Electronic structure of p-type SrTiO$_3$ by photoemission spectroscopy

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The electronic structure of p-type SrTiO$_3$ has been studied by photoemission spectroscopy (PES). Comparing with the PES of n-type SrTiO$_3$, the Fermi level of p type is lower by about 0.7 eV and a prominent feature of Ti 3$d$ character within the band gap, which is formed in the n-type SrTiO$_3$, cannot be found in p-type SrTiO$_3$. It is suggested that the band structure of p-type SrTiO$_3$ follows the rigid-band model. The resonant photoemission study shows that the Ti 3$d$ partial density of states in the valence band of p-type SrTiO$_3$ is much larger than that of n-type SrTiO$_3$. Furthermore, it is also found that the satellite intensities of several core lines in p-type SrTiO$_3$ are stronger than those in n-type SrTiO$_3$. These facts suggest that the hybridization effect between the Ti 3$d$ and O 2$p$ states becomes stronger in p-type SrTiO$_3$. [S0163-1829(98)03312-8]

I. INTRODUCTION

Strontium titanate (SrTiO$_3$) is one of the most typical perovskite-type compounds with a band gap of about 3.2 eV. It is well known that the SrTiO$_3$ crystal has n-type conductivity by doping cations such as Nb$^{5+}$, La$^{3+}$, and Y$^{3+}$ and it becomes a superconductor. The electronic structure of Nb-doped SrTiO$_3$ has been reported in several photoemission spectroscopy studies. In a simple ionic model, a titanium ion in SrTiO$_3$ is tetravalent and has no 3$d$ correlation interactions, the electronic structure of SrTiO$_3$ is essentially ionic. There are no 3$d$ electrons nominally that bring appreciable correlation interactions, the electronic structure of SrTiO$_3$ is possibly described by the energy-band picture. In fact, a lot of theoretical calculations of electronic band structures have also been performed on n-type SrTiO$_3$. In SrTiO$_3$, the top of the valence band is mainly composed of O 2$p$ states and the bottom of the conduction band is formed by the Ti 3$d$ states. However, it is known that the orbital of 3$d$ electrons in titanium is strongly hybridized with those in oxygen. This leads to the situation in which nonvanishing 3$d$ electrons exist in the ground state. Thus, interesting properties in the photoemission spectra are found in the satellite structures of the light transition-metal compounds. Van deer Laan$^7$ observed satellites in the Ti 2$p$ absorption spectra, and strong satellites were observed in the Ti 2$p$ photoemission spectra.$^{3,8-13}$ These satellites are considered to be caused by the charge-transfer (CT) -type satellites.

The Sr$_{1-x}$La$_x$TiO$_3$ has been studied extensively by x-ray absorption and photoemission spectra so far. The 3$d$ state appears due to the La doping in the band gap below the Fermi level.$^{14}$ The small Fermi edge, which should be responsible for the superconductivity, was found.$^{15}$ The intensity of the 3$d$ state in the band gap becomes larger as the La concentration increases.$^{14}$ By O 1$s$ absorption,$^{14}$ the energy shift to the lower energy region was found and the intensity at the absorption edge becomes larger as the La concentration increases.

Recently, it was found that SrTiO$_3$ shows a hole conductivity as well as protonic conductivity when doped with Sc ions.$^{16}$ The protonic conductor is expected to be the hydrogen sensor or fuel cell because of its protonic conductivity at high temperature. The electrical conductivity shows a thermal activation-type behavior with activation energy of about 0.4 eV. It is suggested that proton migrates by hopping from site to site around the oxygen ion in this material.$^{17,18}$

There have been a lot of studies about the application of this material; however, the electronic structure of p-type SrTiO$_3$ has not been studied much. The electronic structure of p-type SrTiO$_3$ has been studied by the absorption spectra of vacuum ultraviolet region.$^{19}$ The energy shift of the absorption edge due to acceptor doping was observed in p type and the band gap was found to increase by increasing the dopant concentration. It is suggested that holes are formed at the top of the valence band of p-type SrTiO$_3$ due to acceptor doping. Thus, this shift is thought to be followed by the rigid-band model.

In this paper, the electronic structure of p-type SrTiO$_3$ (SrTi$_{0.98}$Sc$_{0.02}$O$_3$), in which acceptor ion (Sc$^{3+}$) were introduced into Tr$^{4+}$ ion site in SrTiO$_3$, was studied by photoemission. It is nuclear whether the valence-band structure of the p-type SrTiO$_3$ may be characterized by the rigid-band model. As a reference material, the photoemission of the n-type SrTiO$_3$ (SrTi$_{0.98}$Nb$_{0.02}$O$_3$) was also measured.

