

Unoccupied electronic structure in the surface state of lightly doped SrTiO₃ by resonant inverse photoemission spectroscopy

T. Higuchi, S. Nozawa, and T. Tsukamoto

Department of Applied Physics, Tokyo University of Science, Tokyo 162-8601, Japan

H. Ishii and R. Eguchi

Institute for Solid State Physics, University of Tokyo, Chiba 277-8581, Japan

Y. Tezuka

Faculty of Science and Engineering, Hirosaki University, Hirosaki 036-8561, Japan

S. Yamaguchi

Department of Materials Science, University of Tokyo, Tokyo 113-8656, Japan

K. Kanai* and S. Shin

Institute for Solid State Physics, University of Tokyo, Chiba 277-8581, Japan and RIKEN, Sayo-gun, Hyogo 679-5148, Japan

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The unoccupied electronic structure in the surface state of lightly doped SrTiO₃ has been studied by resonant inverse-photoemission spectroscopy (RIPES). The RIPES spectra show two features whose energy separations match the t_{2g} and e_g subbands of unoccupied Ti 3*d* state. A peak clarified by the Ti 3*p*→3*d* resonance effect is observed at ~6.1 eV above Fermi level (E_F). 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 in the surface state of lightly doped SrTiO₃.

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Stoichiometric SrTiO₃, which normally has a d^0 configuration, is a band insulator with a band gap of about 3.2 eV. It has been extensively used as a substrate for thin-film deposition of high- T_c superconductors and ferroelectrics because of their similar crystal structures and good lattice matching. 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.¹⁻³

Recently, there has been a renewed interest in the electronic structure of SrTiO₃ doped with a charge carrier.⁴⁻¹² When a small number of electrons chemically doped into SrTiO₃, e.g., by La³⁺ substitution for Sr²⁺ site or by Nb⁵⁺ substitution for Ti⁴⁺ site, the doped electrons enter the bottom of the empty Ti 3*d* band. In the limit of lightly doping concentration, there will be no electron correlation between the doped electrons since the probability of electron-electron scattering is vanishingly small. The photoemission spectra have two features in the band-gap region, which are generally believed to be a coherent part at the Fermi level (E_F) and an incoherent part at ~1.5 eV that is attributed to a remnant of the lower Hubbard band.^{5,12} The band-structure calculations that assume a rigid-band filling cannot reproduce the peak at ~1.5 eV, though the bandwidth of the O 2*p* valence band shows a good agreement with the photoemission spectra.⁴ The origin of the ~1.5 eV peak has been studied by several theoretical calculations.^{5,10-12} It is proposed that the ~1.5 eV peak is by a polaronic feature⁵ or a surface structure¹² that is created due to the degree of correlation and

disorder in the surface. A similar feature is also expected in the conduction-band side.¹² However, the detailed electronic structure in the conduction band has not been clarified by experimental methods such as resonant inverse-photoemission spectroscopy (RIPES).

In this paper, we present RIPES spectra of lightly Nb-doped SrTiO₃ (SrTi_{0.98}Nb_{0.02}O₃). RIPES is a powerful technique to investigate the unoccupied electronic structure in the surface state. Although the technique and the physics obtained from RIPES spectra were extensively investigated in rare-earth metal compounds by Kanai and co-workers,¹³⁻¹⁷ the RIPES spectra of lightly 3*d* transition-metal compounds have not been reported thus far.

The SrTi_{0.98}Nb_{0.02}O₃ samples were prepared by the solid-state reaction of SrTiO₃, SrCO₃, and Nb₂O₅ at 1200 °C for about 12 h, and the single crystals were grown by a floating-zone method using 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 the Institute for Solid State Physics, University of Tokyo. A filament-cathode-type electron gun was used for the excitation source. The kinetic energy (E_k) 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.^{18,19} The spectrometer used the Rowland circle geometry that consists of grating with a groove density of 300 lines/mm and a Cs-coated multichannel detector.

