Electronic Structure in the Bulk State of $\text{SrTiO}_{3-\delta}$ by Soft-X-Ray Spectroscopy

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The electronic structure in the bulk state of $\text{SrTiO}_{3-\delta}$ single crystal has studied by X-ray absorption spectroscopy (XAS) and soft-X-ray emission spectroscopy (SXES). The $\text{SrTiO}_{3-\delta}$ exhibits the electrical conductivity in semiconducting region. The Ti 3*d* DOS is created in the band gap energy region by substituting oxygen vacancies. The SXES spectra exhibit the soft-X-ray Raman scattering structures, which correspond to *d-d* transition from occupied Ti 3*d* state to unoccupied Ti 3*d* state. The peak position of the Raman scattering reflects the half on-site Coulomb energy ($U_{dd}/2$).

Keywords: $\text{SrTiO}_{3-\delta}$, soft-X-ray emission spectroscopy (SXES), *d-d* transition, on-site Coulomb energy

1. INTRODUCTION

Perovskite-type oxide SrTiO_3 with a band gap of 3.2 eV exhibits *n*-type conductivity due to doping with electric carriers and becomes a superconductor at low temperature. Such electron doping is known to transform insulating SrTiO_3 readily into a metallic state even with a very small extent of doping [1-4]. Doping can be achieved by altering any of the three sublattices, namely, those of Sr^{2+} , Ti^{4+} and O^{2-} . In particular, La^{3+} substitution at the Sr^{2+} site ($\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$) and Nb^{5+} substitution at the Ti^{4+} site ($\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$) have been extensively studied [1-6]. These samples are used as a substrate for the thin film deposition of ferroelectrics and superconductors because of their similar crystal structures and good lattice matching. On the other hand, $\text{SrTiO}_{3-\delta}$ with oxygen vacancies, which exists as natural ore, might be also expected as substrate for the thin film deposition and other electronic devices. However, details of electronic structure have not been clarified thus far.

In this study, we prepared the $\text{SrTiO}_{3-\delta}$ ($\delta=0, 0.02$) single crystals by floating zone method and measured the electronic structure using X-ray absorption spectroscopy (XAS) and soft-X-ray emission spectroscopy (SXES). The photoemission (PES) spectra were also measured as reference. The SXES spectra reflect the electronic structure of the bulk compared with PES spectra, because the mean free path of a soft-X-ray is very long compared with that of the electron. Furthermore, the Raman scattering observed in the SXES spectra provides useful information about the electronic structure. It is reported that the Raman scattering for 3*d* transition metal compounds is attributed primarily to the *d-d* transition between the 3*d* valence and conduction bands as well as charge transfer (CT) transition from an occupied O 2*p* band to an unoccupied 3*d* band [7-12]. In particular, The observations of *d-d* and CT transitions are useful for the study of electronic structure of strongly correlated electron system. Here, we prove electronic structure

and electron correlation effect of $\text{SrTiO}_{3-\delta}$ single crystals.

2. EXPERIMENTAL

The $\text{SrTiO}_{3-\delta}$ ($\delta=0, 0.02$) samples were prepared by the solid state reaction of SrCO_3 (99.9%, Furuuchi Chemical Co., Ltd.) and TiO_2 (99.99%, Furuuchi Chemical Co., Ltd.) at 1200°C for about 12 h, and the single crystals were grown by a floating-zone method using an Xe-arc imaging furnace. The $\text{SrTiO}_{2.98}$ crystal was obtained in an as-grown sample. The SrTiO_3 crystal was obtained by annealing the as-grown crystal in O_2 atmosphere at 1000°C. The prepared crystals were characterized by X-ray diffraction. The electrical resistivity was characterized by AC impedance method.

SXES and XAS spectra were measured using a soft-X-ray spectrometer installed at an undulator beamline BL-19B (at the Photon Factory), of the High Energy Accelerator Organization. Synchrotron radiation was monochromatized using a varied line spacing plane grating whose average groove density is 1000 lines/mm. The incidence angle of the soft-X-ray was selected to be about 75° in order to avoid the self-absorption effect. The energy resolution was smaller than 0.8 eV at $h\nu=450$ eV.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the XRD patterns of (200) peak as a function of anneal temperature in O_2 atmosphere for $\text{SrTiO}_{3-\delta}$ single crystal. The (200) peak shifts to the lower diffraction angle with increasing anneal temperature. Figure 1(b) shows the lattice constant of *a*-axis as a function of anneal temperature calculated from Fig. 1(a). The lattice constant increases with increasing anneal temperature. The lattice constant of as-grown $\text{SrTiO}_{3-\delta}$ annealed at 1000°C accords with that of pure SrTiO_3 single crystal [13]. This indicates that the oxygen vacancies of $\text{SrTiO}_{3-\delta}$ are compensated by annealing at 1000°C in O_2 atmosphere.

