

Spatial distribution and electronic state of Co in epitaxial anatase $\text{Co}_x\text{Ti}_{1-x}\text{O}_2$ thin films grown by reactive sputtering

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(Received 27 October 2003; accepted 12 February 2004)

The magnetic and phase properties of $\text{Co}_x\text{Ti}_{1-x}\text{O}_2$ anatase thin films grown epitaxially on (001) LaAlO_3 by a reactive rf magnetron cosputter deposition have been examined. $\text{Co}_x\text{Ti}_{1-x}\text{O}_2$ ($x=0.07$) thin films exhibit room-temperature ferromagnetism, as evidenced by hysteresis in $M-H$ loop. Chemical mapping indicates segregation of the Co dopant atoms in these films. However, x-ray photoelectron spectroscopy suggests that the segregated Co is not metallic, but in the Co^{+2} state. These results are consistent with a segregated Ti-Co-O phase being responsible for the ferromagnetic behavior. © 2004 American Institute of Physics. [DOI: 10.1063/1.1691499]

Significant effort has focused on developing dilute magnetic semiconductors (DMS) suitable for spin-based electronic devices. A key component to exploiting DMS materials is the realization of a spin-polarized electron distribution at room temperature.¹⁻⁵ Among the traditional semiconductor materials, (Ga,Mn)As exhibits a Curie temperature (T_C) on the order of 110 K.^{6,7} In recent years, it has been reported that cobalt-doped semiconducting anatase can be ferromagnetic (FM) at room temperature.⁸ This has generated significant interest in the development of spin-based oxide electronics. Thin films of $\text{Co}_x\text{Ti}_{1-x}\text{O}_2$ have been grown on SrTiO_3 (001) and LaAlO_3 (001) by oxygen plasma-assisted molecular-beam epitaxy (MBE).⁹ Spectroscopic studies indicate that the cobalt exists in the +2 formal oxidation state in the TiO_2 thin films, consistent with the ferromagnetism originating from Co substitution on the Ti site. However, examination of cobalt-doped TiO_2 films grown by pulsed-laser deposition (PLD) suggests that the formation of Co nano-clusters is the source for the FM properties.¹⁰

In this letter, we discuss the properties of Co-doped TiO_2 ($\text{Co}_x\text{Ti}_{1-x}\text{O}_2$) epitaxial thin films grown by reactive cosputtering that exhibit FM behavior at room temperature. Previous activities on epitaxially stabilized anatase have focused primarily on PLD- or MBE-grown material. In particular, we have examined the spatial distribution and electronic state of Co dopant atom in these TiO_2 epitaxial films.

$\text{Co}_x\text{Ti}_{1-x}\text{O}_2$ anatase films were epitaxially grown by a reactive rf magnetron cosputter deposition system equipped with a load-lock for substrate exchange. The base pressure of the deposition system was on the order of 5×10^{-8} Torr. For epitaxially stabilized anatase film growth, (001) LaAlO_3 was

chosen as the substrate as it provides a lattice mismatch on the order of -0.26% . The substrates were cleaned in trichloroethylene, acetone, and methanol prior to loading on the sample holder. A water source was created by freezing and evacuating a water-filled stainless cylinder that was attached to the deposition chamber via a leak valve. The total pressure (argon and water vapor) during growth was fixed at 15 mTorr, whereas the water vapor pressure was varied from 10^{-4} and 10^{-2} Torr. We found that $P(\text{H}_2\text{O})=10^{-3}$ Torr is optimal in realizing oxygen deficiency and semiconductor behavior. The substrate temperature during the deposition was 650°C , which was found to be optimum for the growth of Co-doped TiO_2 thin film in the anatase phase.

The crystalline structure was investigated by x-ray diffraction (XRD) with Cu K_α radiation. The quantitative analysis of chemical composition was performed by electron probe microanalysis. In order to extract information regarding chemical states of the element, x-ray photoelectron spectroscopy (XPS) was used with Al K_α radiation ($h\nu=1486.6\text{ eV}$). The surface morphology, backscattered images, and chemical mapping were performed by field-emission scanning electron microscopy (FESEM). Hall effect measurements were performed to measure transport properties of oxygen-deficient Co-doped TiO_2 anatase films. RT $M-H$ loops were measured by a Quantum Design superconducting quantum interference device magnetometer for films with different Co content ($x=0.07,0.02$).

