

# Unoccupied Electronic State at Low Temperature of SrTiO<sub>3-δ</sub> Probed by Resonant Inverse Photoemission Spectroscopy

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The unoccupied electronic structure at low temperature of SrTiO<sub>3-δ</sub> has been studied by resonant-inverse photoemission spectroscopy (RIPES). The RIPES spectra show two peaks whose the energy separations match with the *t<sub>2g</sub>*- and *e<sub>g</sub>*-subbands of unoccupied Ti 3*d* state. A new peak clarified by the Ti 3*p* → 3*d* resonance effect is observed at ~6.1 eV above Fermi level (*E<sub>F</sub>*). The ~6.1 eV peak is not found in the O 1*s* X-ray absorption spectrum, which reflects the electronic structure of the bulk state. The existence of the ~6.1 eV peak suggests the correlation effect at low temperature of SrTiO<sub>3</sub>.

Key words: SrTiO<sub>3</sub>, resonant-inverse photoemission spectroscopy (RIPES), electronic structure, unoccupied state

## 1. INTRODUCTION

SrTiO<sub>3</sub> is one of the most widely studied materials in solid state physics and chemistry, as it exhibits interesting properties including quantum paraelectricity [1], induced ferroelectricity by an electric field [2], uniaxial stress [3], Ca substitution [4], and zone boundary phase transition [5]. In particular, quantum paraelectric behavior is well known for KTaO<sub>3</sub> [6] and SrTiO<sub>3</sub> [7]. The zone boundary phase transition of SrTiO<sub>3</sub> at 105 K does not coincide with the anomaly in the dielectric constant ( $\epsilon_r$ ) that occurs with changes in temperature. The  $\epsilon_r$  in quantum paraelectric SrTiO<sub>3</sub> perpendicular to the *c*-axis increases to approximately 30000 upon cooling, and then remains temperature independent below 3K because of quantum fluctuations.

The electronic structure of SrTiO<sub>3</sub> has been extensively studied by experimental and theoretical methods [8-18]. SrTiO<sub>3</sub>, which normally has a *d0* configuration, is a band insulator with a band gap of 3.2 eV. It has been reported that the electronic structure can be possibly described by standard band calculation, since electron-electron correlation does not play a significant role in the filled O 2*p* valence band and in the empty Ti 3*d* conduction band, unlike in Mott-insulators, where electron correlation in the partially filled Ti 3*d* band plays an important role [8-10]. However, the detailed electronic structure at low temperature region has not been clarified by experimental method.

In this study, the electronic structure at low temperature region of SrTiO<sub>3-δ</sub> has been measured by resonant inverse photoemission spectroscopy (RIPES). The RIPES is a powerful technique to investigate the unoccupied electronic structure in the surface state. Although the technique and new physics obtained from RIPES spectra were investigated in rare-earth metal compounds [19-20], report of RIPES study of lightly 3*d* transition metal compounds is very few.

## 2. EXPERIMENTAL

The SrTiO<sub>3-δ</sub> were prepared by the solid state

reaction of SrCO<sub>3</sub> and TiO<sub>2</sub> 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 single crystal was confirmed as being a single phase with perovskite structure by the powder X-ray diffraction analysis.

The RIPES measurements were carried out at Department of Applied Physics, Tokyo University of Science. A filament-cathode-type electron gun was used for the excitation source. The kinetic energy (*E<sub>k</sub>*) of the electron was calibrated by the electron energy analyzer. The RIPES spectra were measured by the soft-X-ray emission spectrometer, which covers the wide photon energy range from 15 to 1200 eV. The spectrometer used the Rowland circle geometry that consists of grating with groove density of 300 lines/mm and the Cs-coated multichannel detector.

The sample was scraped *in situ* with a diamond file in a vacuum of 2.0×10<sup>-10</sup> Torr in order to obtain the clean surface. The measurement was carried out at 25 K. The intensity axis was normalized by the electron current and measurement time. The bottom axis was normalized by measuring the Fermi edge of Au film. The total energy resolution of the experimental system was approximately 0.5 eV at *E<sub>k</sub>*=60 eV.

## 3. RESULTS AND DISCUSSION

Figure 1 shows the excitation energy dependence of the RIPES spectra of SrTiO<sub>3-δ</sub> in the incident electron energy (*E<sub>k</sub>*) region of Ti 3*p* core level. The abscissa represents the energy above the Fermi level (*E<sub>F</sub>*). The intensity of the peak D at about ~7.3 eV becomes strong at lower electron energy. This is considered to be due to the electron energy dependence of the ionization cross section, indicating the existence of the Sr 4*d* band. The broad bands indicated by arrow are the normal Ti 3*p* fluorescence that is caused by the Ti 3*p* core hole created by the electron excitation. In the energy region from 0 to 5 eV, two prominent peaks A and B are found at ~1.7 and ~3.9 eV, respectively. The intensities of