Fig. 1 (a) XRD patterns and (b) lattice constants as a function of anneal temperature in O_2 atmosphere.

Fig. 2 Electrical resistivity at room temperature as a function of anneal temperature in O_2 atmosphere.

Figure 2 shows the electrical resistivity as a function of anneal temperature in O_2 atmosphere for $\text{SrTiO}_{3-\delta}$ single crystal. The electrical resistivity increases with increasing anneal temperature. The resistivity of as-grown $\text{SrTiO}_{3-\delta}$ annealed at 1000°C accords with that of pure SrTiO_3 single crystal. However, the as-grown $\text{SrTiO}_{3-\delta}$ sample exhibits the resistivity in the semiconducting region. This may indicate that the Ti 3d electron is closely related with the decrease of resistivity.

Fig. 3 PES and SXES spectra in the valence band region of as-grown $\text{SrTiO}_{3-\delta}$.

Fig. 4 Ti 2p XAS spectra of $\text{SrTiO}_{3-\delta}$ and pure SrTiO_3 . The numbers indicate the photon energies where the Ti 2p SXES spectra were measured.

Figure 3 shows the PES and SXES spectra in the valence band region of $\text{SrTiO}_{3-\delta}$. The PES spectrum measured at $h\nu=450$ eV reflects the total density-of-state (DOS). It is well known that the valence band is mainly composed of O 2p state hybridized with Ti 3d state. Although pure SrTiO_3 does not have DOS in the energy gap (E_g) region, the $\text{SrTiO}_{3-\delta}$ exhibits the existence of DOS. The Ti 2p SXES spectrum measured at $h\nu=472$ eV reflects the Ti 3d partial DOS in the valence band region. The Ti 3d partial DOS is observed in the valence band and E_g regions. In particular, the DOS exists at near Fermi level (E_F).

Figure 4 shows the Ti 2p XAS spectrum of $\text{SrTiO}_{3-\delta}$ and SrTiO_3 . The spectrum is mainly derived from two parts of L_3 ($2p_{3/2}$) and L_2 ($2p_{1/2}$). Each part is split into t_{2g} and e_g states by an octahedral ligand field. The spectral shape of SrTiO_3 is similar to that of $\text{SrTiO}_{3-\delta}$. The peak intensity of Ti 2p XAS spectrum is lower in $\text{SrTiO}_{3-\delta}$. This indicates that the Ti 3d electron with oxygen vacancies enters into the Ti 3d conduction band. The vertical bars labeled from 1 to 6 indicate photon energies selected for resonant SXES measurements.

Fig. 5 Ti 2p SXES spectra of $\text{SrTiO}_{3-\delta}$ excited at various photon energies in Fig. 1. Arrow shows the energy position of the excitations photon energy. Vertical broken lines show the energy positions of Ti $3d \rightarrow 2p$ fluorescence.

Figure 5 shows Ti 2p SXES spectra of $\text{SrTiO}_{3-\delta}$ excited at each point of Fig. 1. It is well known that the Ti 2p emission reflects the Ti 3d partial DOS. An arrow shown in each spectrum is attributed to 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 . Then, the peak intensity decreases with increasing excitation energy.

The SXES spectrum 6 excited at $h\nu=472$ eV is an off-resonance spectrum attributed to the normal Ti $3d \rightarrow 2p$ fluorescence spectrum. This spectrum suggests that the Ti 3d state hybridizes with the O 2p state in the valence band, as shown in Fig. 3. Four dashed lines (a, b, c, and d peaks) show the fluorescence bands. The a and b peaks correspond to the bonding state and the nonbonding state in the valence band, respectively. The c and d peaks correspond to the coherent band and the incoherent band in the band gap, respectively.

