W_xN$ and $Ti_{1-x}Mo_xN$, obtained by alloying TiN with W, respectively Mo, in concentrations of up to 50%. The elastic constants as well as the bulk, shear and Young's moduli of these compounds were evaluated using density functional theory calculations within the generalized gradient approximation, and compared with the corresponding properties of TiN and $Ti_{1-x}Al_xN$. Significantly, we found that the addition of W and Mo resulted in substantial increases in bulk modulus values compared to TiN (up to 15%) and $Ti_{1-x}Al_xN$ (up to 30%). At the same time, we observed a dramatic decrease (up to 50%) in the values of C_{44}, and a reversal of the Cauchy pressure, C_{12}-C_{44}, from negative to positive, results indicative of significantly increased ductility in these compounds. Both of these trends are in total contrast to what is known for $Ti_{1-x}Al_xN$, which exhibits increased C_{44}/brittleness and lower bulk modulus values as the Al

content is increased. We also investigated, in the same manner, the effects of alloying $Ti_{0.5}Al_{0.5}N$ with W and Mo, in concentrations of up to 6% and observed a similar trend in increasing hardness and ductility. However, in the case of quarternary TiAl(W/Mo)N, the impact of W and Mo addition was considerably more moderate, as the increase in bulk modulus, respectively decrease in C_{44}, were in the 5% range. As it will be shown, these results demonstrate and help understanding the mechanisms through which W and/or Mo additions modify the atomic bonding in these compounds, from a strong angular/directional character, towards a more metallic type of bonding. This type of electronic structure information is essential in designing compounds with different mechanical properties and tailoring them to a variety of applications.

4:00pm TF-WeA8 Ion Implantation and Annealing Studies on VO_x Films Prepared by Pulsed dc Reactive Sputtering, *C. Venkatasubramanian, M.W. Horn, S. Ashok*, The Pennsylvania State University

Vanadium oxide (VO_x) thin films find extensive use in room-temperature bolometers for IR imaging. It is desirable to control and modify the electronic properties of the material with treatments such as ion implantation and thermal annealing. In this work, we report on the modification of structural and electrical properties of VO_x thin films used in microbolometers. VO_x films of varying compositions were deposited by pulsed dc reactive sputtering of a vanadium target under different oxygen flow rates. The as-deposited resistivities of the films ranged from 0.1 ohm-cm to 100 ohm-cm and the temperature coefficient of resistance (TCR) values varied from -1.1 to -2.7 % K^{-1}. VO_x films used in microbolometer applications need to have a high TCR (> 2 % K^{-1}) and low resistivity values (1 -10 ohm-cm). But, typically, a high TCR is associated with a high resistivity. Hence ion-implantation followed by annealing was performed in order to examine trade-off between TCR and resistivity. Two species - Hydrogen (active) and Helium (inert) were chosen for implantation. Hydrogen is an active species well known for passivating defect states in a wide variety of electronic materials. Helium is an inert species and was chosen mainly to study the effects of bombardment on the film. The implanted films were annealed in an inert atmosphere to allow for redistribution of atoms, and then characterized by current-voltage measurements over a wide temperature range. The effect of thermal annealing alone was evaluated separately by annealing the unimplanted samples. In both cases, an order of magnitude change in resistance, and significant variations in TCR were observed. Further characterization has been done by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) to correlate these resistivity changes with the structure of the films.

4:20pm TF-WeA9 Optical Properties and Structure of Magnetron Sputtered Vanadium Oxide Thin Films, *N.J. Podraza, B.D. Gauntt, N.M. Fieldhouse, K.E. Wells, D. Saint John, E.C. Dickey,* The Pennsylvania State University*, R.W. Collins,* University of Toledo*, M.W. Horn*, The Pennsylvania State University

Vanadium oxide (VO_x) thin films have been used for the last twenty years as the imaging material in uncooled infrared imaging devices. The important material properties for this application are a high thermal coefficient of resistance (TCR), controllable resistivity (ρ), low electrical noise and process compatibility with standard IC fabrication. In this work, device quality VO_x thin films have been fabricated by single and dual-target pulsed dc magnetron sputtering. The deposition parameters of this novel technique include vanadium (V), vanadium dioxide (VO_2), or vanadium trioxide (V_2O_3) sputter targets which can be used individually or two targets simultaneously with separately variable power, variable total pressure, variable oxygen partial pressure, and variable substrate temperature. Variations in these parameters have been shown to result in films with TCR between 1.5 and 4.0 (-%/K) and ρ ranging from 0.1-100,000 Ω cm as measured by a four-point probe technique. The films produced in the region of device interest have been characterized with a wide variety of ex situ techniques to establish what role the deposition parameters play in the final structure and composition of the film, and the resulting effects of these characteristics on the electronic transport and optical properties. Transmission Electron Microscopy (TEM), Rutherford Backscattering (RBS), and Spectroscopic Ellipsometry (SE) have been used to characterize the nanocrystalline structure of these films, their bonding structure, the oxygen content in the film, and the dielectric function spectra ($\varepsilon = \varepsilon_1 + \varepsilon_2$) in the visible range (0.75-6.5 eV), respectively. By utilizing these complementary techniques, correlations between changes in the microstructure and composition determined by TEM and RBS, optical properties determined by SE, and electronic transport properties have been established.

4:40pm TF-WeA10 Multi-Scale Modeling of Thin-Film Epitaxy, *K.A. Fichthorn*, Penn State University **INVITED**

Predicting, with first-principles accuracy, the nanostructures that form during thin-film epitaxy is a current challenge in multi-scale modeling. I will discuss our recent innovations in accelerated molecular dynamics and coarse-grained lattice techniques, which facilitate this task. I will highlight these methods in studies aimed at understanding the morphology in Al(110) homoepitaxy. This system exhibits a number of interesting growth modes as the temperature and deposition rate are varied, including the formation of nanohuts. The nanohuts, which have smooth (111) and (100) facets, arise from a sea of smaller mounds after several layers are deposited, in a bimodal growth mode. We illustrate how first-principles total-energy calculations with density-functional theory, accelerated (ab initio) molecular dynamics, and kinetic Monte Carlo can be extended to yield insight into diffusion, many-body interactions, and growth in this system. I will illustrate the role of oxygen impurities in promoting bimodal growth.

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