Wednesday Morning, October 17, 2007

Thin Film

Room: 613/614 - Session TF-WeM

Thin Film and Nanoparticle Growth and Characterization

Moderator: J.M Fitz-Gerald, University of Virginia

8:00am **TF-WeM1 Dependence of Fiber Texture on Connectivity in Composite Thin Films**, ***J.M.E. Harper***, *D. Carlson, A.M. Brown, D.I. Filoti*, University of New Hampshire

The connectivity of metal-insulator composite thin films varies with composition from a continuous metal phase surrounding insulating islands, through a variety of interconnected networks, to disconnected metal islands within a continuous insulating phase. We show that the strength of the metal fiber texture correlates with the degree of metal connectivity. Composite thin films of Au-SiO_2 and Ag-Si were deposited using dual-source magnetron sputtering and the crystallographic texture was determined using x-ray pole figure measurements. For metal-rich compositions, we observe strong 111 Au or Ag fiber texture perpendicular to the substrate plane, similar to the fiber texture of pure fcc metal films. As the volume fraction of SiO_2 or Si is increased, the strength of the 111 fiber texture decreases monotonically until a random texture is observed. The composition at which the fiber texture is lost correlates well with the composition at which the metal component becomes discontinuous, as determined by resistivity and transmission electron microscopy measurements. We conclude that x-ray pole figure measurements of fiber texture can be used for non-contact determination of the connectivity of phases in composite thin films.

8:20am **TF-WeM2 Morphology Evolution during Growth of Epitaxial $Ti_{1-x}Al_xN$ and $Cr_{1-x}Al_xN$ Films onto MgO(100) and MgO(111)**, ***M. Beckers***, *H. Willmann, J. Birch,* Linköping University, Sweden, *J. v. Borany,* ROBL-CRG at ESRF, France, *P.H. Mayrhofer, C. Mitterer,* University of Leoben, Austria, *L. Hultman*, Linköping University, Sweden

Metastable $Ti_{1-x}Al_xN$ has found widespread industrial use as hard coating for cutting and forming applications, while the knowledge base for $Cr_{1-x}Al_xN$ on structure-property relations still evolves. Here, we report on growth studies of epitaxial $Ti_{1-x}Al_xN$ and $Cr_{1-x}Al_xN$ films deposited onto MgO(100) and MgO(111) substrates by reactive magnetron sputter epitaxy. Both orientations promote cube-on-cube epitaxial growth. However, transmission electron microscopy reveals a smooth single-crystal morphology for the MgO(100) and a facetted columnar morphology for the MgO(111) substrate. This can be ascribed to the highly anisotropic step energies for the corresponding nitride growth surfaces, resulting in a switch between layer-by-layer and island growth mode as characterized by in-situ x-ray diffraction experiments. High-resolution x-ray reciprocal space maps display that films deposited onto MgO(111) grow fully relaxed with lattice parameters that correspond well to literature values at the given compositions. The growth mode on MgO(100) substrates depends on the Al fraction. $Ti_{1-x}Al_xN$ films at low Al fractions that are well lattice-matched to MgO show pseudomorphic strained growth with a small percentage of in-plane strain relaxation due to interfacial misfit dislocations, and exhibit almost defect-free single-crystal morphology. On the contrary, less lattice-matched $(Ti,Cr)_{1-x}Al_xN$ films with x close to the AlN precipitation threshold show an initial pseudomorphic strained layer that relaxes for increasing film thickness. The relaxation starts with interfacial misfit dislocations that gradually evolve into a dislocation network along the {111}<110> slip system. For $Cr_{1-x}Al_xN$ films with an Al fraction of 0.6, this dislocation network is superimposed by crystals of first-order twins about [111] with the orientation relationship $Cr_{1-x}Al_xN$ (122) // MgO (100). The twins overgrow the primary (100) orientated film, likely due to the angular vicinity of fast growing (111) planes. These diverse relaxation mechanisms might be attributed to changed stacking fault energies for different Al fractions. Since polycrystalline $Ti_{1-x}Al_xN$ and $Cr_{1-x}Al_xN$ show AlN precipitation at grain boundaries during annealing, the observed morphology changes for different substrate orientation and stoichiometries have impact for the understanding of age hardening in these systems.

