Electronic Structure of $Bi_4Ti_3O_{12}$ Thin Film by Soft-X-Ray Emission Spectroscopy

Tohru HIGUCHI, Masashi TANAKA, Kazuhide KUDOH, Tomoyuki TAKEUCHI,
Yoshihisa HARADA[1], Shik SHIN[1,2] and Takeyo TSUKAMOTO

Department of Applied Physics, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan
[1]*RIKEN, Sayo-gun, Hyogo 679-5148, Japan*
[2]*Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*

The electronic structure of a ferroelectric $Bi_4Ti_3O_{12}$ (BIT) thin film was investigated by soft-X-ray emission spectroscopy (SXES). In the valence band energy region, Ti $3d$ and O $2p$ partial density of states were observed in O $1s$ and Ti $2p$ SXES spectra. The energy position of the Ti $3d$ state overlapped with that of the O $2p$ state. This finding indicates that the O $2p$ state strongly hybridizes with the Ti $3d$ state in the valence band.

KEYWORDS: $Bi_4Ti_3O_{12}$ thin film, SXES, valence band, hybridization effect, soft-X-ray Raman scattering

1. Introduction

Ferroelectric thin films have attracted considerable attention from the view point of their application to nonvolatile memories or capacitors of high-density dynamic-random-access memories (DRAMs) due to their reversible spontaneous polarization and high dielectric constants. In nonvolatile memories, it is necessary for the polarization to be reversible at a small applied voltage for low-voltage operation and to be free from fatigue over a number of write and read cycles. For practical ferroelectric materials, a bismuth titanate $Bi_4Ti_3O_{12}$ (BIT) thin film is expected to be used in nonvolatile memory devices with nondestructive readout operation due to the small coercive field along the *c*-axis. Thus far, deposition of BIT thin films has been studied by several techniques such as metalorganic decomposition (MOD),[1–4] metalorganic chemical vapor deposition (MOCVD),[5–7] and sputtering techniques.[8,9] Furthermore, the electrical properties have also been studied in terms of the application to nonvolatile memory devices.

In this study, the electronic structure of ferroelectric BIT thin film has been investigated by soft-X-ray emission spectroscopy (SXES). We believe that understanding the electronic structure of ferroelectric thin films is a very important issue in terms of the science and technology of materials. However, the studies of the electronic structure of oxide thin films seem to be very few. Although photoemission spectroscopy (PES) has been a powerful method for study of the electronic structure, PES is surface-sensitive, because the mean free path of an electron is very short compared with that of light.[10] Therefore, it is difficult to study the electronic structure of a thin film by PES as it requires a clean surface under the ultrahigh vacuum. On the other hand, the SXES technique can investigate the electronic structure of the bulk state compared with PES spectra, because the mean free path of a soft-X-ray is very long compared with that of an electron. Furthermore, the SXES has a clear selection rule regarding the angular momentum due to a dipole transition, as it occurs mainly within the same atomic species. Thus, the partial density of state (PDOS) localized at the atom can be obtained by SXES spectra.

2. Experimental

A ferroelectric BIT thin film was deposited on a $Pt/Ti/SiO_2/Si$ substrate by the radio-frequency (RF) magnetron sputtering method with Bi_2O_3 and TiO_2 ceramic multitargets. The RF powers of Bi_2O_3 and TiO_2 were 100 W and 200 W. The total gas flow of Ar and O_2 was 10 sccm. The thickness of the film deposited at 700°C was estimated to be about 400 nm. The X-ray diffraction (XRD) pattern is shown in Fig. 1. One can see the BIT thin film with high *c*-axis orientation and most in the single phase. The detailed electrical and structural properties will be published elsewhere.[11]

Soft-X-ray absorption and emission spectra were measured using a soft-X-ray spectrometer installed at the undulator beamline BL-2C (in Photon Factory) at the High Energy Accelerator Organization. Synchrotron radiation was monochromatized using a varied-line spacing plain grating whose average groove density is 1000 lines/mm. The spectra were measured in a polarized configuration. The energy resolution was about 0.4 eV at $h\nu = 450$ eV. The bottom axis was calibrated by measuring the $4f$ core level of Au.

