Tuesday Afternoon, October 21, 2008

Electronic Materials and Processing
Room: 210 - Session EM-TuA

Complex and Multifunctional Oxides
Moderator: A. Herrera-Gomez, Cinvestav-Unidad Queretaro, Mexico

1:40pm **EM-TuA1 Understanding Metastable Structures in Sputter Deposited Hafnia-Alumina, Hafnia-Zirconia, and Hafnia-Titania Nanolaminates**, ***C.R. Aita***, *E.E. Hoppe, M.C. Cisneros-Morales*, University of Wisconsin-Milwaukee

The formation of metastable nanocrystalline phases during reactive sputter deposition of HfO_2-Al_2O_3, HfO_2-ZrO_2, and HfO_2-TiO_2 nanolaminates on unheated substrates is discussed. In addition to being technologically useful, these nanolaminates are archetypical because their bulk pseudobinary phase diagrams predict three different modes of interfacial mixing: complete immiscibility (HfO_2-Al_2O_3), complete miscibility (HfO_2-ZrO_2) and limited miscibility without a common end-member lattice (HfO_2-TiO_2). Of these individual constituents, all but Al_2O_3 (which has structural complexity) form both intralayer and interfacial nanocrystalline phases. However, these are often not bulk equilibrium phases and are termed here metastable. This paper addresses two questions: (1) By what mechanisms do these metastable phases arise? (2) How thermally stable are they at temperatures that a device may see during routine processing? We discuss metastable phases resulting from finite crystal size effects (tetragonal and orthorhombic HfO_2 in HfO_2-Al_2O_3) and heteroepitaxy (tetragonal $Hf_{1-x}Zr_xO_2$ in HfO_2-ZrO_2). We discuss the formation of a complex interface in HfO_2-TiO_2 nanolaminates that includes monoclinic $Hf_{1-x}Ti_xO_2$, a metastable phase which here results from a second order phase transition of orthorhombic $HfTiO_2$ (a stable interfacial phase) to accommodate the larger Hf atom at aHfO_2-on-TiO_2 interface. In all cases, these metastable structures represent self-assembly into the lowest possible energy structures in the absence of long-range diffusion.

2:00pm **EM-TuA2 Band Edge Engineering of Barium Strontium Titanate Thin Films by Ni-doping Driven Changes in Bonding Symmetry of Ti and O**, ***H. Seo***, North Carolina State University, *Y.B. Kim*, Hanyang University, Korea, *G. Lucovsky*, North Carolina State University

Suppression of the transition from direct to trap-assisted Fowler-Nordheim tunneling in metal-insulator-metal (MIM) capacitors is reported when approximately one percent Ni-doped barium strontium titanate (BST) thin film dielectrics are substituted for undoped BST. A significant leakage current reduction and improved breakdown resistance are observed for Ni-doped BST compared to undoped BST. The origin of such a large reliability enhancement of Ni-doped BST was investigated by spectroscopic studies includng spectroscopic ellipsometry (SE) and synchrotron X-ray absorption spectroscopy (XAS) measurements. For Ni-doping at the one percent level, the spectral dependence of the imaginary part of the complex dielectric constant,ε_2, obtained from SE shows significant differences in the band edge trap depth and density relative to undoped BST revealing defect states 0.2 eV shallower in energy and seven-fold reduced in density. This change in the defect state energy in Ni-doped BST is accompanied by a change in symmetry of the Ti atom empty t_{2g} states from either monoclinic/orthorhombic to tetragonal: the two t_{2g} states higher lying in the undoped BST O K1 edge and spectroscopic ellipsomtery ε_2 spectra are merged into to a single state in Ni-doped BST, while preserving the average t_{2g} d-state energy. The physical origin of these changes in the band edge defects is the substitution of divalent Ni^{2+} for tetravalent Ti^{4+} in band edge divacancy defects. Electrical measurements of J-V traces for Ni-doped BST show a symmetric direct tunneling process while undoped BST revealed asymmetric trap assistant tunneling/Fowler-Nordheim conduction process responsible for a rapid current rise. The results on improved Ni-doped BST suggest an approach for BST MIM capacitor in gigabit dynamic random access memory as well as identify a novel band edge state engineering approach based on transition metal doping which should be applied to other oxides with perovskite structures, e.g., $PbTiO_3$ and $PbZrO_3$.

