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Electronic state changes of Cu nanoparticles on reduced $TiO_2(110)$ by oxygen exposure

Kazuma Ide, Takeru Yagi, Kei Mitsuhara, and Masaru Takizawa
Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, 525-8577, Japan

It is well known that Cu based catalysts are used in the reactions such as water gas-shift, methanol oxidation, CO oxidation, and so on. In spite of many efforts, however, the mechanism leading to strong catalytic activities of Cu nanoparticles is still a debatable issue. In previous study, we have found the oxidation of Cu nanoparticles on oxygen-rich $TiO_2(110)$ (O-TiO_2) by measuring the core-level shifts and the work functions. In this work, we have measured the electronic properties of oxygen-exposed Cu nanoparticles on reduced $TiO_2(110)$ (R-TiO_2) by photoelectron and photo-induced secondary electrons emission 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. Ti 3*p* and O 2*s* spectra were obtained by irradiating SR light of 120 eV. Secondary electron spectra were obtained with a bias voltage of -3.0 eV. The all measurements were performed at room temperature (RT) under ultrahigh vacuum (UHV) of $\sim 1 \times 10^{-7}$ Pa. The R-TiO_2 were prepared by Ar^+ sputtering and annealing at 870 K for 10 min in UHV. Cu was deposited on the clean surfaces at RT with a Kundsen cell under UHV condition. The deposition rate was 0.055 ML/min. Here, 1 ML means 1.77×10^{15} atoms/cm^2, corresponding to the areal density of Cu(111).

Figure 1 shows Ti 3*p* and O 2*s* spectra for Cu (0.5 ML)/R-TiO_2 as a function of oxygen exposure. It is clearly seen that the binding energies of both the O 2*s* and Ti 3*p* lines shift toward a lower binding energy side.

Figure 2 shows the binding energy shifts of Ti 3*p* and O 2*s* and the change of work function as a function of oxygen exposure for Cu (0.5 ML)/R-TiO_2 and R-TiO_2. The electronic state change for R-TiO_2 indicates an upward band bending by changing to O-TiO_2 after O_2 exposure [1]. The electronic state for Cu (0.5 ML)/R-TiO_2 changes more significantly than that for R-TiO_2. These results indicate that Cu nanoparticles oxidized to Cu_2O by oxygen exposure and then the additional upward band bending is caused by a p-n junction between Cu_2O and TiO_2 substrate.

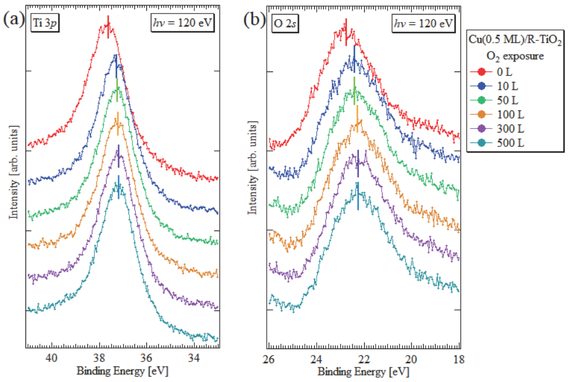

Fig. 1 Ti 3*p* (a) and O 2*s* (b) spectra for Cu coverage of 0.5 ML on R-TiO_2 as a function of O_2 exposure.

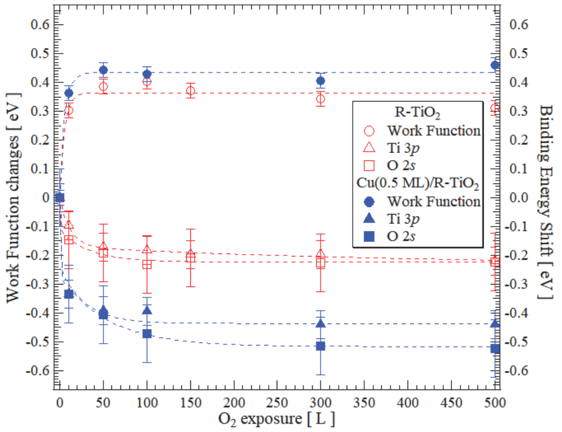

Fig. 2 Work function changed (circles) and binding energy shifts of Ti 3*p* (triangles) and O 2*s* (squares) for R-$TiO_2(110)$ (red) and Cu (0.5 ML)/ R-$TiO_2(110)$ (blue) as a function of oxygen exposure. The broken curves are guides to an eye.

References

[1] K. Mitsuhara, H. Okumura, A. Visikovskiy, M. Takizawa, Y. Kido, J. Chem. Phys. Lett. **513**, 84 (2011).