Structural and electronic properties of anatase Ti$_{1-x}$Fe$_x$O$_{2-\delta}$ thin film prepared by RF magnetron sputtering

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Abstract. Ti$_{1-x}$Fe$_x$O$_{2-\delta}$ thin films have been deposited on Nb-doped SrTiO$_3$ substrate by RF magnetron sputtering. The as-deposited thin films prepared at $T_{\text{sub}} = 300 \sim 500 ^\circ$C exhibit anatase structure. The lattice constant depends on the crystallization temperature. The substitution of Fe ions is confirmed by photoemission spectra. The Ti 2$p$ X-ray absorption spectra exhibit that Ti $3d$-band occupancy is increased as a result of the oxygen vacancies. The thin film prepared at 500$^\circ$C has the Ti $3d$-DOS at the Fermi level. These findings indicate that Ti $3d$ electrons created by the oxygen vacancies contribute to the electrical conductivity.

1. Introduction

Nb-doped TiO$_2$ exhibits $n$-type conductivity and becomes a metallic in the heavily doping region. Such a behavior has been also reported in TiO$_{2-\delta}$ thin film with oxygen vacancies. The $n$-type TiO$_2$ is expected in practical applications such as transparent electrodes and sensors. In recent years, Matsumoto et al. have discovered that the Co-doped TiO$_2$ (Ti$_{1-x}$Co$_x$O$_{2-\delta}$) thin film becomes a diluted magnetic semiconductor, which realizes practical application of spintronics device [1-3]. The ferromagnetism of Ti$_{1-x}$Co$_x$O$_{2-\delta}$ thin film is driven by the exchange interaction between the Co spins and the $n$-type carriers in the Ti 3$d$ band. The oxygen vacancies of this material have an important role for magnetic properties. Yan et al. have reported that the oxygen vacancies induce a spin-split donor impurity band with a $t_{2g}$ character in the band gap energy region [4]. Although similar behavior has been also expected in Fe-doped TiO$_2$ thin film prepared by pulsed laser deposition [5], the details have not been clarified thus far.

In this study, the authors have prepared the Fe-doped TiO$_2$ (Ti$_{0.993}$Fe$_{0.007}$O$_{2-\delta}$) thin films by RF magnetron sputtering and proved its electronic structure by X-ray absorption spectroscopy (XAS) and photoemission spectroscopy (PES). The oxygen vacancies of the thin film can form by controlling the deposition parameters. In this paper, the authors present that the oxygen vacancy of the thin film is closely related with the electrical and magnetic properties in terms of electronic structure.

2. Experiment

Ti$_{0.993}$Fe$_{0.007}$O$_{2-\delta}$ thin films were deposited on 0.1 wt. % Nb-doped SrTiO$_3$ (100) single crystals with metallic conductivity, which were supplied by Crystal-Base Co. Ltd. The target was sintered ceramics prepared by solid state reaction of TiO$_2$ and Fe$_2$O$_3$, and pressed into cylinders ($\phi$ 53× 3 mm) at 27 MPa, then sintered in air at 1250$^\circ$C for 6 h. The prepared target was examined using X-ray diffraction (XRD).
The RF magnetron sputtering system was arranged in a symmetric configuration with a rotating substrate holder for compositional uniformity. For the deposition, the Ar gas flow rate, deposition pressure and the RF power of ceramics target were fixed at 0.7sccm, 4.0×10^{-3} Torr and 50 W, respectively. The substrate temperature (\(T_{\text{sub}}\)) was changed from 300°C to 500°C. The film thickness was approximately 100 nm for the deposition time of 1 h.

The structural properties of the prepared thin films were characterized by XRD. The electronic structure was measured by XAS and PES installed at an undulator beamline BL-2C in Photon Factory at the High Energy Accelerator Research Organization in Tsukuba, Japan [6]. The energy resolutions of XAS and PES at \(h\nu=730\) eV were 60 meV and 100 meV, respectively.

### 3. Results and Discussions

**Figure 1.** (a) XRD patterns and (b) lattice constants of the thin films prepared at \(T_{\text{sub}}=300^\circ\text{C}, 400^\circ\text{C}\) and 500°C.

Figure 1(a) shows the XRD patterns of Ti_{0.993}Fe_{0.007}O_{2-\delta} thin films prepared at various \(T_{\text{sub}}\). The XRD patterns exhibit single phase of anatase (004). The peak position shifts to the higher 2\(\theta\) side with increasing \(T_{\text{sub}}\). The lattice constant calculated from figure 1(a) is shown in figure 1(b). The lattice constant decreases with increasing \(T_{\text{sub}}\). These results are considered to be due to the oxygen vacancies with Fe doping.