8:40am **TF-WeM3 A Mesoscopic View on Complex, Stress-Governed Phenomena in Submonolayer Ag-films on Pt(111) at High Temperature**, ***B. Poelsema***, *E. Van Vroonhoven*, University of Twente, The Netherlands

The growth of ultrathin silver films at 750 K on Pt(111) has been studied with LEEM. The STM-based previous reports on surface confined alloying in this bulk immiscible system are confirmed. This information is inferred from the evolution of the electron reflectivity as well as indirectly from the distribution of adatom islands indicative of highly unconventional nucleation behavior extending to extremely high coverages. De-alloying as previously reported is also confirmed basically. The in-situ mesoscopic data, however, reveal a number of previously unnoticed features. For instance de-alloying is accompanied by strong segregation effects. Platinum-rich disks evolve during de-alloying, showing up as persistent "dark spots" in a bright field measurement, irrespective of the energy of the probing electrons. Also no additional diffraction features spots are observed, indicative of the Pt-disks being highly disordered, amorphous or possibly liquid. In a very narrow coverage window around 85% of a monolayer µ-LEED measurements demonstrate a sudden stress relieve. At this point the de-alloying reaches a summit and the film temporarily releases stress by expansion. This goes together with enhanced segregation. Further along the route to monolayer completion we observe reentrant alloying which actually persists during the growth of a few more layers. Also the film quickly resumes its pseudomorphic structure.

9:00am **TF-WeM4 Field Emission Suppression from Stainless Steel Using Silicon Oxynitride Coatings**, ***N.D. Theodore***, *B.C. Holloway,* The College of William and Mary, *C. Hernandez-Garcia, H.F. Dylla,* Jefferson Lab, *D. Manos*, The College of William and Mary

We have developed a new RF inductively-coupled, plasma-based, reactive sputtering procedure to deposit high-purity silicon oxynitride (SiO_XN_Y) films. Oxynitride formation was verified using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). Using profilometry, we determined that increasing the nitrogen plasma pressure or the RF power raises the deposition rate. However, FTIR results show that adjusting the plasma pressure also altered the amount of bound nitrogen in the silicon oxynitride layer. The resulting silicon oxynitride coatings have also been characterized with Auger electron spectroscopy (AES), Rutherford backscattering spectrometry (RBS), and elastic recoil detection analysis (ERDA) to determine their elemental composition and density. This silicon oxynitride coating drastically reduced field emission from large area, stainless steel electrodes. High voltage tests showed that a polished, 180 cm^2, stainless steel electrode exhibited 27 µA of field-emitted current at 15 MV/m; however, by applying a silicon oxynitride coating to a similarly polished electrode, emission current was drastically reduced to less than 300 pA at 30 MV/m. The field emission from these silicon oxynitride coatings seems to follow the electron emission mechanisms proposed by Schottky and Poole-Frenkel. Both of their emission equations predict that increasing the band gap, dielectric constant, and electron affinity of the silicon oxynitride coatings could further reduce field emission. Our most recent high voltage tests of two polished electrodes coated with a 'graded' silicon oxynitride layer supports these predictions; at 30 MV/m, the field emitted current was below 4 pA, the detection limit of our high voltage test system.

9:20am **TF-WeM5 A Study of Tungsten Silicon Nitride Films Used for Thermal Inkjet Printheads**, ***J. Wonnacott***, *E. Whittaker, G.S. Long, B. Risch*, Hewlett-Packard Company

Thin ternary films of tungsten and silicon nitride (WSiN) have been studied for use as heater resistors in thermal inkjet printheads. Product applications require films with the appropriate bulk resistivity and thermal stability at process and performance temperatures. A typical resistor may be required to heat and eject several billion ink drops over the lifetime of the printhead. The heating of the WSiN causes changes in film properties that adversely effect ink drop ejection and the subsequent print quality. Specific electrical annealing procedures have been used to stabilize the as deposited WSiN film for resistor firing conditions during printing. Various analytical techniques including X-Ray Diffraction (XRD), X-Ray Reflectance (XRR), X-Ray Fluorescence (XRF), X-Ray Photoelectron Spectroscopy (XPS), and Transmission Electron Microscopy (TEM) have been used to study the WSiN film characteristics after the initial Physical Vapor Deposition (PVD), after actual use in printheads, and after simulated use by rapid thermal processing on blanket deposited films. The PVD processing parameters and WSiN target composition have been varied to study the impact the resulting performance of the resistor film. Employing these analytical techniques optimized resistor films have been explored for high temperature stability characteristics.

