

Site-specific valence-band x-ray photoelectron spectra of a SrTiO₃ single-crystal by x-ray standing wave technique

Tatsuo Fujii^a, Masahiro Kimura^b, Hideki Yoshikawa^b, and Sei Fukushima^b

^a Faculty of Engineering, Okayama University, Tsushima-naka 3-1-1, Okayama 700-8530, Japan

^b Harima Office, National Institute for Materials Science, Kouto 1-1-1, Sayo-cho, Hyogo 679-5198, Japan

Site-specific valence-band x-ray photoelectron spectra (XPS) of a SrTiO₃(111) single-crystalline surface were successfully obtained by using an x-ray standing wave technique [1]. The SrTiO₃(111) has a cubic perovskite structure and consists of two different atomic layers along the <111> axis: one is the Ti⁴⁺ layer and another is the SrO₃⁴⁻ layer. To apply the XPS combined with an x-ray standing wave technique, contributions of the Ti and SrO₃ derived electronic states to the valence-band spectra could be clearly separated.

Moreover, the high-energy XPS spectra provided not only site-specific but also bulk-sensitive information on the SrTiO₃ crystal because of the large escape depth of the photoelectrons. The high-energy XPS measurements were performed at BL15XU in SPring8, the National Institute for Materials Science beam line equipped with an angle resolved XPS system (ULVAC-PHI DAPHNIA). The incident x-ray beam was monochromated by using a Si(111) double-crystal monochromator to a photon energy of about 4,750 eV. The sample crystal was placed on a motorized rotating sample stage and the incident x-ray angle was fixed to about 36° to confirm the Bragg diffraction condition of the SrTiO₃(111) plane. A hemispherical electron energy analyzer with a high energy resolution of about 0.2eV at a pass energy of 23.5 eV was placed normal to the sample surface. Because of a good insulating nature of stoichiometric SrTiO₃, a neutralizer gun was used to compensate for the large charging effects. The binding energy in all XPS spectra was calibrated to assume the O 1s line of 530.1 eV.

The XPS spectra emitted by the controlled x-ray standing wave under the Bragg diffraction conditions had a good spatial resolution. The Ti derived states in the valence-band was mainly contributed to the deeper levels in the valence-band due to the formation of the covalent bonding between Ti 3d and O 2p orbitals. While the spectrum derived from the SrO₃ layer had clear double peaked structure at the valence-band, mainly attributed to the O 2p component. The structures of the observed valence-band spectra derived from both Ti and SrO₃ layers were in good agreement with those of the DV-X α calculation results by using the (Sr₈Ti₂₇O₁₀₈)⁹²⁻ cluster model. The partial density of states of both Ti and Sr ions in SrTiO₃ were mainly distributed over the bottom of the valence-band to produce the covalent bonding with O ions.

[1] T. Fujii, M. Kimura, H. Yoshikawa, S. Fukushima, Solid State Commun., **136**(2005) 375.