

High-resolution soft-X-ray photoemission study on SrTi_{0.99}Sc_{0.01}O₃ thin film

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1 Introduction

Undoped SrTiO₃ is one of dielectric materials with cubic perovskite structure. The SrTiO₃ transfers from the insulator to metal or semiconductor by small carrier doping. The doping can be achieved by alternating of the three sublattices, namely, those of Sr²⁺, Ti⁴⁺, and O²⁻. The Sc³⁺-doped SrTiO₃ single crystal exhibits proton conductivity as well as hole conductivity in the temperature region of 200~400 °C. The proton conduction of Sc-doped SrTiO₃ is useful for electrochemical applications of solid state oxide fuel cell and hydrogen sensor in the energy source industry.

In this study, the electronic structure of Sc-doped SrTiO₃ (SrTi_{0.99}Sc_{0.01}O₃) thin film has been probed by high-resolution photoemission spectroscopy (HRPES) and X-ray absorption spectroscopy (XAS). As a reference, the electrical conductivity was also measured. Understanding the detailed structural and electrical properties of the thin film is one of the important subjects in term of electrochemical application. However, the details of the thin film have not been clarified thus far. In this paper, the authors would like to propose that the SrTi_{0.99}Sc_{0.01}O₃ thin film becomes *p*-type oxide semiconductor in comparison with undoped SrTiO₃ and Nb-doped SrTiO₃ single crystals.

2 Experiment

The SrTi_{0.99}Sc_{0.01}O₃ thin films were prepared on 0.1 wt.% Nb-doped SrTiO₃ (100) single crystals by RF magnetron sputtering using ceramic target. The RF power, deposition pressure and substrate temperature were fixed at 40 W, ~3.0×10⁻³ Torr and 500 °C, respectively. The film thickness was approximately 100 nm. The prepared thin film was examined using X-ray diffraction and atomic-force microscope. The detailed structural properties have been reported in Ref. [1]. The electrical conductivities were measured by A.C impedance method. The XAS and HRPES spectra were measured using a soft-X-ray spectrometer installed at an undulator beamline BL-19B and BL-2C (in Photon Factory) at the High Energy Accelerator Organization in Tsukuba, Japan. The energy resolutions of XAS at $h\nu=400\sim500$ eV and HRPES at $h\nu=800$ eV were 50 meV and 120 meV, respectively. The energy axis was calibrated by measuring the HRPES spectrum of the 4*f* core level of Au film.

3 Results and Discussion

Figure 1(a) shows the Ti 2*p* XAS spectra of the SrTi_{0.99}Sc_{0.01}O₃ thin film and SrTiO₃ single crystal. Each XAS spectrum was measured on different beam line.

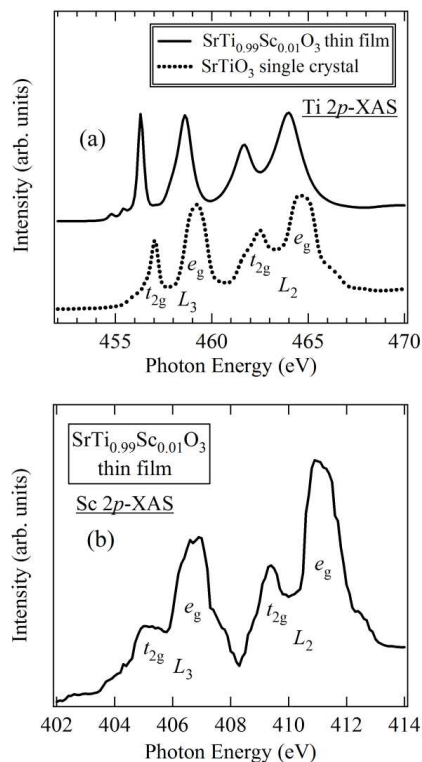


Fig. 1 (a) Ti 2*p* XAS spectra of the SrTi_{0.99}Sc_{0.01}O₃ thin film and SrTiO₃ single crystal. (b) Sc 2*p* XAS spectrum of the SrTi_{0.99}Sc_{0.01}O₃ thin film.

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 further split into the *t*_{2*g*} and *e*_g states by the octahedral ligand field. Comparing with the SrTiO₃ single crystal, the peak of the thin film shifts to the lower energy side. This corresponds to the rigid band shift. Furthermore, the intensity of the *t*_{2*g*} peak for *L*₃ state is higher in the SrTi_{0.99}Sc_{0.01}O₃ thin film. This may indicate that the Sc³⁺ ions are substituted into Ti⁴⁺ site in SrTiO₃.

