

## Site-specific valence-band x-ray photoelectron spectra of a SrTiO<sub>3</sub> single-crystal by x-ray standing wave technique

Tatsuo Fujii<sup>a</sup>, Masahiro Kimura<sup>b</sup>, Hideki Yoshikawa<sup>b</sup>, and Sei Fukushima<sup>b</sup>

<sup>a</sup> Faculty of Engineering, Okayama University, Tsushima-naka 3-1-1, Okayama 700-8530, Japan

<sup>b</sup> 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 SrTiO<sub>3</sub>(111) single-crystalline surface were successfully obtained by using an x-ray standing wave technique [1]. The SrTiO<sub>3</sub>(111) has a cubic perovskite structure and consists of two different atomic layers along the <111> axis: one is the Ti<sup>4+</sup> layer and another is the SrO<sub>3</sub><sup>4-</sup> layer. To apply the XPS combined with an x-ray standing wave technique, contributions of the Ti and SrO<sub>3</sub> 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 SrTiO<sub>3</sub> 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 SrTiO<sub>3</sub>(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 SrTiO<sub>3</sub>, 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 SrO<sub>3</sub> 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 SrO<sub>3</sub> layers were in good agreement with those of the DV-X $\alpha$  calculation results by using the (Sr<sub>8</sub>Ti<sub>27</sub>O<sub>108</sub>)<sup>92-</sup> cluster model. The partial density of states of both Ti and Sr ions in SrTiO<sub>3</sub> 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.