

Thursday Afternoon, October 21, 2010

Thin Film

Room: Ruidoso - Session TF-ThA

Multifunctional Thin Films and Characterization

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

2:00pm **TF-ThA1 Structural and Dielectric Properties of Epitaxial BiFeO₃:BiMnO₃ Nanocomposite Films on Flexible Hastelloy**, *J. Xiong, J. Zhai, V. Matias, G. Zou, M. Zhuo, Y. Zhang, D.T. Trugman*, Los Alamos National Laboratory, *B. Tao, Y. Li*, University of Electronic Science and Technology of China, *J. Driscoll*, University of Cambridge, UK, *Q. Jia*, Los Alamos National Laboratory

Growth of multifunctional thin films on flexible substrates is of great technological significance since such a platform is needed for the fabrication of flexible electronics. In this study, we report the growth of nanocomposite (BiFeO₃)_{0.5}:(BiMnO₃)_{0.5} [BFO:BMO] films on polycrystalline hastelloy. To grow epitaxial BFO:BMO films on polycrystal substrates, we have used a template consisting of biaxially aligned TiN seed layer deposited by ion-beam-assisted deposited (IBAD) and a La_{0.7}Sr_{0.3}MnO₃ (LSMO) buffer layer deposited by pulsed laser deposition. It should be noted that LSMO is used not only as a buffer layer but also as the bottom electrode of the nanocomposite dielectric films. Microstructural characterization by X-ray diffraction and transmission electron microscopy showed that the nanocomposite thin films were epitaxy with orientation relations of (001)_{BFO:BMO}||[(001)_{LSMO}](001)_{TiN} and [100]_{BFO:BMO}||[100]_{LSMO}||[100]_{TiN}. Electrical measurements indicated good dielectric and ferroelectric properties which are comparable to that reported for ferroelectric films on single crystal substrates.

2:20pm **TF-ThA2 Comparison of Ion Beam and Magnetron Sputtered Vanadium Oxide Thin Films**, *O.M. Cabarcos, B.D. Gaunt, J. Li*, The Pennsylvania State University, *S. Antrazi, 4Wave Inc., E.C. Dickey, D.L. Allara, M.W. Hom*, The Pennsylvania State University

Uncooled Infrared (IR) focal plane arrays are an enabling technology for both military and commercial high sensitivity night vision cameras. The IR imaging is accomplished using MEMS microbolometers fabricated on read-out integrated circuits (ROIC's) and depends critically on the material used to absorb the incoming IR radiation. A typical detector works by monitoring changes in the electrical resistance of the detector material as it absorbs the radiation. Thus, suitable detector materials must exhibit a large temperature coefficient of resistance (TCR) and low noise characteristics to efficiently detect IR photons while also maintaining compatibility with standard IC processing. The most commonly used material in uncooled infrared imaging detectors is vanadium oxide deposited by reactive ion beam sputtering. Here we present a comparison of vanadium oxide thin films grown via reactive ion beam sputtering to films grown using reactive pulsed DC magnetron sputtering. Films deposited using both methods were optically and structurally characterized using Raman spectroscopy, transmission electron microscopy, atomic force microscopy, grazing incidence X-ray diffraction and Rutherford backscattering spectroscopy. Electrical properties of the films were also measured and were found to be very sensitive to the deposition conditions used. The ion beam sputtered films were determined to contain twinned FCC VOx nanocrystals with sub-nanometer scale twin spacing, in the form of large 10-20 nm wide columnar/conical grains. In contrast, the magnetron sputtered films consisted of equiax grains of FCC VOx (5-10 nm) encapsulated in an amorphous matrix. Subtle differences in composition and structure could also be determined from the Raman spectra of the films. These differences in microstructure and composition were then correlated to the measured resistivities and TCRs of the films.

2:40pm **TF-ThA3 Mapping Li-ion Diffusion on the Nanoscale in Thin Film Battery Materials**, *S.V. Kalinin*, Oak Ridge National Laboratory
INVITED

The electrochemical energy storage systems based on Li-based insertion and reconstitution chemistries are a vital aspect of energy technologies. Despite the wealth of device-level and atomistic studies, little is known on the mesoscopic mechanisms of ion diffusion and electronic transport on the level of grain clusters, individual grains, and extended defects.