Figure 1(b) shows the Sc 2*p* XAS spectrum of the SrTi_{0.99}Sc_{0.01}O₃ thin film. The Sc 2*p* XAS spectrum corresponds to the transition from the Sc 2*p* core level to the unoccupied Sc 3*d* state. The spectrum splits into the *t*_{2*g*}- and *e*_g-subbands of *L*₃ (2*p*_{3/2}) and *L*₂ (2*p*_{1/2}) by the octahedral ligand field. The existence of the peak structure indicates that the Sc³⁺ ions are substituted for Ti⁴⁺ site in the SrTi_{0.99}Sc_{0.01}O₃ thin films.

Figure 2 shows the HRPES spectrum in the valence band region of the $\text{SrTi}_{0.99}\text{Sc}_{0.01}\text{O}_3$ thin film. The spectral shape is in a good agreement with the PES spectra of Nb-doped SrTiO_3 single crystal. The valence band has two structures of A and B. It is known that the peak A corresponds to the nonbonding state and the peak B corresponds to the bonding state that is well mixed with Ti 3d state. On the other hand, the Fermi level (E_F) of the thin film locates at ~ 1.2 eV from the top of the valence band. The E_F locates at ~ 2.6 eV from the top of the valence band in the case of $\text{SrTi}_{0.98}\text{Sc}_{0.02}\text{O}_3$ single crystal. The E_F of the thin film locates at the valence band side. Furthermore, the additional structures within the band gap, which are commonly observed at oxide surfaces with defects or disorders, are hardly visible in the present spectra, indicating that a well-defined surface is obtained. These results indicate that the band bending effect of the single crystal is suppressed by postannealing in O_2 atmosphere. From Figs. 1 and 2, the E_F of the $\text{SrTi}_{0.99}\text{Sc}_{0.01}\text{O}_3$ thin film corresponds to that of p -type oxide semiconductor.

The energy band-DOS curves in the valence band, which are obtained by two authors of Matheiss *et al.* [3] and Toussaint *et al.* [4], are also shown as histogram lines. The DOS curves of solid lines are obtained by convoluting the original DOS with Gaussian broadening functions widths of 0.1 eV. Matheiss *et al.* calculated the DOS using the APW and Slater-Coster linear combination of atomic orbital interpolation method. Toussaint *et al.* calculated the DOS using the tight-binding method with a Green function.

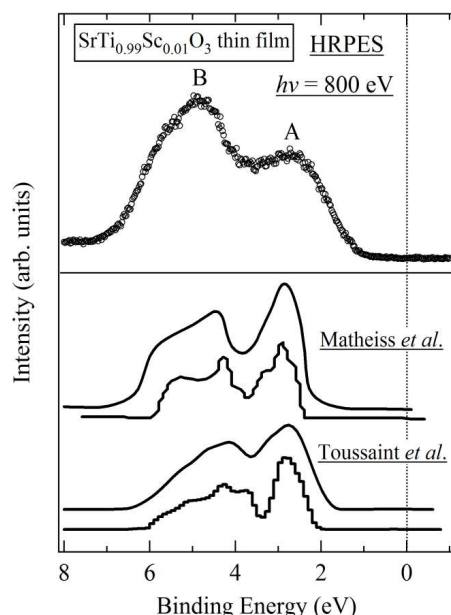


Fig. 3 (a) Valence band of the $\text{SrTi}_{0.99}\text{Sc}_{0.01}\text{O}_3$ thin film measured by HRPES, which is shown as open circles. (b) The band-DOS curves calculated by two authors, Matheiss *et al.* [3] and Toussaint *et al.* [4], which are also shown as solid lines.

The influence of electron correlation is not calculated in the two DOS. The spectral shape and bandwidth of HRPES spectrum are in good agreement with two band DOS curves. However, the ratio of the peak intensity of the HRPES spectrum is different from that of two DOS curves. This is considered to be due to the change of the Ti-O hybridization effect in the valence band.

4 Conclusion

The authors have studied the electronic structure of the $\text{SrTi}_{0.99}\text{Sc}_{0.01}\text{O}_3$ thin film using XAS and HRPES. The Ti 2p and Sc 2p XAS spectra exhibit that Sc^{3+} ions are substituted into Ti^{4+} site. The electrical conductivity exhibits the thermal activation-type behavior. The E_F of the $\text{SrTi}_{0.99}\text{Sc}_{0.01}\text{O}_3$ thin film locates to the valence band side. The energy separation between E_F and the top of valence band corresponds to the E_a , which is estimated from the Arrhenius plot of conductivity. The valence band consists of the O 2p state hybridized with the Ti 3d state. The hybridization effect between the O 2p and Ti 3d states in the valence band is weaker in the thin film. These results indicate that the $\text{SrTi}_{0.99}\text{Sc}_{0.01}\text{O}_3$ thin film become p -type oxide semiconductor with the large E_a .

Acknowledgement

The present work was supported by the Grant-In-Aid for Science Research C (No. 22560670) from the Ministry of Education, Culture, Sports, and Technology in Japan.

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