II. EXPERIMENT

The single crystal of p-type SrTiO$_3$ was grown by the floating-zone method using Xe-arc imaging furnace. The hydrostatically pressed rod that consists of SrTiO$_3$, SrCO$_3$, and
Sc$_2$O$_3$ powder was used. The crystals were examined using x-ray diffraction. The single crystals of $n$-type SrTiO$_3$, which were grown by the Czochralski method, were obtained from Earth Jewelry Co. Ltd.

The photoemission spectra were measured at BL-2 of SOR-RING of the Synchrotron Radiation Laboratory, Institute for Solid State Physics (ISSP), University of Tokyo. Synchrotron radiation was monochromatized using a grazing-incidence spherical grating monochromator. The kinetic energy of the photoelectron was measured with a double-pass cylindrical mirror analyzer. The total resolution of the experimental system was about 0.3 eV. The x-ray photoemission spectroscopy (XPS) spectra were also measured by the Mg $K\alpha$ line (1253.6 eV) as the excitation light source. The photoelectron was measured by the electrostatic hemispherical spectrometer whose radius is 100 mm. The total-energy resolution was about 1.0 eV.

The samples were scraped in situ with a diamond file in a vacuum of $3.0 \times 10^{-10}$ Torr in order to obtain the clean surface. Since the $p$-type SrTiO$_3$ has little conductivity at room temperature, the sample is charged. On the other hand, the sample has a finite conductivity at high temperature. Thus, the measurement was carried out at 393 K to avoid the charging. The position of the Fermi level has been determined by measuring the Fermi edge of Au.

III. RESULTS AND DISCUSSION

Figure 1 shows the comparison of several energy distributions curves (EDC’s) between $n$-type SrTi$_{1-x}$Nb$_x$O$_3$ and $p$-type SrTi$_{1-x}$Sc$_x$O$_3$. The figure shows the spectra of Ti $3s$, $3p$, $2p$, and $2s$ core regions measured at $h\nu=1253.6$ eV, respectively. Solid and dotted lines show the comparison of EDC’s of $n$- and $p$-type SrTiO$_3$, respectively. The intensities of these spectra are normalized by the peak intensities of the main lines. Satellite structures having energy separations of about 13.6 eV are found in all these core lines. The binding energy ($E_B$) of Ti $3p$ core levels in $n$-type is 37.6 eV, and that in $p$-type is 36.9 eV. The Ti $3s$, $2p$, and $2s$ core lines are located at 62.4, 459, and 39.4 eV in $n$ type, and at 61.7, 458.3, and 564.7 eV in $p$ type. That is, every Ti line undergoes a core-level shift to lower binding energy by about 0.7 eV in $p$-type SrTi$_{1-x}$Sc$_x$O$_3$. This fact means the Fermi level becomes lower in $p$-type SrTiO$_3$.

Figure 2 shows the comparison of the EDC spectra in the valence-band energy region.

FIG. 1. Comparisons of several core lines in the photoemission spectra of $n$- and $p$-type SrTiO$_3$. The ordinates are normalized by the intensities of the main peaks. Solid and dashed lines indicate the $p$- and $n$-type SrTiO$_3$.

FIG. 2. Comparison of EDC’s between $n$- and $p$-type SrTiO$_3$ in the valence-band energy region.
well mixed with the Ti 3d states. Feature C is considered to be the defect of oxygen at the surface.² It has been reported by Betrel²⁰ that the doublet structures at around 20 eV are the O 2s and Sr 4p lines. The intensities of both n- and p-type spectra are normalized by the peak intensities of Sr 4p. The peak position of A and B are different in the spectra of n- and p-type. Features A and B are observed at 4.7 and 6.7 eV in n-type, while at 4.0 and 6.0 eV in p-type. Therefore, the position of the valence-band top is shifted to lower binding energy by about 0.7 eV in p-type SrTiO₃. This fact seems to be consistent with the energy shifts in Ti core lines. This shift of the Fermi level indicates the effect of the doping on the rigid-band model.

