Thursday Afternoon, October 18, 2007

Thin Film

Room: 613/614 - Session TF2-ThA

Computational Aspects of Thin Films

Moderator: B.C. Holloway, The College of William and Mary

2:00pm **TF2-ThA1 Computational Study of the Interfacial Structure of Aluminum/α-Alumina**, ***B.D. Devine***, University of Florida, *A. McGaughey*, Carnegie-Mellon University, *S.R. Phillpot*, *S.B. Sinnott*, University of Florida

Several experimentally observed orientations for the interface between FCC aluminum grown on the (0001) face of α-alumina were studied through molecular dynamics using a modified variable charge potential. This many-body, empirical potential allows for the realistic modeling of both the metallic and ceramic phases in large-scale, atomistic simulations. The effects of temperature, surface terminations and coherency on the interfacial structure and energy were investigated. The efficiency of the molecular dynamics simulation allows for study of periodic systems oriented with minimal strain along the preferred relationship of $<1010>_{Al2O3} \parallel <110>_{Al}$ as well as secondary orientations along $[2112]_{Al2O3} \parallel [011]_{Al}$ and $[2112]_{Al2O3} \parallel [231]_{Al}$. The results are compared to experimental data and to the results of density functional theory calculations. This work is supported by the National Science Foundation (DMR-0426870).

2:20pm **TF2-ThA2 Analytical Simulation of Conformal and Super-Conformal CVD on High Aspect Ratio Vias and Trenches**, *Y. Yang*, ***J.R. Abelson***, University of Illinois at Urbana-Champaign

The need to coat or fill recessed features such as trenches or vias is frequently encountered in micro- and nano-fabrication processes. Chemical vapor deposition is commonly used because of the combination of good conformality and high growth rate. With the continuous scaling down of feature sizes and the increase of aspect (depth/width) ratios, it has become a major challenge to maintain the growth conformality and filling efficiency. We developed a numerical model that is capable of simulating the film thickness profiles produced by CVD in trenches and vias with aspect ratios ≥ 10:1. In this model, the precursor transport is described by Knudson diffusion, and the precursor concentration and reaction rate distributions are solved numerically from the continuity equation. The evolution of the deposition profile during a filling process can also be predicted. We employ this model to understand the critical issues associated with CVD on high aspect ratio features. We show that the precursor reaction probability is the key factor that governs the deposition conformality. The model predicts the precursor reaction probability that is required to conformally coat or to completely fill trenches with aspect ratios ranging from 5:1 to 100:1. These simulations are in close agreement with the experimental profiles we have obtained for HfB_2 and CrB_2 films grown using single-source borohydride precursors. Traditionally the precursor reaction probability is controlled primarily by the growth temperature. We show that if a Langmuir surface reaction mechanisms is operative then the precursor pressure is a far more effective parameter to reduce the reaction probability. We have developed a new approach to obtain super-conformal coating (bottom-up filling) of high aspect ratio features, and we have demonstrated proof-of-concept with CrB_2 and HfB_2 films. In this method, a suppressor species is introduced into the growth system to reduce the surface reaction rate of the precursor. We simulate the deposited film profile as a function of the suppressor pressure, precursor pressure, trench aspect ratio, and the relative reaction rates of the suppressor and precursor species. We will discuss methods to optimize the filling process by varying the suppressor pressure in time during film growth.

2:40pm **TF2-ThA3 Computational Investigation of Surface Polymerization by Ion Assisted Deposition**, *W.-D. Hsu*, University of Florida, *S. Tepavcevic*, *L. Hanley*, University of Illinois at Chicago, ***S.B. Sinnott***, University of Florida **INVITED**

Density functional theory-MD (DFT-MD) simulations are used to study surface polymerization by ion-assisted deposition (SPIAD) of thiophene on alpha-terthiophene oligomers on a silicon surface to determine the dominant mechanisms responsible for the SPIAD process. Polythiophene is a conductive polymer that has attracted much interest in recent years because its properties are desirable for applications that include light emitting diodes, field effect transistors, and photovoltaics. Optimization of the performance of polythiophene in these devices requires the development of processing methods that can simultaneously control its chemistry and morphology on the nanometer scale. One such method is SPIAD, where conducting polymer thin films are grown on substrates by the simultaneous deposition of hyperthermal polyatomic ions and thermal neutrals in vacuum. Both neutral and positively charged systems are considered in the DFT-MD simulations in order to assess the effect of charge on the results, which were compared to experimental data. The incident energies range from 100 to 500 eV. The simulations indicate that the differences in the collision outcomes between the neutral and positively charged events are small in most cases, but the atoms in the +1 charged system experienced slightly larger forces and velocity variations than the atoms in the neutral system. Several key bond dissociation and polymerization mechanisms are predicted in the simulations that are also observed experimentally. The most important prediction is that incident thiophene ions break apart on collision with the 3T film. Both the experiments and simulations indicate that incident thiophene ions chemically modify the structure of the oligomer film by covalently bonding to the 3T oligomers. The insight gained from this integrated experimental and computational work can be used to optimize the SPIAD process for polythiophene and other conducting polymer systems. This work is supported by the National Science Foundation (CHE-0200838).

