Polarization-dependent X-ray absorption spectroscopy on rutile TiO$_2$(110)

Daichi Yuyama, Kei Mitsuhara, and Masaru Takizawa

Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University, Kusatu, Shiga 525-8577, Japan

X-ray absorption fine structure (XAFS) measurements are powerful technique to elucidate a valence state of a specific element, especially a transition metal. For transition metal oxides, O K-edge XAFS spectra are also important due to a strong hybridization between oxygen and the transition metal [1]. Rutile TiO$_2$(110) surface, which is the most stable surface, is well studied as a typical oxide surface because it is a few systems which can obtain a flat single crystal surface with an atomic level. This surface contains two specific rows of bridging oxygen and 5-fold-coordinated Ti atoms along [001] direction, which alternatively align along [1$\bar{1}$0] direction. In contrast, SrTiO$_3$(100) surface has an isotropic TiO$_2$ surface. In order to see the effect of highly anisotropic surface on the XAFS spectra, we have performed polarization-dependent XAFS measurements of TiO$_2$(110) and SrTiO$_3$(100) surface.

The TiO$_2$(110) were prepared by 0.75 keV Ar$^+$ sputtering and annealing at 870 K for 10 min in UHV and the SrTiO$_3$(100) were prepared by the chemical methods [2]. The XAFS measurements were carried out at the BL-8 of SR Center, Ritsumeikan University. O K-edge XAFS spectra were obtained by the total electron yield (TEY) method. In order to see the polarization dependence, all XAFS spectra were collected with two polarization geometries.

Figure 1 (a) shows O K-edge XAFS spectra of the TiO$_2$(110) surface with two polarization geometries. The t_{2g} ($\sim$ 530.5 eV) and the e_g ($\sim$ 533.5 eV) bands are separated by the ligand field splitting. The ratio of t_{2g} and the e_g peak intensities changed depending on the polarization direction. This result is well reproduced by theoretical results [3] as shown in Fig. 1 (b), which reflect the relationship between O $2p$ orbital-dependent DOS in the unoccupied state and the polarization of SR. On the other hand, the energy difference Δd [= E(e_g)-E(t_{2g})] taken for [1$\bar{1}$0]-azimuth is larger than that for [001]-azimuth [Fig. 1(a)]. It may suggest the oxygen vacancy (V$_o$) affect this result. Figure 1 (c) shows the effect of the oxygen vacancy. As the number of oxygen vacancy increases, Δd becomes larger, which is similar to the experimental result. However, the ratio of peak intensities also changes. Figure 1 (d) shows O K-edge XAFS spectra of SrTiO$_3$(100) surface with two polarization geometries. Both of the spectrum does not change depending on the polarization direction. This result is well reproduced too.
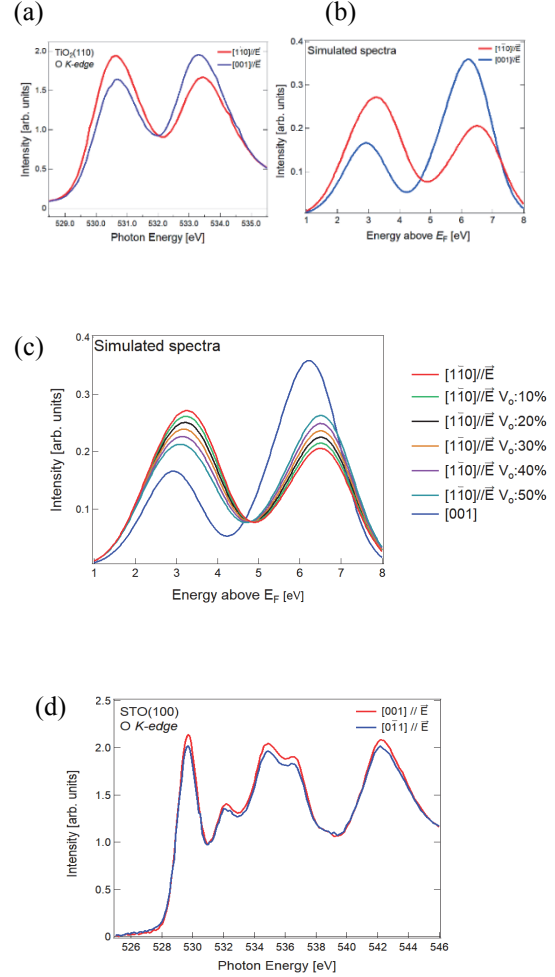

Fig. 1 (a) O K-edge XAFS spectra of TiO$_2$(110) surface. (b) Theoretical prediction from ref. [3]. (c) Effect of oxygen vacancy. (d) O K-edge XAFS spectra of SrTiO$_3$(100) surface.

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