9:40am **TF-WeM6 Ti as an Interface Stabilizer for Fe-Al Interfaces***, ***W. Priyantha***, *A. Comouth, A. Kayani, M. Finsterbusch, H. Chen, M. Kopczyk, D. Tonn, R.J. Smith,* Montana State University*, D.E. McCready, P. Nachimuthu*, Pacific Northwest National Laboratory

The use of ultra-thin metal interlayers to stabilize metal-metal interfaces and to limit interdiffusion has drawn much attention over the past few years, driven by a variety of technological applications. Earlier, we reported using a Ti monolayer as an interlayer to promote epitaxial growth and to minimize diffusion at the Fe/Al(001) interface. These findings encouraged us to explore the use of interlayer structures for thin films of technological interest deposited on Si wafers using RF sputtering. AlFe and FeAl metal bi-layers, with and without a Ti stabilizing interlayer, were studied using Rutherford backscattering (RBS) and X-ray reflectivity (XRR). Analysis revealed that FeAl and AlFe films without a Ti interlayer on SiO2/Si wafers showed considerable Fe-Al intermixing, especially when the Fe layer was deposited on top of the Al layer. With a Ti interlayer present the interfaces exhibited less interdiffusion.

* This work was supported by the National Science Foundation, NSF Grant DMR 0516603.

10:40am **TF-WeM9 Size-Selected Clusters: From 3D Atomic Structure to Applications in Biochips**, ***R.E. Palmer***, The University of Birmingham, UK **INVITED**

In this talk I will address both atomic-scale characterisation and biological applications of size-selected atomic clusters. Today's advancements in nanotechnology present new challenges for the quality, speed and precision of nanostructure characterization. Here we show that the new generation of aberration-corrected scanning transmission electron microscopes (STEM), coupled with simple imaging simulation, is capable of providing three-dimensional structural information[1] with atomic resolution in a single shot, revealing not only the size but also the shape, orientation and atomic arrangement, for size-selected gold nanoclusters that are preformed in the gas phase and soft-landed on an amorphous carbon substrate. The structures of gold nanoclusters containing 309 (@+=@5%) atoms can be identified with either decahedral, cuboctahedral or icosahedral geometries. The work illustrates a new and efficient means to study the atomic structure and the stability of supported, ultra-small metal clusters in the nanometre range, e.g. catalyst and extracellular particles, with single atom sensitivity. The controlled deposition of such size-selected Au clusters, of size 1-10nm, also provides a route to the fabrication of novel surface binding sites for individual biological molecules, notably proteins. We report the pinning[2,3] of size-selected Au_N clusters (N = 1-100) to the (hydrophobic) graphite surface to create films of arbitrary, sub-monolayer density. Gold presents an attractive binding site for sulphur and thus for cysteine residues in protein molecules. AFM measurements in buffer solution[4,5] show that GroEL chaperonin molecules (15 nm rings), which contain free cysteines, bind to the clusters and are immobilised.[5]. Peroxidase[6] and oncostatin molecules behave similarly. By contrast, green fluorescent protein (GFP) does not bind, consistent with detailed analysis of the protein surface; the cysteine residues lie in the interior of the folded protein. The results provide "ground rules" for residue-specific protein immobilisation by clusters. The extension of the approach to optical surfaces is enabling the production of prototype biochips (microrarrays) for protein analysis, e.g., early stage cancer-marker detection.

[1] Z.Y. Li, J. Yuan, Y. Chen, R.E. Palmer and J.P. Wilcoxon, Adv. Mater. 17 2885 (2005).

[2] S. Pratontep, P. Preece, C. Xirouchaki, R.E. Palmer, C.F. Sanz-Navarro, S.D. Kenny and R. Smith, Phys. Rev. Lett. 90 055503 (2003).

[3] S.J. Carroll, S. Pratontep, M. Streun, R.E. Palmer, S. Hobday and R. Smith, J. Chem. Phys. (Comms) 113 7723 (2000); M. Helmer, Nature (News & Views) 408 531 (2000).

[4] R.E. Palmer, S. Pratontep and H.-G. Boyen, Nature Materials 2 443 (2003).

[5] C. Leung, C. Xirouchaki, N. Berovic and R.E. Palmer, Adv. Materials 16 223 (2004).

