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XAS Characterization of Growth Parameter Effects for Pulsed Laser Deposited $\text{Co}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ Films

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Abstract

Films of cobalt-doped titanium dioxide ($\text{Co}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$) can be stabilized in the thermodynamically unfavorable anatase phase if they are grown on appropriate substrates. We performed X-ray Absorption Spectroscopy (XAS) measurements at the oxygen, titanium, and cobalt edges of PLD grown samples. Our data shows the success of this substrate-induced stabilization of the anatase phase occurs only at elevated temperatures ($\sim 700^\circ\text{C}$ or more) and elevated oxygen partial pressures ($\sim 1 \times 10^{-5}$ Torr or more). The effects of post annealing in vacuum are also considered.

1. Introduction

Magnetic semiconductors have recently received considerable attention because of their potential applications in combining conventional semiconductor technology and spin transport electronics. Spin polarized current injection in semiconductors is an obstacle of particular concern that may be overcome by the development of a suitable ferromagnetic semiconductor. When injecting spin polarized electrons from ferromagnetic metals into traditional semiconductors, scattering can occur because of band structure mismatch [1]. Ferromagnetic semiconductors, if successfully synthesized, could solve this problem.

Cobalt doped anatase TiO_2 has been shown to have a hysteretic signature at and above room temperature [2–4]. However, it is thermodynamically unfavorable [5] and will, at elevated temperatures, revert to the more stable rutile structure [6]. For most spin transport electronics applications, it is essential that these materials be grown as thin films. As has been well demonstrated in other systems, it is possible to stabilize the anatase phase by growing it on an appropriate substrate. Two substrates have been identified by the scientific community as good candidates to stabilize the anatase phase: $\text{SrTiO}_3(001)$ and $\text{LaAlO}_3(001)$ [5, 7, 8]. The lattice match between the cubic SrTiO_3 ($a = 3.905 \text{ \AA}$) and the tetragonal anatase TiO_2 ($a = 3.784 \text{ \AA}$, $c = 9.515 \text{ \AA}$) helps promote the growth of anatase with the c axis perpendicular to the film plane. The rutile structure of TiO_2 is also a tetragonal crystal but with a poor lattice match ($a = 4.585 \text{ \AA}$, $c = 2.953 \text{ \AA}$) [9].

The Co-doped anatase is properly described by $\text{Co}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$, where the “ δ ” represents oxygen vacancies, which must exist to maintain charge neutrality of the sample by compensating for the cobalt (valence 2+) substituted titanium (valence 4+) atoms. It is therefore not surprising that the sample’s structure depends strongly on the oxygen partial pressure during growth. Note additionally that oxygen vacancies are necessary for conductivity. According to Chambers *et al.* [1], oxygen vacancies make TiO_2

an n-type semiconductor; it would otherwise be an insulator. They also suggests the ferromagnetic coupling between cobalt atoms is electron mediated and would not be possible without oxygen vacancies in excess of those required for charge neutrality.

2. Experimental

In this study, $\text{Co}_x\text{Ti}_{1-x}\text{O}_{2-\delta}$ films ($x = 1\%$ and 7%) were grown on SrTiO_3 by pulsed laser deposition (PLD) at various temperatures and partial pressures of oxygen (PO_2). Rutherford backscattering, X-ray diffraction, and vibrating sample magnetometry measurements on some of the samples have been published elsewhere (see Shinde *et al.* [3]). The samples were shown to exhibit ferromagnetism at high temperatures and high temperature treatment was found to dramatically enhance Co incorporation in the matrix. Subsequent XAS results (this study) allowed us to determine the necessary conditions that enable the substrate induced stabilization of the desired anatase structure. We used X-ray Absorption Spectroscopy (XAS) to measure the $L_{2,3}$ edges of cobalt and titanium, and the K edge of oxygen. Measurements were performed at the MSU Materials X-ray Characterization Facility located at beamline U4B of the National Synchrotron Light Source at Brookhaven National Laboratory.

Rutile and anatase TiO_2 have been studied extensively. The XAS intensity profiles of oxygen and titanium, in rutile or anatase, are available for comparison with our spectra. Our spectra are in fair agreement with calculations by F. M. F. de Groot [10, 11] and in very good agreement with XAS spectra measured by Ruus *et al.* [12] and Soriano *et al.* [13]. By comparing our oxygen and titanium XAS spectra with previously measured spectra we can determine whether our Co-doped samples are in the anatase, rutile, or some other TiO_2 structure.

3. Results

To make the structure identification, the revealing feature is a double peak at around 460 eV. For the anatase structure the left peak dominates while for the rutile structure the right peak is the larger of the two. Similarly, the oxygen spectral shapes reveal whether the probed oxygen is in an anatase or rutile structure. Having both oxygen and titanium spectra for comparison allows us to determine our sample’s structure with confidence.