Figure 2(a) shows the PES spectra in Fe 3\(p\) core level of the thin films prepared at \(T_{\text{sub}}=400^\circ\text{C}\) and 500°C. The Fe 3\(p\) peak is observed at ~65 eV, although the peak intensity is weak. This indicates that Fe ions are doped into TiO\(_2\) Thin films. The peak position accords with Fe\(^{3+}\). Figure 2(b) shows the Ti 2\(p\) XAS spectra of the thin films prepared at \(T_{\text{sub}}=400^\circ\text{C}\) and 500°C. The Ti 2\(p\) XAS spectra correspond to the transition from the Ti 2\(p\) core level to the unoccupied Ti 3\(d\) state. The spectra consist of two parts derived from the spin orbit split of \(L_3\) (2\(p_{3/2}\)) and \(L_2\) (2\(p_{1/2}\)) states. They are split into the \(t_{2g}\) and \(e_g\) states by the octahedral ligand field. The spectral shapes of thin films are in good agreement with anatase TiO\(_2\) single crystal [7]. The intensity of the \(t_{2g}\) peak for \(L_3\) state is lower in the thin film prepared at \(T_{\text{sub}}=500^\circ\text{C}\). This indicates that the Ti 3\(d\)-band occupancy is increased as a result of the oxygen vacancies.

Figure 3 shows the PES spectra in the valence band region of the thin films prepared at various \(T_{\text{sub}}\). The spectral shapes and peak positions do not depend on \(T_{\text{sub}}\). The thin films prepared at \(T_{\text{sub}}=300^\circ\text{C}\) and 400°C have broad DOS in the band gap energy region. However, the thin film prepared at \(T_{\text{sub}}=500^\circ\text{C}\) has an apparent Fermi edge at \(E_F\). The existence of the Fermi edge indicates that the thin film prepared at \(T_{\text{sub}}=500^\circ\text{C}\) exhibits metallic conductivity at room temperature.
Figure 2. (a) PES spectra in the Fe 3p core level and (b) Ti 2p XAS spectra of the thin films prepared at $T_{\text{sub}} = 300^\circ\text{C}, 400^\circ\text{C}$ and $500^\circ\text{C}$.

Figure 3. PES spectra in the valence band region (Solid line) and in the band gap energy region (Closed circles) of the thin films prepared at $T_{\text{sub}} = 300^\circ\text{C}, 400^\circ\text{C}$ and $500^\circ\text{C}$.

Figure 4(a) show the off- and on-resonance spectra in the valence band region of the thin films prepared at $T_{\text{sub}} = 500^\circ\text{C}$. The excitation energies of the off- and on-resonance spectra are shown in figure 2(b). The spectral shape is in a good agreement with O 2p band-DOS curve calculated by Thomas et al. [8]. The B peak is resonantly enhanced by the Ti 2p $\rightarrow$ 3d excitation in the on-resonance spectrum. The difference spectrum, which is obtained by subtracting from the on-resonance to off- spectra, is shown in figure 4(b). The difference spectrum is Ti 3d partial DOS (PDOS) in the valence band region. The PDOS distributes in the valence band region. The existence of Ti 3d-PDOS indicates that the Ti 3d state strongly hybridized with O 2p state in the valence band. Therefore, the peak A is the O 2p non-bonding state and the peak B is the O 2p bonding state hybridized with Ti 3d state [9]. On the other hand, the Ti 3d-PDOS is also observed at around the $E_F$. The Ti 3d-PDOS corresponds to the large Fermi edge shown in Fig. 3. When the Fe$^{3+}$ ions are substituted into Ti$^{4+}$ site, the thin film forms a lot of oxygen vacancies in order to keep the charge neutral condition. Therefore, the number of Ti 3d electron increases by Fe substitution. Thus, the electrical conductivity is mainly achieved by Ti 3d electron created by the oxygen vacancies during deposition, although the Fe 3d electron may also contribute to electrical and magnetic properties.
4. Conclusion

The authors have studied the electronic structures of the anatase Ti$_{0.993}$Fe$_{0.007}$O$_{2-\delta}$ thin films prepared at various $T_{\text{sub}}$ using XAS and PES. The Fe 3$p$ PES spectra exhibit that Fe ions are doped into TiO$_2$ thin films. The Ti 2$p$ XAS spectra exhibit that the Ti 3$d$-band occupancy is increased as a result of the oxygen vacancies. The PES spectrum of thin film prepared at $T_{\text{sub}} = 500^\circ$C has an apparent Fermi edge, which corresponds to Ti 3$d$-PDOS, at $E_F$. These results indicate that Ti 3$d$ electrons created by the oxygen vacancies contribute to the electrical conductivity.

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