

Monday Afternoon, October 28, 2013

Magnetic Interfaces and Nanostructures

Room: 202 A - Session MI+EM+MG-MoA

Frontiers of Complex Oxides

Moderator: G.J. Szulczewski, The University of Alabama,
Z. Gai, Oak Ridge National Laboratory

2:00pm **MI+EM+MG-MoA1 Deposition of AgFeO₂ Thin Films with the Delafossite Structure by Combinatorial Sputtering.** *F. Mao, T. Nyberg, T. Thersleff, U. Jansson*, Uppsala University, Sweden

Delafossites AMO₂ (A= Cu, Ag, Pd, Pt; M=Fe, Co, Ni, Cr, Al, Mn, etc) have received considerable attention due to their potential applications as transparent conducting oxides, photocatalysts, luminescent materials, batteries and thermoelectric materials. Recently, high temperature superconductivity was also suggested for doped members of this type of oxide compounds. Many of the interesting properties of delafossites are related to the crystal structure where linear O-A-O bonds connect layers of slightly distorted edge-sharing MO₆ octahedra. Consequently, the delafossites can be described as natural nanolaminates of MO₂ layers separated by A atoms.

Copper-based delafossite materials have been studied intensely through synthesis of solid-state reaction, hydrothermal synthesis method, sol-gel methods and, in a few cases, reactive sputtering with high temperature post-annealing ($\geq 700^\circ\text{C}$). To our knowledge, however, no studies have previously been published on silver-based delafossite films deposited directly by sputtering. The main challenge is that the silver based delafossites tend to decompose at high temperature ($>400^\circ\text{C}$). Furthermore, the synthesis of Ag-based delafossites by reactive sputtering is usually restricted to small window of stoichiometric composition and also the sputtering condition.

The combinatorial materials science enables rapid discovery and optimization of new or known materials for creating "library" of composition-structure-property relationship. Compared with the "one-at-a-time" sputtering, the combinatorial sputtering with large composition gradient is powerful tool for time-saving and economical development of silver-based delafossite films.

In this work, we demonstrate the combinatorial deposition of delafossite AgFeO₂ thin films using co-sputtering of silver and iron targets in a reactive Ar-O₂ mixture atmosphere. Rapid screenings of XRD, XPS, XRF were employed to determine the chemical composition and phase structure. The most interesting parts of the materials were studied by TEM. Optical and electrical properties have also been investigated. Our results show that the AgFeO₂ films have been successfully deposited by the combinatorial reactive sputtering without post-annealing but the process window is very narrow and strongly dependent on deposition temperature, sputtering power ratio, pulse frequency, O₂ flow rate, working pressure, etc. The XRD and TEM showed that the AgFeO₂ films grew epitaxially with the direction of (001) in the optimal sputtering condition.

2:20pm **MI+EM+MG-MoA2 MBE Growth and Properties of SrCrO₃ Thin Films.** *Y. Du, H. Zhang, R.J. Colby, V. Shutthanandan, S.A. Chambers*, Pacific Northwest National Laboratory

Complex oxides with the perovskite structure exhibit a range of interesting electronic, magnetic, and optical properties. Material synthesis of those structures in thin-film form is of fundamental importance to realize their full potential. SrCrO₃ was first reported to be a paramagnetic metallic oxide with a cubic structure, but the property measurements thereafter have been controversial. Almost all SrCrO₃ structures have been synthesized through higher pressure and high temperature conditions and no epitaxial thin-film form has been reported to our knowledge. In this talk, we will present on the growth of epitaxial, near-stoichiometric SrCrO₃ films on LaAlO₃(001) substrates by molecular beam epitaxy using O₂ as the oxidant. Coherently strained films are shown to grow in a layer-by-layer fashion. The cation stoichiometry was determined by XPS and RBS. *In-situ* XPS Cr 2p core-level spectra show that majority of the Cr cations in SrCrO₃ films are in the 4+ oxidation state, although there is a small amount of Cr³⁺ and higher oxidation states, which could be a result of charge disproportionation. The films are appreciable oxygen deficient, as judged by XPS, RBS, and STEM. The structure and properties of SrCrO₃ films will be compared to that of LaCrO₃ films grown with similar conditions in the same chamber.

