

Ti–O Hybridization Effect of Nb-Doped SrTiO₃ by Resonant Photoemission Spectroscopy

Tohru HIGUCHI, Takeyo TSUKAMOTO, Shu YAMAGUCHI¹, Yasuhisa TEZUKA² and Shik SHIN^{3,*}

¹Department of Applied Physics, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

²Faculty of Science and Engineering, Hirosaki University, 1 Bunkyo-chou, Hirosaki 036-8561, Japan

³Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

³Institute for Solid State Physics, University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8581, Japan

(Received December 12, 2000; accepted for publication January 10, 2001)

The electronic structure of Nb-doped SrTiO₃ (SrTi_{1-x}Nb_xO₃) has been investigated by resonant photoemission spectroscopy (RPES). The valence band is well described by the band calculation. The RPES spectra show that the Ti 3d partial density of states in the valence band increases with increasing Nb dopant concentration. This finding suggests that the hybridization effect between the Ti 3d and O 2p states depends on the Nb dopant concentration.

KEYWORDS: SrTi_{1-x}Nb_xO₃, RPES, valence band, DOS, hybridization effect

Strontium titanate (SrTiO₃) is a very typical perovskite-type compound with a band gap of about 3.2 eV.¹⁾ Its electrical conductivity is successfully controlled by substitution doping similar to that in semiconductors. It has been used in practical applications such as electrodes and gas sensors. In particular, Nb-doped SrTiO₃ (SrTi_{1-x}Nb_xO₃) is 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. Thus, understanding the electronic structure of SrTi_{1-x}Nb_xO₃ is one of the most important subjects in terms of the science and technology of materials.

The electronic structure of SrTiO₃ has been reported in many photoemission studies²⁻⁷⁾ and in theoretical band calculation.⁸⁻¹¹⁾ The electronic structure can be described by the energy band picture since there are only nominal 3d electrons that bring about appreciable correlation interaction. The top of the valence band is mainly composed of O 2p states and the bottom of the conduction band is formed by the Ti 3d states. It is known that the Ti 3d orbital is strongly hybridized with the O 2p orbital. This leads to a situation in which nonvanishing 3d electrons exist in the ground state. Recently, it has been reported that the hybridization effect between the Ti 3d and O 2p states depends on the dopant concentration of carriers in Sc-doped *p*-type SrTiO₃.^{3,4)} However, the hybridization effect of the dopant concentration for SrTi_{1-x}Nb_xO₃ has not been well studied thus far.

In this study, the electronic structure of SrTi_{1-x}Nb_xO₃ (*x* = 0.01, 0.02, and 0.05) has been investigated by resonant-photoemission spectroscopy (RPES). To investigate the valence band of SrTiO₃ more extensively, RPES measurements were performed near the Ti 3p → 3d resonant region. We present the RPES spectra in order to study the hybridization effect between the Ti 3d and O 2p states in the valence band of SrTiO₃ in terms of Nb dopant concentration.

Single crystals of SrTi_{1-x}Nb_xO₃ were grown by the Czochralski method. The doping concentrations are *x* = 0.01, 0.02, and 0.05. The crystals were examined using X-ray diffraction. RPES measurements were carried out at the revolver undulator beamline BL-19B at the Photon Factory (PF) of the High Energy Accelerator Organization (KEK), Tsukuba, Japan. Synchrotron radiation from the undulator was monochromatized using a grating monochromator. The revolver undulator covers a wide energy range from 10 to

1200 eV in the first harmonic. Photoelectron energies were measured with an electrostatic hemispherical analyzer with a radius of 100 mm. The total-energy resolution was about 40 meV. The samples were scraped *in situ* with a diamond file in a vacuum of 3.0 × 10⁻¹⁰ Torr in order to obtain a clean surface. The position of the Fermi level was determined by measuring the Fermi edge of Au film.

Figure 1(a) shows the constant final state (CFS) spectrum of SrTi_{0.99}Nb_{0.01}O₃ measured at the kinetic energy where the secondary electron has a maximum intensity. This spectrum is regarded as the approximate absorption spectrum of Ti 3p → Ti3d. The CFS spectrum shows a broad maximum at about 47 eV. The vertical bars, numbered from 1 to 6, indicate the selected photon energies for the RPES measurements.