The development of the capability for probing ion transport on the nanometer scale is a key to deciphering complex interplay between structure, functionality, and performance in these systems. Here we demonstrate how Scanning Probe Microscopy can be utilized to measure Li-ion mobility based on the strong strain-bias coupling in the system when local Li concentrations are changed by electrical fields. The imaging capability, as well as time- and voltage spectroscopies analogous to

traditional current based electrochemical characterization methods are developed. The reversible intercalation of Li and mapping electrochemical activity in LiCoO₂ is demonstrated, illustrating higher Li diffusivity at non-basal planes and grain boundaries. In Si-anode device structure, the direct mapping of Li diffusion at extended defects and evolution of Li-activity with charge state is explored. The electrical field-dependence of Li mobility is studied to determine the critical bias required for the onset of electrochemical transformation, potentially allowing reaction and diffusion processes in the battery system to be separated at each location. The Scanning Probe Microscopy measurements are compared with classical characterization methods such as cyclic voltammetry and electrochemical impedance spectroscopy. The prospects of Scanning Probe Microscopy for battery characterization are discussed.

This material is based upon work supported as part of the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number ERKCC61. Part of work is performed as a user proposal in the Center for Nanophase Materials Sciences at ORNL.

3:40pm **TF-ThA6 Composition and Intermixing at the LaAlO₃/SrTiO₃ Interface by Rutherford Backscattering Spectrometry**, *S.V. Shuthanandan, A. Cohen, L. Qiao, S.A. Chambers*, Pacific Northwest National Laboratory

There is a strong and growing interest in complex oxide interfaces because of the wide range of functional properties exhibited. It is well known that the LaAlO₃/SrTiO₃ (LAO)/(STO) interface exhibits novel electronic conductivity when grown in certain ways. LAO and STO are both band insulators in the bulk, but their interface exhibits n-type electrical conductivity when LAO is grown on TiO₂-terminated STO. Rutherford backscattering spectrometry (RBS) was used to determine interface composition in several pulsed laser deposition (PLD) grown LAO/STO samples prepared at leading laboratories. RBS data collected on these samples clearly show that La diffuses deep into the STO substrate. The clear presence of a shoulder between the low energy side of the La peak and the high energy side of the Sr peak suggests La interdiffusion, although this shoulder could also be caused by pulse pile up in the detector, straggling, and/or multiple/dual scattering effects. Therefore, RBS data were taken as a function of beam current, incident beam energy, and film thickness to determine if this shoulder is due to these artifacts, or La interdiffusion. It was determined that none of the aforementioned artifacts occur, thereby implicating La interdiffusion. The presence of substitutional La at Sr sites in the substrate provides a plausible explanation for the observed n-type conductivity, as La is a shallow donor in STO.

4:00pm **TF-ThA7 Low Work Function CsI Coatings for Enhanced Field Emission Properties**, *P.T. Murray*, University of Dayton, *T.C. Back, S.B. Fairchild*, Air Force Research Laboratory

The use of CsI coatings on graphite fiber cathodes has been shown to reduce the field strength required for field emission from approximately 10⁴ V/cm to 250 V/cm. Interestingly, the mechanism for enhanced field emission is poorly understood. We have explored the enhancement mechanism by using simulated cathode structures consisting of CsI films deposited (by thermal evaporation and by pulsed laser deposition) onto graphite and Si surfaces; the films were characterized by x-ray photoelectron, Auger electron, ultraviolet photoelectron, and electron energy loss spectroscopy. Two aspects of the enhancement mechanism have been explored. The first, cathode conditioning, was addressed by characterizing the surfaces of CsI-coated cathodes and (stainless steel) anodes before and after conditioning. The results allow us to assess the change in cathode surface chemistry as well as the extent to which material is transferred between electrodes during conditioning. The second aspect concerns the reported observation that CsI coated cathodes, after use, exhibit the disappearance of I and the appearance of a coating that appears to have wetted the cathode surface. We hypothesize that I depletion leaves behind a film of Cs which, with its low melting point, will flow during cathode operation. To test this hypothesis, we have characterized I depletion from CsI by carrying out electron and photon stimulated desorption from CsI surfaces. The talk will conclude with a discussion of our findings and their relevance to the enhancement mechanism.

4:20pm **TF-ThA8 Characterization of SiO₂ Thin Films Prepared by Pulsed Electron Deposition**, *V.C. Rincon, S. Kotru, H.V. Nampoori, M. Chen, R.M. Frazier*, The University of Alabama

Pulsed Electron Deposition (PED) is an ablation-based physical vapor deposition technique similar to Laser Deposition (PLD), where electrons are used as the ablation source. Silicon dioxide is a material which is

extensively used by the microelectronic industry and also finds various applications as insulators, protective layers, antireflection coatings etc. There are many different techniques as thermal oxidation of silicon, low pressure chemical vapor deposition (LPCVD), plasma enhanced chemical vapor deposition (PECVD), to grow SiO₂. This work presents growth of thin films of SiO₂ deposited on Si (100) using PED. Films were deposited at oxygen pressure of 4.1mTorr and a pulse frequency of 3 Hz. Substrate temperature was varied from RT- 850 °C, along with varying the source's voltage in the range of 18-12 KV. Characterization tools such as ellipsometry, FTIR and AFM were employed to study the dependence of optical constants and roughness on the quality of SiO₂ films.

