1C/2004G007

ARPES Study on the Electronic Structure of Deposited Cu on ZnO(10-10)

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Introduction

Zinc oxide (ZnO) is a material that is widely used in many applications such as optoelectronic devices, chemical sensors, catalysts, etc. As a catalyst, the Cu/ZnO system show high activity for synthesis of methanol and higher alcohol, water gas shift reaction and steam reforming of methanol. Activity of oxide-supported metal catalysts should be closely related to the morphology and the electronic structure of metals on oxide surfaces. In the present study, we have performed angle-resolved photoemission spectroscopy (ARPES) measurements of the Cu/ZnO(10-10) surface to elucidate the valence electronic structure of the Cu overlayers at various Cu coverages.

Experimental

The ARPES measurements were carried out at beam line 1C. The ZnO(10-10) surface was cleaned by an Ar^+ bombardment and annealing at 1050 K. Cu was deposited on the surface at room temperature using a commercial evaporation source (Omicron EFM3).

Result and Discussions

FIG. 1 shows the normal emission spectra from the ZnO(10-10) surface at various Cu coverages. Cu deposition leads to the gradual evolution of the Cu 3d peak in the band gap region of ZnO. The Cu 3d peak locates at 3.0 eV at 0.2 ML and shifts to 2.5 eV up to 3.2 ML. In the energy region between the Fermi level (E_F) and the Cu 3d peak, the step structure is formed by the emission from the Cu 4sp band, which represents the total density of state (DOS) of the Cu 4sp states. The onset position of the 4sp DOS also shifts to the lower binding energy side with increasing the Cu coverage in a similar manner to the Cu 3d peak. Formation of the step-like sp DOS from the low coverage region and the shift of the onset position towards E_F with increasing coverage are characteristic of noble-metal/oxide systems, where the deposited noble-metal atoms aggregate to form clusters and the size of the cluster is enlarged with increasing the coverage [1]. Thus, growth of Cu on ZnO(10-10) is characterized by the cluster formation, in good agreement with a recent scanning tunnelling microscopy study [2].

An interesting point to note is that the magnitude of the shift as a function of the Cu coverage is larger for the onset of the Cu 4sp DOS than for the Cu 3d peak. For the Cu 4sp DOS, the onset position moves from 0.75 eV at 0.2 ML to 0.12 eV at 3.2 ML. Both the Cu-induced bending of the ZnO band, which causes the shift of the ZnO peaks (the Zn 3d and O 2p-Zn 4sp hybrid peaks), and the final state screening of the photohole remain in the Cu cluster affect the Cu 3d and 4sp states equally. Thus, the extra shift for the Cu 4sp DOS should be caused by initial state effects. The small noble-metal clusters have semiconducting electronic structure with an energy gap between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO), and the HOMO-LUMO gap is reduced with increasing the cluster size [3]. Since the onset of the Cu 4sp DOS corresponds to the HOMO of the Cu cluster, the extra shift should be due to the change in the HOMO-LUMO gap width. Comparison of the coverage dependent shift of the Cu 4sp DOS with that of the Cu 3d peak suggests that the HOMO-LUMO gap may close at ca. 1 ML.

References

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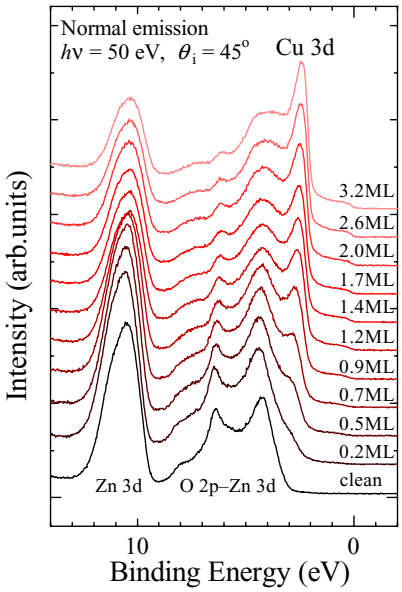

FIG.1 Change in the normal emission spectrum of the ZnO(10-10) surface as a function of the Cu coverage. One monolayer (ML) is equivalent to the coverage where the substrate surface is covered entirely with the Cu overlayer with a single atomic thickness.

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