3:40pm **TF2-ThA6 Modelling, Growth and Characterisation of Stress-Balanced Thin Films on Stress-Free Virtual Substrates**, ***S.G. Turner***, Imperial College London, UK, *L. Yu*, Chinese Academy of Sciences, China, *K. Chua*, *M.R. Levy*, Imperial College London, UK, *X. Li*, University of Oxford, UK, *J. Zhang*, Imperial College London, UK

The Si/SiGe material system on a Si platform gives opportunities to develop Si-based optoelectronic devices, allowing monolithic integration.[1] The 4% mismatch requires strain to be properly managed in structures that exceed the critical thickness for relaxation. Growing a stress-balanced structure on a virtual substrate (VS) allows such control. This work characterises the composition, tilt and strain state of the VS, and that of thin layers. Growth was carried out under ULPCVD & GSMBE modes in a modified VG Semicon system. We grew a fully-relaxed SiGe VS on Si(001), compositionally graded from pure Si. We show that a composition overshoot in the graded layer is needed to achieve the required in-plane lattice parameter, and determine its value. We examined x-ray reciprocal space maps (RSM) about the 004 and 224 reflections, obtaining average tilt of the VS with respect to the substrate and tilt distribution. Results from misoriented substrates show that the VS tilts to reduce the difference between low-index planes and the physical surface by >5%, explained by the preferential introduction of misfits with certain Burgers vectors. A fully-relaxed VS provides a good template for stress-balance between thin metastable layers by considering average force in the structure.[2] Predictions from linear elasticity (LE) theory (assuming linear interpolation of alloy elastic constants) were tested by depositing a DBR on a fully-relaxed VS.[3] The DBR consisted of 25 repeats of a Si/SiGe (32%) bilayer of ~190nm thickness, grown at 590°C and 520°C respectively. RSMs (giving lattice parameters) revealed the bilayer was coherent to the VS, supporting the validity of the linear extrapolation. This was compared to density functional theory calculations of the elastic constants. Reflectivity was 75% at 1.4 microns, and x-ray analysis showed fringes typical of well-ordered interfaces, suggesting a good stress-balance was realised. The composition overshoot part of the VS remains under compressive strain and coherent to the subsequent grown layers. We propose to compensate this using tensile Si, obtaining a true stress-free structure. We demonstrated this for varying VS compositions. We thus show that the precise strain state of thin films can be accurately manipulated.

[1]Kuo et al., Nature Vol. 437 p1334
[2]Ekins-Daukes et al., Crystal Growth & Design Vol. 2 p287.
[3]Kawaguchi et al., APL Vol. 79 p476.

4:00pm **TF2-ThA7 Intra- and Interlayer Mass Transport Rates during Layer-By-Layer Homoepitaxial Pt(111) Growth from Hyperthermal Beams (5-50 eV)**, ***V. Chirita***, *D. Adamovic*, *E.P. Münger*, *L. Hultman*, Linköping University, Sweden, *J.E. Greene*, University of Illinois, Urbana-Champaign

We employ multi-billion time step embedded-atom method molecular dynamics simulations to study homoepitaxial growth of Pt(111) using low-energy (0.2 - 50 eV) hyperthermal Pt fluxes. We deposit 5 monolayers at 1000K and with deposition rates approaching experimental conditions. The results reveal a transition from a three-dimensional (3D) multilayer growth mode to layer-by-layer growth at ~ 20 eV which is maintained for energies of up to 50 eV. In order to determine the mechanisms responsible for the observed change in the growth mode, we resolve, with picosecond resolution, both irradiation-induced and thermally activated processes. This

allows us to determine, with unprecedented accuracy, the energy dependence of the net intra- and interlayer migration rates during the deposition process. Results show, that for all energies, irradiation events are completed within 10 ps following energetic impacts and that these processes dictate the growth mode. As expected, thermal migration is not affected by the deposition energy. For Pt deposition energies above 20 eV, the net interlayer migration induced by irradiation is towards the surface. This type of mass transport occurs via exchange mechanisms between surface and sub-surface atoms. On the growing layers, we observe primarily the descent of adatoms at step-edges and the recombination of adatoms with surface vacancies, i.e. mainly thermally activated processes. However, thermally activated net downward migration is an order of magnitude less than irradiation-induced upward migration. Intralayer migration is shown to depend strongly on adatom surface coverage. Results show that adatoms are the primary source of in-layer mass transport, which is observed to peak at a coverage of ~ 0.05 ML. Sputtering is observed to occur for energies higher than 25 eV. However, the yield is too small, less than 1% at 50 eV, to have a significant effect on island nucleation and coalescence kinetics.

