

Skewing of electronic band along the direction of electric polarization in ferroelectrics

Ferroelectric materials have a spontaneous polarization due to the relative ionic displacement involving inversion symmetry breaking that plays an essential role in high dielectric capacitors, piezo-actuators, pyro-sensors, and nonlinear optics. In the research and industry fields, the majority treats ferroelectric material as a typical insulator owing to its high resistivity and wide optical band gap, and this is the fact that we learned in textbooks. Modern theoretical work has revealed an approach showing the electronic structure of ferroelectrics using the Berry phase formulation, which is a revolutionary breakthrough that opens the doors to new methodologies for developing novel functioning electronic devices using ferroelectric oxide materials, such as a nonvolatile random access memory and memristors, for realizing a future artificial neural network. The principle of the work for such ferroelectric devices is based on a characteristic electron tunneling. Electrons can be transferred in the heterostructure of a ferroelectric oxide thin film sandwiched by two different electrodes, e.g., Pt/BaTiO₃ (BTO)/Nb-SrTiO₃, the so-called ferroelectric tunneling junction (FTJ) [1]. In FTJs, electrons can move in the film along the potential slope depending on the polarization direction (Fig. 1). In the Schottky barrier formed at the interface near the doped semiconductor, its height and depletion regions can be switched by electric polarization reversal. This behavior originates from the skewed electronic structure of ferroelectrics. The depolarization field generated by electric polarization causes an electrostatic potential gradient along the polarization direction, forming a skewed band structure. Such a gradual potential affects the Schottky barrier and drives the rectification of electron transfer in FTJs. Thus, the ferroelectric band skewing (FEBS) structure is a crucial physical property for developing functional FTJs. The concept of the FEBS structure was predicted in 1973 [2]. The first-principles calculation is performed for FEBS in the ferroelectric BTO thin film [3]; however, the actual structure has not yet been demonstrated.

We have recently succeeded in showing experimental evidence for FEBS, which was obtained from the depth profiles of atomic orbitals of angle-resolved hard X-ray photoemission spectra of ferroelectric BTO thin films [4]. We prepared epitaxial BTO thin films of various thicknesses by pulsed laser deposition. We used the experimental equipment of angle-resolved hard X-ray photoemission

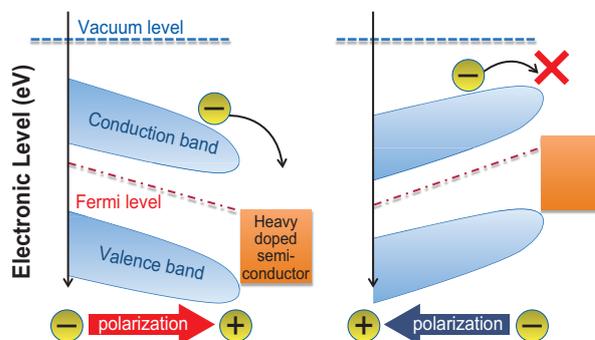


Fig. 1. The schematic figure of the FEBS structure. The electronic band is skewed along the direction of the electric polarization. This slope can be switched by the polarization reversal.

spectroscopy (AR-HAXPES) at SPRING-8 BL47XU, which allows for the direct observation of the FEBS structure in ferroelectric materials. AR-HAXPES with synchrotron radiation has the advantage of providing a 20-nm-deep profile of photoelectron emission spectra. The AR-HAXPES unit installed at BL47XU is equipped with an objective lens with a wide acceptance angle of 64°, which is a significant advantage for our study. In a conventional AR-HAXPES unit without a wide-angle objective lens, the optical angle between the incident beam and the sample is often required to be mechanically adjusted, a feature that causes difficulty in achieving accurate angular resolution and beam positioning within the micrometer domain on samples. The emission angle of the photoelectron almost corresponds to the depth of the sample, but this estimation is theoretically invalid. We must consider the depth sensitivity, which is affected by the inelastic mean free path of photoelectrons, and the optical geometry between the sample surface and incident X-ray/irradiated photoelectrons. As a future task, we are developing an analytical technique for the accurate measurement of the depth profile.

Our results show that electronic core levels and the valence band shift to higher energy following electrical polarization orientation in BTO thin films. Figure 2 shows AR-HAXPES spectra of the valence band in 5-nm-thick BTO, observed at various depths. The valence band of BTO consists of three electronic states: one pure O-2p orbital and two O-2p and Ti-3d hybridized states. The position of the three states shifts to the high-energy side from the surface to a deeper region. Since the direction of electric

polarization of this sample points into the substrate, the binding energy of atomic orbitals increases along with the electric polarization. The energy shift depends on the magnitude of the electric polarization. We also demonstrated that the slope of FEBS could be changed by switching the polarization, as shown in Fig. 3. Our experimental result proves the ferroelectric origin of the band-skewed structure, which agrees with the theoretical prediction.

