

Monday Morning, October 29, 2012

Oxide Heterostructures-Interface Form & Function

Focus Topic

Room: 7 - Session OX+EM+MI+NS+TF-MoM

Structure-Property Relationships in Epitaxial Oxide Interfaces

Moderator: E.I. Altman, Yale University

8:20am **OX+EM+MI+NS+TF-MoM1 Role of Dual-laser Ablation in Controlling Mn Oxide Precipitation during the Epitaxial Growth of Mn Doped ZnO Thin Films with Higher Doping Concentrations.** D. Mukherjee, M. Hordagoda, R.H. Hyde, N. Bingham, H. Srikanth, P. Mukherjee, S. Witanachchi, University of South Florida

The low solubility of Mn (equilibrium limit of 13 %) and precipitation of Mn oxides at slightly higher Mn doping (> 4 %) have remained major obstacles in the growth of Mn doped ZnO (ZnO:Mn) thin films for potential spintronic applications. In this work, epitaxial ZnO:Mn thin films were deposited on c-cut Al₂O₃ (0001) substrates, with increasing Mn concentrations from 2 to 12 %, using the dual-laser ablation process. In this process, an excimer (KrF) laser and a CO₂ laser pulses are spatially and temporally overlapped onto the target surface. Initially the target is heated by the CO₂ laser to produce a transient molten layer, from which the slightly time-delayed KrF laser initiates the ablation. Ablation for a momentary liquid target not only results in a drastic reduction of particulates in the deposited films but also overcomes the problem of non-congruent ablation of the ZnO:Mn target, leading to stoichiometric film deposition. Moreover, the optimum coupling of the laser energies produces an ablation plume that has a broader angular distribution, compared to the plume generated by KrF pulse alone, as observed from the intensified-charge-coupled-detector (ICCD) images of the ablated plumes. This allows the deposition of uniform films over larger area. Further, the higher ionization of the ablated species as seen in the optical emission spectra (OES) of the dual-laser ablated plumes leads to enhanced gas phase reaction and better film morphology and crystallinity. X-ray diffraction studies revealed that the dual-laser deposited ZnO:Mn films were single crystalline with no secondary phase formation even at 12 % doping while single-laser deposited ZnO:Mn films showed secondary Mn oxide phases. Room temperature magnetic measurements showed ferromagnetism (FM) with enhanced saturation magnetization (M_s) values from 1.3 emu/cm³ for 2 % ZnO:Mn films to 2.9 emu/cm³ for 12 % ZnO:Mn films. In- and out-of-plane magnetization revealed absence of magnetic anisotropy. Further, temperature dependent Hall measurements showed a strong correlation between the effective carrier densities and the observed FM. All these measurements suggested a carrier mediated mechanism of FM in ZnO:Mn thin films. Using both the experimental data and theoretical analysis the FM in less conducting ZnO:Mn films was described by a bound magnetic polaron model whereas that in highly conducting films was consistent with a carrier mediated interaction via RKKY exchange mechanism.

8:40am **OX+EM+MI+NS+TF-MoM2 Structural Characterization of Heterojunction n-ZnO/p-NiO Thin Films Epitaxially Deposited on (0002)Al₂O₃ Substrates.** Y.H. Kwon, Sungkyunkwan University, Republic of Korea, J.H. Lee, KAIST, Republic of Korea, S.H. Chun, Sungkyunkwan University, Republic of Korea, J.Y. Lee, KAIST, Republic of Korea, H.K. Cho, Sungkyunkwan University, Republic of Korea

Recently, oxide semiconductors with superior electrical properties have been considered as candidates to replace Si based electronics. Furthermore, their thermally and chemically stable characteristic is preferable for devices. Especially, among a lot of oxides, ZnO based semiconductors have been extensively investigated to apply in wide application such as thin film transistor and light emitting diode. ZnO is an intrinsic *n*-type semiconductor which characteristic comes from Zn interstitials and O vacancies. And band-gap and exciton binding energy are 3.37 eV and 60 meV, respectively, which is suitable for optical application operating in ultra-violet region. Therefore, *p-n* homojunction diode structure combined with *n*-ZnO and *p*-ZnO having well matched interface had been studied by a lot of researchers.[1] However, it was not reliable since *p*-type ZnO synthesized by doping of group V elements is unstable and return to the *n*-type by self-compensation.[2]

Therefore, *p-n* heterojunction diode composed of *n*-ZnO and stable *p*-type oxide such as Cu₂O and NiO was alternatively studied.[3] Among the *p*-type oxides, NiO with wide direct band-gap (3.7 eV) have been expected to apply in optical applications. And conductivity of NiO could be significantly controlled by Li⁺ doping. Furthermore, according to T. Dutta

et. al., (111) plane of NiO could well matched with (0002) of ZnO by domain match epitaxy.[4]

In this study, heterojunction diode structure was fabricated with *n*-type ZnO and *p*-type NiO on [0002] oriented Al₂O₃ substrates. RF magnetron sputtering method was used for deposition of NiO and ZnO films. After the deposition of NiO films at 400°C in O₂ atmosphere, ZnO films were grown at 600°C and in Ar and O₂ mixed gas atmosphere. XRD result showed the NiO films were fabricated with high crystallinity and preferred orientation of [111]_{NiO}. And sixfold symmetry of (100)_{NiO} plane obtained by phi-scan indicates that the NiO films were bi-epitaxially grown on Al₂O₃ substrates. In addition, electrical properties of NiO showed relatively low resistivity (1.648 Ωcm) and high mobility (14.52 cm²/Vs) due to Li⁺ doping. Sixfold symmetry of (1-102)_{ZnO} observed at phi-scan result indicates that ZnO films were also epitaxially grown on [111] oriented NiO films.