11:20am **TF-WeM11 Formation of Robust, Freestanding Tantalum Oxide Films with Controlled Morphology**, ***P. Kruse****, S. Singh*, McMaster University, Canada

We have previously shown that electropolishing of tantalum in concentrated acid mixtures can reproducibly lead to very flat surfaces with dimples tens of nanometers in diameter, regular in shape, monodispersed in size and arranged in highly ordered arrays which even transverse grain boundaries. In this work, we are demonstrating the anodic growth of nanometer thick, detachable, amorphous tantalum oxide films with tuneable morphology (porosity) on these surfaces. Large (sqcm) sections of these flexible tantalum oxide films can be separated as sheets from the base tantalum surface by a Lift- Off-Float-On technique. The sheets can then be transferred to a wide variety of substrates, like Si wafers, glass slides, TEM grids etc. We have thoroughly characterised the films and are studying their growth conditions with the intention of gaining even better control over their morphology. Potential applications include nanotechnology, photonics and catalysis.

11:40am **TF-WeM12 Fabrication of Poly-Crystalline Silicon Thin Film by Using a Neutral Beam Deposition Method at a Low Temperature**, ***S.-K. Kang***, SKKU Advanvced Institute of Nano Technology (SAINT), Korea*, B.J. Park, S.W. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea

Poly-crystalline silicon (p-Si) thin films are generally applied to electronic and optoelectronic devices because of its higher carrier mobility than that of amorphous silicon (a-Si) film and excellent potential in fabricating higher speed, higher resolution and brighter TFT-LCD. Currently, p-Si film is fabricated by re-crystallizing an a-Si film with post-treatment method such as excimer laser annealing (ELA), solid phase crystallization (SPC), metal-induced crystallization (MIC), etc. However, these troublesome post-treatment requires high processing temperature (500~600 °C) which is higher than glass transition temperature. Furthermore, throughput and cost issues will become more critical as the substrate size is increased. Therefore, to simplify process steps and increase production throughput, direct p-Si deposition at a low temperature is definitely required. Chemical assisted neutral beam deposition (CANBD) is investigated as a new approach to fabricate and develop p-Si which has more excellent properties in this study. The difference of CANBD to the conventional PECVD is that the p-Si thin film formation energy of CANBD is supplied by controlled neutral beam energies. Decomposition of source gas (SiH_4) is enhanced by assisted neutral beam which is generated by low energy Ar neutral beam, resulting in the formation of low temperature p-Si. The p-Si made by the neutral beam deposition method shows better electrical property compared to silicon deposited by other processes at low temperature. Resistivity of grown silicon film is measured by 4-point probe measurement. Carrier concentration and carrier mobility are evaluated by Hall measurement. Film crystallinity is investigated by HRTEM, Raman spectroscopy, and X-ray diffraction analysis.

12:00pm **TF-WeM13 Properties of Nano-Crystalline Silicon Grown by Internal Linear Antenna-Inductively Coupled Plasma-type Plasma-Enhanced Chemical Vapor Deposition**, ***H.C. Lee****, H.B. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea

Considerable attentions have been paid to hydrogenated nano-crystalline silicon film deposited a low temperature because of its promising application to stable high efficient solar cell, thin film transistors, and color sensors. In particular, the development of nano-crystalline silicon film is one of the key issues in developing active matrix liquid crystal displays (AMLCD) and active matrix organic light emitting displays (AMOLED). For this purpose, good field effect mobility in the range of $2\sim5cm^2/Vs$ is required to have high quality resolution displays along with higher stability than amorphous silicon thin films due to the less hydrogen bonded to silicon in the film. In this study, nano-crystalline silicon was deposited using an internal-type inductively coupled plasma (ICP) source, and the properties of the nano-crystalline silicon were investigated as a function of operating pressure, SiH_4/H_2 gas mixture, additive gas, etc. Especially, the effect of initial nucleation condition by controlling gas combination on the crystalline size and crystalline percentage was investigated. The crystallinity and orientation of the deposited hydrogenated silicon thin film was estimated by using micro-Raman spectroscopy (Invia Basic Renisaw) and a high-resolution X-ray diffraction (HRXRD, D8 Discover Bruker). The dark conductivity was calculated by using the I-V characteristics of the films. Field effect mobilities were measured by the fabricated thin film trasnsistors. At the temperature lower than 200°C, nano-crystalline having the size of 30nm could be deposited and the volume fraction of the crystalline calculated by the Raman spectroscopy was higher than 40%. In the presentation, more detailed characteristics of nano-crystalline film deposited by the internal linear ICP film will be discussed.

Authors Index

Bold page numbers indicate the presenter