

Friday Morning, November 4, 2011

Thin Film Division

Room: 110 - Session TF-FrM

Thin Films: Growth and Characterization II

Moderator: S. Gupta, University of Alabama

8:20am **TF-FrM1 Low-temperature CVD with Growth Inhibitors to Afford Uniform, nm-thick Films in Structures with Aspect Ratio ~ 200.** *S. Babar, J. Abelson*, University of Illinois at Urbana Champaign

In order to grow uniform, smooth and pinhole-free films of nm thickness, the nucleation step must occur with high areal density on the substrate and the nuclei must have a narrow size distribution. If the film must be deposited inside of a deep structure of very high aspect ratio, then the growth process must be strictly governed by the surface reaction rate of the precursor species rather than by the rate at which precursor is transported to the growth surface. Here, we present a method of control in chemical vapor deposition that simultaneously meets both of the above criteria.

We previously reported that the steady-state film growth rate is reduced when a molecular species, called the *inhibitor*, is added to the CVD process. The inhibitor interacts transiently with the growth surface but does not decompose and incorporate its elements into the film, i.e., the inhibitor is not consumed. We also reported that the inhibitor greatly improves the film nucleation step, e.g. for the growth of HfB_2 , a high performance diffusion barrier, on SiO_2 substrates. In the absence of the inhibitor the nucleation density is low and the size distribution is broad, such that some islands attain a height of > 10 nm before the film even coalesces. In the presence of the inhibitor, nuclei attain a height of ~ 1 nm, but then grow only very slowly. Additional nuclei continue to form and fill in the bare substrate, such that coalescence occurs at a thickness of ~ 2 nm with a rms surface roughness of ≤ 0.5 nm.

The use of a growth inhibitor allows the *nucleation regime of film growth* to afford excellent nm-thick coatings in extremely high aspect ratio features. Note that when the film growth rate is low, so also is the consumption of precursor, such that a partial pressure of precursor species persists to the bottom of the feature. The inhibitor further assures that the nucleation process will be uniform. In features of aspect ratio > 200 , we show that a film is deposited on all surfaces with a rms roughness of 0.6 nm. We also discuss the mechanisms that can afford the observed results. We suggest that the ability to reduce (homogenize) the size distribution and increase the areal density of nuclei will greatly extend the useful range of CVD precursor-substrate combinations which can afford nm-thick coatings in very high aspect ratio features.

8:40am **TF-FrM2 Understanding the Role of Hydrogen Impurity Scattering in Manganese Thin Films on the Si(001) Surface.** *A.J. Stollenwerk, B.J. Friend*, University of Northern Iowa

Interest in energy production via hydrogen has been increasing due to the fact that it does not emit harmful greenhouse gases associated with fossil fuels. Unfortunately, hydrogen is an explosive gas that is both colorless and odorless. This will make hydrogen sensors an important piece of safety equipment in a hydrogen based economy. Diffusion of hydrogen to the Mn/Si interface is believed to have an amphoteric effect on the interface characteristics making it a possible hydrogen sensor. This motivates a need to better understand electron transport properties through Mn/Si Schottky diodes. We performed ballistic electron emission microscopy (BEEM) on Mn/Si(001) Schottky diodes to study hot electron transport properties through this system. Samples were fabricated using electron-beam deposition of Mn onto n-type Si(001) with thickness ranging from 10 to 40 Å. Scattering in the Mn films as function of energy has been measured and compared to results obtained on Au/Si(001) Schottky diodes. Schottky heights on these samples were determined from the corresponding BEEM spectra using the Bell-Kaiser model. Future plans include introducing an atmosphere consisting of varying amounts of hydrogen and measuring the resulting effects on hot electron transport in the Mn film as well as the Schottky height. Should electron scattering or the Schottky height be affected by the presence of hydrogen, this system may prove useful as an inexpensive hydrogen sensor.

9:00am **TF-FrM3 Elimination of Indium Surface Segregation in InGaN Grown Throughout the Miscibility Gap.** *M.W. Moseley, B. Gunning, J.E. Lowder*, Georgia Institute of Technology, *G. Namkoong*, Old Dominion University, *W.A. Doolittle*, Georgia Institute of Technology

InGaN alloys have great potential in optoelectronics due to the tunable bandgap which spans the visible spectrum. However, these alloys are difficult to obtain as a result of thermal decomposition, indium surface

segregation, and spinodal decomposition. To solve these problems, low growth temperatures, fast growth rates, and in situ surface analysis must be used. These limitations make Metal-Modulated Epitaxy (MME) a promising growth candidate. Using MME, smooth InGaN has been grown without phase separation throughout the miscibility gap.