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- [4] T. Dutta, P. Gupta, A. Gupta, J. Narayan, Journal of Applied Physics, 108 (2010) 083715.

9:00am **OX+EM+MI+NS+TF-MoM3 Manipulating the Electrostatic Boundary Conditions of Polar Interfaces.** Y. Hikita, SLAC National Accelerator Laboratory

INVITED

Transition metal oxides (TMO) offer various functionalities ranging from electronic devices to environmental catalysts [1, 2]. Often, the central part of such devices is the interface between different materials. In order to improve their device performance, control of charge transport across these interfaces is essential. Originally developed in semiconductor heterostructures, interface band alignment control is based on the interface electrostatic boundary conditions and is one of the most fundamental methods to tune the carrier transport across interfaces [3]. Given their strongly ionic nature and their accessibility to multiple valence states, the TMO interface should be more suitable than covalent semiconductors for manipulating interface band alignments. Here we focus on epitaxial metal-semiconductor Schottky interfaces between perovskite oxides to demonstrate the effectiveness of this technique. I will present two SrTiO₃ based perovskite Schottky junctions in which the interface energy barriers were modulated by interface dipoles controlled on the atomic scale [4]. Further, I will present the application of this technique in the form of an all-oxide hot electron transistor [5].

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3. F. Capasso *et al.*, Appl. Phys. Lett. 46, 664 (1985).
4. Y. Hikita *et al.*, Phys. Rev. B 79, 073101 (2009).
5. T. Yajima *et al.*, Nature Mater. 10, 198 (2011).

11:20am **OX+EM+MI+NS+TF-MoM10 Strain-induced Oxygen Vacancy Ordering at SrTiO₃/La_{0.5}Sr_{0.5}CoO₃ Interfaces, and its Impact on Magnetic "Dead" Layers.** S. Bose, M. Sharma, M. Torija, University of Minnesota, J. Gazquez, M. Varela, Oak Ridge National Laboratory, J. Schmitt, C. He, University of Minnesota, S. El-Khatib, American University of Sharjah, United Arab Emirates, M. Laver, J. Borchers, NIST Center for Neutron Research, C. Leighton, University of Minnesota

The remarkable functionality and epitaxial compatibility of complex oxides provides many opportunities for new physics and applications in oxide heterostructures. Perovskite cobaltites provide an excellent example, being of interest for solid oxide fuel cells, oxygen separation membranes, catalysis, ferroelectric RAM, resistive switching memory, and oxide spintronics. However, the same delicate balance between phases that provides this diverse functionality also leads to a serious problem - the difficulty of maintaining desired properties close to the interface with other oxides. Although this problem is widespread, manifests itself in several ways, and could present a significant roadblock to the development of heterostructured devices for oxide electronics, there is no consensus as to its origin. In our work, using SrTiO₃(001)/La_{1-x}Sr_xCoO₃ as a model system, we have combined epitaxial growth via high pressure oxygen sputtering [1] with high resolution x-ray diffraction, atomic resolution scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS), and detailed magnetic, transport, and neutron scattering measurements to determine the fundamental origin of the deterioration in interfacial transport and magnetism [2,3]. The effect is

found to be due to nanoscopic magnetic phase separation in the near-interface region driven by a significant depletion in interfacial hole doping due to accumulation of O vacancies. This occurs due to a novel mechanism for accommodation of lattice mismatch with the substrate based on formation and long-range ordering of O vacancies [4]. This fundamental link between strain state and O vacancy formation and ordering is explored in detail in this presentation. We demonstrate that the O vacancy density, depth profile, and ordering vector can all be controlled via strain, leading to a potential mechanism to substantially improve interfacial properties.

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[3] Sharma *et al*, Phys. Rev. B., **84** 024417 (2011). [4] Gazquez *et al*, Nano. Lett. **11** 973 (2011).

11:40am **OX+EM+MI+NS+TF-MoM11 Fabrication and Characterization of Titanium Oxide Films with Tunable Stiffness**, K. Gotlib-Vainshtein, O. Girshevitz, C.N. Sukenik, Bar Ilan University, Israel, D. Barlam, Ben Gurion University, Israel, E. Kalfon-Cohen, S.R. Cohen, Weizmann Institute of Science, Israel

The design of surfaces with controlled stiffness is attractive for a variety of applications ranging from controlling cell growth to mechanical and electrical engineering design. Here, the creation of layered composites with tunable surface stiffness has been achieved by coating a soft PDMS polymer with a stiff film of amorphous titanium oxide with thickness varying from 2 to 50 nm. The oxide layer is smooth (6 nm rms roughness at 2 μm^2 image size), and crack-free. Air plasma treatment was used to form a silica surface layer on the soft polymer base to promote adhesion of the titania overlayer. To gain insight into the mechanics of the layered structure, nanomechanical quantification has been performed using different experimental approaches, as well as modeling studies. The surface mechanical properties of the samples have been probed using both instrumented nanoindentation and atomic force microscopy—based nanomechanical characterization. These results have been compared to finite element analysis (FEA) simulations.

By fitting the FEA simulations with experimental curves it is shown that the hard titania film and softer PDMS substrate individually maintain their characteristic elastic moduli, while the stiffness of the vertical nanocomposite can be controllably modified by changing the thickness of the stiff layer. Liquid phase deposition of the oxide allows control of its thickness at the nm level. During an indentation cycle, the stiff layer transmits the stress to the underlying PDMS base by deformation of its overall shape, but only negligible compression of the film thickness.

This synthetic approach can be quite versatile, and can, in principle, be extended to different oxides and a wide range of thicknesses. It allows control of surface properties while maintaining bulk material properties. This exploratory work is a first step towards defining the range of surface stiffnesses that can be achieved in this way, as well as developing general methodologies for their characterization.

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