

Analysis of interstitial Ti formed in Rutile TiO₂(110): Effect of sample thickness

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Rutile Titania (TiO₂) with the most stable (110) face [TiO₂(110)] has been used as a model support to investigate the chemical activities of metal clusters. The origin of the defect state in the band gap seen in ultraviolet photoelectron spectra (UPS) for reduced (R-) and hydroxylated (H-)TiO₂(110) surfaces has been recently debated excitingly. It has been recognized that creation of oxygen vacancy (V_O) gives an electronic charge to underlying Ti atoms making the Ti⁴⁺ state into Ti³⁺ state. Recently, however, Wendt *et al.* claimed that the gap state comes from the Ti interstitial (Ti-int) acting as an electron donor condensed near the surface by annealing in UHV [1]. Since annealing in UHV is necessary to obtain a model surface, it is important to evaluate the contributions from V_O and Ti-int. Taking a diffusion of Ti-int into account, sample thickness would affect the condensation of Ti-int near the surface. In this study, we have evaluated the contributions from V_O and Ti-int by photoelectron spectroscopy using synchrotron radiation (SR) light.

The photoelectron spectroscopy (PES) measurements were performed at beamline 8 named SORIS set up at SR center, Ritsumeikan University. Valence band spectra were obtained by irradiating synchrotron radiation (SR) light of 50 eV. The all measurements were performed at room temperature (RT) under ultrahigh vacuum (UHV) of $\sim 1 \times 10^{-7}$ Pa. Two different thicknesses of TiO₂(110) substrates (0.5 mm and 1.0 mm) were prepared. To create the gap state, repeated cycles of Ar⁺ sputtering (0.75 kV) and annealing at 870 K for 5 min in UHV were conducted.

Figure 1 shows the valence band PES spectra for TiO₂(110) substrate with thickness of 1.0 mm after the several cycles. The intensity of defect state around 1 eV increases with increasing the number of cycles. The increased intensity of defect state is likely caused by an increase V_O and/or Ti-int. Figure 2 shows the defect state intensities as a function of the cycles for TiO₂(110) substrates with thickness of 0.5 mm and 1.0 mm. Interestingly, the intensities for the substrate with thickness of 0.5 mm saturate faster than those with thickness of 1.0 mm. Since the annealing temperature was controlled by measuring near the surface, the temperature in the bulk could be different between the substrates. Therefore, this result suggests that the creation of

Ti-int near the surface is different depending on the thickness of the substrate because of the bulk Ti-int diffusion during annealing.

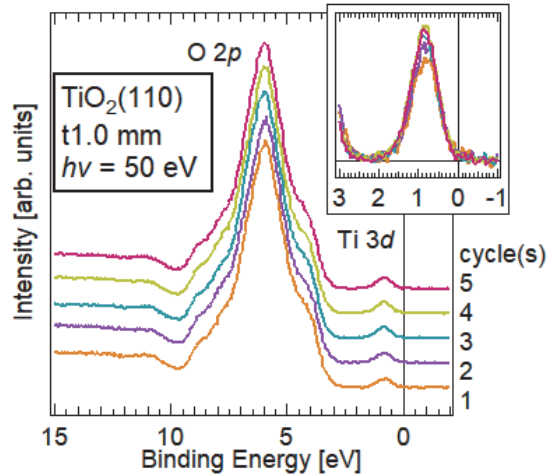


Fig. 1 Valence band spectra for TiO₂(110) substrates with thickness of 1.0 mm after the several cycles. Inset: Magnified spectra around the defect state.

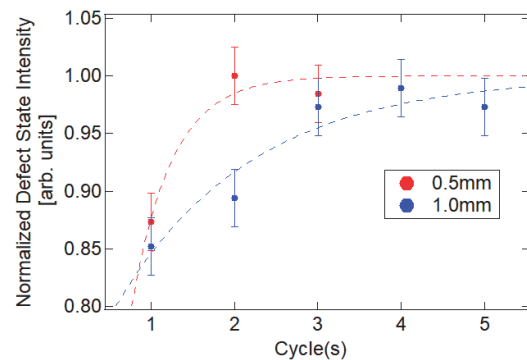


Fig. 2 Normalized intensities of Ti 3d defect state as a function of the cycles for the TiO₂(110) substrates with thickness of 0.5 mm (red) and 1.0 mm (blue). The broken curves are guides to an eye.

References

- [1] S. Wendt *et al.*, Science **320**, 1755 (2008).