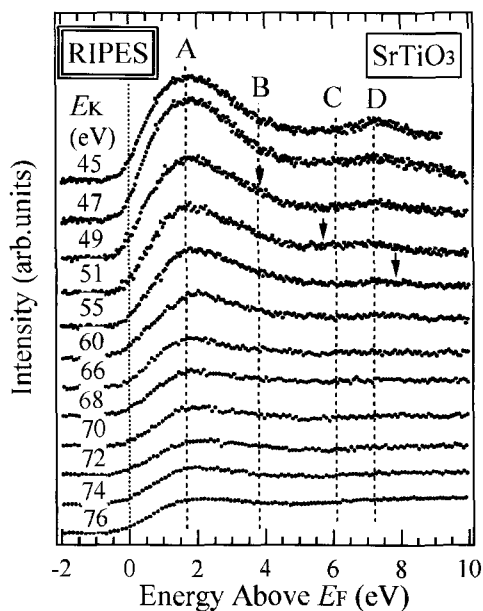
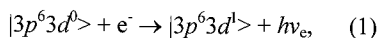


Fig. 1: IPES spectra of  $\text{SrTiO}_{3-\delta}$  near the Ti  $3p \rightarrow 3d$  absorption edge measured by various  $E_k$ . The abscissa is the energy above Fermi level ( $E_F=0$  eV). Arrow shown in each spectrum indicates the normal fluorescence.

the peaks A and B increase with decreasing  $E_k$  and decrease at  $E_k=45$  eV. This indicates the resonance effect of the IPES spectra at  $E_k=47$  eV. These enhancements resemble with the resonance effect of the photoemission spectra on the valence band region [13]. In the energy region above 5.0 eV, the peaks C and D are found at  $\sim 6.1$  eV and  $\sim 7.3$  eV, respectively. The details of the peaks B and C, which seem to only a long tail of the peaks A, are clarified in Figs. 2 and 3.

Figure 2 shows the excitation energy dependences of the intensities of three peaks A, B and C estimated from Fig.1. These curves are obtained by plotting the intensities of the three peaks against  $E_k$ , which correspond to the constant final state (CFS) spectra. The intensities of the three peaks A, B, and C increase with decreasing  $E_k$ . These intensities have a maximum intensity at  $E_k=47$  eV. As references, the CFS spectrum used in the RPES spectrum is also shown [13]. The CFS spectrum of  $\text{SrTiO}_3$  has been already measured at the kinetic energy, where the secondary electron has a maximum intensity. The CFS spectrum is approximately regarded as the absorption spectrum of Ti  $3p \rightarrow 3d$ . It is reported that the bonding state in the valence band is resonantly enhanced at the photon energy of 47 eV [13]. The CFS spectra in both PES and IPES have maximum at near  $E_k=47$  eV, indicating the Ti  $3p \rightarrow 3d$  resonant effect of IPES.

The normal IPES process is represented for the transition to Ti  $3d$  states as follows:



where  $e^-$  and  $hv_e$  are the incident electron and the emitted photon. For the incident energy range of the present study, the conduction from non- $d$  conduction bands also coexists with the  $3d$  contribution in the

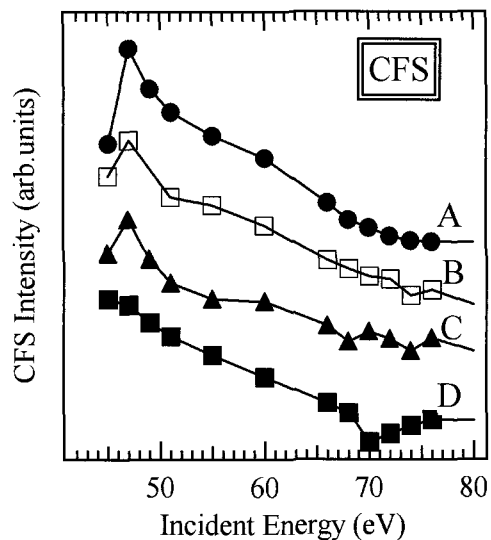
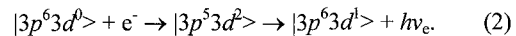


Fig.2: Intensities as a function of  $E_k$  of four peaks, A, B, C, and D, which are observed in Fig. 1.

normal IPES. In the RIPES study, on the other hand, the resonant processes are expressed by the following processes:



Since the initial and final states are the same in these two processes (1) and (2), they interfere with each other. Therefore, the  $3d$  cross section increases when the excitation energy is tuned to Ti  $3p \rightarrow 3d$  absorption edge and we can extract the Ti  $3d$  contribution in the conduction band.

The excitation energy dependence of the intensity of the peak D estimated from Fig.1 is also shown in Fig. 2. This curve is obtained by plotting the intensity of the peak D against the kinetic energy of the electron. The intensity increases with decreasing  $E_k$ , though the intensity has minimum at  $E_k \sim 70$  eV. These behaviors accord with the electron energy dependence of the ionization cross-section of  $4d$  state in  $4d$  transition metal [21]. Therefore, the peak D might be estimated to be the Sr  $4d$  state.