The sample was scraped *in situ* with a diamond file in a vacuum of 2.0×10^{-10} Torr in order to obtain the clean sur-

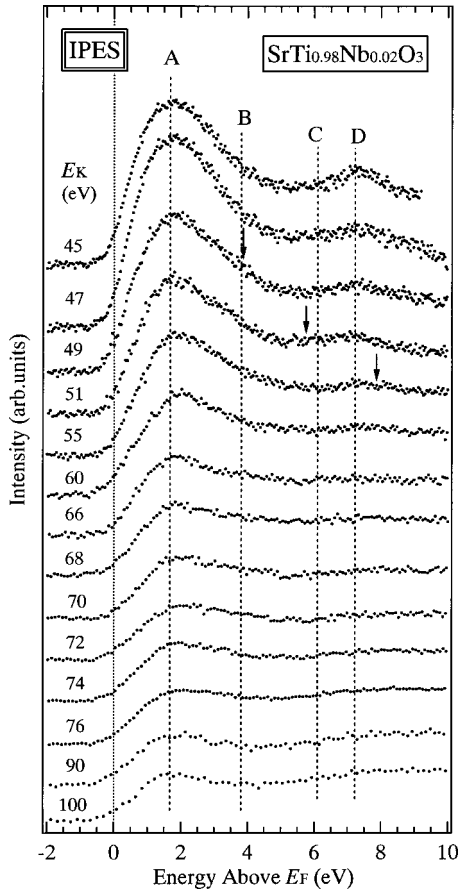


FIG. 1. IPES spectra of $\text{SrTi}_{0.98}\text{Nb}_{0.02}\text{O}_3$ near the $\text{Ti } 3p \rightarrow 3d$ absorption edge measured by various kinetic energy of the electron (E_K). The abscissa is the energy above Fermi level ($E_F = 0$ eV). Arrows shown in each spectrum indicate the normal fluorescence.

face. 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 the Au film. The total-energy resolution of the experimental system was about 0.5 eV at $E_K = 60$ eV.

Figure 1 shows the excitation energy dependence of the RIPES spectra of $\text{SrTi}_{0.98}\text{Nb}_{0.02}\text{O}_3$ in the incident electron energy (E_K) region of Ti $3p$ core level. The abscissa represents the energy above the Fermi level (E_F) that was calibrated by the Fermi edge of Au. The experimentally determined E_F is located almost at the bottom of the conduction band because the sample used in this study has n -type conductivity. The intensity of the feature 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 $4d$ band. The broad bands indicated by arrows are the normal Ti $3p$ fluorescence caused by the Ti $3p$ core hole created by the electron excitation. In the energy region from 0 to 5 eV, two prominent features A and B are found at ~ 1.7 and ~ 3.9 eV, respectively. The intensities of the features 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 the resonance effect

of the photoemission spectra on the valence-band region.⁶⁻⁸ In the energy region above 5.0 eV, the features C and D are found at ~ 6.1 and ~ 7.3 eV, respectively. The details of features B and C , which seem to be only a long tail of the features A , are clarified in Figs. 2 and 3.

Figure 2(a) shows the excitation energy dependences of the intensities of three features A , B , and C estimated from Fig. 1. These curves are obtained by plotting the intensities of the three features against E_K , which correspond to the constant final-state (CFS) spectra. The intensities of the three features A , B , and C increase with decreasing E_K . As references, the CFS spectrum used in the RPES spectrum is also shown.⁶⁻⁸ The CFS spectrum of $\text{SrTi}_{0.98}\text{Nb}_{0.02}\text{O}_3$ 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.⁶⁻⁸ The CFS spectra in both PES and IPES have their maxima 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:

$$|3p^6 3d^0\rangle + e^- \rightarrow |3p^6 3d^1\rangle + h\nu_e, \quad (1)$$

where e^- and $h\nu_e$ 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 normal IPES. In the RIPES study, on the other hand, the resonant processes are expressed by the following processes:

$$|3p^6 3d^0\rangle + e^- \rightarrow |3p^5 3d^2\rangle \rightarrow |3p^6 3d^1\rangle + h\nu_e. \quad (2)$$

Since the initial and final states are the same in these two processes, Eqs. (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.

Figure 2(b) shows the excitation energy dependence of the intensity of the feature D estimated from Fig. 1. This curve is obtained by plotting the intensity of the feature 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 the $4d$ state in the $4d$ transition metal. Therefore, the feature 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 features, A and B , are resonantly enhanced by the Ti $3p \rightarrow 3d$ excitation in the on-resonance spectrum, though the resonance effect of the feature B is very weak in comparison with that of feature 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 $1s$

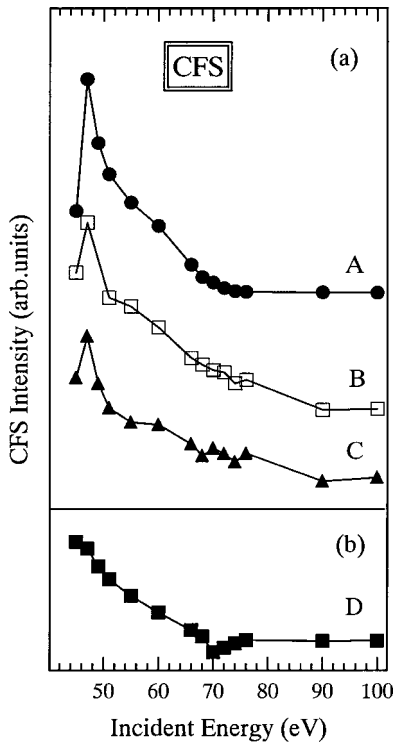


FIG. 2. Intensities as a function of E_k of four peaks, (a) A, B, C, and (b) D, which are observed in Fig. 1.

