

# Wednesday Afternoon, October 17, 2007

## Electronic Materials and Processing

Room: 612 - Session EM-WeA

### Growth and Characterization of Complex Oxides

**Moderator:** C.H. Swartz, University of Canterbury, New Zealand

1:40pm **EM-WeA1 Spatially and Energy Resolved Imaging of Nucleation Centers in Ferroelectrics**, *S.V. Kalinin, S. Jesse, B.J. Rodriguez*, Oak Ridge National Laboratory, *I. Vrejoiu, D. Hesse, M. Alexe*, Max Planck Institute of Microstructure Physics, Germany, *Y.H. Chu, R. Ramesh*, University of California, Berkeley, *S. Choudhury, L.Q. Chen*, Pennsylvania State University, *E.A. Eliseev, A.N. Morozovska*, National Academy of Science of Ukraine

Ferroelectric polarization switching in non-volatile memory and high density data storage devices is governed by a number of nucleation centers that account for the experimentally observed low values of coercive fields. Despite 50 years of research, the microstructural origins of the Landauer paradox (switching fields corresponding to implausibly large nucleation activation energies) are still a mystery. Here, Switching Spectroscopy Piezoresponse Force Microscopy (SS-PFM) is developed as a quantitative tool for real-space mapping of polarization dynamics in ferroelectrics. SS-PFM is an extension of PFM spectroscopy that involves the acquisition and analysis of multiple hysteresis curves at every point in an image to extract maps of parameters describing the local switching properties. In nanodots, the non-uniform work of switching was imaged with ~10 nm resolution within 50 nm ferroelectric nanoparticles. In epitaxial lead zirconate-titanate thin film, the spatial distribution of the switching centers is obtained and the components of thermal (variation in depolarization energy of domain wall energy) and field (built-in polarization) disorder are extracted independently. Phase-field modeling of PFM switching yields nearly quantitative agreement between experimentally measured and calculated nucleation biases on the free surfaces and in the vicinity of the in-plane domains. This indicates that switching in PFM is close to the intrinsic thermodynamic limit. Further prospects of SS-PFM studies of ferroelectric devices and nanostructures for information technology are discussed. Research supported by the Division of Materials Science and Engineering, Basic Energy Sciences, U.S. Department of Energy at Oak Ridge National Laboratory, which is managed by UT-Battelle, LLC.

2:00pm **EM-WeA2 Strain-Enhanced Ferroelectrics and Multiferroics Grown by MBE\***, *D.G. Schlom*, Penn State University **INVITED**

Aided by theoretical predictions, we have used epitaxy and the misfit strain imposed by an underlying substrate to enhance the ferroelectric properties of SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, and BaTiO<sub>3</sub>/SrTiO<sub>3</sub> superlattices grown by MBE. The enhancements include shifting the paraelectric-to-ferroelectric transition temperature by hundreds of degrees and maintaining ferroelectricity in BaTiO<sub>3</sub> layers as thin as one unit cell in BaTiO<sub>3</sub>/SrTiO<sub>3</sub> superlattices. The effect of strain on EuTiO<sub>3</sub> will also be presented.

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2:40pm **EM-WeA4 Molten Salt Synthesis and Luminescence Properties of Rare-Earth Doped Yttrium Oxide and Rare-Earth Zirconate/Hafnate**, *Y. Mao, J. Dorman, J.P. Chang*, University of California at Los Angeles

A molten salt synthetic method is described in this work for synthesizing rare-earth doped yttrium oxide (RE:Y<sub>2</sub>O<sub>3</sub>) and rare-earth zirconate/hafnate (RE<sub>2</sub>(Zr<sub>x</sub>Hf<sub>1-x</sub>)<sub>2</sub>O<sub>7</sub>) (0 ≤ x ≤ 1), since it is one of the simplest, most versatile, and cost-effective approaches available for obtaining crystalline, chemically purified, single-phase powders at lower temperatures and often in overall shorter reaction times with little residual impurities as compared with conventional solid-state reactions. RE:Y<sub>2</sub>O<sub>3</sub> are promising rare-earth-ion-activated phosphor materials with wide applications including amplifiers,

