

Cu Clusters on the Polar ZnO Surfaces: Surface-Termination-Dependence of the Cu Valence Band

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Introduction

Zinc oxide (ZnO) is a widely used oxide as optoelectronic devices, chemical sensors, catalysts, etc. As a catalyst, Cu/ZnO is industrially utilized for methanol synthesis, water gas shift reaction and steam reforming of methanol. Catalytic activity of oxide-supported metals should be closely related to the morphology and the electronic structure of metals on oxide surfaces. Wurtzite ZnO has stable low-index surfaces of (10-10), (0001) and (000-1). Both (0001) and (000-1) surfaces are the polar surfaces with the Zn- and O-termination, respectively. Recent scanning tunneling microscopy (STM) study has revealed that many triangular pits and terraces are formed on the Zn-terminated (0001) surface, whereas the hexagonal terraces exist on the O-terminated (000-1) surfaces [1]. Deposition of Cu on these polar surfaces results in the Cu clusters [2]. However, it is not clear how the difference in the surface termination affects the morphology and the electronic structure of the Cu clusters. In the present study, therefore, we have carried out angle-resolved photoemission spectroscopy (ARPES) measurements for the Cu/ZnO(0001) and Cu/ZnO(000-1) systems to elucidate the effect of the surface termination of ZnO on the electronic structure of the Cu clusters.

Experimental

The ARPES measurements were carried out at beam line 28A. A single crystal ZnO sample with the (0001) orientation used in the present study was mounted on the goniometer (R-Dec, *i* GONIO LT) [3]. The ZnO surfaces were cleaned by an Ar⁺ bombardment and annealing at 1000 K. The clean surfaces exhibited a hexagonal (1x1) low-energy electron diffraction pattern. Cu was deposited on the surfaces at room temperature using a commercial evaporation source (Omicron EFM3).

Result and Discussions

Solid curves in FIG. 1 are the normal emission spectra from the Zn-terminated ZnO(0001) and O-terminated ZnO(000-1) surfaces. The photon energy used was 50 eV. Both spectra bear a sharp peak at around 10 eV and the broad structure between 3 and 9 eV. The former corresponds to the Zn 3d bands and the latter to the O 2p-

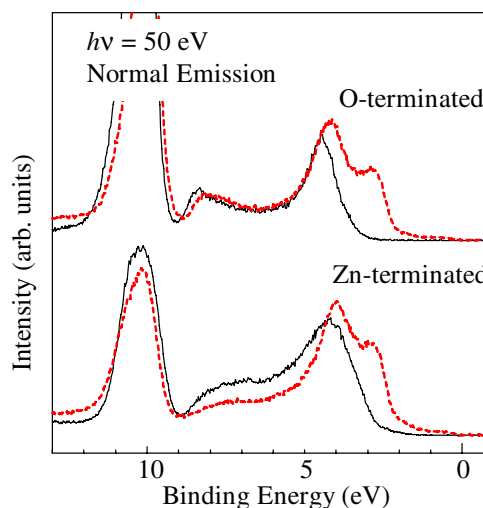


FIG.1 The normal emission spectra of the clean Zn- and O-terminated ZnO surfaces (solid lines) and the Cu-covered surfaces (dotted lines). The photon energy used was 50 eV. The Cu coverage, not determined precisely, is less than a monolayer for both adsorption systems.

Zn 4sp hybrid bands. As the surfaces are being covered with a small amount of Cu, the emission from the Cu 3d bands appears from 2 to 4 eV. The emission structure is similar for both surfaces, i.e., the peaks are formed at 2.8 and 4 eV. However, a close examination reveals that the Cu 3d bands on the O-terminated surface lie deeper than those on the Zn-terminated surface. This may result from the difference in the direction of bending of the ZnO band at the surfaces; the ZnO band bends downwards on the O-terminated surface, whereas upward band bending is induced on the Zn-terminated surface.

References

- [1] O. Dulub et al., *Surf. Sci.*, **519**, 201 (2002).
- [2] L.V. Koplitz et al., *J. Phys. Chem. B*, **107**, 10583 (2003).
- [3] Y. Aiura et al., *Rev. Sci. Instrum.*, **74**, 3177 (2003).

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