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Spectroscopic Studies of Electronic Structure of Elemental and Complex Transition Metal Oxides: d-state Occupation and Device Functionality

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1. Introduction

Complex oxides including transition metal, TM, and/or lanthanide rare earth, LRE atoms, are of interest for added functionality in Si ULSI circuits. These oxides must display room temperature magnetic properties that can be modulated by electrical input. This cannot genrally be obtained with multi-ferroic perovskites where anti-ferromagnetic behavior based super-exchange generally prevails [1]. This paper takes a different path based on a double exchange mechanism with stronger spin correlation in metallic TM and LRE oxide films [2]. The prototype thin film is CrO_2.

2. Experimental Methods

$Gd(Sc_{1-x}Ti_x)O_3$ alloys > 5 nm thick with x = 0.0, 0.01, 0.05, 0.18 and 0.25 were deposited at room temperature in an ultra-high vacuum system onto (i) $LaAlO_3$ substrates to promote epitaxial growth, and onto (ii) superficially oxidized Si(001) to produce nano-grain films. Ti is in a Ti^{3+} ionic state, and as such the complex oxide is changed from a d^0 to a d^1 oxide with an occupied Ti $S^{1/2}$ state. Nano-grain dimensions in as-deposited films are < 2-2.5 nm, and too small for Jahn-Teller distortions and ordering of Ti atoms on the Sc sub-lattice. The exchange correlation energy is estimated from the energy difference between the localized Ti band edge impurity state and the first d-state feature of Sc. Annealing at 900°C in Ar increases grain size enabling Jahn-Teller distortions, producing an insulator to metal transition for the alloy films with x = 0.18 and 0.25, a first for intentional doping of a d^0 complex oxide, $GdScTiO_3$.
This transition was confirmed by a novel application of X-ray absorption spectroscopy, XAS, using numerical integration of O K edge spectra that extends into the pre-edge and vacuum continuum regimes for X-ray energies < 530 eV, and > 545 eV, respectively.

3. X-ray Spectra/Data Reduction

Figure 1 display O K edge spectra for the epitaxial films that indicate a novel way to detect the insulator to metal transition. High levels of charging in the insulating films, x - 0.0, x = 0.01 and x = 0.05 reduce the signal level by more than factor of 30 with respect to substantially higher signal levels with no evidence of charging in metallic films x = 0.18 and 0.25. The total energy yield, TEY, detection method relies on current flow through the surface of the epitaxial film to balances positive charge associated with photoelectron emission during X-ray irradiation.

The most significant aspects of the O K spectra in Figs 2 and 3 are the shift to lower eV of the Ti defect state and the spitting of that feature into strong and weaker opposite spin bands that bracket the uncorrelated feature in the nano-grain X-ray amorphous film. An energy difference of ~ 1 eV, with respect to the band edge shoulder feature in the as-deposited film identifies a discrete and separated feature in the annealed film is evident in Fig. 2. Moving on to Fig. 3, the lower arrow, labeled "1" indicates an energy difference, or ~1 eV between the Ti impurity level and the Sc T_{2g} feature that has been identified in Fig. 2. The upper arrow, labeled "2" indicates the energy difference between the strongly correlated spin band at lower eV, and the weaker opposite spin band, also ~1 eV. The equality of these two energy differences is discussed in the next section, and is an important consequence of the double exchange mechanism.

Another important feature in the 25% epitaxial film are the positions of the Ti strongly correlated spin state band and the Fermi level in the SXPS spectrum of Fig. 4. The correlated spin band is below the Fermi level and this is a characteristic signature of ferro- or ferri-magnetic behavior in general, and therefore present in metal films, as well as in complex oxides in which there is an insulator to metal transition [2].

4. The Insulator to Metal Transition in $Gd(Sc_{1-x}Ti_x)O_3$

There are two different mechanisms for coupling of electron spins in TM and LRE elemental and complex oxides. The super exchange mechanism prevails in d^n TM elemental oxides, with n≥1, and is based on TM dπ - O atom pπ - TM dπ coupling which results in symmetry determined anti-ferromagnetism [1]. Two exception are CrO_2 and Fe_2O_3, where a double exchange mechanism prevails in the mixed valence oxide Fe_30_4, from a homogeneous alloy mix of FeO and Fe_2O_3 with formally divalent and trivalent Fe [2]. A similar mechanism prevails in CrO_2 [2].

The objective of the research described in this abstract is to demonstrate that the insulator-metal transition required for the double exchange mechanism could be achieved in an "intelligently-designed" complex oxide and detected spectroscopically as well. The double exchange mechanism is based on many-body theory in which the metallic state is a mixture of multiple ionic states with different formal valence [2,3,4]. The alloy system that we have chosen was anticipated to have an insulator to metal transition when the concentration of Ti^{3+} on the Sc sub-lattice exceeds a volume percolation threshold of 16% [5]. The means that the occupied Ti d-states in the d^1 configuration experience a

substantial degree of connectedness so that a strongly correlated spin up or spin down band is obtained. This is indeed the case as illustrated in the spectra in Figs. 2 and 3. The magnitude of the exchange correlation energy determines whether ferro- or ferri-magnetic behavior prevails. In this system that energy is ~1 eV, and comparable to width of the occupied strongly correlated spin band, so that ferri-, rather than ferro-magnetism occurs.

