Effect of Sputtering and Annealing for Rutile $TiO_2(110)$

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Rutile Titania (TiO_2) with the most stable (110) face [$TiO_2(110)$] has been used as a model support to investigate the chemical activities of metal clusters. The in-gap state of $TiO_2(110)$, which has been observed in photoelectron spectroscopy (PES) spectra, is also known to influence the activity. As for the origin of this in-gap state, it has been recognized that creation of oxygen vacancy (V_O) gives an electronic charge to underlying Ti atoms making the Ti^{4+} state into Ti^{3+} state. Recently, however, Wendt *et al.* [1] claimed that the in-gap state comes from the Ti interstitial (Ti-int) acting as an electron donor condensed near the surface by annealing in ultrahigh vacuum (UHV). In this study, we have evaluated the contributions from V_O and Ti-int, which may depend on the combination of sputtering and annealing, by synchrotron radiation (SR) PES analysis.

The PES measurement was carried out at the linearly polarized soft X-ray beamline BL-7 of SR center, Ritsumeikan University, using a hemispherical electron energy analyzer, SCIENTA SES2002. The valence band spectra were obtained by irradiating SR light of 50 eV. The energy resolution was set to be ~200 meV. The measurements were performed at room temperature under the UHV of ~5×10^{-8} Pa. $TiO_2(110)$ substrate surfaces were cleaned by Ar^+ sputtering (1.0 kV) and/or newly installed electron bombardment annealing at 870 K for 10 min in UHV. Ar^+ sputtering creates V_O, while annealing partially heals V_O and creates Ti-int to form (110) surface. Indeed, low energy electron diffraction (LEED) showed the 1×1 pattern after the sputtering and annealing treatment.

Figure 1 shows the valence band spectra for the cleaned $TiO_2(110)$ substrates. The prominent structures around the binding energy (E_B) of 6 eV mainly come from O 2*p* states. As for the sputtered $TiO_2(110)$, the in-gap Ti 3*d* state around E_B of 1 eV is clearly seen due to the large amount of V_O. Furthermore, the spectral shape of O 2*p* states for the sputtered $TiO_2(110)$ is quite different from those for the annealed and the sputtered and annealed $TiO_2(110)$. This is considered as the difference between the angle-integrated PES spectrum and the angle-resolved PES spectrum, i.e., the total density of state and the band structure of $TiO_2(110)$, which is consistent with the observation of LEED 1×1 pattern for the sputtered and annealed $TiO_2(110)$.

Figure 2 shows the normalized Ti 3*d* state for the cleaned $TiO_2(110)$ substrates. As described above, the prominent Ti 3*d* state for the sputtered $TiO_2(110)$ comes from the V_O. As for the sputtered and annealed $TiO_2(110)$, the spectral shape of the Ti 3*d* state is very similar to that for the sputtered $TiO_2(110)$ since annealing partially heals V_O and creates Ti-int. As for the annealed $TiO_2(110)$, the Ti 3*d* state is quite different: the broad states connecting with the O 2*p* states, indicating that the surface is not completely clean.

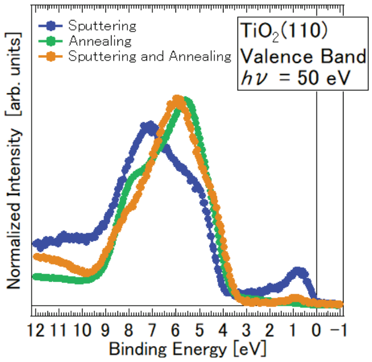

Fig. 1 Valence band spectra for the cleaned $TiO_2(110)$ substrates.

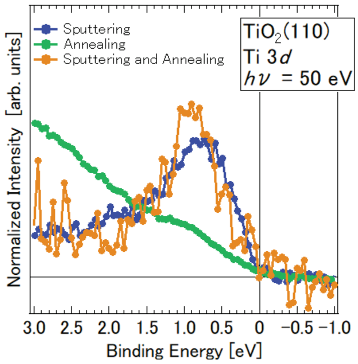

Fig. 2 Ti 3*d* states for the cleaned $TiO_2(110)$ substrates.

References

[1] S. Wendt, P.T. Sprunger, E. Lira, G.K.H. Madsen, Z. Li, J.Ø. Hansen, J. Matthiesen, A. Blekinge-Rasmussen, E. Lægsgaard, B. Hammer, and F. Besenbacher, Science **320**, 1755 (2008).