3. Results and Discussion

Figure 2(a) shows the Ti $2p$ X-ray absorption spectroscopy (XAS) spectrum of the BIT thin film. The spectrum is derived from two parts of L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$). Further-
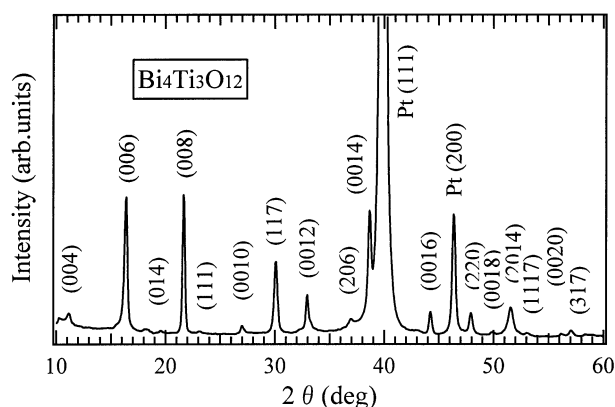

Fig. 1. XRD pattern of stoichiometric BIT thin film deposited on $Pt/Ti/SiO_2/Si$ substrate by RF magnetron sputtering method.
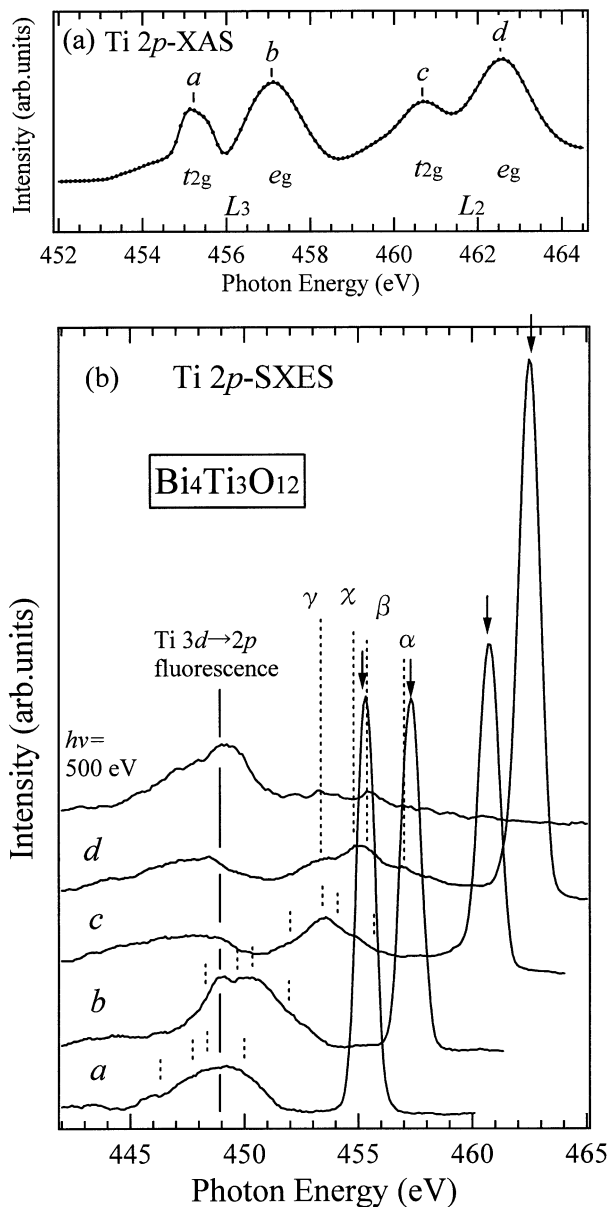
Fig. 2. (a) Ti $2p$ XAS spectrum of BIT thin film. (b) Ti $2p$ SXES spectra excited at various photon energies indicated in (a). An arrow shows the energy position of the excitation photon energy. Vertical lines show the energy position of Ti $3d \rightarrow 2p$ fluorescence.

