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Electronic Structure of the $Cu_2O(111)$ Thin Film on ZnO(0001)-Zn : Angle-Resolved Photoelectron Spectroscopy Study

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Introduction

Cuprous oxide (Cu_2O) is a *p*-type semiconductor with direct band-gap energy of 2.17 eV. Cu_2O is regarded as one of the most promising materials for photovoltaic devices because high conversion efficiency is theoretically predicted. For the photovoltaic application, *n*-type ZnO is often chosen as a counterpart of *p*-type Cu_2O to fabricate *p-n* heterojunctions. However, the achieved conversion efficiency of the Cu_2O/ZnO-based cell so far is below 2%. One of the key factors to improve a photovoltaic performance is to achieve good crystallinity of the composite films, i.e. the Cu_2O and ZnO films [1]. It is known that ZnO(0001) [or ZnO(000-1)] and $Cu_2O(111)$ are crystalographically matched so that the ZnO(0001) [or (000-1)] surface can be a good template for the $Cu_2O(111)$ film. In the present study, we have prepared the $Cu_2O(111)$ thin film on the Zn-terminated ZnO(0001) surface by oxidizing the Cu overlayer on ZnO(0001) and have investigated the valence electronic structure of the $Cu_2O(111)$ film by angle-resolved photoelectron spectroscopy (ARPES). The $Cu_2O(111)$ film on ZnO(0001) exhibits a strong *p*-type semiconducting nature with the valence band maximum (VBM) at 0.1 eV below the Fermi level.

Experimental

The ARPES measurements were carried out at beam line 1C. Cu was deposited on the clean ZnO(0001) surface and was oxidized by annealing at 650 K in O_2 at 1.3×10^{-4} Pa for 10 min. This oxidation treatment results in the formation of Cu_2O and determined from the shift of the Cu 3p core-level shift. Low energy electron diffraction (LEED) measurements revealed that the Cu_2O film was (111) oriented (the inset of Fig. 1a). When the Cu overlayer at 5 monolayer (ML) was oxidized, the Cu_2O film with the average thickness of 1.4 nm was obtained.

Results and Discussion

Normal emission spectra of the clean Zn-terminated ZnO(0001) surface, the 5-ML Cu-covered surface and the Cu_2O-covered surface are shown in Fig. 1a. The spectrum of the Cu-covered surface bears a sharp peak at 2.7 eV and a step structure in the band gap region of ZnO. These are associated with the emission from the Cu 3d and 4sp bands, respectively. The observation of the step structure indicates the metallic nature of the Cu overlayer at 5 ML. Upon oxidation, the sharp peak at 2.7 eV is broadened and the step structure is quenched. Alternatively, new peaks, labelled D1, E1 and F1, are emerged at 2.3-2.5 eV, 1.5-1.6 eV and 0.4 eV, respectively. These are associated with the Cu_2O states. In comparison with the corresponding states of bulk Cu_2O, the states are found to have smaller binding energies by 0.4-0.5 eV [2]. The VBM is also shifted by the same amount. Fig. 1b shows an energy band diagram of the $Cu_2O(111)$/ZnO(0001) system. The $Cu_2O(111)$ film exhibits a strong p-type semiconducting character, whereas the ZnO substrate has an *n*-type feature. Thus, the *p-n* heterojunction is realized.

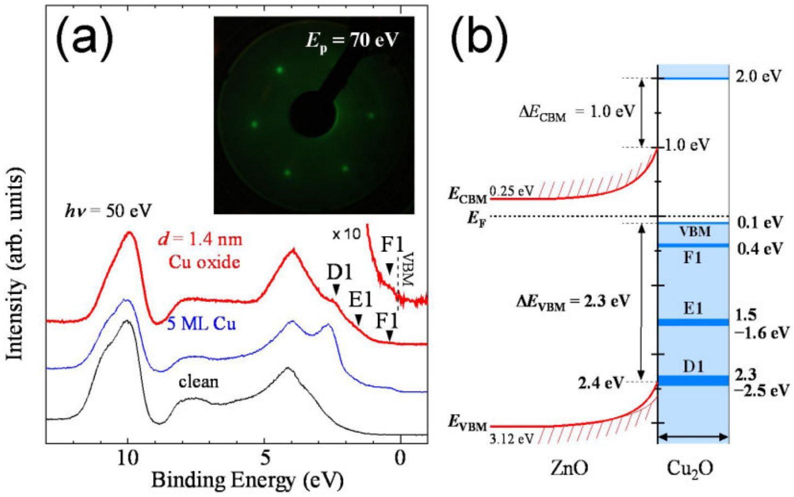

Fig. 1 (a) Normal emission spectra of the clean, 5-ML Cu-covered and Cu_2O-covered ZnO(0001) surface. Positions of the Cu_2O-related peaks (D1, E1 and F1) are indicated by triangle marks. The inset shows a LEED image of the Cu_2O-covered ZnO(0001) surface. (b) Energy band diagram of the $Cu_2O(111)$ /ZnO(0001) system.

References

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