MME is a growth technique applied to molecular beam epitaxy of III-nitrides in which metal and dopant cell shutters are periodically opened and closed while active nitrogen flux remains constant. This technique uses metal-rich fluxes that would accumulate droplets in traditional MBE, taking advantage of the enhanced adatom mobility provided by excess metal. The periodic shuttering of the effusion cells allows the excess metal to be consumed, providing smooth, dry surfaces required for devices that demand abrupt interfaces.

In this study, MME is applied to the growth of InGaN and transient RHEED intensities are monitored for differing metal shutter open times (Fig. 1). It is found that these RHEED transients are the result of a RHEED oscillation associated with the buildup and consumption of the metal adlayer. This allows for observation and control of fractions of adsorbed metal layers. However, there is a drastic difference between the RHEED transients of low and high metal shutter open times. This difference is attributed to indium surface segregation, resulting in leftover In on the surface that does not form InN at these elevated temperatures. A model for adlayer buildup and consumption is developed, and a key RHEED signature is identified as the onset of surface segregation. The thickness of the adsorbed metal at this onset is found to be between 1 and 2 ML for various compositions. Samples grown throughout the miscibility gap using this technique exhibited single phase XRD spectra and < 1 nm RMS roughnesses (Fig. 2). High hole concentrations in p-InGaN are also achieved by MME (Fig. 3).

At the low temperatures required for high indium-content InGaN, an intermediate growth regime in MBE does not exist. Thus, traditional MBE cannot produce metal-rich InGaN without droplets or surface segregation. Because the onset of surface segregation ($1 < x < 2$ ML) occurs below droplet accumulation (< 2.3 ML), this study confirms that for metal-rich InGaN growth, some form of modulation must be employed.

This work was supported by the Air Force Office of Scientific Research under a basic science grant managed by Kitt Reinhardt.

9:20am **TF-FrM4 Aging Effect on the Hydrophilicity of Metal Nanorod Arrays.** *N. Albarakati, D. Ye*, Virginia Commonwealth University

Time dependent wettability of nickel nanorod arrays were studied by measuring the water contact angles on the samples. Nickel nanorods arrays were deposited on silicon substrates by sputtering oblique angle deposition with an 85° incident angle. The substrates are rotated at a speed of 0.5 rps by a stepper motor. Samples with varying nanorod heights were prepared. Water contact angles were measured for each sample on a sequence of time up to three months. The water contact angles on the fresh nanorod arrays are less than 10° . However, the contact angle increases with time after the samples were exposed to air. We observed that the contact angles on the samples with short nanorods increase quickly to an angle close to hydrophobic and that on the samples with long nanorods increase slowly and remain in the hydrophilic region. X-ray photoelectron spectroscopy was employed to study the change of the surface composition due to oxidation and hydrocarbon contamination. We believe that the change of water contact angles is due to the accumulation of hydrocarbon on the nanorod surface.

9:40am **TF-FrM5 Cubic ZnMgO and NiMgO for UV-C Applications.** *R.C. Boutwell, J.W. Mares, M. Wei, W.V. Schoenfeld*, University of Central Florida

We will report on two new ternary cubic oxides offering close lattice matching to MgO, ZnMgO and NiMgO, and compare the properties of films grown by both RF Plasma-Assisted MBE and a much more economical sol-gel deposition process. Using both methods we have successfully demonstrated band gap tuning in the UV-C spectral region, with ZnMgO films producing band gaps ranging from ~ 5 eV to 7.8eV and NiMgO films having band gaps ranging from 3.5eV to 7.8 eV. XRD revealed 2θ FWHM values as narrow as 0.19° , and atomic force microscopy of ZnMgO films demonstrated surface roughness of 3.4nm with NiMgO films having roughness below 1Å. Optical, compositional, and morphological results from films produced using both synthesis methods will be presented. We will also report on initial photodetectors with 5µm interdigitated fingers that produced peak responsivities of 12 mA/W at 250 nm.