Fig. 3. The Ti $3d \rightarrow 2p$ SXES spectra of BIT thin film presented as the relative emission energy to the elastic scattering. Vertical dashed lines show the energy position of the soft-X-ray Raman scattering.

more, they are split into t_{2g} and e_g states due to the octahedral ligand field.[12–15] The vertical bars, which are labeled from a to d, indicate the selected photon energies for resonant SXES measurements.

Figure 2(b) shows the Ti $2p$ SXES spectra of the BIT thin film. The Ti $2p$ emission reflects the Ti $3d$ PDOS. The arrow shown in each spectrum indicates the excitation photon energy. The peak beneath the arrow is attributed to the elastic scattering of the excitation photon. The elastic peak is enhanced at the excitation energy corresponding to the t_{2g} absorption peak of L_3. On the other hand, the SXES spectrum excited at $hv = 500\,\text{eV}$ is an off-resonance spectrum attributed to the normal Ti $3d \rightarrow 2p$ fluorescence spectrum. A vertical line shows the position of the fluorescence band for each SXES spectrum.

Four features shown with vertical bars α, β, χ, and γ represent the energy positions that have energy separation of 5.5,
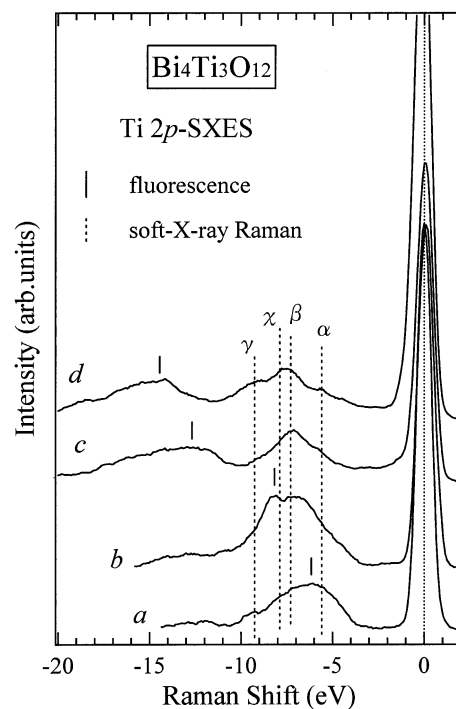
7.2, 7.8, and 9.2 eV, respectively, from the excitation energy. They shift as the excitation energy is varied. These features are attributed to the soft-x-ray Raman scattering, that is, inelastic scattering. The inelastic scattering that is excited in the L_3 absorption spectral region overlaps with the Ti $3d \rightarrow 2p$ fluorescence.

Figure 3 shows the SXES spectra of BIT thin film where the abscissa represents the Raman shift, which is the energy shift from the elastic scattering. The elastic scattering peak is located at 0 eV. The Ti $3d \rightarrow$ Ti $2p$ fluorescence peak shifts to a higher energy as the excitation energy increases. It is known that the elementary excitation of the soft-X-ray Raman scattering is the valence band transition.[10, 12] In the SXES study on $3d^0$ compounds such as TiO_2 and $SrTiO_3$, four soft-X-ray Raman scatterings (α, β, χ, and γ) shown by dashed lines have been observed, which is attributed to a charge-transfer (CT) transition from occupied O $2p$ states to unoccupied Ti $3d$ states.[12–15]

Figure 4 shows the occupied valence band by O $1s$, Ti $2p$ SXES and the unoccupied conduction band by O $1s$ XAS of the BIT thin film. The O $1s$ and Ti $2p$ SXES spectra measured at $hv = 550\,\text{eV}$ and $500\,\text{eV}$ reflect the partial density of state (PDOS) of the O $2p$ state and Ti $3d$ state in the valence band. One can find that the O $2p$ state overlaps with the Ti $3d$ state. This result indicates that the O $2p$ state hybridizes with the Ti $3d$ state in the valence band. Thus, it is clear that feature A corresponds to the nonbonding state and feature B corresponds to the bonding state that is well mixed with the Ti $3d$ state.