2:40pm **MI+EM+MG-MoA3 Oxygen Stoichiometry and Topotactic Phase Reversal in SrCoO_x Epitaxial Films.** *H.N. Lee*, Oak Ridge National Laboratory **INVITED**

Strontium cobaltites (SrCoO_x) exhibit a wide spectrum of magnetic and electronic phases, ranging from antiferromagnetic insulator to ferromagnetic metal, depending on the oxygen stoichiometry (*x*). The Co valence state change due to the modification of *x* in SCO mainly governs the physical properties. In particular, the redox reactions and subsequent changes in the physical properties are essential ingredient in applications such as solid oxide fuel cells, gas sensors, and many other devices that exploit the redox reactions. In this work, we examined the topotactic transformation between two structurally distinct perovskite (SrCoO_{3-d}) and brownmillerite (SrCoO_{2.5}) phases. Temperature dependent, ambient controlled real-time x-ray diffraction and ellipsometry conspicuously showed that the topotactic phase transitions accompany a rapid, drastic change in the crystallographic and electronic structures. Interestingly, the topotactic phases were found to be reversible through oxygen (de)intercalation at greatly reduced temperatures. Therefore, we envision that the phase stability of strontium cobaltites may lead to discovery of new oxygen membranes and cathode materials for high performance energy storage.

*The work was supported by the U.S. Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division.

3:40pm **MI+EM+MG-MoA6 Medard W. Welch Award Lecture - Complex Oxide Interfaces: Conquering the (Polar) Catastrophe.** *C.G. Van de Walle**, University of California, Santa Barbara **INVITED**

The formation of a two-dimensional electron gas (2DEG) at the interface between two insulators, SrTiO₃ (STO) and LaAlO₃ (LAO), has sparked huge interest in oxide electronics. In spite of almost a decade of research, the mechanisms that determine the density of this 2DEG have remained controversial. The electronic behavior of these polar/nonpolar interfaces is often modeled using electrostatics based on an ionic representation of the solids. This leads to a "polar catastrophe" in which the potential in the overlayer diverges—similar to the case of (001) interfaces between heterovalent semiconductors (e.g., Ge/GaAs) that were studied 35 years ago [1].

In fact, if the electrons resulting from the polar discontinuity can be confined at the interface, the "catastrophe" can be entirely avoided, and a 2DEG with an electron density of $3.3 \times 10^{14} \text{ cm}^{-2}$ (0.5 electrons per unit cell) can be generated. However, experimentally observed densities at the STO/LAO interface are more than an order of magnitude lower.

We have used a combination of first-principles calculations and Schrödinger-Poisson simulations to investigate this problem [2]. The termination of the wider-band-gap overlayer is key: surface states that act as a sink for electrons limit the 2DEG density. I will discuss the effects of LAO surface reconstructions, including hydrogenation. These results apply to oxide interfaces in general, and explain why the SrTiO₃/GdTiO₃(GTO) interface has been found to exhibit the full density of 0.5 electrons per unit cell [3].

An interesting question can be raised now: why is it that oxide interface can sustain this huge 2DEG density, while semiconductor interfaces are commonly accepted to undergo atomic reconstructions to eliminate the polar catastrophe? I will suggest that the insights gained from oxide interfaces may be used to design semiconductor interfaces that could sustain similar 2DEGs.

Work performed in collaboration with L. Bjaalie, L. Gordon, K. Krishnaswamy, and A. Janotti, and supported by the ARO, ONR, and NSF.

[1] W. A. Harrison, E. A. Kraut, J. R. Waldrop, and R. W. Grant, *Phys. Rev. B* **18**, 4402 (1978).