Epitaxial anatase films were realized for a growth temperature of 650°C and water vapor pressure at 10^{-3} Torr, with crystalline quality similar to that seen in previous work on undoped films.^{11,12} The magnetization properties of the 7 at. % Co-doped TiO_2 films are shown in Fig. 1. For these films, $M-H$ hysteresis loops are observed at RT. Note that for films doped with 2 at. % or 7 at. % Co, hysteresis in the

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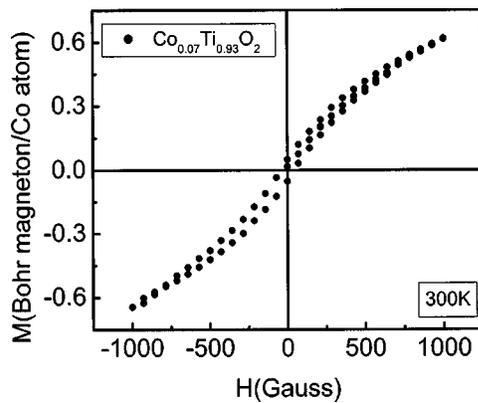


FIG. 1. An $M-H$ curve for $\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_2$ thin films on $\text{LaAlO}_3(001)$ taken at RT. Magnetic field was applied parallel to the film surface.

$M-H$ plot is observed, although the 7 at. % Co-doped TiO_2 film exhibits a larger magnetization than the 2 at. % doped sample. XRD data taken along the surface normal for films deposited in water vapor pressure of 10^{-3} Torr at 650°C indicate epitaxial anatase with a small amount of secondary rutile phase. There was no evidence for Co or cobalt oxides phases from the diffraction data.

The elemental composition for the $\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_2$ thin films was determined by XPS. An XPS spectrum for the film is shown in Fig. 2, indicating the following peaks: $\text{Ti } 2p_1$ at 464.24 eV and $\text{Ti } 2p_3$ at 458.49 eV, $\text{Co } 2p_1$ at 796.21 eV and $\text{Co } 2p_3$ at 780.12 eV, $\text{O } 1s$ at 529.9 eV, and a carbon peak ($\text{C } 1s$ at 285.16 eV). The shift caused by charging effects has been corrected using a standard peak, $\text{O } 1s$ at 529.9 eV from TiO_2 , as a reference. The oxidation state of the Ti atoms matched well with standard $\text{Ti } 2p_1$ and $\text{Ti } 2p_3$ peaks, indi-

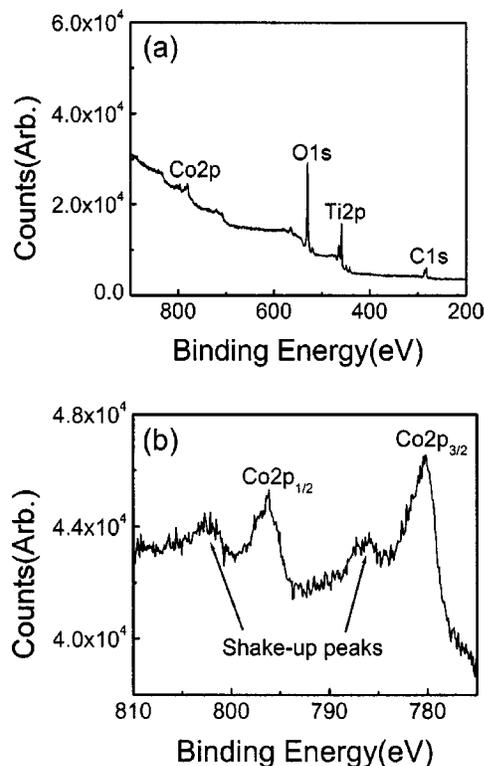


FIG. 2. XPS spectrum of $\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_2$ on $\text{LaAlO}_3(001)$: (a) General spectrum, and (b) $\text{Co } 2p$ band.