3.1. Substrate growth temperature dependence

Titanium and oxygen XAS measurements on samples grown at various substrate temperatures (see Fig. 1) reveal a lower limit to the temperature at which films can be stabilized in the

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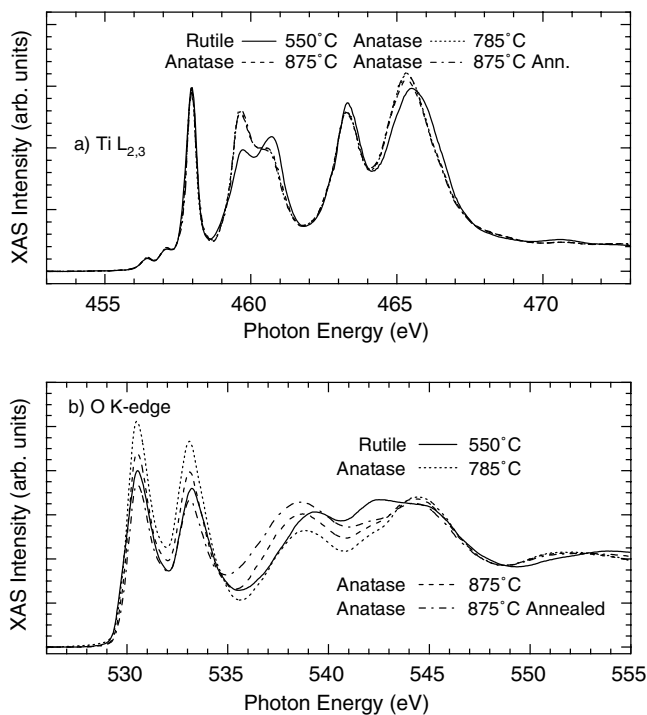


Fig. 1. The titanium $L_{2,3}$ XAS (a) for 7% cobalt doped TiO_2 films grown at various substrate temperatures. Only the lowest growth temperature yielded the rutile structure while all others resulted in anatase. Annealing the sample resulted in no significant difference in the titanium spectra. The oxygen K edge spectra (b) confirm the titanium results. Spectra from all samples have the same general features except for that of the sample grown at 550°C , which is characteristic of the rutile structure.

anatase structure for Co-doped TiO_2 . For successful substrate induced stabilization, the titanium, cobalt, and oxygen atoms must have a minimum mobility, allowing them to conform to the substrate. At low temperatures the reduced mobility causes the substrate induced anatase structure growth to be lost and the films then revert to the more thermodynamically stable rutile structure.

3.2. Dependence on oxygen partial pressure during growth

The oxygen partial pressure (PO_2) dependence was determined for two sets of samples grown at 700°C with 1% and 7% cobalt doping. There is a minimum PO_2 required to obtain the anatase structure (see Fig. 2). Indeed, below a certain PO_2 the films grow in the rutile structure, or at very low PO_2 , they may adopt the so-called TiO_2 -II structure. Although the TiO_2 -II XAS spectral shape resembles a mixture of anatase and rutile, this structure is an entirely different (orthorhombic) structure [12]. We understand the PO_2 effect by recognizing that oxygen has a lower sticking coefficient on a fully oxidized surface. Titanium then, likely dictates film growth kinetics and anatase growth must occur at an overpressure of oxygen (well above stoichiometric ratios). Oxygen deficiency will again compromise the substrate induced anatase structure stabilization. Interestingly, at the threshold oxygen partial pressure between the formation of anatase and rutile there appears to be a region of mixed phase. This was revealed by the sample grown at the threshold PO_2 of 2×10^{-5} T, for which the surface region is in the rutile structure while the bulk appears to be in the anatase structure (as revealed by XRD measurements by Shinde *et al.* [3]). The titanium spectra and oxygen spectra share the same general features whether samples are grown with 1% or 7% cobalt doping so the 7% spectra

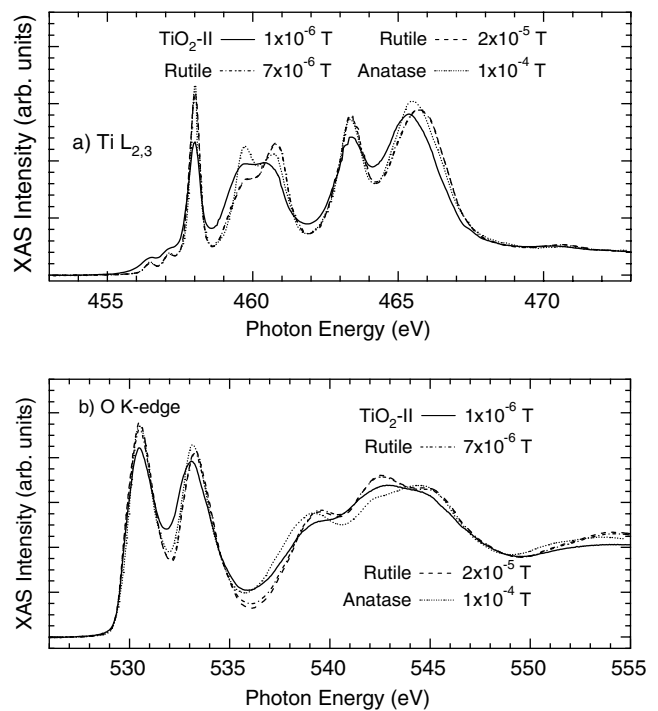


Fig. 2. Titanium spectra (a) for 1% Co samples grown at various PO_2 . Oxygen partial pressures above 1×10^{-4} are necessary to ensure growth in the anatase structure. The oxygen spectra (b) for the same samples confirm the conclusions reached from the titanium spectra. For partial pressures below approximately 5×10^{-6} Torr we obtain a spectrum similar to that of the $CoTiO_2$ -II structure.