Figure 1(b) shows the RPES spectra in the valence band region of SrTi_{0.99}Nb_{0.01}O₃ measured at various photon energies.

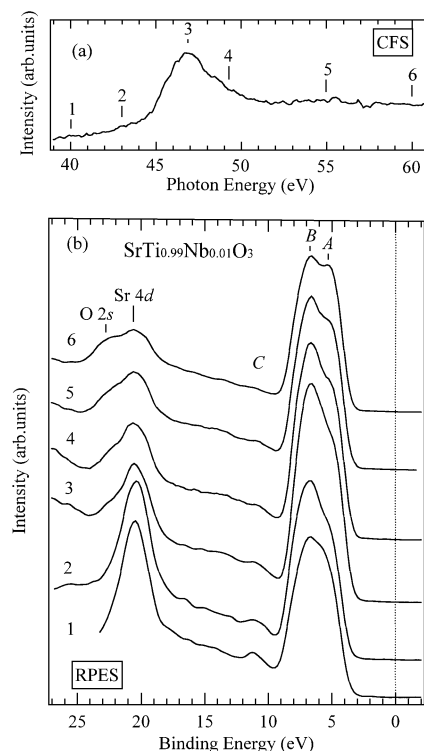


Fig. 1. (a) CFS spectrum of SrTi_{0.99}Nb_{0.01}O₃, corresponding to the Ti 3p → 3d absorption spectrum. The numbers indicate the photon energies at which the RPES spectra were measured. (b) Valence band spectra of SrTi_{0.99}Nb_{0.01}O₃ excited at various photon energies.

*Also from RIKEN, Sayo-gun, Hyogo 679-5148, Japan.

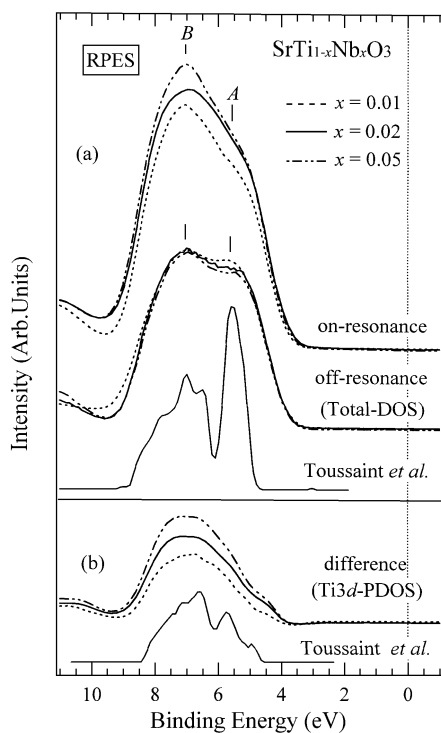


Fig. 2. Doping dependence of on-resonance and off-resonance spectra of $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$ ($x = 0.01, 0.02, \text{ and } 0.05$): (a) On-resonance spectra measured at 47 eV and off-resonance spectra measured at 60 eV. (b) Difference spectra obtained by subtracting the off-resonance from the on-resonance spectra. As a reference, total DOS and Ti 3d PDOS curves calculated by Toussaint *et al.*¹⁰⁾ are shown.

The valence band spectra have two features indicated by A and B which mainly consist of O 2p states mixed with Ti 3d states. It is known that feature A corresponds to the nonbonding state and that feature B corresponds to the bonding state that is well mixed with the Ti 3d states. In the PES spectrum of $h\nu = 47$ eV, the intensity of the bonding peak is enhanced by the Ti 3p \rightarrow 3d absorption. Feature C is considered to be due to oxygen defects at the surface.⁸⁾ The doublet structures at around 20 eV are the O 2s and Sr 4d lines. The bonding peak of the valence band is enhanced at the photon energy of 47 eV (Label 3). The intensity of the Sr 4p peak at 23.2 eV increases at lower excitation energies. This is evidently due to the excitation energy dependence of the ionization cross section of the Sr 4p electron.¹²⁾ Since the Sr 4p line is strongly observed, the O 2s line is distinguished as a shoulder on the tail of the Sr 4p line.