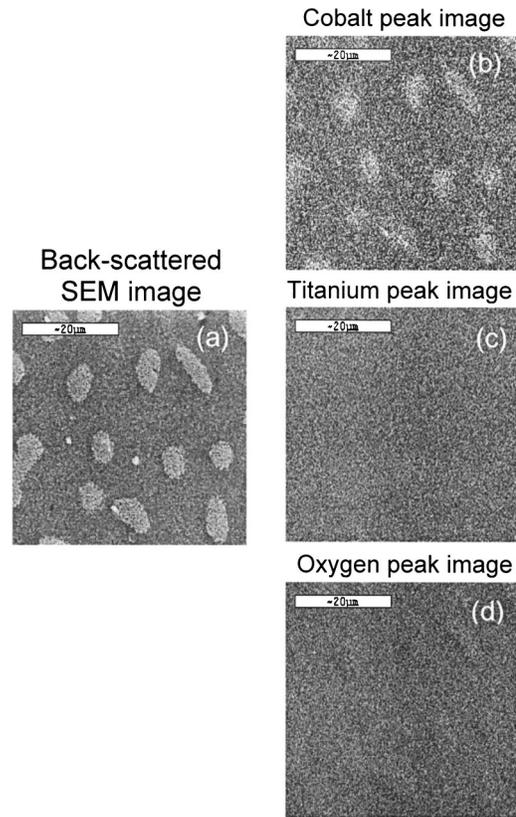


FIG. 3. BSE image and EDS mapping of $\text{Co}_{0.07}\text{Ti}_{0.93}\text{O}_2$: (a) BSE image, (b) Co mapping, (c) Ti mapping, and (d) O mapping.

cating that these two peaks originate from anatase TiO_2 .¹³ The line separation between $\text{Ti } 2p_{1/2}$ and $\text{Ti } 2p_{3/2}$ was 5.75 eV, consistent with 5.7 eV as the standard binding energy. The oxidation state of the Co atoms can be inferred from the shape of the $\text{Co } 2p$ lines. The satellite structure on the high binding energy side of the principal $2p_{1/2}$ and $2p_{3/2}$ lines is a typical characteristic of high spin Co^{2+} ,¹³ although the resolution of the XPS measurement is insufficient to resolve multiplet splitting that would delineate the Co spin state. The shake-up peak is a more easily identified characteristic of the chemical state of the Co than either the absolute binding energy or the line separation between $\text{Co } 2p_{1/2}$ and $\text{Co } 2p_{3/2}$.¹⁴ The result of XPS spectra from the original surface is consistent with the Co existing in the +2 formal oxidation state in $\text{Co}_x\text{Ti}_{1-x}\text{O}_2$ thin films. As reported by Rizzetti *et al.*, small peaks associated with unoxidized cobalt were observed after 4 min sputtering with Ar ion.¹⁵ However, the metallic Co likely results from reducing oxidized Co via Ar ion bombardment, but could also indicate metallic cobalt in the film below the surface.

The surface microstructure of the films was examined by FESEM measurements. Figure 3(a) shows the backscattered electron (BSE) image of a 7 at. % Co-doped TiO_2 anatase thin film grown on $(001)\text{LaAlO}_3$. The sample surface is clearly decorated with secondary phase precipitates that are not observed for undoped epitaxial TiO_2 films. Figure 3 also shows a chemical mapping image, obtained by energy dispersive spectrometry (EDS) in the FESEM, of the Co-doped TiO_2 film ($x=0.07$). First note that the Ti and oxygen peaks were uniformly distributed across the film surface. If the secondary phase was Co metal, we would expect a drop in Ti

signal intensity in the precipitates relative to the remainder of the films. This is not observed. However, when the Co signal is mapped, the secondary phase particles clearly possess a higher Co content than the TiO₂ film area between the particles. These results indicate that the secondary precipitates are a Ti–Co–O phase, which is consistent with the results for MBE-grown films.^{9,16,17} Note also that the secondary phase particles are brighter in the backscattered SEM image due to charging, indicating insulating behavior. Co particles would be metallic. From this surface structure and the result of XPS measurements, we conclude that the material of surface segregation in Co-doped TiO₂ thin films is Ti–Co–O particles.

From the XPS survey spectrum, the Co atoms appear to exist as Co²⁺ in the Co_xTi_{1-x}O₂ precipitate phase, causing FM behavior at RT. In order to make clear the origin of ferromagnetism in Co-doped TiO₂ thin films grown by reactive sputtering system, further research is required, including high-resolution transmission electron microscopy and selected area diffraction of the precipitate phases.

In conclusion, we have investigated ferromagnetism in semiconducting anatase Co-doped TiO₂ thin films grown by the reactive sputter deposition technique. Surface segregation from Ti–Co–O particles was observed in highly doped films. Our results from XPS clearly show that Co is primarily in the +2 formal oxidation state in these doped thin films. Further activities will focus on the crystal structure of the secondary phase.

This work was partially supported by the Army Research Office through research grant DAAD 19-01-1-1508 and by a grant from the NSF (DMR0101856). The authors would also like to acknowledge the staff of the Major Analytical Instrumentation Center, Department of Materials Science and Engineering, University of Florida, for their assistance with this work.

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