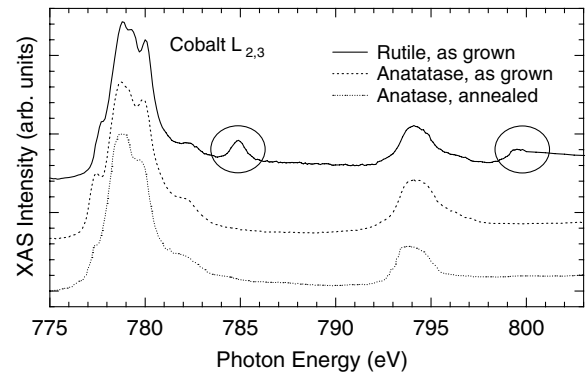


Fig. 3. Cobalt $L_{2,3}$ spectra. Samples that were shown to be in the rutile phase from the oxygen and titanium spectra have additional features that are circled in the figure. The effect of annealing on the cobalt spectra of 7% Co-doped samples is also shown. The sharpening, and partial loss of shoulder features suggests a partial transformation to metallic cobalt.

were omitted in Fig. 2. The conclusions we draw concerning PO_2 effects on growth are by and large independent of cobalt doping concentration.

3.3. Cobalt Spectra

The cobalt $L_{2,3}$ XAS spectra shown in Fig. 3 are in agreement with those published by Chambers *et al.* for Co doped anatase TiO_2 [1]. They very closely resemble $CoTiO_3$ spectra, providing evidence that cobalt atoms take on substitutional lattice sites [4]. The spectral shapes display minimal change with varying growth conditions or resultant structure. Nevertheless, we identified an additional sharp feature above both the L_2 and L_3 edges in the Co spectra from samples that were determined to be in the rutile phase (by inspection of the oxygen and titanium scans). The origin of this spectral feature (circled in Fig. 3) is still

unknown but is currently being investigated by band structure calculations.

Also included in Fig. 3 is the cobalt $L_{2,3}$ XAS spectrum for a sample that was post annealed in vacuum at 875°C to create conductivity enhancing oxygen vacancies and disperse clustered cobalt atoms in the film [3]. Although cobalt clusters in a semiconducting matrix exhibit macroscopic ferromagnetism, an intrinsic ferromagnetic semiconductor is necessary to achieve successful interfacing with traditional semiconductors. Cluster dispersal is therefore desirable. The present work shows that annealing is therefore desirable. The present work shows that annealing also causes out-diffusion towards the surface. This is substantiated by the sharpening and loss of shoulder features of the L_3 edge of the annealed spectrum in Fig. 3, which both suggest a partial transformation to metallic cobalt. Because XAS is surface sensitive, and previous work shows dispersal in the bulk [3], we conclude that metallic clustering occurs near the surface. Our conclusions apply to our sample which was annealed in vacuum. Other studies show that annealing in an oxygen environment leads to similar results [14] and annealing in argon caused dispersal but no clustering [3].

4. Conclusion

We have determined suitable oxygen partial pressure and substrate temperature conditions that allow for substrate induced stabilization of cobalt doped anatase TiO_2 grown by PLD. The phase diagram shown in Fig. 4 best describes our conclusions. High enough growth temperatures are necessary to induce mobility of deposited atoms and epitaxial conformation to the substrate. A minimum PO_2 ensures enough oxygen is present during growth in spite of oxygen's higher volatility compared to titanium and cobalt. Post-annealing leads to out-diffusion of cobalt and metallic surface clustering. Finally, we have identified a new feature in the cobalt scans of Co-doped rutile TiO_2 that is absent for samples in the anatase structural phase.

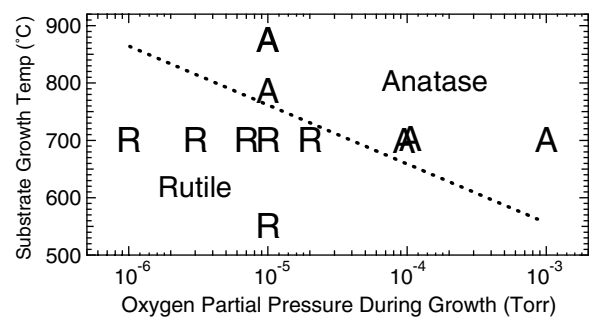


Fig. 4. Phase diagram for partial oxygen pressure and substrate growth temperature requirements that allow for substrate induced anatase structure stabilization on SrTiO_3 .

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