Electronic Structure of Silver on ZnO(10-10)

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Introduction

Zinc oxide (ZnO) is one of the most important semiconductors because of several applications such as optoelectronic devices, chemical sensors, catalysts, etc. As a catalyst, the Cu/ZnO systems exhibit high activity for synthesis of methanol and higher alcohol, water gas shift reaction and steam reforming of methanol. Similar catalytic activity is also found for Ag/ZnO systems. The purpose of the present study is to elucidate the valence electronic structure of the Ag film on ZnO(10-10) by angle-resolved photoelectron spectroscopy (ARPES).

Experimental

The ARPES measurements were carried out at beam line (BL) 1C and 11C. The sample surface was cleaned by an Ar\textsuperscript{+} bombardment and annealing at 1050 K. Ag was deposited on the surface at room temperature using a commercial evaporation source (Omicron EFM3).

Result and Discussions

FIG. 1 shows the Ag-coverage dependence of the evolution of the Ag 4d bands along the ΓX’ axis. On the clean surface, the O 2p dangling-bond band is seen between 3.5 and 4.5 eV with a periodic dispersion. Detailed discussions of the valence band structure of the clean surface are found in Ref. [1]. As the surface is covered with Ag, the emission from the O 2p band becomes weaker and several Ag 4d states grow at the higher binding energy side of the O 2p band. The states form two-dimensional bands with a dispersing feature already at 0.12 ML (1 ML = 1.4 x 10\textsuperscript{15} cm\textsuperscript{-2}). This means that the lateral Ag-Ag interaction is emerged from relatively low coverages as a result of the formation of the Ag islands. Increase in the Ag coverage leads to the enhancement of the emission from the Ag 4d bands as shown in FIG. 1. Moreover, the bands shift slightly to the lower binding energy side with increasing coverage. A similar shift is also observed for the O 2p band as well as the Zn 3d bands. We thus conclude that Ag adsorption results in the upward bending of the ZnO valence band. The magnitude of the bending upon Ag adsorption is estimated to be 0.15 eV.

Another interesting feature of the Ag 4d states is that the basic structure of the band dispersion is essentially the same irrespective of the coverage. This implies that the local atomic structure within the Ag island is preserved in the submonolayer region.

References


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