In n-type material, the E,F is located just at the bottom of the conduction band because the band gap is about 3.2 eV and the energy between the top of the valence band and the E,F is about 3.2 eV in Fig. 2. In the case of p-type material, the top of the valence band is found to be located at about 2.6 eV below the E,F, while the band gap of p-type SrTiO₃ was obtained at 3.54 eV.¹⁹ This fact indicates that the Fermi level is located close to the conduction band in the band gap. If the electronic structure obeys the rigid-band model exactly, the position of the E,F of the p type one would be located below the half of the band gap. Thus, the energy shift observed in this measurement seems to be small. This fact may reflect the band bending effect at the surface. It is known that the bands at the surfaces of ordinary semiconductors bend upward or downward in the n- or p-type samples, respectively.³¹ This effect may depend on the space charge trapped by the surface state. The surface state has been studied well in n-type semiconductors, while it has not been studied well in p-type semiconductors. It is known that Sc-doped SrTiO₃ has a lot of oxygen defects. It is believed that the extra charge is trapped by defects at the surface. Another possible origin of the apparent discrepancy is that the photoemission is a spatially localized phenomenon, whereas the E,F observed in conductivity measurement is macroscopic. Here, the location of the E,F cannot be explained quantitatively. However, the difference of the E,F between n and p type is consistent with the rigid-band model.

**FIG. 3.** Photoemission spectra near the Fermi level on an expanded scale for n- and p-type SrTiO₃. The donor band exists only in the band gap of the n-type SrTiO₃.

**FIG. 4.** The CFS spectra of n- and p-type SrTiO₃ corresponding to the Ti 3p absorption spectra. Closed and open circles indicate p- and n-type SrTiO₃. The numbers indicate the photon energies, where the resonant-photoemission spectra were measured.

**FIG. 5.** Valence-band spectra of n-type SrTiO₃ excited at various photon energies numbered in Fig. 4. Labels A and B indicate the nonbonding and bonding band between the O 2p and Ti 3d states.
Figure 3 shows the detailed photoemission spectra in the band-gap energy region below the Fermi level, where the open and closed circles indicate the EDC spectra of $p$- and $n$-type SrTiO$_3$. A prominent feature that has a $3d$ character was found at around $E_B = 1$ eV in the band gap. The feature mainly originates from the donor band formed by doping. There is a Fermi edge for $n$-type SrTiO$_3$, though the intensity at $E_F$ is very little. However, there is no structure in the band gap below the Fermi level in $p$-type SrTiO$_3$. This fact is consistent with the rigid-band model, which suggests that there is a structure in the band gap above the Fermi level in the case of $p$-type SrTiO$_3$.

A $3d$ character band has been found in the band gap of La-doped $n$-type SrTiO$_3$. There is the difference of binding energy from the donor band, which is considered to be 1.5 eV in La doped, and $\sim 0.8$ eV in Nb doped. The origin of the formation of the gap state has not been clear. In $n$-type La-doped SrTiO$_3$, Fujimori et al. interpreted that the density of states (DOS) observed in the band gap is not simply a donor band. Impurity potential due to the La$^{3+}$ ions substituting Sr$^{2+}$ produces donor levels, but the binding energy of such a donor level would be orders of magnitude too small to account for the $\sim 1.5$ eV peak. And, the long-range Coulomb interaction combined with potential disorder might cause a pseudogap in metallic systems, since it is known to produce a Coulomb gap in insulators. Such an effect, however, depends on the mean distance between doped electrons and hence should diminish with decreasing $X$. In this study, one can find there is no structure in the band gap in the $p$-type SrTiO$_3$. This fact supports at least that this band comes from the donor bands, though there are a lot of questions regarding the origin of the formation of this band.

Figure 4 shows the constant final state (CFS) spectra of $p$- and $n$-type SrTiO$_3$ measured at the kinetic energy, where the secondary electron has a maximum intensity. These spectra are approximately regarded as the absorption spectra of Ti $3p \rightarrow Ti 3d$. The vertical bars, which are numbered from 1 to 10, indicate the selected photon energies for the resonant-photoemission measurements.

Figures 5 and 6 show the valence-band EDC’s of $n$- and $p$-type SrTiO$_3$ measured at various photon energies numbered in Fig. 4. Labels A and B indicate the nonbonding and bonding bands of the O 2$p$ and Ti 3$d$ states. The bonding peak of the valence band is enhanced around the photon energy 47 eV. The Ti $3p \rightarrow 3d$ resonance enhancement of bonding peak in $p$ type is larger than that in $n$ type. The intensity of the Sr $4p$ peak at about 23.2 eV becomes strong at lower excitation energies. This is obviously due to the excitation-energy dependence of the ionization cross section of the Sr $4p$ electron. Since the Sr $4p$ line is observed...
strongly, the O 2s line is distinguished as a shoulder on the tail of the Sr 4p line.