lasers, waveguides, X-ray imaging, bioimaging, and field emission or electroluminescent displays due to their luminescent characteristics and stability in high vacuum. RE<sub>2</sub>(Zr<sub>x</sub>Hf<sub>1-x</sub>)<sub>2</sub>O<sub>7</sub> are of great interest in recent years for their possible applications as high-temperature heating elements, oxidation catalysts, thermal barrier coatings, nuclear waste hosts, and host materials for luminescence centers. The as-prepared nanoparticles have sizes around 100 nm for RE:Y<sub>2</sub>O<sub>3</sub> and around 30 nm for RE<sub>2</sub>(Zr<sub>x</sub>Hf<sub>1-x</sub>)<sub>2</sub>O<sub>7</sub>. They are thoroughly characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution TEM (HRTEM), selected area electron diffraction (SAED), energy-dispersive X-ray spectroscopy (EDS), and UV-vis spectroscopy to delineate the structure and composition of these nanoparticles. Their room temperature luminescent properties (photoluminescence and cathodoluminescence) are measured as a function of the particle size and distribution. In order to process these materials for device fabrication, they are made water soluble by surface modification of these nanoparticles with DMSA (2,3-dimercaptosuccinic acid). We will discuss the effect of these nano-coatings on the optical properties of the nanoparticles.

3:00pm **EM-WeA5 Thermoelectric Properties of Concentration Graded Bulk Co-Doped TiO<sub>2</sub>**, *N. Nguyen*, University of Washington, *A. Yamamoto*, Advanced Institute for Science and Technology, Japan, *D. Kukuruzyak, T. Chikyow*, National Institute of Materials Science, Japan

There has been a recent increased interest in using segmented thermoelectric elements to improve the performance of the thermoelectric devices. Concentration graded of dopants in the oxides can be regarded as a segmented component composed of a single parent based material. In terms of material processing and operating temperature, concentration graded oxides is more advantageous, and may result in higher efficiency at elevated operating temperature, especially for bulk thermoelectric devices. In this work, concentration graded n-typed Co-doped TiO<sub>2</sub> synthesized by solid state reaction method by mixing the powder of Ti and Co oxides, followed by hot-pressed under vacuum of 3x10<sup>-5</sup> torr and temperature of 1473 K. The distribution of the Co doping concentration in the graded samples was mapped out by using Energy Dispersive X-ray Fluorescence Spectrometer scanning technique. The 2D X-ray diffraction measurements indicate polycrystalline Co-doped TiO<sub>2</sub> rutile were fabricated. The Current-Voltage characteristics under the presence of the temperature gradient were generated for selected samples by applying a current source in such a way that the thermopower current was suppressed by applied current in the opposite direction. Power factors (S<sup>2</sup>Σ) were then evaluated over a temperature range from 300 K – 800 K. Surprisingly, uniform Co doping shows parallel declined in both conductivity and thermopower magnitude, whereas graded Co doping enhanced the power factor. This implies the enhancement of the power factor could be related to electron spin entropy effect induced by Co doping to TiO<sub>2</sub>

4:00pm **EM-WeA8 Growth and Characterization of Vanadium Dioxide (VO<sub>2</sub>) Thin Films Prepared by Reactive Biased Target Deposition (RBTd)**, *K.G. West, J. Lu, W. Chen, J. Yu, Y. Pei, S.A. Wolf*, University of Virginia

Vanadium dioxide (VO<sub>2</sub>) undergoes a well known first order metal to semiconductor structural phase transformation just above room temperature at 341K. The abruptness of the phase transformation from its high temperature tetragonal phase to its low temperature monoclinic phase is accompanied by large changes in its electrical conductivity and infrared transmission characteristics, making it an excellent candidate for sensor and switching applications. Also recently it has been observed that an electric field can induce an abrupt transition and change in electrical conductivity below the phase transition temperature, owing even greater potential for its use in practical devices. The growth of high quality VO<sub>2</sub> thin films can be problematic since several distinct oxide states exist. Growth conditions, such as O<sub>2</sub> flow rate, process pressure, and substrate temperature can highly influence the phase of the growing film. Using a novel growth technique called reactive bias target deposition (RBTd), we have prepared highly oriented VO<sub>2</sub> thin films on Al<sub>2</sub>O<sub>3</sub> (0001) substrates at various growth temperatures ranging from 250C-550C. The influence of the growth parameters on the microstructure, and transport properties of VO<sub>2</sub> thin films was systematically investigated. A change in electrical conductivity of 10<sup>3</sup> was measured at 341K associated with the well known structural phase transition (SPT). It was observed that the SPT temperature can be tuned to higher temperatures by mixing VO<sub>2</sub> and other vanadium oxide phases. In addition a current/electric-field induced metal-insulator transition (MIT) was observed at room temperature with a change in electrical conductivity of 8x. The current densities required to induce the MIT in VO<sub>2</sub> are on order of 6x10<sup>4</sup> A/cm<sup>2</sup>. The switching time of the MIT, as measured by high frequency current pulsed measurements, was determined to be roughly