2:20pm **EM-TuA3 Growth and Properties on Multifunctional Epitaxial Oxide Structures**, ***C.H. Ahn***, Yale University **INVITED**

Complex oxides exhibit a wide range of phenomena, including magnetism, ferroelectricity, superconductivity, and colossal magnetoresistance. The epitaxial growth of these complex oxides in crystalline heterostructure form allows these functionalities to be combined and utilized for fundamental science and technical applications. The ability to integrate this class of materials with others, and silicon in particular, multiply these research and technical opportunities. To fully realize this potential, the interfaces between materials must be understood, controlled, and optimized on the atomic level. We have developed techniques for the determination of such interface structures with sub-Angstrom accuracy, and informed by first-principles calculations, we have developed real-space models for complex oxide heteroepitaxy.

3:00pm **EM-TuA5 Structure and Properties of Polar Oxide Hetero-Interfaces: Hematite on Magnesia (111) and Alumina (0001)**, ***M. Gajdardziska-Josifovska***, *P. Dey, K. Pande, A. Celik-Aktas, S.H. Cheung, M. Weinert*, University of Wisconsin – Milwaukee, *S.A. Chambers*, Pacific Northwest National Laboratory

The most fundamental differences between oxide surfaces and those of metals and elemental semiconductors arise from the strong ionic character of the metal-oxygen bond, presenting opportunities to use polarity in design of novel oxide hetero-interfaces. For example, controlled growth of hematite and magnetite films has been a subject of intense studies inspired by their many technological applications in catalysis, gas sensing, sequestration of toxic metals, and magnetic devices. Surface and interface polarities add novel and desirable properties to these complex multi-functional oxide materials. In this work we integrate experimental and theoretical methods to study the atomic structure and electronic properties of hematite films grown on unreconstructed hydrogen-stabilized and on reconstruction stabilized polar oxide surfaces. We find that different modes of polar surface stabilization have profound effects on the growth mode, phase composition and magnetic properties of polar hematite films grown by OPA-MBE on magnesia and alumina single crystal substrates. Growth on reconstruction stabilized magnesia results in formation of an interfacial magnetite-like phase that offers a new way to create materials of interest in spintronics. This polarity-induced self-organized magnetite buffer persists after growth, in contrast to the transient maghemite detected by recent in-situ studies of the early stage of growth on unreconstructed sapphire surfaces. Indeed, pure phase Fe_2O_3 (0001) that is macroscopically antiferromagnetic is obtained on the hydrogen stabilized unreconstructed MgO(111) and Al_2O_3(0001) substrates. Theoretical modeling by DFT predicts unusual ferrimagnetic properties at the atomically abrupt α-Fe_2O_3 (0001)/MgO(111)-(1x1) interfaces.

4:00pm **EM-TuA8 The Metal-Insulator Transition in Vanadium Dioxide: A View at Bulk and Surface Contributions for Thin Films and the Effect of Annealing**, *W. Yin, K. West, J. Lu*, University of Virginia, *Y. Sun*, Stanford University, *S.A. Wolf*, ***P. Reinke***, University of Virginia

