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Valence Band Structure of the Cu/ZnO(0001) Surface: Angle-Resolved Photoemission Spectroscopy Study

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Introduction

Electronic and atomic structures of metals on oxide surfaces are of great importance from the view point of catalyst activity. Chemical activity of the oxide-supported metal clusters is influenced by their morphology as well as the electronic structure. Therefore, great efforts have been made to elucidate the characteristics of deposited metals on oxide surfaces using various surface science techniques. Cu-deposited ZnO is known as a catalyst for methanol synthesis. X-ray photoelectron spectroscopy, ion scattering spectroscopy and scanning tunneling microscopy studies have revealed that Cu adsorption proceeds via a cluster formation on single-crystal ZnO surfaces [1]. However, only limited information is available as to the valence electronic structure, especially the evolution of the valence band, of the Cu clusters on ZnO.

In the present study, the valence electronic structure of the Cu clusters on the Zn-terminated ZnO(0001) surface has been studied by angle-resolved photoelectron spectroscopy. The coverage-dependent measurements of the work function, the Zn 3p and Cu 3p core-level peaks and the valence band structure have been carried out.

Experimental

The ARPES measurements were carried out at beam line 1C. A single crystal ZnO sample with the Zn-terminated (0001) surface was cleaned by an Ar^+ bombardment and annealing at 1000 K. No contaminant such as carbon and sulfur was detected by the Auger electron spectroscopy measurements. Cu was deposited on the surfaces at room temperature using a commercial evaporation source (Omicron EFM3). The Cu coverage Θ_{Cu} was estimated from the attenuation curve of the Zn 3p core-level peak as a function of the deposition time.

Result and Discussions

Fig. 1 shows the normal emission spectra of the Cu-covered ZnO(0001) surface as a function of Θ_{Cu}. Upon Cu adsorption, the work function decreases by 0.57 eV followed by a gradual increase. Downward bending of the ZnO band is also induced. These indicate that charge is transferred from Cu to ZnO at low coverages. Valence charge should be transferred from the Cu 4sp to the empty Zn 4sp band. On the Cu-covered surface, the step structure by the emission from Cu 4sp band is observable at > 5 ML. The mid-point of the onset of the step locates at 0.3 eV below E_F at 5.6 ML and shifts to 0.25 eV at 8.9 ML. This means that the Cu clusters on ZnO(0001) at 8.9 ML have an electronic structure which is not equivalent to that of bulk Cu. However, the low-energy electron diffraction measurements reveal that the upper terrace of the Cu cluster is terminated by an hexagonal (111) structure at 8.9 ML, i.e. the atomic arrangement of the Cu cluster is already equivalent to that of bulk Cu.

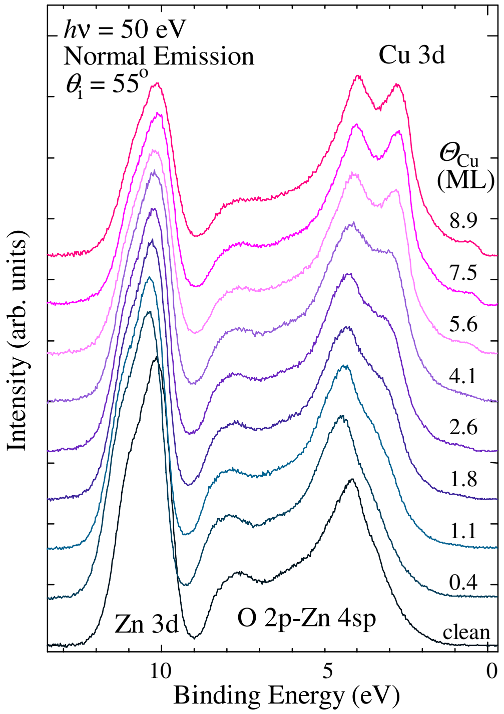

FIG.1 Change in the normal emission spectrum of the Zn-terminated ZnO(0001) surface as a function of the Cu coverage. The photon energy used was 50 eV.

References

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