Electronic state analysis of Cu nanoparticles on SrTiO₃(001)

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Cu based catalysts exhibits strong catalytic activities for the water-gas shift reaction, methanol oxidation, methanol synthesis and others [1,2]. However, their performance is not fully understood and is highly dependent on the synthesis conditions or the nature of the oxide support. In this study, we have analyzed the electronic state of Cu nanoparticles on TiO₂-terminated SrTiO₃(001) (STO) surface by photoelectron and photon-induced secondary electrons emission spectroscopy using synchrotron-radiation (SR) light.

The Photoelectron Spectroscopy (PES) measurements were carried out at the BL-8 of SR Center, Ritsumeikan University. O 2s, Sr 4p and Ti 3p spectra were obtained by irradiating SR light of 140 eV. Work Function spectra were obtained with retarding voltage of -3 V. The mirror-finished STO substrates were sonicated in organic solvents and then etched by BHF (pH \sim 4.5) [3]. The clean (1×1) surfaces were checked by RHEED. The substrates were annealed at 800 °C for 10 minutes in UHV to remove surface contamination. SrO precipitates on the surface ($\sim 33\%$) after annealing. Then this substrates sonicated in hot water(\sim 70°C) to remove surface SrO and annealed at 200 °C for 10 minutes in UHV to remove surface contamination. The surface structure of this substrate is forming TiO₂double layer. Cu nanoparticles were deposited on the clean surfaces at RT with a Knudsen cell at a rate of 0.055 ML/min under UHV condition. Here, 1 ML means 1.77×10^{15} atoms/cm², corresponding to the areal density of Cu(111). The all measurements were performed at room temperature under ultrahigh vacuum of $\sim 1 \times 10^{-7}$ Pa.

Figure 1 shows O 2*s*, Sr 4*p* and Ti 3*p* spectra as a function of Cu coverage. All peaks shifted toward a lower binding energy side with increasing Cu coverage at more than 0.1 ML. On the other hand, the work function increased with increasing Cu coverage more than 0.1 ML. (Fig. 2). These results suggest that electron charge transfer takes place at Cu/STO interface from STO support to Cu nanoparticles due to a larger work function of Cu than that of STO. The electron deficiencies are created near the STO surface, which leads to an upward band bending, just like a Schottky contact. However, the reason why work function decreases with Cu coverage of less than 0.1 ML is unknown.



Fig. 1. O 2s (a) and Ti 3p (b) spectra as a function



Fig. 2. Work Function as a function of Cu coverage.

Reference

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