Four parts denoted by small vertical bars in each Ti 2p SXES spectrum represent the energy sites shifted from the excitation energy shown in Fig. 4, to be 5.6, 6.9, 8.0, and 9.3 eV, respectively. They shift as the excitation energy is varied. These features are attributed to the soft-X-ray Raman scattering (or inelastic scattering). The soft-X-ray Raman scattering that is excited in the L_3 absorption spectral region overlaps with the Ti $3d \rightarrow 2p$ fluorescence. The SXES spectrum 1 excited immediately below the Ti 2p threshold shows an apparent feature at a lower energy than the elastic scattering. Since the excitation energy is lower than the binding energy of Ti 2p, the Ti $3d \rightarrow 2p$ fluorescence cannot be observed. It is attributed to a normal Raman scattering, where the intermediate is a virtual state.

Figure 6 shows SXES spectra of $\text{SrTiO}_{3-\delta}$, where the abscissa is the Raman shift (or energy loss) that is the energy shift from the elastic scattering. The energy of

Fig. 6 Ti $3d \rightarrow 2p$ SXES spectra of $\text{SrTiO}_{3-\delta}$ presented as the relative emission energy to the elastic scattering. Inset shows the optical conductivity spectrum of $\text{SrTiO}_{3-\delta}$.

each elastic scattering peak in Fig. 5 is normalized at 0 eV. The Ti $3d \rightarrow 2p$ fluorescence peaks shown by four vertical dashed bars shift to the higher energy with increasing the excitation energy. Four vertical solid lines α , β , γ , and ϵ indicate the Raman scatterings. These Raman scatterings can be compared with the optical conductivity spectrum [3], since the elementary excitation of the Raman scattering is the valence band transition. Therefore, the optical conductivity spectrum of $\text{SrTiO}_{3-\delta}$ is shown as dashed spectral line in inset of Fig. 6. Compared with the SXES spectra, the four Raman scatterings are in good accordance with the optical conductivity spectrum, as shown by the four dashed lines. This fact indicates that these Raman scatterings can be attributed to a charge-transfer (CT) transition from the occupied O 2p state to the unoccupied Ti 3d state [11,12].

Figure 7 shows a comparison of the t_{2g} -resonanced SXES spectra between SrTiO_3 and $\text{SrTiO}_{3-\delta}$. As reference, the $\text{La}_{0.10}\text{Sr}_{0.90}\text{TiO}_3$ (LSTO) with the electron correlation effect is also shown in this figure. The δt_{2g} peak is observed at about 2.0 eV in $\text{SrTiO}_{3-\delta}$, although the peak is not observed in SrTiO_3 . The PES spectrum in Fig. 3 indicates that two peaks attributed to Ti 3d states are observed just below the Fermi level (E_F). The peaks are the coherent band at E_F and the incoherent band at about 1.5 eV below E_F . In the t_{2g} excitation, there is typically no large band splitting so that the contribution to the Raman scattering is due to the electron correlation energy (U_{dd}). The Raman scattering of the δt_{2g} peak at approximately ~ 2.0 eV corresponds to the $d-d$ transition from the occupied incoherent band to the unoccupied coherent band. Therefore, the Raman shift of the δt_{2g} peak reflects the effective $U_{dd}/2$. The magnitude is in good agreement with the results of the PES and inverse-PES studies [12]. On the other hand, the intensity at Raman shift=0 eV is

Fig. 7 Comparison of the t_{2g} -resonance SXES spectra of $\text{SrTiO}_{3-\delta}$ and pure SrTiO_3 . This t_{2g} -resonance spectrum obtained for $\text{SrTiO}_{3-\delta}$ corresponds to the spectrum 2 in Fig. 6. As reference, the spectrum of $\text{La}_{0.10}\text{Sr}_{0.90}\text{TiO}_3$ (LSTO) is also shown.

larger in $\text{SrTiO}_{3-\delta}$. This behavior indicates the Drude photoresponse which is attributed to the d - d transition between the coherent bands [9, 12].

4. CONCLUSION

The authors have studied the electronic structure in the bulk state of $\text{SrTiO}_{3-\delta}$ using the SXES, PES and XAS. The electronic structure in the valence band region of the SXES spectrum reflects that of the PES spectrum. The CT Raman scattering, which corresponds to the transition from O $2p$ to Ti $3d$ states in the virtual state, agrees with the optical conductivity spectrum. The Raman scattering, which is attributed to the d - d transition between the incoherent and the coherent bands, is directly observed in the t_{2g} -resonance SXES spectra of $\text{SrTiO}_{3-\delta}$. The Raman shift corresponds to the magnitude of the effective $U_{dd}/2$. The existence of the Raman scattering indicates that the $\text{SrTiO}_{3-\delta}$ has weak electron correlation effect.

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