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Photoelectron energy-loss functions of SrTiO₃, BaTiO₃, and TiO₂: Theory and experiment

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We compare experimental O 1s electron energy-loss structures below 30 eV of single crystalline SrTiO₃, BaTiO₃, and TiO₂ with their theoretical electron energy-loss functions. The photoelectron energy-loss structures of in situ fractured surface in ultrahigh vacuum can be approximated by a sum of four components for SrTiO₃ and BaTiO₃, and of three components for TiO₂. Electronic structures were calculated from first principles using the full-potential linearized augmented plane-wave method in the local-density approximation. The momentum matrix elements between Bloch functions were evaluated to determine the electron energy-loss functions. The theoretical electron energy-loss functions agree well with experimental spectra except a structure at around 20 eV of SrTiO₃ and that at around 18 eV of BaTiO₃. The difference of high binding energy peaks is explained from the positions of semicore states.

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I. INTRODUCTION

Perovskite-type oxides have been a great interest in both the field of basic research and thin-film applications for superconductivity and ferroelectricity. The electronic structure of SrTiO₃ is of interest since stoichiometric SrTiO₃ is highly insulating, but slightly reduced one shows the superconductivity. SrTiO₃ crystallizes in the simple cubic perovskite structure Pm3m (O h₃) at room temperature (a = 3.9051 Å). Above the ferroelectric Curie point BaTiO₃ has the same structure while below the temperature a slight tetragonal distortion C₄ᵥ modifies the perovskite structure. For tetragonal phase BaTiO₃ the difference between the lattice constants of the c and a axes is 1% (a = 3.9920, b/a = 1.000, and c = 4.0361 Å). The difference in electronic structure between the ferroelectric and paraelectric BaTiO₃ is also interesting since the deviation of crystal structure below and above the Curie point is so small, though the dielectric property changes largely. In these materials a titanium atom is surrounded by six oxygen atoms. In spite of difference from the cubic crystal structure, TiO₂ of rutile structure P4₁/mmm(D₁₄h) has the same Ti-O coordination as SrTiO₃ and BaTiO₃. The lattice constants are a = 4.5936 and c = 2.9587 Å, and the internal coordinate u is 0.3048. In the unit cell rutile including two TiO₂ molecules, Ti atoms are positioning at the sites of (0,0,0) and (1/2,1/2,1/2), and four coordinated O atoms occupy at the sites of ±(u,u,0) and ±(u+1/2,1/2−u,1/2).

Reported fundamental absorption edges of SrTiO₃, BaTiO₃, and TiO₂ (Ref. 6) at room temperature are 3.22, 3.15, and 4.0 eV, respectively. The closeness of the absorption edge of SrTiO₃, BaTiO₃, and TiO₂ suggests that the edge is predominantly due to transitions between the O 2p to Ti 3d states with admixture of Sr or Ba wave functions. Although the similarity in the crystal field among these materials, there are great discrepancies in superconducting and ferroelectric characteristics. For these materials the differences in detail of electronic structure and dielectric functions are still of fundamental interest. Simple cubic SrTiO₃ offers a natural starting point for the study of the electronic structure and dielectric functions. The crystal-field splitting of the O 2p states occurs because the oxygen resides at a site of tetragonal D₁₄h (4/mmm) point symmetry in SrTiO₃. The structure of the empty conduction band (CB) could play a decisive role as well as that of the filled valence band (VB) in the electronic properties of SrTiO₃.

X-ray photoelectron spectroscopy (XPS) is suitable to examine the electronic structure of the filled levels and dielectric response of a solid. The XPS satellite structures are generated by intrinsic and extrinsic processes. The intrinsic satellites are caused by several mechanisms under the influence of a core hole. On the other hand, the extrinsic satellites are caused by the dielectric response to the photoexcited electrons. During the approach of an excited electron to the solid surface, the Coulomb field accompanied with the moving electron interacts with the electrons of the solid via long-range dipole fields. The long-range Coulomb interactions...
bring about interband transitions and plasma excitations. Thus the electron energy-loss structure observed in high-resolution XPS can probe unoccupied electronic states of insulators.\(^7\)

In the previous paper,\(^8\) we examined the XPS satellites for SrTiO\(_3\) by comparing with theoretical electron energy-loss functions and experimental electron energy-loss spectroscopy (EELS) spectra. It was found that the O 1\(s\), Sr 3\(d\), and Ti 2\(p\) satellites have common features which can be ascribed to extrinsic energy-loss structures. The O 1\(s\) and Sr 3\(d\) spectra agree well with theoretical energy-loss functions while the Ti 2\(p\) spectra show more complicated structure due to intrinsic satellites.

