XAFS Study of $Co_xTi_{1-x}O_{2-x}$-Anatase

S.M. Heald, S.A. Chambers, T. Droubay
Pacific Northwest National Laboratory (PNNL), Richland, WA, U.S.A.

Introduction

Co-doped TiO_2-anatase is a promising candidate as a dilute magnetic semiconductor (DMS). DMS materials have potential applications as spin injectors in spintronics devices. These devices, which utilize the spin of carriers, offer the promise of enhanced functionality. DMS materials can have spin-polarized states in their valence or conduction bands. At interfaces with nonmagnetic semiconductors, they can then be used for spin-polarized carrier injection, thereby allowing for the fabrication of novel devices that use spin. Theory and measurements indicate that DMS materials could be much more efficient spin injectors than ferromagnetic metals.

Most traditional DMS materials require cryogenic cooling, which is impractical. Therefore, extensive theoretical and experimental searches have been underway to find DMS materials that exhibit ferromagnetic behavior above room temperature. To date, the most robust candidate appears to be Co-doped TiO_2-anatase. The ferromagnetic properties of this material were first discovered by Matsumoto et al. [1]. Their films were produced by pulsed laser deposition (PLD) on $LaAlO_3$ and $SrTiO_3$ substrates. The saturation moment was found to be 0.3 μ_B/Co atom.

Methods and Materials

In the present work, molecular beam epitaxy (MBE) techniques were used to grow the films. Either oxygen plasma or atomic oxygen was used in an attempt to prevent the production of Co nanoparticles. The oxygen-plasma-assisted MBE (OPAMBE) films showed a saturation moment of 1.26 μ_B/Co [2]. Bulk Co has a saturation moment of 1.7 μ_B/Co atom, and its formation can complicate the measurement of magnetic properties. Here we demonstrate that the use of x-ray absorption near-edge measurements is a sensitive and simple way to probe for the formation of metallic particles. The Co is primarily in the 2+ oxidation state, although metal is detected in some of the films. We also use extended x-ray absorption fine structure (EXAFS) to determine the Co site in the anatase lattice.

Results and Discussion

Results from five samples are presented. Two of the samples were grown on $LaAlO_3$(100) [5], and three of the samples were grown on $SrTiO_3$/Si. The samples on $LaAlO_3$ were grown by OPAMBE and are referred to as LAO1 and LAO2. Sample LAO1 showed no evidence of Co-rich particles, while LAO2 had about 1% of its surface area covered by Co-rich particles that seemed to contain most of the Co in the film. The samples grown on $SrTiO_3$/Si were grown by MBE, with atomic oxygen used in an attempt to maintain stoichiometry. These three nominally identical films are referred to as STO1, STO2, and STO3. All the films were approximately 20-nm thick with a Co concentration of about 5%.

X-ray absorption measurements were made in fluorescence mode by using a sample spinner to minimize Bragg peak interference from the single-crystal substrate. A glancing incident angle of 1-2° was used to enhance the signal. Measurements were made with the x-ray polarization parallel to the c axis and in the ab plane.

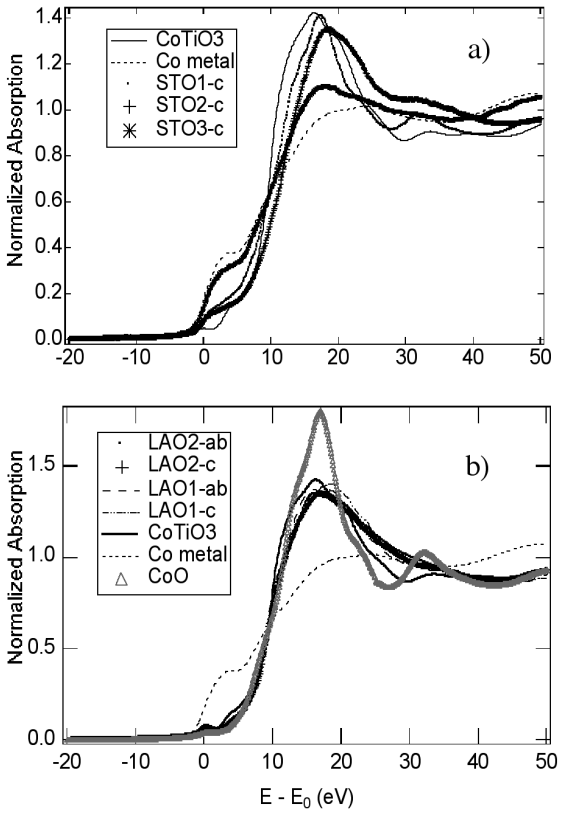

FIG. 1 Near-edge plots for the Co-doped anatase samples as compared to CoO, $CoTiO_3$ (Co+2), and Co metal. a) The three samples grown on $SrTiO_3$ on Si. Only the c axis polarization is shown since the ab data were similar. b) The two samples grown on $LaAlO_3$ are shown. ab indicates the polarization is in the ab plane, and c indicates the x-ray polarization is out of the plane of the film.