The electric polarization induces FEBS, which indicates a gradual change in electrostatic potential in a ferroelectric crystal. In our experiment, an electronic structure skewed by the electric polarization is revealed by the binding energy shift of atomic orbitals. All atomic orbitals show similar behaviors, but the magnitude of the energy shift derived from FEBS is different. We attributed the electric polarization in the ion crystal to the atomic contribution. It is well known that the amplitude of the polarization calculated from the relative ionic displacement is underestimated. Born effective charges, which are different from nominal ionic charges, are defined by the actual amplitude of the polarization divided by the ionic displacement [5]. We found that the magnitude of the energy shift of each atomic orbital has good correlation with the Born effective charge. We also estimated an effective screening length and a depolarizing field using the

magnitudes of the binding energy shift and electric polarization at various thicknesses. The values are in good agreement with the results of first-principles calculation and depend on the film thickness. The direct observation of FEBS has been performed by AR-HAXPES, which proves to be a useful technique for observing the ferroelectric characteristic electronic structure and facilitates its understanding.

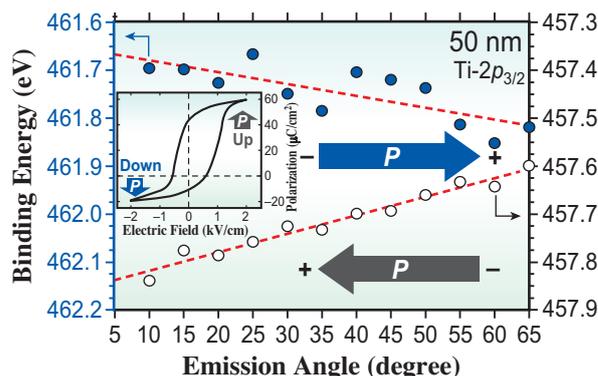


Fig. 3. Depth dependence of binding energies of $Ti-2p_{3/2}$ atomic orbital in 50-nm-thick BTO with different polarization directions. Open circles indicate the energy shift when the electric polarization points upward. Blue closed circles are for electric polarization the pointing downward. Black and blue arrows show the directions of electric polarization upon switching induced by applying an electric field. The inset shows the $P-E$ hysteresis loop.

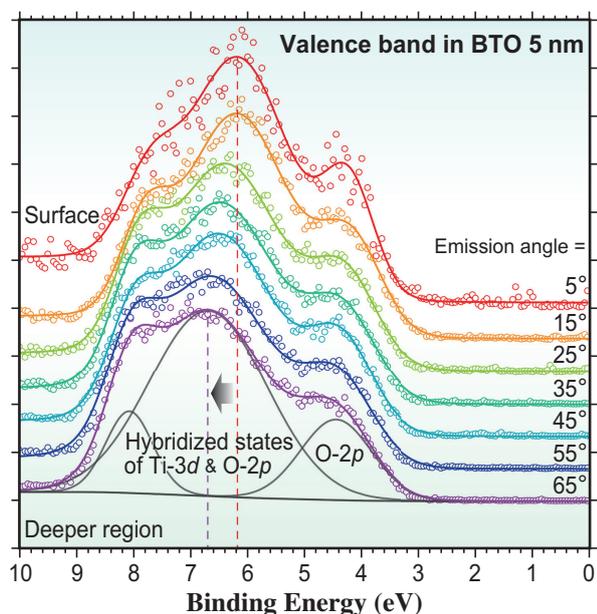


Fig. 2. AR-HAXPES spectra of the valence band in the 5-nm-thick BTO observed at each emission angle. The valence band consists of three densities of states. In the spectrum at emission angle = 65° , the fitted curves of background and Voigt function are drawn as gray lines. Binding energy is referenced to the energy of the Au Fermi edge.

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References

- [1] E.Y. Tsymbal and A. Gruverman: Nat. Mater. **12** (2013) 602.
- [2] P. Wurfel and I.P. Batra: Phys. Rev. B **8** (1973) 5126.
- [3] X. Liu *et al.*: Phys. Rev. Lett. **116** (2016) 197602.
- [4] N. Oshime, J. Kano, E. Ikenaga, S. Yasui, Y. Hamasaki, S. Yasuhara, S. Hinokuma, N. Ikeda, P.-E. Janolin, J.-M. Kiat, M. Itoh, T. Yokoya, T. Fujii, A. Yasui, H. Osawa: Sci. Rep. **10** (2020) 10702.
- [5] R. Resta *et al.*: Phys. Rev. Lett. **70** (1993) 1010.