Vanadium dioxide is investigated as potential oxide barrier in spin switches, and undergoes a first order metal-to-insulator (MIT) transition at 340 K, which will provide an actively switchable interlayer as a critical element in the device. In order to incorporate VO2 layers in a complex multi-layer devices it is necessary to understand the relation between bulk and surface/interface properties in order to optimize device performance. Our study focuses on the comparison of the MIT in the bulk and at the surface of thin VO2 layers, and establishes an irreversible modification of the crystallite structure and surface for temperatures exceeding the MIT. The surface modification impacts on the strategies which are employed to build the magnetic contact on a VO2 layer. Highly oriented VO2 thin films were grown on (0001) sapphire single crystal substrates with a novel growth technique called reactive bias target ion beam deposition. In the analysis of the VO2 films we employed bulk-sensitive methods (x-ray diffraction, transport measurements) and surface sensitive techniques (photoelectron spectroscopy, STM). The samples were subjected to a heating cycle with repeated cycling through the MIT, and annealing to at least 100 K above the MIT. The VO2 films exhibit the the transition from the monoclinic to the tetragonal phase, with the concurrent change in conductivity by 10-3. The cycling across the MIT temperature and annealing have no impact on the abruptness and magnitude of the transition, and the bulk-dominated process exhibits therefore the requisite long-term stability. The stability of the surface with respect to annealing is dramatically lower, and electronic and structural changes occur. The observation of the valence band with PES as the film transits through the MIT temperature and the subsequent annealing clearly show that the surface partially retains its high-temperature metallic character. The onset of oxygen depletion at the surface is held responsible for this behavior, and a critical issue in tailoring the interface to the top contact. In addition to the changes on an atomic level, the annealing triggers a rearrangement in the orientation and shape of the crystallites, which is shown in a quantitative analysis of the STM images of the VO2 surface. The in-situ observation of the temperature-induced changes of the surface with STM will provide additional information on the oxygen-depletion and morphological changes in the VO2 surface.

4:20pm **EM-TuA9 Some High k Potential for MIM or RRAM Applications**, ***C. Vallee***, *P. Gonon, E. Gourvest, C. Jorel, M. Mougenot, M. Bonvalot,* CNRS - France, *V. Jousseaume,* CEA/LETI/D2NT - France, *O. Joubert*, CNRS - France

Metal Insulator Metal (MIM) capacitors in silicon analog circuit applications have attracted great attention due to their high conductive electrodes and low parasitic capacitance. Silicon oxide and nitride were commonly used in conventional MIM capacitors. Though they can provide good-voltage linearity and low temperature coefficients, their capacitance density are limited due to their low dielectric permittivity. In order to increase the surface density of MIM capacitors, several technological ways are investigated: realization of capacitors according to 3D architectures and integrating high or medium k materials. First MIM high k investigations dealt with Ta_2O_5. Among various high k dielectric materials, medium k such has HfO_2, ZrO_2 and rare earth oxides should give better performances owing to larger band gap than Ta_2O_5 and higher permittivity than silicon nitride. Flash technology is expected to reach its limits by the beginning of the next decade. In this context, existing research efforts are exploring a variety of novel memory concepts including: i) FeRAMs (Ferroelectric RAMs), ii) MRAMs (Magnetic RAMs), iii) PCRAMs (Phase Change RAMs). More recently, the semiconductor research community has shown a growing interest for RRAM (Resistive RAM) which exploits the resistive switching properties of oxides (mainly NiO) to store information. Its main advantages are good compatibility with current CMOS technology, high speed, and low power switching and good temperature stability of the data retention. A PVD process is usually used for the deposition of the oxide. Hence, for both applications (MIM capacitors and RRAM devices) high k dielectrics deposited with a low thermal budget should be a solution. This study is then focused on the deposition and characterization of several high k dielectrics such as HfO_2 or Y_2O_3 on different metallic electrodes (Pt,TiN,…) for MIM capacitors or RRAM devices. These materials are deposited by ALD or PE-MOCVD processes. The electrical behavior of the structures will be presented and discussed in terms of capacitance density, capacitance linearity and current-voltage characteristics with a special care to the switching mechanism of the high k RRAM. They will be correlated to chemical analysis results (XPS, ATR and FUV-SE), with special attention devoted to metal/oxide interface investigations.

