

## Analysis of interstitial Ti atoms formed in rutile TiO<sub>2</sub> (110)

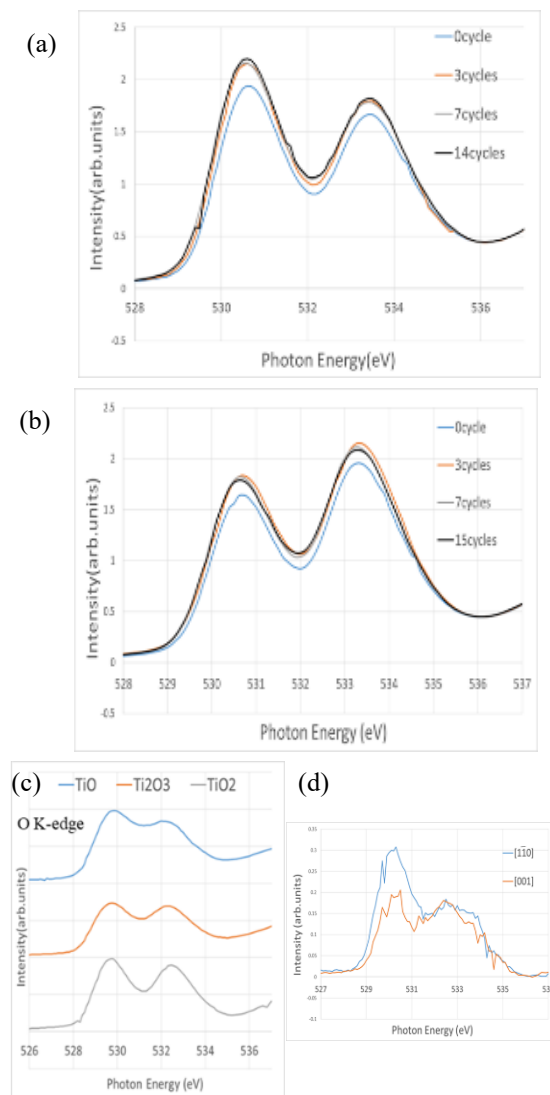
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Metal oxides play an important role such as catalysis and gas sensing. In the case of rutile TiO<sub>2</sub>(110), the electronic excess charge appears in the band gap, which was identified as a Ti 3d electron bound by a positive core of Ti<sup>4+</sup> ion, namely existing as a Ti<sup>3+</sup> ion. The gap state originates from (i) bridging O vacancy (V<sub>O</sub>), which delivers an excess electronic charge to underlying lattice site of Ti<sup>4+</sup> ions, and (ii) interstitial Ti<sup>3+</sup> ions (Ti-int) condensed near the surface by annealing in a vacuum. Because gas phase redox reactions on oxide surfaces progress via transfer of an electronic excess charge, it is important to understand distribution of V<sub>O</sub> and Ti-int separately. In this study, we have investigated the distribution of Ti-int for reduced (R-) TiO<sub>2</sub>(110) by X-ray absorption fine structure (XAFS) measurements.

The R-TiO<sub>2</sub>(110) were prepared by several cycles of 0.75 keV Ar<sup>+</sup> sputtering and annealing at 870 K for 10 min in UHV. 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 method (TEY). In order to see the polarization dependence, all XAFS spectra were collected with the electric vector of SR parallel to [1 $\bar{1}$ 0] and [001].

Figure 1 (a) and (b) show O K-edge XAFS spectra of R-TiO<sub>2</sub>(110) with several sputtering / annealing cycles for the polarization parallel to [1 $\bar{1}$ 0] and [001], respectively. The  $t_{2g}$  (~ 531 eV) and the  $e_g$  (~ 533 eV) bands are separated by the ligand field splitting. This splitting is also observed for other titanium oxides [Fig. 1(c)]. These ligand field splitting  $\Delta d$  were estimated by the energy difference in the peak positions. Since  $\Delta d$  depends on the valence of Ti, we could estimate the valence of Ti from O K-edge spectrum. Although  $\Delta d$  depends on the polarization of SR for the TiO<sub>2</sub>(110) single crystal, the average  $\Delta d$  is consistent with that for Ti<sup>4+</sup> (powder TiO<sub>2</sub>). The polarization-dependent  $\Delta d$  can be explained by the theoretical calculation considering the O-Ti bonds [1]. As both  $t_{2g}$  and  $e_g$  intensities increased with increasing the number of cycles, we extracted the difference spectra between 0 cycle and 14 (or 15) cycles [Fig. 1(d)]. Since the amount of V<sub>O</sub> does not depend on the cycles [2], it may suggest that the difference spectra represents the Ti-int component. The average  $\Delta d$  of the difference spectra was coincident with that of Ti<sup>3+</sup> (Ti<sub>2</sub>O<sub>3</sub>). This result also suggests that this component corresponds to Ti-int.



**Fig. 1** O K-edge XAFS spectra taken at [1 $\bar{1}$ 0]-azimuth (a) and [001]-azimuth (b) for R-TiO<sub>2</sub>(110) with several sputter/annealing cycles. (c) O K-edge XAFS spectra for powder samples. (d) Difference spectra of O K-edge XAFS spectra between 0 cycle and 14 (or 15) cycles for two measurement geometries.

### References

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- (2) K. Mitsuhashi, H. Okumura, A. Visikovskiy, M. Takizawa, and Y. Kido, *J. Chem. Phys.* **2012**, 136, 124707.