10:00am **TF-FrM6 Growth of Fe-Pd Nanoparticles and Thin Films via Pulsed Laser Deposition and the Matrix Assisted Pulsed Laser Evaporation of Metal Based Acetates**, M.A. Steiner, J.M. Fitz-Gerald, University of Virginia

Nanoparticle and thin film magnetic alloys of 3d-4d/5d metals such as Fe-Pt, Co-Pt, and Fe-Pd are of technological interest due to their ordered L1₀ tetragonal phase which exhibits high magnetocrystalline anisotropy. Hard magnetic properties combined with ductility and corrosion resistance make these alloys ideal for applications including micro-electro-mechanical systems and ultra high-density magnetic storage. These materials have also been shown to possess a unique strain-induced chessboard eutectoid microstructure between their hard L1₀ and soft L1₂ magnetic phases that features exchange coupling effects. Within this class of materials Fe-Pd alloys possess a low order-disorder transition temperature making them a good candidate for ordered structure studies.

Nanoparticles and thin films of eutectoid (61.5 at% Pd) Fe-Pd were deposited by pulsed laser deposition. Additionally ordered nanoparticles were deposited utilizing a novel technique involving the matrix assisted decomposition of metal-organic precursors. Nanoparticles and films were subsequently characterized by x-ray diffraction, vibrating sample magnetometry, high resolution transmission electron microscopy, and scanning electron microscopy.

10:40am **TF-FrM8 Surface Plasmon Resonance Excited in RuO₂ Films Grown on Glass and on Crystalline (001) TiO₂**, L. Wang, K. Yang, C. Clavero, E. Crisman, V. Dinavahi, I. Novikova, R.A. Lukaszew, College of William and Mary

PLEASE NOTE YOU MUST IDENTIFY A DIFFERENT PRESENTER FOR THIS ABSTRACT. YOU MAY PRESENT ONE PAPER ONLY (ORAL OR POSTER) AT THE CONFERENCE. YOU ARE ALREADY LISTED AS PRESENTER OF ABSTRACT #554Surface Plasmon Resonance (SPR) excitation in metallic thin films and nanostructures has been widely applied to study biomolecules absorption, bio-imaging, bio-sensing, and sensitivity enhanced Raman spectroscopy [1,2,3]. However, although the theoretical principles underlying SPR excitation are applicable to any conductive material, only metals, and in particular Au and Ag, have been considered for practical applications. Here we investigate SPR excitation in a conducting metal oxide such as RuO₂. Due to the optical properties frequency dependence, SPR excitation is more intense in the infrared region for this material. The RuO₂ thin films investigated were grown using reactive magnetron sputtering on two different substrates resulting on amorphous RuO₂ films when deposited on glass and crystalline RuO₂ films when epitaxially deposited on TiO₂ (001) substrates. We have used Atomic Force Microscopy (AFM) and Reflection High-Energy Electron Diffraction (RHEED) to characterize the surface morphology and microstructure of these samples. Four-point probe was used to investigate the electrical conductivity properties and ellipsometry was used to characterize the optical properties of the films. We will show a comparison of the physical properties including the SPR excitation between these two kinds of thin film RuO₂ samples. The investigation of SPR in conducting metal oxide materials provides a significant advancement for thin film characterizations as well as opens new venues for photonic and plasmonic applications.

This work was financially supported by NSF (DMR-1006013).

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11:00am **TF-FrM9 Towards Achieving a High Degree of Carbon Ionization in Magnetron Sputtering Discharges**, A. Aijaz, K. Sarakinos, D. Lundin, U. Helmersson, Linköping University, Sweden

Physical vapour deposition (PVD) methods, which are characterized by highly ionized deposition fluxes of the film forming species, provide added means for the synthesis of tailor-made materials. They can, for instance, facilitate the growth of meta-stable phases, nanostructures as well as selective deposition on complex-shaped substrates. In such methods, the generation of highly ionized deposition fluxes stems from high electron (plasma) densities. Cathodic arc and pulsed laser deposition are examples of such discharges where electron densities in the order of 10²¹ m⁻³ can be obtained. These techniques, while providing as high as 100% degree of ionization of the deposition flux, exhibit several drawbacks, such as macroparticle ejection from the target, lack of lateral film uniformity, and in some cases are difficult to scale up. Magnetron sputtering based techniques