Figure 2(a) shows off-resonance spectra of the valence band of $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$ measured at $h\nu = 60$ eV. The energy band density-of-state (DOS) curve shown under the off-resonance spectra obtained by Toussaint *et al.*¹⁰⁾ is also

exhibited. The DOS curve, which is calculated by the tight-binding method, is obtained by convoluting the original DOS with Gaussian broadening functions with a width of 0.5 eV. The off-resonance spectra are in good accordance with the band DOS. The PES spectra also show the two peaks A and B (nonbonding and bonding states), although the intensity of peak A is lower than that of peak B. We note that the intensity of peak A decreases with increasing Nb dopant concentration. Furthermore, the Ti 3d components in both peaks, A and B, are resonantly enhanced by the Ti 3p \rightarrow 3d excitation in the on-resonance spectrum. The effect strongly depends on the Nb dopant concentration.

Figure 2(b) shows the difference spectra by subtracting the off-resonance from the on-resonance spectra. It is known that the difference spectra correspond to the Ti 3d components in the valence band. In fact, the difference spectra are in good agreement with the calculated Ti 3d partial DOS (PDOS), which is shown below the three difference spectra. Comparing the difference spectrum of $x = 0.01, 0.02, \text{ and } 0.05$, the Ti 3d state increases with increasing Nb ions. This result implies that the hybridization between the Ti 3d state and O 2p state becomes more extensive with Nb dopant concentration, indicating a decrease in the effective charges of Ti^{4+} and O^{2-} ions. Thus, it shows that the bond distance between Ti and O ions or the crystal symmetry changes with a small amount of doping cations.

We measured the RPES spectra on $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$ using synchrotron radiation. The PES spectra are in good agreement with the band calculation. The RPES spectra show that the Ti 3d PDOS in the valence band increases with increasing Nb dopant concentration. It is concluded that the hybridization effect depends on Nb dopant concentration.

- 1) M. Cardona: Phys. Rev. A **140** (1965) 651.
- 2) Y. Tezuka, S. Shin, T. Ishii, T. Ejima, S. Suzuki and S. Sato: J. Phys. Soc. Jpn. **63** (1994) 347.
- 3) T. Higuchi, T. Tsukamoto, N. Sata, M. Ishigame, Y. Tezuka and S. Shin: Phys. Rev. B **57** (1998) 6978.
- 4) T. Higuchi, T. Tsukamoto, N. Sata, M. Ishigame, Y. Tezuka and S. Shin: Solid State Ionics **108** (1998) 349.
- 5) T. Higuchi, T. Tsukamoto, K. Kobayashi, Y. Ishiwata, M. Fujisawa, T. Yokoya, S. Yamaguchi and S. Shin: Phys. Rev. B **61** (2000) 12860.
- 6) Y. Haruyama, Y. Aiura, H. Bando, Y. Nishihara and H. Kato: J. Electron Spectrosc. Relat. Phenom. **88-91** (1998) 695.
- 7) Y. Haruyama, H. Fukutani, Y. Aiura, Y. Nishihara, T. Komeda, S. Kodaira, T. Maruyama and H. Kato: Jpn. J. Appl. Phys. **32** (1993) 543.
- 8) B. Reihl, J. G. Bednorz, K. A. Muller, Y. Jugnet, G. Landgren and J. F. Morar: Phys. Rev. B **30** (1984) 803.
- 9) L. F. Mattheiss: Phys. Rev. B **6** (1972) 4718.
- 10) G. Toussaint, M. O. Selme and P. Pecheur: Phys. Rev. B **36** (1987) 6135.
- 11) P. Pertosa and F. M. Michel-Calendini: Phys. Rev. B **17** (1978) 2011.
- 12) J. J. Yeh and I. Lindau: A. Data & Nucl. Data Tables **32** (1993) 1.