4:20pm **TF2-ThA8 Synthesis and Theoretical Modeling of Fullerene-like Phospho-Carbide Compounds**, ***A. Furlan***, *G.K. Gueorguiev, H. Högberg, S. Stafström, L. Hultman*, Linköping University, Sweden

First-principles DFT calculations predict that Fullerene-like (FL) CPx compounds can have resilient mechanical behavior similar to FL-CNx, but for a lower V element concentration. P is a higher period element compared to N. This means a higher freedom with respect to chemical bonding which is likely to affect the structure of the CPx compounds compared to FL-CNx. The results of theoretical simulation of synthetic growth of FL-CPx structures show that the substitution of N with P makes the formation of tetragon defects energetically favorable and that P-P bonds are plausible. This implies stronger curvature and interlocking of graphene planes. Concurrent inter- and cross-linking of the bent graphene planes induced by the P atom leads to cage- and onion-like structures which promise improved mechanical properties of the FL solids. In this paper we also present results from magnetron sputtering deposition of CPx thin films. The films were deposited by DC magnetron sputtering in Ar atmosphere from a compound graphite-P target containing between 5 and 15 at.% of P. Higher proportions of P in the target should be avoided since P-rich species in the deposition flux might result in P-segregation during film growth. The substrates were Si and NaCl wafers kept at a bias voltage in the range of -20 V to -50 V, and substrate temperature ranging from 150 ^{o}C to 780 ^{o}C. As-deposited coatings were analyzed using XPS, nanoindentation, SEM, and TEM. The preliminary results show that incorporation of P into the film is promoted at lower substrate temperatures and higher bias voltages. Nanoindentation experiments show that resistance to indentation and hardness of the CPx increases for decreasing substrate temperature and increasing bias voltage.

4:40pm **TF2-ThA9 High-Throughput Determination of Sputtered Film Composition: The Importance of Resputtering**, *J.M. Gregoire, M.B. Lobovsky, M.F. Heinz, F.J. DiSalvo,* ***R.B. van Dover***, Cornell University

The use of traditional characterization techniques to determine elemental compositions in composition spread thin films is time-intensive. Combinatorial, high-throughput studies of thin film materials demand high-throughput determination film composition. We discuss the possibility of calculating codeposited film compositions from deposition profiles obtained during single-source sputtering. In the context of DC magnetron sputtering, we find that while this technique is appropriate for the Pd,Pt,Ti system, it yields atomic ratios in a Pt,Pb composition spread thin film that vary significantly from values measured with wavelength dispersive x-ray spectroscopy. A model for resputtering during codeposition is presented to account for these discrepancies, and the model is used to calculate resputter rates during Pt,Pb codeposition. We also employ our model to estimate the resputtering susceptibility of commonly sputtered elements.

5:00pm **TF2-ThA10 General Theory of Optical Reflection from a Thin Film on a Solid and its Application to Heteroepitaxy**, *Y.Y. Fei, X.D. Zhu,* ***X. Wang***, University of California at Davis, *H.B. Lu, G.Z. Yang*, Chinese Academy of Sciences

Light reflection from an optically smooth yet atomically rough film on a smooth solid substrate formed by deposition or erosion is a convenient source of information on morphology and chemical make-up of the film. We show that changes in optical reflectivity for s-polarized (TE mode) and p-polarized (TM mode) components, defined as $(r_p - r_{p0})/r_{p0} - (r_s - r_{s0})/r_{s0} = \Delta_p - \Delta_s$, induced by such a film, is generally related to structural and chemical properties of such a film through a mean-field theory. Here r_{p0} and r_{s0} are the reflectivity of a bare substrate, and r_p and r_s are the reflectivity when the film is added onto the substrate. According to the theory, $\Delta_p - \Delta_s$ consists of a term that is proportional to the thickness of the rough portion of the film, a term that is proportional to the density of unit cells embedded in terraces, and a term that is proportional to the density of unit cells situated at step edges. The proportionality constants are functions of the overall thickness and chemical make-up of the film. We apply the theory to analysis of a wide range of growth and adsorption experiments studied with the oblique-incidence reflectivity difference (OI-RD) technique.

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