Figure 3(a) shows the comparison of on- and off-resonance spectra of the conduction band measured at  $E_k=47$  and 45 eV. One can find that the Ti  $3d$  components in both the peaks A and B are resonantly enhanced by the Ti  $3p \rightarrow 3d$  excitation in the on-resonance spectrum, though the resonance effect of the peak B is very weak in comparison with that of the peak A. The difference spectrum from on-resonance to off-resonance spectra is also shown. It is known that the difference spectrum corresponds to the Ti  $3d$  partial density-of-state (DOS) in the conduction band. The O  $1s$  X-ray absorption (XAS) spectrum of  $\text{SrTiO}_3$  is also shown in Fig.3 (b). From the dipole selection rule, it is indicated that the O  $1s$  XAS spectrum of  $\text{SrTiO}_3$  correspond to transitions into O  $2p$  character hybridized into the unoccupied Ti  $3d$  states [13-14]. The  $E_F$  of the XAS spectrum is determined from the binding energy of the O  $1s$  photoemission peak. The energy position of

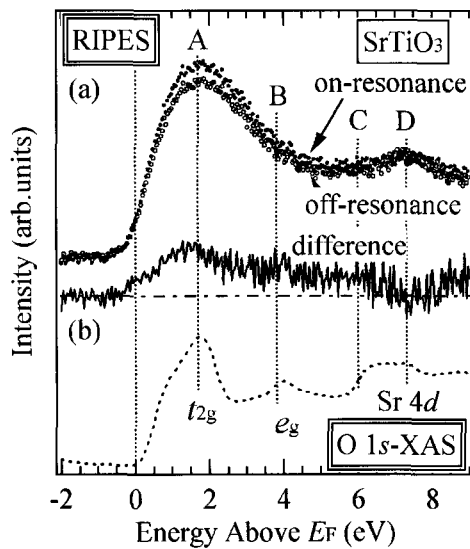


Fig.3 (a) On-resonance (closed circle) and off-resonance (open circle) spectra measured at  $E_k = 47$  eV and 45 eV, respectively. Difference spectrum (solid line) subtracted from on- and off-resonance spectrum is also shown. (b) O 1s XAS spectrum.

Sr 4d state of the O 1s XAS spectrum matches with the broad band at  $\sim 7.3$  eV (peak D) in the RIPES spectra. The difference spectrum at  $\sim 7.3$  eV is negative since the cross-section increases with decreasing  $E_k$ , indicating the existence of Sr 4d state. On the other hand, two peaks at  $\sim 1.7$  eV and  $\sim 3.9$  eV of O 1s XAS spectrum reflect the  $t_{2g}$ - and  $e_g$ -subbands of the Ti 3d states. The energy separation between the  $t_{2g}$ - and  $e_g$ -subbands (crystal-field splitting) accords with Ti 2p XAS spectrum and the band calculation for the O 1s XAS spectra by Fujimori *et al.*[12]. It is striking that the energy positions of the  $t_{2g}$  and  $e_g$  subbands of O 1s XAS spectrum are in good agreement with the peaks A and B of the RIPES spectra, as shown in two vertical dashed lines. These positions of the peaks A and B mismatch with those of the coherent and incoherent parts, which are expected from the disordered Hubbard model [12].

In the difference spectrum of Fig.3 (b), the peak C at  $\sim 6.1$  eV, which shows the Ti  $3p \rightarrow 3d$  resonant effect in Fig.2, does not match with the O 1s XAS spectrum. The peak C has not been observed in the RIPES spectra at room temperature [22]. The existence of the peak C might be attributed to the surface-induced structure, because the O 1s XAS spectrum is the bulk sensitive. In recent years, the band structure in the conduction band region of the  $\text{SrTiO}_{3-\delta}$  has been calculated by Sarma and co-workers [17-18]. They used the linearized muffin-tin orbital (LMTO) method within the atomic-sphere approximation. From the second order perturbation applied to the DOS obtained from LMTO supercell calculation, a correlation-induced satellite appears outside the one-electron bandwidth in the unoccupied states [18]. The energy position of the correlation satellite structure matches with that of the peak C observed in Fig.3 (b). This fact indicates that the correlation effect exists in the surface state of low temperature region of  $\text{SrTiO}_{3-\delta}$ .

#### 4. CONCLUSION

We have studied the unoccupied electronic state at low temperature of  $\text{SrTiO}_{3-\delta}$  using RIPES. The resonance enhancement of the RIPES is observed at the Ti  $3p \rightarrow 3d$  absorption edge. The RIPES spectra show two peaks, which correspond to the  $t_{2g}$ - and  $e_g$ -subbands of the O 1s XAS spectrum. On the other hand, a new peak clarified by the Ti  $3p \rightarrow 3d$  resonance effect is observed at  $\sim 6.1$  eV above  $E_F$ . The  $\sim 6.1$  eV peak is not found in the O 1s XAS spectrum that reflects the electronic structure of the bulk state. The energy position of the  $\sim 6.1$  eV peak match with that of the correlation satellite, which is expected from LMTO supercell calculation.

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