x-ray absorption spectrum of $\text{SrTi}_{0.98}\text{Nb}_{0.02}\text{O}_3$ is also shown in Fig. 3(b). From the dipole selection rule, it is indicated that the O 1s x-ray absorption spectrum (XAS) of SrTiO_3 corresponds to transitions into O 2p character hybridized into the unoccupied Ti 3d states.⁷ The E_F of the XAS spectrum is determined from the binding energy of the O 1s photoemission peak. The energy position of Sr 4d state of the O 1s XAS spectrum matches with the broad band at ~ 7.3 eV (feature D) in the RIPES spectra. The difference spectrum at ~ 7.3 eV is negative since the cross section increases with decreasing E_k , indicating the existence of the Sr 4d state. On the other hand, two features at ~ 1.7 and ~ 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 the Ti 2p XAS spectrum and the band calculation for the O 1s XAS spectra by Fujimori *et al.*⁴ It is striking that the energy positions of the t_{2g} and e_g subbands of the O 1s XAS spectrum are in good agreement with features A and B of the RIPES spectra, as shown in two vertical dashed lines. These positions of features 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 feature C at ~ 6.1 eV, which shows the Ti $3p \rightarrow 3d$ resonant effect in Fig. 2, does not match the O 1s XAS spectrum. The existence of feature C might be attributed to the surface-induced structure, because the O 1s XAS spectrum is bulk sensitive. In recent years, the band structure in the conduction-band region of the lightly doped SrTiO_3 has been calculated by Sarma and co-workers.¹⁰⁻¹² They used the linearized muffin-

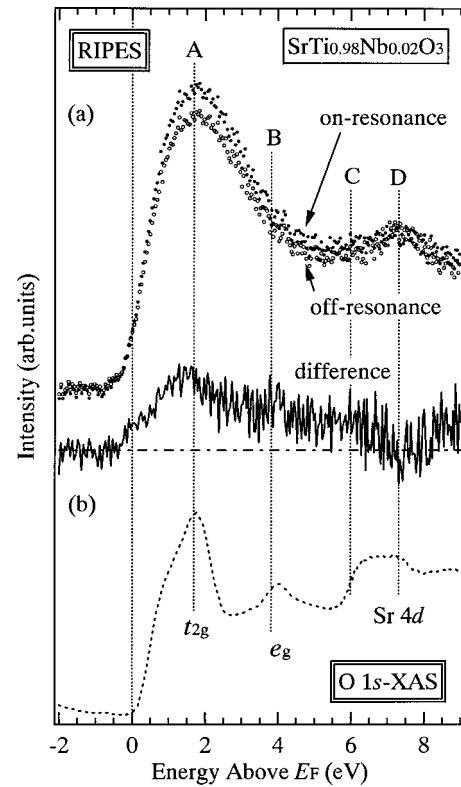


FIG. 3. (a) On-resonance (closed circle) and off-resonance (open circle) spectra measured at $E_k=47$ and 45 eV, respectively. (b) Difference spectrum (solid line) subtracted from on- and off-resonance spectrum is also shown. (c) O 1s XAS spectrum.

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.¹² The energy position of the correlation satellite structure matches that of the feature C observed in Fig. 3(b). This fact indicates that the correlation effect exists in the surface state of lightly doped SrTiO_3 .

In conclusion, we have studied the unoccupied electronic state of lightly doped SrTiO_3 using RIPES. The resonance enhancement of the RIPES is observed at the Ti $3p \rightarrow 3d$ absorption edge. The RIPES spectra show two features, which correspond to the t_{2g} and e_g subbands of the O 1s XAS spectrum. On the other hand, a peak clarified by the Ti $3p \rightarrow 3d$ resonance effect is observed at ~ 6.2 eV above E_F . The ~ 6.1 eV peak is not found in the O 1s x-ray absorption spectrum that reflects the electronic structure of the bulk state. The energy position of the ~ 6.2 eV peak matches that of the correlation satellite in the surface state, which is expected from LMTO supercell calculation.

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- *Present address: Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan.
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