In this paper, we extend the analysis to the experimental O 1\(s\) photoelectron energy-loss functions of SrTiO\(_3\), BaTiO\(_3\), and TiO\(_2\). We discuss their similarities and differences from the viewpoint of the electronic structures. We show that all compounds have similar peaks in the electron energy-loss functions because they have a common Ti-O coordination as a local structure unit. We also show that the energy-loss functions have differences which are attributed to the positions of semicore states in energy-loss functions because they have a common Ti-O coordination as a local structure unit.

In this paper, we extend the analysis to the experimental O 1\(s\) photoelectron energy-loss functions of SrTiO\(_3\), BaTiO\(_3\), and TiO\(_2\). We discuss their similarities and differences from the viewpoint of the electronic structures. We show that all compounds have similar peaks in the electron energy-loss functions because they have a common Ti-O coordination as a local structure unit. We also show that the energy-loss functions have differences which are attributed to the positions of semicore states in energy-loss structures.

We calculated the bulk electronic structures of SrTiO\(_3\), BaTiO\(_3\), and TiO\(_2\) within the local-density approximation (LDA),\(^9\) using the WIEN97 package\(^10\) which is based on the full potential linearized augmented plane-wave method. The LDA succeeded to describe the valence and conduction bands of various compounds,\(^9\) however, the LDA failed to

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**II. EXPERIMENT**

For XPS at room temperature we used a Surface Science Laboratories Model SSX-100 spectrometer with monochromatized Al K\(\alpha\) source having a diameter of 300 \(\mu\)m spot on the sample surface. The pass energy of the spectrometer was set to 50 eV. The solid angle of the input lens of the energy analyzer was 30°. The spectrometer was calibrated utilizing the Au 4\(f_{7/2}\) electrons (83.79 eV) and the full width at half maximum (FWHM) of the Au 4\(f_{7/2}\) peak was 1.03 eV.

Fracturing of single crystals \textit{in situ} in ultrahigh vacuum (UHV) is the only reliable way to prepare almost perfect and stoichiometric surfaces indispensable for studying intrinsic surface properties of oxides. The gross electronic structure of the fractured surfaces reflects that of perfect surfaces. At first, single crystals of SrTiO\(_3\), BaTiO\(_3\), and TiO\(_2\) from K&R Creation Inc. (Japan) have been cut to smaller pieces (\(\approx 0.5 \times 0.5 \times 3\) mm\(^3\)) for the measurements. Then, the bar of crystals were attached to Cu sample holders and introduced into a measurement chamber. The samples were fractured in a vacuum of \(5 \times 10^{-10}\) Torr at the analyzing position of the measurement chamber, and then we immediately started the measurement of \textit{as-fractured} spectra. No contamination signals could be detected for 20 min after the fracturing.

The binding energies of the measured spectra were corrected with C 1\(s\) of 284.7 eV of the contaminated carbon on the surfaces after a long exposure to the vacuum. Since the samples are nonconductive, conditions for a neutralizer were optimized to obtain XPS spectra. Although the peak positions changed from sample to sample, the O 1\(s\) spectra had symmetrical single Gaussian profile and excellent reproducibility.

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**III. CALCULATIONS**

We calculated the bulk electronic structures of SrTiO\(_3\), BaTiO\(_3\), and TiO\(_2\) within the local-density approximation (LDA),\(^9\) using the WIEN97 package\(^10\) which is based on the full potential linearized augmented plane-wave method. The LDA succeeded to describe the valence and conduction bands of various compounds,\(^9\) however, the LDA failed to
reproduce the band gaps of semiconductors and insulators. Typically, the band gap obtained by the LDA is only half of the experimental values. Thus the transition energies between valence and conduction bands are also underestimated more or less.

We used cubic structures for SrTiO$_3$ and BaTiO$_3$. The TiO$_2$ has a tetragonal structure. The Muffin-tin sphere radii $R$ were chosen as (in a.u.): Sr and Ba, 2.5; Ti, 1.9; O, 1.5. The cutoff $K_{\text{max}}$ for basis functions is set to $RK_{\text{max}}=7.0$ where $R$ is minimum sphere radius, i.e., 1.5 for oxygen. The self-consistent calculations were performed by using $20 \times 20 \times 20$ k-point sampling for SrTiO$_3$ and BaTiO$_3$, and $13 \times 13 \times 21$ for TiO$_2$.