5. Summary

Nano-grain and epitaxial thin films of $Gd(Sc_{1-x}Ti_x)O_3$ alloys > 5 nm thick with x = 0.0, 0.01, 0.05, 0.18 and 0.25 have been prepared and studied by XAS and SXPS. These studies have identified an insulator to metal transition for films with x = 0.18 and 0.25, consistent with a strongly correlated Ti 3d state metallic conductivity band. Future studies will oxides, and combine XAS, SXPX spectroscopic studies with electrical and magnetic measurements as well

Acknowledgements

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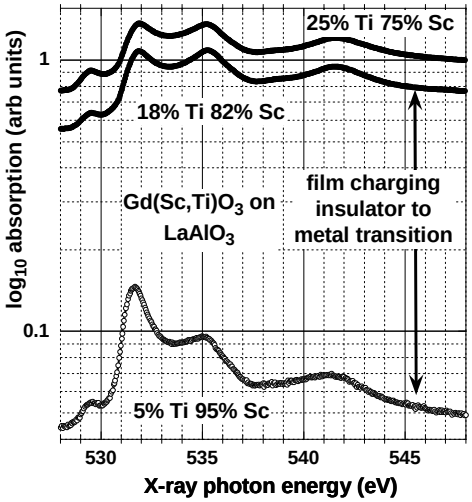

Fig. 1. XAS O K edge spectra of epitaxial $GdSc_{1-x}Ti_xO_3$ alloys

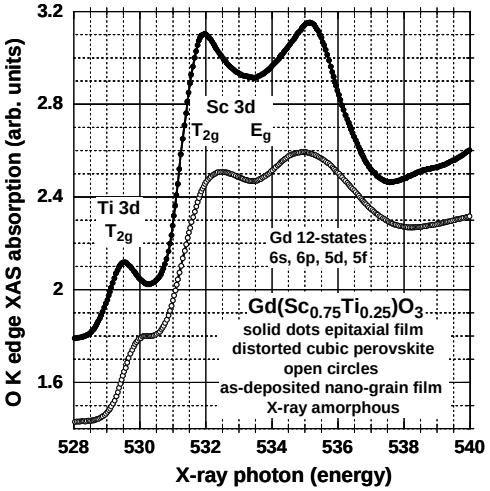

Fig. 2. XAS O K edge spectra if a $GdSc_{1-x}Ti_xO_3$ alloy with x - 0.25.

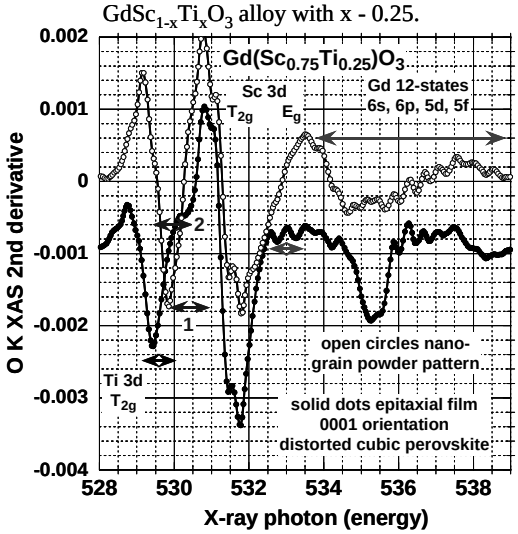

Fig. 3. 2nd derivative XAS O K edge spectra of a $GdSc_{1-x}Ti_xO_3$ alloy with x - 0.25.

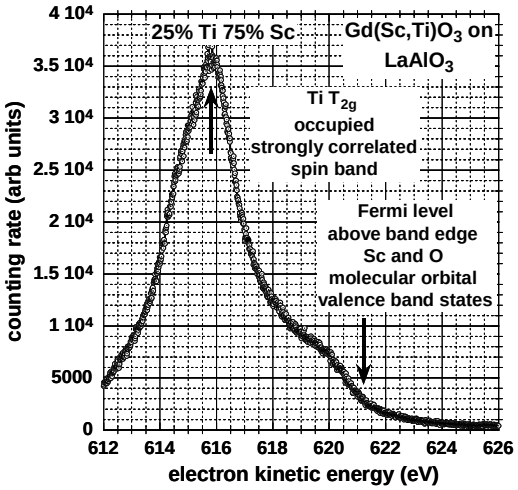

Fig. 4. SXPS valence band spectrum of a $GdSc_{1-x}Ti_xO_3$ epitaxial alloy with x = 0.25.