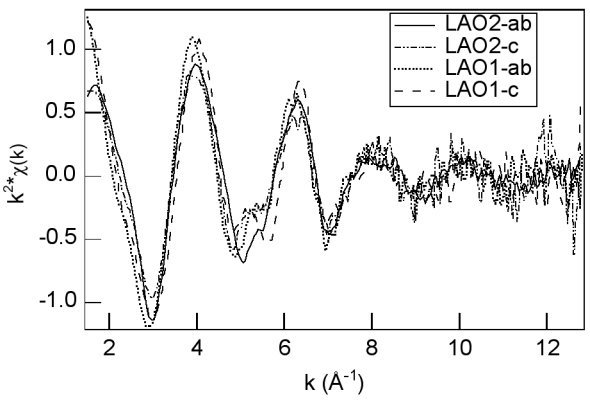

FIG. 2 k^2 weighted $\chi(k)$ for the two samples grown on $LaAlO_3$. ab indicates the x-ray polarization is in the ab plane, and c indicates the polarization is along the c-axis.

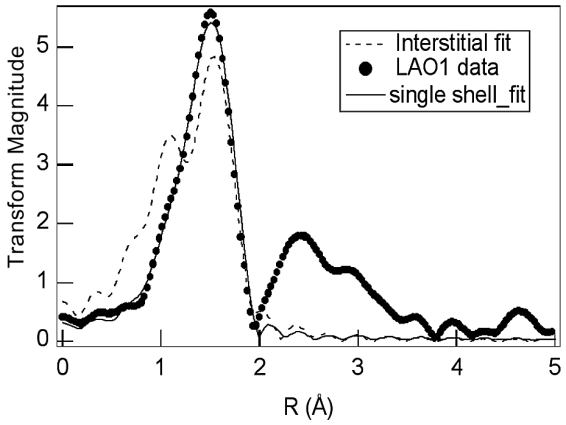

FIG. 3 Fitting for sample LAO1. The transform range is 2-11 $Å^{-1}$, and the fitting was carried out over the r-space range of 0.8-1.9 Å.

The near-edge data are shown in Fig. 1. For the LAO data in Fig. 1(b), there is no evidence for Co metal, while the STO samples clearly contain Co metal. The edge position for the LAO samples indicates that the Co is predominant in the 2+ valence.

The EXAFS data are shown in Fig. 2. The Co site is found to be highly disordered, with a Co-O distance (2.03) intermediate between the Ti-O distance (1.96) in anatase and typical Co(2+)-O distances (2.13). For charge neutrality, we expect an O vacancy to be formed for each Co substitution. Because of its large size, the Co ion may prefer to have a vacancy as a neighbor. In the EXAFS, there is some indication of reduced Co-O coordination, but the reduction is close to our error bars and is not a full O neighbor. Therefore, the correlation, if it exists, is only partial [4].

Another issue that EXAFS can answer is whether the Co is in an interstitial site. Theory indicates this could be the preferred position. Our data, however, seem to rule this out, at least in the configuration predicted by theory. Figure 3 compares the Fourier transforms for fits to our data for a single Co-O distance and to the model predicted for an interstitial site.

Acknowledgments

This work was supported by the PNNL Nanoscience and Technology Initiative; the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES); and the Defense Advanced Research Projects Agency (DARPA) Spins in Semiconductors Initiative. PNC-CAT facilities and research at these facilities are supported by DOE Office of Science Grant No. DE-FG03-97ER45628. Use of the APS was supported by the DOE BES under Contract No. W-31-109-ENG-38.

References

[1] Y. Matsumoto et al., Science **291**, 854 (2001).
[2] S.A. Chambers et al., Appl. Phys. Lett. **79**, 3467 (2001).
[3] S.A. Chambers et. al., Thin Solid Films **418**, 197 (2002).
[4] For a more detailed discussion see S.A. Chambers, S.M. Heald, and T. Droubay, Phys Rev. B **67**, 100401(R) (2003).