[2] A. Janotti, L. Bjaalie, L. Gordon, and C. G. Van de Walle, *Phys. Rev. B* **86**, 241108(R) (2012).

[3] P. Moetakef, T. A. Cain, D. G. Ouellette, J. Y. Zhang, D. O. Klenov, A. Janotti, C. G. Van de Walle, S. Rajan, S. J. Allen, and S. Stemmer, *Appl. Phys. Lett.* **99**, 232116 (2011).

4:20pm **MI+EM+MG-MoA8 Magnetic Reconstructions in Ultrathin Oxide Heterostructures.** *H. Hwang*, Stanford University **INVITED**

Complex oxides are fascinating systems which host a vast array of unique phenomena, such as high temperature (and unconventional) superconductivity, 'colossal' magnetoresistance, all forms of magnetism and ferroelectricity, as well as (quantum) phase transitions and couplings

* Medard W. Welch Award Winner

between these states. In recent years, there has been a mini-revolution in the ability to grow thin film heterostructures of these materials with atomic precision. With this level of control, the boundary conditions at oxide surfaces and interfaces have been used to form new electronic phases. Here we focus on the magnetic reconstructions found in perovskites heterostructures, particularly for manganite thin films and rectifying junctions. In the later case, a direct correlation is found between the junction properties and the reconstructions at the interface.

5:00pm **MI+EM+MG-MoA10 A New Tool to Manipulate the Transition Metal Crystal Field: Creating Local Dipoles via Cation Ordering.** *B. Nelson-Cheeseman*, University of St. Thomas, *H. Zhou, J. Hoffman*, Argonne National Laboratory, *P. Balchandran, A. Cammarata, J.M. Rondinelli*, Drexel University, *A. Bhattacharya*, Argonne National Laboratory

In complex oxides, the intriguing electronic, magnetic and orbital properties often result from how the oxygen anions surround the transition metal cation. Altering this bonding geometry, and thus the transition metal crystal field, can stabilize new and exciting ground states. Here, we present a novel method to tune the positions of the oxygen anions--and, thus, the crystal field--by creating polar interfaces *within* a single thin film material. By using the atomic monolayer control of molecular beam epitaxy (MBE), we are able to introduce "artificial" interfaces into a thin film of LaSrNiO₄--a material in which the La and Sr dopant cations are usually randomly arranged over the A-sites. Using MBE, we interleave full layers of SrO (+0) and LaO(+1) in a series of chemically equivalent LaSrNiO₄ films, varying the pattern of SrO and LaO layers relative to the NiO₂ layers. This technique allows us, in one material, to capitalize on the polar interface phenomena found in more traditional multi-component systems (e.g. LAO/STO). Through synchrotron surface x-ray diffraction and Coherent Bragg Rod Analysis (COBRA) performed at the Advanced Photon Source, we directly investigate the La and Sr cation order and the resulting atomic displacements throughout the film thickness for each ordering pattern. We correlate these results with theoretical calculations and transport measurements of the layered nickelate films. For a particular interface pattern, we find that the nickel-oxygen bond lengths change by as much as 10% compared to the random alloy control films. The ability to modify the bond lengths by such a significant amount, while still maintaining the overall chemical equivalency of the material, could have broad implications for re-envisioning the electronic, magnetic and orbital properties of well-known oxide materials.