The calculated densities of states (DOS) shown in Figs. 2–4 are consistent with the previous calculations.$^{11-18}$ As common characteristics to all compounds, the band gaps appear between the O 2p valence bands and the Ti 3d conduction bands. As shown in the partial densities of states, the O 2p orbitals and Ti 3d orbitals are hybridized. Below the O 2p bands, the semicore states by O 2s orbitals appear from −16 to −18 eV. For SrTiO$_3$ and BaTiO$_3$, additional semicore states originate from A-site cation orbitals: Sr 4p from −14 to −15 eV and Ba 5p from −9 to −10 eV.

The states at the bottom of the empty conduction bands arise from the threefold degenerate Ti 3d $t_{2g}$ orbitals which are lower in energy than the twofold degenerate Ti 3d $e_g$ orbitals. In higher energy region (6−12 eV) for SrTiO$_3$ and BaTiO$_3$, the bands are predominantly formed by Sr 5s, 4d and Ba 6s, 5d orbitals partially overlapping with the Ti 3d $e_g$ bands, but for TiO$_2$ such A-site cation contribution does not exist. As a result, the Ti 3d $e_g$ bands distribute a wider energy region for BaTiO$_3$ and SrTiO$_3$ than for TiO$_2$. The conduction bands above 14 eV are mainly composed of Ti 4s and 4p orbitals.

The extrinsic energy-loss structures are generated by the inelastic scattering of photoexcited electrons. Within the Born approximation, the cross section of the inelastic scattering is related to dielectric functions $\varepsilon$ as$^{19}$

$$K(E_0, \omega) = -\frac{\text{Im} [\varepsilon(\omega)^{-1}]}{\pi a_0 E_0} \ln \left( \frac{\sqrt{E_0^2 + \hbar \omega}}{\sqrt{E_0^2 - \hbar \omega}} \right),$$

where $E_0$ is the kinetic energy of the electron and $a_0$ is the Bohr radius. Here the $\text{Im}(\varepsilon^{-1})$ is assumed to be independent of wave vector. Thus the electron energy-loss structure can be approximated by the $-\text{Im}(\varepsilon^{-1})$ if we ignore multiple-scattering effects. To obtain the theoretical electron energy-loss structures, the inelastic scattering of photoexcited electrons was calculated using the complex dielectric function $\varepsilon$.
loss functions, the imaginary part $\text{Im}(\epsilon)$ of dielectric functions was calculated from the momentum matrix elements between the occupied and unoccupied wave functions. The real part $\text{Re}(\epsilon)$ was evaluated from the $\text{Im}(\epsilon)$ by the Kramers-Kronig transformation. The electron energy-loss functions of bulk $\text{Im}(\epsilon_{21})$ and surface $\text{Im}(\epsilon_{11})$ were derived from the $\text{Re}(\epsilon)$ and $\text{Im}(\epsilon)$ of the calculated dielectric functions. The $\text{Im}(\epsilon_{21})$, $\text{Im}(\epsilon_{11})$, and $\text{Im}(\epsilon_{11})$ are shown in Fig. 5–7. Since TiO$_2$ has tetragonal symmetry, the dielectric functions depend on polarization directions. We present the direction averaged functions in Figs. 5–7. The peaks in the $\text{Im}(\epsilon_{21})$ tend to shift to the lower energy side than in the $\text{Im}(\epsilon_{11})$.

IV. DISCUSSION

In Fig. 5, calculated dielectric functions $\text{Im}(\epsilon)$ show several broad peaks which can be ascribed to various interband transitions. At 0–15 eV, all compounds have two broad peaks which is caused by the transition from O 2$p$ valence bands to Ti 3$d$ $t_{2g}$ and $e_g$ bands. The second peaks in SrTiO$_3$ and BaTiO$_3$ are broad which is in contrast with the sharp peak for TiO$_2$. This is because Ti 3$d$ $e_g$ bands in TiO$_2$ is narrower than in BaTiO$_3$ and SrTiO$_3$. At 15–30 eV, all compounds show broad peaks centered at 20 eV. They are ascribed to two types of transitions which are from O 2$s$ semicore states to Ti 3$d$ conduction bands and from O 2$p$ valence bands to high-energy conduction bands (Ti 4$s$ and 4$p$). Additional structures appear around 22–24 eV for SrTiO$_3$ and 18–20 eV for BaTiO$_3$. They are caused by the transition from Sr 4$p$ (Ba 5$p$) semicore states to Sr 5$d$ (Ba 6$d$) conduction bands. Since the momentum matrix elements between np and $(n+1)d$ orbitals can be large, these peaks are larger than those from O 2$s$ semicore states.