10ns. RBTU utilizes a low energy broad beam ion source that reliably produces a very high density of low energy (5-50eV) inert gas ions. A large negative potential bias is applied to the metal sputtering target. The high density of low energy inert gas ions in front of the sputtering target, seeing a very large potential difference, are accelerated to the target surface at a near normal incidence angle at high enough energies to induce sputtering. A pulsed DC bias is used to avoid target poisoning during reactive processing.

**4:20pm EM-WeA9 Elaboration, Chemical and Electrical Analyses of Intermixed and Nanolaminate HfO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> MIM Capacitor Structures.** *M. Bonvalot, M. Kahn, C. Vallee, C. Dubourdieu, O. Joubert, CNRS, France*

High quality MIM capacitors are seeing increased use in CMOS, BICMOS and bipolar chips. The economic demand for smaller devices directly leads to the request for higher MIM charge storage densities. Therefore new high  $\epsilon$  dielectric materials, such as Al<sub>2</sub>O<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub> and HfO<sub>2</sub>, are being evaluated as MIM dielectrics and are or will be used in future applications. Among those materials, it is generally admitted that Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> show good potentials for this purpose. Al<sub>2</sub>O<sub>3</sub> exhibits a lower  $k$  value but has a larger breakdown field than HfO<sub>2</sub>, and thus the simultaneous use of these two materials in a MIM structure may lead to some improved electrical properties. In this work, we investigated the behaviour of nanolaminate and intermixed HfO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> MIM capacitor structures. HfO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> have both been deposited by Atomic Layer Deposition (ALD) on WSi<sub>x</sub> ( $x=2.3$ ) substrates. Numerous materials stackings have been realised, such as simple HfO<sub>2</sub>/WSi<sub>x</sub> and Al<sub>2</sub>O<sub>3</sub>/WSi<sub>x</sub>, bilayered HfO<sub>2</sub>/ Al<sub>2</sub>O<sub>3</sub>/WSi<sub>x</sub>, sandwiched Al<sub>2</sub>O<sub>3</sub>/ HfO<sub>2</sub>/ Al<sub>2</sub>O<sub>3</sub>/WSi<sub>x</sub>, and nanolaminate Al<sub>2</sub>O<sub>3</sub>/ HfO<sub>2</sub>/ Al<sub>2</sub>O<sub>3</sub>/ HfO<sub>2</sub>/ Al<sub>2</sub>O<sub>3</sub>/WSi<sub>x</sub>, as well as intermixed (HfO<sub>2</sub>)<sub>x</sub>( Al<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub>/WSi<sub>x</sub> compounds. All these structures were carefully analysed by UV ellipsometry up to 8 eV, and show an overall thickness of 13 nm. ATR and variable angle XPS analyses have been performed for interface analysis. C(V) and I(V) electrical characterizations were also carried out after metallic deposition of top electrodes (Au, Al, Ni, Pt). Comparisons of these measurements are useful for identification of individual contributions to the overall electrical behaviour of the MIM structures. In particular, we studied the gain obtained in the linearity of the C(V) curves and the overall capacitance value of these numerous MIM structures. A detailed discussion will be presented on the multiple advantages of using nanolaminate and intermixed compound structures.

**4:40pm EM-WeA10 Suppression of Metal-Insulator-Metal (MIM) Capacitor Leakage Current in BaSrTiO<sub>3</sub> (BST) Dielectrics by Ni Doping : Spectroscopic Studies Changes in Conduction Band Edge Defects States with Ni Doping.** *H. Seo, North Carolina State University, Y.B. Kim, Hanyang University, Korea, G. Lucovsky, North Carolina State University*