Figure 7(a) shows off-resonance spectra of the valence band of n- and p-type SrTiO₃. The excitation energy for the spectra is 60 eV. The binding energy of the p-type SrTiO₃ is shifted to higher binding energy by 0.7 eV in order to compare the line shape with that of the n-type one. Two energy-band DOS curves shown under off-resonance spectra obtained by several authors, Mattheiss and Toussaint, Selme, and Pecheur, are also exhibited. Each of the DOS curves are obtained by convoluting the original DOS with Gaussian broadening functions with widths of 0.5 eV. Mattheiss calculated his DOS curves using the augmented plane wave and Slater-Coster linear combination of atomic orbitals interpolation method. Toussaint et al. calculated DOS curves using the tight-binding method, together with a Green’s function. The off-resonance spectra are in good accordance with the calculated Ti 3d partial density of states (PDOS) by Toussaint, Selme, and Pecheur, which is shown under two difference spectra.

Figure 7(b) shows the difference spectra from on-resonance to off-resonance spectra.

It is known that the difference spectra by the resonant photoemission correspond to the 3d components in the valence band. One can find that the difference spectrum of p-type SrTiO₃ has a stronger intensity than n-type material. This fact shows that the 3d component of p-type SrTiO₃ is more than that of n-type SrTiO₃. Thus, one can know that the hybridization between O 2p and Ti 3d increases in p-type SrTiO₃. In fact, the difference spectra are in good agreement with the calculated Ti 3d partial density of states (PDOS) by Toussaint, Selme, and Pecheur, which is shown under two difference spectra.

Figure 8 shows the XPS and ultraviolet photoemission spectroscopy spectra in several core levels. The abscissa represents the relative binding energy, the zero of which is located at the main peak. The core levels are indicated on the left-hand sides of the spectra. The vertical bars in EDC spectra indicate the location of the charge-transfer satellites. The core-level XPS spectra of SrTiO₃ have been already reported by Kim and Winograd et al. and Tezuka et al. The present results are consistent with their results. It is known that these satellites are closely related to the hybridization effect between Ti 3d and O 2p in SrTiO₃.

It is recognized that the charge-transfer satellites are observed in every spectrum about 13.6 eV from the main peak. If only the hybridization of the Ti 3d and O 2p states becomes stronger in the p-type one, the energy position of the satellite in p type would be larger than that in n type. Recently, Okada and Kotani calculated the charge-transfer (CT) satellite in the Ti 2p core region of Ti compounds. The energy separation of the satellite structure is well reproduced by calculation, where the energy separation is mainly due to the large hybridization effect V and the CT energy (Δ). It is roughly determined to be \( \sqrt{\Delta^2 + 4 V_{\text{eff}}^2} \), where \( V_{\text{eff}} \) is \( 6V(t_{2g})^2 + 4V(e_g)^2 \), and \( V(t_{2g}) \) and \( V(e_g) \) are the hybridization energies of \( t_{2g} \) and \( e_g \) states. Since the energy separation does not change much, the other parameters are changed between n- and p-type SrTiO₃. These changes of the parameters may be due to the slight change of the lattice constant and the screening effect by the free carriers in n-type SrTiO₃.

The vertical dashed lines show the plasmon satellites. The dashed line in the Ti 3s is due to the plasmon of Ti 3p core line. A plasmon satellite is observed at about 28 eV. Frandon, Brousseau, and Pradal observed the plasmon peak at 26 eV by means of electron-energy-loss study. Sen, Riga,
IV. CONCLUSION

We measured photoemission spectra on \( p \)-type SrTiO\(_3\) using synchrotron radiation, and compared the results with those of the Nb-doped \( n \)-type SrTiO\(_3\). The valence-band and Ti core levels are shifted by about 0.7 eV. The donor band is found in the band gap below Fermi level in the \( n \)-type SrTiO\(_3\), but cannot be found in the \( p \)-type one. These results can be understood by the rigid-band model. In the resonant-photoemission study, the Ti 3\( d \) state in the valence band is much stronger in \( p \)-type SrTiO\(_3\). It is concluded that the hybridization with O 2\( p \) and Ti 3\( d \) is increased in \( p \)-type SrTiO\(_3\).

and Verbiest\(^1\) also observed the satellites at 26 eV in the Ti 2\( s \) and Ti 2\( p \) spectra. In this study, the plasmon satellite is observed in the Ti 2\( s \) and Ti 3\( p \) spectra, though it is not observed clearly in the Ti 2\( p \) and Ti 3\( s \) spectra.

In the Ti 2\( s \) spectrum, the charge-transfer satellite is formed at about 10 eV from the main peak. These structures may be nonbonding-type charge-transfer satellites, which are found in on-resonance spectra of early transition-metal compounds, such as ScF\(_3\) (Ref. 27) and TiO\(_2\).\(^{3,8-13}\) This nonbonding satellite becomes stronger in \( p \)-type SrTiO\(_3\), which is also consistent with the larger hybridization in \( p \)-type SrTiO\(_3\).