are technologically more relevant, owing to their inherent advantages of conceptual simplicity, upscalability, and film uniformity. However, electron densities in magnetron discharges are significantly smaller, in the range of 10¹⁴–10¹⁶ m⁻³ and therefore generation of a highly ionized deposition flux is often difficult. This difficulty is overcome by high power impulse magnetron sputtering (HiPIMS), where plasma densities on the order of 10¹⁹ m⁻³ are achieved. HiPIMS has been successful in enhancing the ionization for most common metals (Cu, Al, Ta, Ti), but it is challenged when non-metals such as carbon is considered. Previous investigations have shown that C⁺/C ratio in HiPIMS does not exceed 5%, which does not provide efficient control over the physical properties and synthesis of carbon in various technologically relevant forms, e.g. tetrahedral amorphous carbon. In the present study we address the low degree of ionization of carbon in magnetron discharges. We have developed a new HiPIMS based process, which provides a plasma characterized by high electron temperature and plasma density as determined by time-resolved Langmuir probe measurements. The C⁺ ion energy distribution functions (IEDFs) determined by time-averaged energy resolved mass spectrometry demonstrate an energetic C⁺ ion population and an overall five-fold increase of the C⁺ ion fraction as compared to standard HiPIMS methods. The enhanced ionized fraction of carbon facilitates the growth of carbon films with mass densities as high as approx. 2.8 g/cm³ as determined by high resolution x-ray reflectivity measurements. Determination of the D-peak to G-peak ratio (I(D)/I(G)) and full width at half maximum of the G-peak in Raman spectra indicate that the films contain a large fraction of diamond-like bonded (sp³) carbon.

11:20am **TF-FrM10 Kinetics of Sputtered Metal Film Growth on Vertically Aligned Carbon Nanotube Arrays**, C. Muratore, A. Reed, A. Waite, J. Bultman, J. Hu, T. Smith, A.A. Voievodin, Air Force Research Laboratory

Controlling the surface morphology of metallized arrays of vertically aligned nanotubes (VACNTs) is useful for diverse technological applications, such as interface materials for thermal management of high-heat flux electronics and electrical contacts for MEMS switches. We have observed variation of the morphology of metal films sputtered on carbon nanotubes, ranging from thin continuous films surrounding individual bundles of carbon nanotubes along their entire length for tubes up to 100 microns in length, to metal canopies covering the surface, with only minimal penetration (10–20 microns) into the nanotube forest. There is a strong link between flux of metal ions and their kinetic energy and the morphology of metal films of technological interest, including titanium, nickel, copper, gold and aluminum. To explore the mechanisms dictating metal film architectures on VACNT arrays, we systematically altered the flux and energy of incident metal and inert gas ions. These processing conditions were characterized using a mass spectrometer and energy analyzer adjacent to VACNT substrates. For conditions of interest, film growth was carried out for different times in an ultra high vacuum processing chamber, followed by electron microscopy of VACNT film cross sections, which were examined to observe different stages of growth and identify mechanisms of film nucleation and growth on nanotube sidewalls and tips. Comparison of growth kinetics of metal films on planar (002) graphite surfaces to that observed on VACNTs was used to identify effects of curvature on film growth. Switch performance was shown to be strongly dependent on morphology.

11:40am **TF-FrM11 Crystallographic Orientation of Vanadium Dioxide Nano-Grains on Various Single-Crystal Sapphire Substrates**, F. Rivera, Brigham Young University, J. Nag, R.F. Haglund Jr., Vanderbilt University, R. Davis, R. Vanfleet, Brigham Young University

Vanadium dioxide (VO₂) is a material of particular interest due to the reversible semiconductor to metal phase transition that VO₂ exhibits near room temperature (~ 68 °C) and the accompanied hysteresis. Recent studies suggest that external stresses applied to VO₂ crystals have an effect on the transition temperature and hysteresis. Thin films of VO₂ were deposited on three different cuts of sapphire by Pulsed Laser Deposition (PLD). Electron Back-Scattered Diffraction (EBSD) was used to study the orientation of the crystalline VO₂ grains obtained and showed epitaxial relationships between the different single-crystal substrates. A predominant family of crystallographic relationships is present in all cuts of sapphire wherein the rutile VO₂ {001} planes tend to lie parallel to the substrate's {10-10} and the rutile VO₂ {100} planes lie parallel to the substrate's {1-210} and {0001}. This family accounts for the majority of the VO₂ grains observed on all substrates with specific orientations (and stresses) depending upon the substrate's normal direction. Transmission Electron Diffraction patterns taken from cross-section of particles of the A and R cut sapphire substrates helped to lift the ambiguity present in the rutile {100} axes. EBSD showed additional families of relationships in the C and R cuts of sapphire, most related to the aforementioned predominant family. Variations in the

transition temperatures of the deposited thin films mentioned in this study are attributed to the stresses generated by the epitaxial relationships.

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