A significant reduction of leakage current in MIM capacitors in Ni-doped BST dielectrics is reported. Ni-doping increases the breakdown voltage from ~10-12 V to >35 V, and reduces the leakage current by several orders of magnitude,  $10^2 \sim 10^3$ , as compared to un-doped BST. The conduction mechanism is changed from i) tunneling injection plus Poole-Frenkel transport in un-doped BST to ii) Fowler-Nordheim tunneling in the Ni-doped BST. These decreases are explained by a spectroscopic study of changes in conduction band, and band edge defect states. The large changes in breakdown voltage and leakage current between doped and un-doped BST have been correlated with changes in band edge oxygen vacancy defects detected by spectroscopic ellipsometry (SE). The  $\epsilon_2$  spectrum from the SE measurements on Ni-doped BST is qualitatively different than that from un-doped BST. Changes in conduction band states from 3.5 to 6 eV are assigned to Ni<sup>2+</sup>/Ni<sup>3+</sup> transitions, and changes in band edge defect state features between 2.5 and 3 eV due to reduction of Ti<sup>3+</sup> bonding at O-atom vacancies. In particular, the defect state difference is attributed to charge transfer between Ni<sup>2+</sup> states, and Ti<sup>4+</sup> band states, as well as Ti<sup>3+</sup> pre-existing defect states of the BST host. The band edge vacancy defect is ~0.2 eV shallower in Ni-doped BST and this leads to the significant changes in transport and trapping, accounting for reductions in leakage current, and improved resistance to breakdown in the Ni-doped BST. The study demonstrates that addition of transition metal doping atoms with different valence states than Ti in BST, and/or Zr in other insulating perovskites, can have a significant effect on transport by providing a way to reduce/control leakage current and breakdown. These doping effects will be important in transition metal/rare earth atom complex oxides that have been identified for device applications, not only as high- $k$  capacitors or gate dielectrics, but for ferro-electric devices as well.

**5:00pm EM-WeA11 Comparison Between Film Characteristics and Gas-Phase Diagnostics in Magnetron Sputtering Deposition of Superconducting YBaCuO.** *K. Fukaya, K. Sasaki, J. Gao, T. Kimura, M. Watanabe, M. Inoue, A. Fujimaki, Nagoya University, Japan, H. Sugai, Chubu University, Japan*

YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-d</sub> (YBaCuO) thin films are promising materials for high-temperature superconducting integrated-circuit devices. Magnetron sputtering deposition is a useful method for preparing YBaCuO thin films because of the cheaper process cost than pulsed laser deposition and metal organic chemical vapor deposition. This work reports gas-phase diagnostics of magnetron sputtering deposition of YBaCuO thin films. Because of the lack in detailed plasma diagnostics, the precursors for the deposition of YBaCuO films have not been identified yet. In this work, we measured two-dimensional distributions of the densities of Y, Ba, Cu, YO, BaO, and CuO by laser-induced fluorescence imaging spectroscopy. In addition, we adopted two-photon absorption laser-induced fluorescence for measuring one-dimensional distribution of the O atom density. By comparing the results of the gas-phase diagnostics with the properties of YBaCuO films, we identified the deposition precursors for obtaining fine YBaCuO films. A YBaCuO powder target, Ar/O<sub>2</sub> mixture gas and a conventional rf magnetron sputtering source at 13.56 MHz were used in this experiment. The densities of Y, Ba, and Cu atoms were measured with varying the O<sub>2</sub> flow ratio from 0 to 100% at a total gas pressure of 400 mTorr. The Cu density decreased gradually with the O<sub>2</sub> flow ratio from 0 to 100%, which may be due to the decrease in the plasma density with the O<sub>2</sub> flow ratio, resulting in the decrease in the sputtered Cu flux. In contrast, the Ba and Y densities decreased drastically with the O<sub>2</sub> flow ratio, which is due to oxidation reaction in the gas phase. We observed the increases in the YO and BaO densities with the O<sub>2</sub> flow ratio from 0 to 10%, indicating the production of YO and BaO from Y and Ba in the gas phase, while the CuO density was below the detection limit at all the discharge conditions. On the other hand, the O atom density increased with the O<sub>2</sub> flow ratio from 0 to 20% and was saturated at O<sub>2</sub> flow ratios higher than 20%. The O atom density was estimated to be much higher than the Cu density. According to the analysis of YBaCuO films deposited on MgO substrates (670 °C) placed at a distance of 3 cm from the target, fine YBaCuO films with high crystallinity were obtained at O<sub>2</sub> flow ratios from 50 to 70%. Therefore, it is known by the present work that the deposition precursors for obtaining fine YBaCuO films are Cu, YO, BaO, and O.

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