5:20pm **MI+EM+MG-MoA11 Hybridized L1' Ordered Phase Induced by Strain in Epitaxial Fe_{38.5}Pd_{61.5} Thin Films,** *M.A. Steiner, R.B. Comes, J.A. Floro, W.A. Soffa, J.M. Fitz-Gerald*, University of Virginia

Thin films of 3d-4d/5d magnetic alloys such as Fe-Pt, Co-Pt, and Fe-Pd are of technological interest due to their ordered L1₀ tetragonal intermetallic phase which exhibits a high magnetocrystalline anisotropy of $K \sim 10^7$ to 10^8 ergs/cm³, comparable to that of 3d-4f rare earth magnets. Strong hard-magnet properties, combined with the ductility and chemical inertness from their ennobled metallic nature, make these alloys ideal for applications in ultra-high-density magnetic storage or micro-electro-mechanical systems where the thermally induced KV/k_BT superparamagnetic limit is an important constraint. The Co-Pt system has been shown to decompose under bulk conditions into a novel, strain-induced chessboard microstructure at the eutectoid composition between its ordered L1₀ and L1₂ intermetallic phases, and related 3d-4d/5d material systems may also be expected to produce strain-induced microstructural behavior. Within this class of materials, Fe-Pd alloys possess comparatively moderate magnetocrystalline anisotropies relative to Co-Pt and Fe-Pt. The Fe-Pd phase diagram, however, exhibits a considerably lower order-disorder transition temperature range that renders the material well-suited for nanostructured magnetic applications by enabling lower processing temperatures.

Epitaxial films of Fe_{38.5}Pd_{61.5} at the L1₀-L1₂ eutectoid composition have been grown on MgO (001) oriented substrates by pulsed laser deposition. It is found that ordered thin films of Fe_{38.5}Pd_{61.5} are deposited as a single phase, initially surmised to be L1₂ due magnetic data and the location and orientation of the X-Ray Diffraction (XRD) peaks. Careful analysis of peak intensities, however, results in an anomalously large long-range ordering parameter. Quantitative XRD analysis of the films shows that this is due to a perturbation in the Pd-site occupancy of the non-stoichiometric Fe atoms in the films; resulting in a hybridization of the L1₀ and L1₂ ordered structures. This L1'hybridized ordered structure, first postulated by thermodynamic principles to exist for the Au-Cu system[†], is believed to be induced by the accommodation of epitaxial strain from the substrate. In addition to its verification, the thermodynamic behavior of this new strain-induced phase is addressed in relation to the equilibrium phase diagram.

[†] W. Shockley, J. Chem. Phys. **6**, 130 (1938)

Authors Index

Bold page numbers indicate the presenter

— B —

Balchandran, P.: MI+EM+MG-MoA10, 2
Bhattacharya, A.: MI+EM+MG-MoA10, 2

— C —

Cammarata, A.: MI+EM+MG-MoA10, 2
Chambers, S.A.: MI+EM+MG-MoA2, 1
Colby, R.J.: MI+EM+MG-MoA2, 1
Comes, R.B.: MI+EM+MG-MoA11, 2

— D —

Du, Y.: MI+EM+MG-MoA2, 1

— F —

Fitz-Gerald, J.M.: MI+EM+MG-MoA11, 2
Floro, J.A.: MI+EM+MG-MoA11, 2

— H —

Hoffman, J.: MI+EM+MG-MoA10, 2
Hwang, H.: MI+EM+MG-MoA8, 1

— J —

Jansson, U.: MI+EM+MG-MoA1, 1

— L —

Lee, H.N.: MI+EM+MG-MoA3, 1

— M —

Mao, F.: MI+EM+MG-MoA1, 1

— N —

Nelson-Cheeseman, B.: MI+EM+MG-MoA10, 2
Nyberg, T.: MI+EM+MG-MoA1, 1

— R —

Rondinelli, J.M.: MI+EM+MG-MoA10, 2

— S —

Shutthanandan, V.: MI+EM+MG-MoA2, 1
Soffa, W.A.: MI+EM+MG-MoA11, 2
Steiner, M.A.: MI+EM+MG-MoA11, 2

— T —

Thersleff, T.: MI+EM+MG-MoA1, 1

— V —

Van de Walle, C.G.: MI+EM+MG-MoA6, 1

— Z —

Zhang, H.: MI+EM+MG-MoA2, 1
Zhou, H.: MI+EM+MG-MoA10, 2