The theoretical energy-loss functions $-\text{Im}(\epsilon^{-1})$ show several peaks corresponding to various features in $\text{Im}(\epsilon)$. It was shown that theoretical energy-loss functions for SrTiO$_3$ have three prominent features. These three features also appear for BaTiO$_3$ and TiO$_2$. Feature I is caused by the splitting of the Ti 3$d$ bands into $t_{2g}$ and $e_g$ subbands. Feature II arises from the resonance of the O 2$p$ valence electrons. Feature III at 20–30 eV is most dominant and corresponds to the plasmonlike collective excitation of the valence and semicore electrons. Feature III of BaTiO$_3$ appears to be lower energy than that of SrTiO$_3$. Feature III of TiO$_2$ has lowest energy among three compounds and becomes wide. These differences can be explained by the positions of semi-
core states. For BaTiO$_3$, the broad peaks by Ba 5$p$ states in $\text{Im}(\epsilon)$ appear at about 5 eV lower energy than that by Sr 4$p$ in SrTiO$_3$. Thus feature III which is resonance of valence and semicore electrons appears at lower energy for BaTiO$_3$. The A-site cation semicore state is absent for TiO$_2$ and O 2$s$ is the only semicore state. Therefore feature III of TiO$_2$ has lowest energy. It is broad because the peak by O 2$s$ semicore state in $\text{Im}(\epsilon)$ is weak.

The theoretical electron energy-loss functions for all compounds agree with experimental spectra except the structure C in SrTiO$_3$ and BaTiO$_3$. The positions of structure D shift to lower energy in the order of SrTiO$_3$, BaTiO$_3$, and TiO$_2$. This trend is reproduced by Feature III in theoretical spectra. It means that the positions of structure D are affected by the semicore states in A-site cation atoms. Such semicore states are ignored for the discussion of physical properties of these compounds. For low-energy phenomena, it is justified because their positions are far below the valence-band maximum and the excitation from these states are unlikely. However, they would influence the high-energy spectra as shown for electron energy-loss functions.

As described above, for the perovskites the structure of photoelectron energy-loss spectra differs from that of the calculated energy-loss functions, though for TiO$_2$ the energy-loss structures by experiment and theory agreed with each other. The O 1$s$ energy-loss and EELS spectra of SrTiO$_3$, BaTiO$_3$, and TiO$_2$ are shown in Figs. 8–10, respectively. The intensities of the spectra are normalized with the zero-loss peaks. In the EELS the kinetic energy of primary electrons ($E_p$) was set to be 1000 eV, which was nearly equal to 950 eV for that of the O 1$s$ photoelectrons. In EELS the angle between the incident and measured electron beams is a right angle. Then the directly reflected electrons were not included in the EELS spectrum. However, the intensity ratio of inelastic scattering to elastic scattering peaks in EELS was smaller than that of the O 1$s$ photoelectrons for the perovskites. The energy-loss structures by EELS and XPS agree with each other except for the intensity of structure C at around 20 eV for SrTiO$_3$ and 18 eV for BaTiO$_3$. In the EELS for SrTiO$_3$ and BaTiO$_3$ relative intensities at around 20 and 18 eV, respectively, corresponding to structure C of XPS are so small and in agreement with the calculated energy-loss function in Fig. 6. At present, for SrTiO$_3$ and BaTiO$_3$ origins of the disagreement between XPS and EELS, and between XPS and theory, have not yet become clear.

Figure 10 shows the O 1$s$ energy-loss and EELS spectra of TiO$_2$ in situ fractured in UHV. The electrons in EELS twice travel in the sample surface but photoelectrons do once. So EELS spectrum having the same kinetic energy as photoelectrons has more information about the surface than photoelectron spectrum. The shift by $-1$ eV of EELS spectrum reflects the effect of surface loss function. The photoelectron energy loss at around 5.5, 12.5, and 25 eV of the O 1$s$ structures coincided essentially with those of present EELS and those by theoretical calculation.

V. SUMMARY

We have presented the experimental and theoretical results on the electron energy-loss functions of SrTiO$_3$, BaTiO$_3$, and TiO$_2$. No intrinsic surface states in the energy
gaps for *in situ* fractured samples brought about an agreement between the results of a first-principles calculation and the energy-loss structure in the core-level spectra. The XPS with first-principles band calculation can reveal the DOS of unoccupied states since the energy-loss structure of the core-level spectra resulted from the single-particle excitation and collective excitations of valence electrons. For the perovskite-type structure SrTiO$_3$ and BaTiO$_3$ there remained apparent disagreement in the energy-loss structures between XPS and theory. Both theory and EELS could not predict additional structure $C$ by XPS of the perovskites. The appearance and energy change of the structure $C$ for the perovskites suggests that $A$-site cation affects their origins and the lower energy excitation reflects only the Ti $d$–O $p$ hybridization. It is found that the positions of structure $D$ are affected by the semicore states in $A$-site cation atoms.

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