5:00pm **EM-TuA11 Study of Luminescence and Epitaxy of Green Light Emitting ZnO Thin Films Prepared by MOCVD**, ***J.H. Liang***, *Y.J. Chen, J.H. Du, H.Y. Lai*, National Dong Hwa University, Taiwan

ZnO is one of the potential candidates for application on the green light LED, since ZnO has a broad PL peak in the green light region. Since the green light emission is caused by defect level transition in ZnO, epitaxial relationship could affect the behavior of green light emission due to the formation of different types of defects. Therefore, we studied intensively the dependence of luminescence of the ZnO film on the epitaxial relationship between film and substrate in order to get high intensity of green light emission. In our experiment, we prepared ZnO thin films on sapphire substrates by metal organic chemical vapor deposition (MOCVD), using dimethylzinc (DMZn) and oxygen, respectively, as zinc and oxygen source. We changed the Ⅵ-Ⅱ ratios and the growth temperature, and annealed the ZnO thin film at various temperature of 600°C - 1000°C in three kinds of atmospheres (Argon, nitrogen and oxygen). We used XRD to analyze the crystal structure, PL to analyze light emission, FESEM to observe the morphology and TEM to observe the epitaxial relationship between the film and the substrate. We reported the successful growth of dense (002)-oriented ZnO thin films with nearly 100 nm of grain size. We found that the XRD intensity of (002) and the grain size of ZnO grown under all three kinds of atmospheres increase with increasing temperature. We also found that the intensity of UV and green light emission were the highest at 1000°C in oxygen atmosphere, and the improvement of the intensity of green light emission was even more significant. We suggested that the defects of oxygen dominate the intensity of green light emission. We will show the TEM results about epitaxial relation between the film and the substrate to prove that there are 30-degree rotated epitaxial relationship between the film and the substrate. We will discuss about how the epitaxial relationship may affect the green light luminescence.

5:20pm **EM-TuA12 Investigation of Conductive Channel on GaInZnO Surface**, ***J. Lee***, *J. Chung, H.I. Lee, E. Lee, T. Kim, D. Kang,* Samsung Advanced Institute of Technology, Korea, *H.J. Kang*, Chungbuk National University, Korea

GaInZnO (GIZO) is a promising material for oxide thin film transistor which has transparent and high electric mobility. However GIZO has very sensitive to ambient environment. To understand the surface sensitive electrical property of GIZO, the physical properties of GIZO surfaces such as energy band gap, work function, and surface composition were investigated at the GIZO (70nm thick) fabricated by radio frequency sputter deposition on Si(100) and Glass substrate. The energy band gap of GIZO was measured using electron energy loss spectroscopy (EELS) against the energy of primary electron beam. The energy band gap of GIZO (Ga:In:Zn=3:2:1) was increased from 3.0eV to 3.5eV when the energy of primary electron beam increased from 300eV to 2000eV. Because of lower the primary electron beam energy of EELS, more sensitive to of surface, the result says that the energy band gap of surface is about 0.5eV lower than that of bulk of GIZO. When the Ga concentration in the GIZO increased from Ga:In:Zn=2:2:1 to 4:2:1, the energy band gap slightly increased from 3.3eV to 3.6eV. A depth profiling analysis of GIZO by Secondary Ion Mass Spectrometry (SIMS) indicated that GIZO was divided by 4 layers such as Zn+Ga rich, Ga rich, In rich, and balanced GIZO layers. The thickness of altered layer was about 3nm. The concentration of Zn at the surface was higher when the oxygen partial pressure during sputter deposition was higher. The Zn+Ga rich layer was just top monolayer (~0.2nm thickness). The thickness of Ga rich layer was about 0.45nm. The thickness of altered layer of GIZO was well agreement with that of estimated by EELS results. The previous results suggest the existence of a conductive channel on GIZO surface. The characteristics of GIZO based thin film transistor are strongly influenced by the conductive channel which formed near surface. In this report, the existence of conductive channel on GIZO surface will be discussed in detail.

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