From the dipole selection rule, it is understood that the O $1s$ XAS spectra of the Ti compound correspond to transitions from O $1s$ to O $2p$ character hybridized into the unoccupied Ti $3d$ states. Generally, the O $1s$ spectra of Ti oxides shift to a
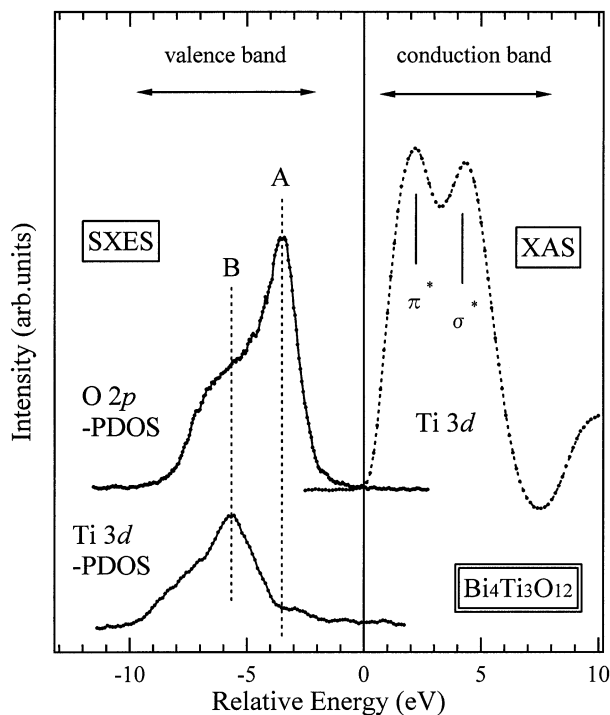
Fig. 4. O $1s$, Ti $2p$ SXES and O $1s$ XAS spectra of BIT thin film. The Ti $2p$ SXES spectrum is excited at $hv = 500$ eV in Fig. 2(a). Features A and B indicate the nonbonding state and bonding state, respectively.

lower energy by about 0.5 eV due to core hole potential. Thus, the bottom axis of the O $1s$ XAS spectrum is calibrated by considering the core hole potential effect. The lower-energy peak is attributed to the O $2p\pi$ state, while the higher-energy peak is attributed to the O $2p\sigma$ state. These states are hybridized with Ti $3d\pi^*$ (t_{2g}) and Ti $3d\sigma^*$ (e_g) states, respectively. The energy separation between the top of the valence band and the bottom of the conduction band reflects the band gap (E_g). However, the observed E_g is not the true value due to the core hole potential effect.

The electronic structures of the single crystals of Ti oxides such as TiO_2 and $SrTiO_3$ have been extensively studied by SXES as well as PES.[12–17] These compounds are also examined for the hybridization effect between Ti $3d$ and O $2p$ states in the valence band. Furthermore, the four CT Raman scatterings that correspond to α, β, χ, and γ in Fig. 3 are also observed. However, the energy position of these compounds is different from that of the BIT thin film. In this study, the incidence angle of the soft-X-ray was about 70° in order to avoid the self-absorption effect. The SXES and XAS spectra were measured at a polarized configuration. The polarization vector of the emitted photon rotates by 90° from the polarization vector of the incident photon. When the SXES spectra are measured in the polarization configuration, the polarization vector of the emitted photon contains the same polarization vector as that of the incident photon. Although the de-

tailed description has been reported by Harada *et al.*,[13] it is clearified that the SXES and XAS spectra at the polarization reflect the electronic structure within the *a-b* plane. Thus, it is considered that the energy difference of the CT Raman scattering of the BIT thin film reflects the change of the Ti–O bond length in comparison with other Ti oxides.

4. Conclusions

We have studied the electronic structure of a BIT thin film by SXES. The O $2p$ state of the BIT thin film hybridizes with the Ti $3d$ state in the valence band. Furthermore, four soft-X-ray Raman scatterings were observed, which is attributed to a charge-transfer (CT) transition from occupied O $2p$ states to unoccupied Ti $3d$ states. Comparing with TiO_2 and $SrTiO_3$, the energy positions of the CT Raman scattering change in the BIT thin film. This finding indicates the change of the Ti–O bond length in the BIT film.

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