4:40pm **TF-ThA9 Growth and Characterization Studies of CdS_{1-x}Se_x (0.0 ≤ x ≤1.0) Alloy Thin Films by Spray Pyrolysis, E. Masumdar, Rajarshi Shahu Mahavidyalaya, India**

The n-CdS_{1-x}Se_x thin films of variable composition have been deposited on amorphous glass and FTO coated glass substrates by simple and cost effective spray pyrolysis technique. The various deposition parameters have been optimized by using photoelectrochemical technique. The structural, surface morphological, compositional, optical and electrical properties have been studied. The X-ray diffraction studies indicated that all the films are polycrystalline in nature with hexagonal structure irrespective of the composition. The lattice parameter 'a' and 'c' varies from 4.1034 to 4.2615Å and 6.6664 to 6.9243 Å respectively with change in composition parameter from x = 0.0 to x = 1.0. Polycrystalline texture with nearly smooth surface and clearly defined grains has been observed for all samples from scanning electron microscopy (SEM). EDAX studies confirmed that CdS_{1-x}Se_x films have approximately same stoichiometry both initially and finally. The absorption coefficient 'α' is of the order of 10⁴ cm⁻¹. The optical absorption studies reveal that direct allowed transition with band gap energy between 2.44 and 1.74 eV. It is found that resistivity of the films decreased with increase in 'x' up to 0.8 and further it increases for x = 1.0. Semi-conducting behavior has been observed from resistivity measurements.

Key words: X-ray diffraction; Cadmium compounds; Semiconducting II-VI materials; Optical Properties; Electrical properties.

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5:00pm **TF-ThA10 In situ Stoichiometry Control using Reflection-High-Energy-Electron-Diffraction Generated X-rays, C. Keenan, S. Chandril, West Virginia University, T.H. Myers, Texas State University - San Marcos, D. Lederman, West Virginia University**

One major challenge in the stoichiometric growth of complex oxides, such as YMnO₃, is the control of the relative compositions of the constituent materials. Desirable properties of oxide materials, such as ferroelectricity, are highly dependent upon material stoichiometry, making stoichiometry control an important issue. While RHEED (Reflection High Energy Electron Diffraction) analysis is typically used as a qualitative tool, RHEED generated x-rays can be used to give quantitative compositional information. The relative compositions of Y and Mn in MBE grown YMnO₃ samples were studied using the grazing exit x-rays generated by RHEED electrons. Comparing the results with RBS characterization suggested that the technique has the potential for real-time compositional analysis.

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Authors Index

Bold page numbers indicate the presenter

— A —

Allara, D.L.: TF-ThA2, 1
Antrazi, S.: TF-ThA2, 1

— B —

Back, T.C.: TF-ThA7, 1

— C —

Cabarcos, O.M.: TF-ThA2, **1**
Chambers, S.A.: TF-ThA6, 1
Chandril, S.: TF-ThA10, 2
Chen, M.: TF-ThA8, 1
Cohen, A.: TF-ThA6, 1

— D —

Dickey, E.C.: TF-ThA2, 1
Driscoll, J.: TF-ThA1, 1

— F —

Fairchild, S.B.: TF-ThA7, 1
Frazier, R.M.: TF-ThA8, 1

— G —

Gauntt, B.D.: TF-ThA2, 1

— H —

Horn, M.W.: TF-ThA2, 1

— J —

Jia, Q.: TF-ThA1, 1

— K —

Kalinin, S.V.: TF-ThA3, **1**
Keenan, C.: TF-ThA10, **2**
Kotru, S.: TF-ThA8, 1

— L —

Lederman, D.: TF-ThA10, 2
Li, J.: TF-ThA2, 1
Li, Y.: TF-ThA1, 1

— M —

Masumdar, E.: TF-ThA9, **2**
Matias, V.: TF-ThA1, 1
Murray, P.T.: TF-ThA7, **1**
Myers, T.H.: TF-ThA10, 2

— N —

Nampoori, H.V.: TF-ThA8, 1

— Q —

Qiao, L.: TF-ThA6, 1

— R —

Rincon, V.C.: TF-ThA8, **1**

— S —

Shutthanandan, S.V.: TF-ThA6, **1**

— T —

Tao, B.: TF-ThA1, 1
Trugman, D.T.: TF-ThA1, 1

— X —

Xiong, J.: TF-ThA1, **1**

— Z —

Zhai, J.: TF-ThA1, 1
Zhang, Y.: TF-ThA1, 1
Zhuo, M.: TF-ThA1, 1
Zou, G.: TF-ThA1, 1