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ScienceDirect
Surface Science 601 (2007) 4053–4057
SURFACE SCIENCE
www.elsevier.com/locate/susc

Angle-resolved photoemission study of Cu on ZnO(10$\bar{1}$0); room temperature deposition and annealing effect

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Available online 19 April 2007

Abstract

The valence electronic structures of the Cu-covered ZnO(10$\bar{1}$0) surfaces have been studied by angle-resolved photoemission spectroscopy utilizing synchrotron radiation. The coverage dependent change in the Cu valence band indicates the cluster formation of Cu at room temperature. The Cu 3d state forms a band with an energy dispersion, and the coverage dependence of the Cu 3d band structure suggests that the electronic structure of the Cu cluster is initially two-dimensional and turns to be three-dimensional at high coverages. The annealing effect on the morphology and the electronic structure of the Cu clusters is also examined and discussed.

Keywords: Angle-resolved photoemission spectroscopy; Copper; Zinc oxide; Valence band structure

1. Introduction

The Cu/ZnO system has attracted considerable attention because of its widespread application in various catalytic reactions such as synthesis of methanol from CO_2, CO and H_2 [1], steam reforming of methanol [2], water–gas shift reaction [1], etc. Because of the low heat of oxide formation of noble metals [3], the interaction between noble metals and oxide surfaces is so weak that the deposited metals form nanometer-size clusters on the surfaces. Cu on ZnO is not an exception. The adsorption process of Cu on well-defined low-index surfaces of single crystal ZnO has been investigated by Auger electron spectroscopy (AES) [4], ion-scattering spectroscopy (ISS) [5,6] and scanning tunneling microscopy (STM) [7,8]. It is found that, on ZnO(0001), (000$\bar{1}$) and (11$\bar{2}$0), the Cu clusters grow initially two-dimensionally and then three-dimensionally [4–7], whereas exclusively three-dimensional (3D) clusters are formed on ZnO(10$\bar{1}$0) from the very low Cu coverage region [8].

The morphology and the electronic structure of the metal cluster determine its chemical properties so that understanding of the atomic and electronic structures is desired to reveal the origin of catalytic activity of the metal clusters on the oxide surfaces. Although the morphology of Cu on ZnO has been investigated extensively, only limited information is available for the electronic structure, especially in the valence band region [9]. In the present study, therefore, angle-resolved photoemission spectroscopy (ARPES) has been utilized to elucidate the valence electronic structure of the Cu clusters on ZnO(10$\bar{1}$0). The coverage dependent measurements have been carried out, and the evolution of the Cu 3d band has been examined. We have also assessed the annealing effect on the Cu clusters by measuring the change of the valence electronic structure. Ripening of the Cu clusters and the interface reaction to form Cu oxides are found to proceed by the heat treatment.

2. Experimental section

The experiments were performed at beam lines 1C and 11C of the Photon Factory, High Energy Accelerator Research Organization (KEK), utilizing the linearly polarized

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doi:10.1016/j.susc.2007.04.058

synchrotron radiation. The measurements were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of 2×10^{-10} Torr. Details of the analysis chamber used in the present study were described elsewhere [10]. The ARPES spectra were measured at room temperature with the total energy resolution of ~0.2 eV. The angular resolution was ±1°.

In the ARPES spectra presented below, the binding energy (BE) is referenced to zero at the Fermi energy (E_F). The intensity of the spectra is normalized by the sample current measured during data acquisition.

The ZnO(1 0 $\bar{1}$ 0) surface was cleaned in the UHV condition by cycles of Ar^+ sputtering (2 kV, ~1 μA) and annealing at 1000 K. Then, the sample was annealed at 700 K in O_2 atmosphere and 600 K in UHV. Sample temperature was monitored by a chromel–almel thermocouple attached to the sample holder.

Cu was deposited onto the surface at room temperature from a commercial evaporation source (Omicron EFM3). The Cu coverage Θ_{Cu} was determined from the O KLL and Zn LMM AES peak intensities. One monolayer (ML) is defined as the coverage at which the substrate surface is covered with Cu with a monoatomic thickness.

3. Results and discussion

3.1. Cu adsorption process

The left panel of Fig. 1 shows the normal emission spectra of the whole valence band region, and the magnified spectra around E_F are shown in the right panel. The photon energy ($h\nu$) used was 50 eV. On the Cu-free surface, the emissions from the Zn 3d/4sp–O 2p hybrid states and the Zn 3d states are observed at 3–9 and 10–12 eV, respectively. As the surface is being covered with Cu, the Cu 3d peak is emerged at the lower BE side of the leading edge of the ZnO valence band. The Cu 3d peak is observed at 3.1 eV at $\Theta_{Cu} = 0.2$ ML and shifts to 2.4 eV up to 3.0 ML. The Cu 3d emission, which is obvious at high Θ_{Cu}, also appears as a hump at 3–5 eV.

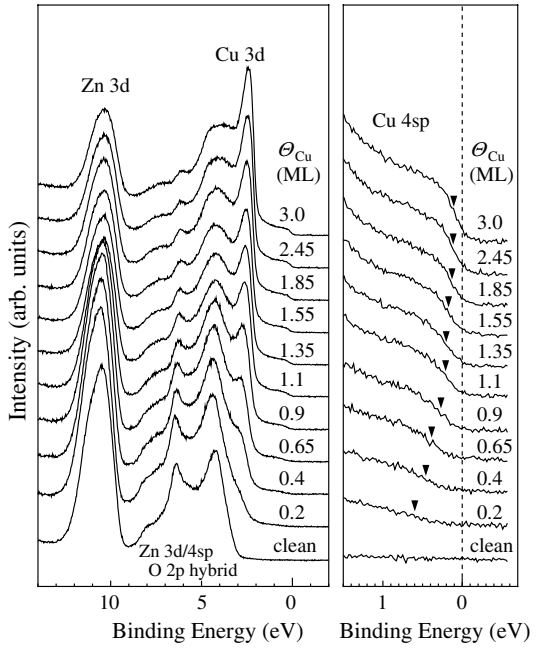

Fig. 1. Normal emission spectra of Cu/ZnO(1 0 $\bar{1}$ 0) at various Θ_{Cu}. The incidence angle of the light was 45° from the surface normal. The left panel shows the whole valence region, and the magnified spectra around E_F are shown in the right panel. The triangle marks indicate the mid point of the onset of the Cu 4sp states.

In the vicinity of E_F, the emission from the Cu 4sp states is observed. It appears from the low Θ_{Cu} region as a step structure, which is characteristic of the emission structure from condensed Cu [11]. This suggests that the Cu adatoms should aggregate into clusters. The cluster formation is also inferred from the Θ_{Cu}-dependent shift of the onset position of the step structure. The triangle marks in the right panel of Fig. 1 indicate the mid point of the onset. It shifts monotonically from 0.58 eV (0.2 ML) to 0.10 eV (3.0 ML). A similar shift is commonly observed for the noble-metal/oxide systems, where the noble-metal adatoms form clusters and these clusters grow in size with increasing coverage [10,12–14]. Therefore, the Cu cluster formation and their growth on ZnO(1 0 $\bar{1}$ 0) can be deduced from the ARPES study.

In an attempt to obtain further information on the electronic structure of the Cu clusters on ZnO(1 0 $\bar{1}$ 0), we have carried out the off-normal emission measurements of the spectra at three different Θ_{Cu}. The results are shown in Fig. 2. All the spectra were measured with the detection plane of the photoelectrons being set parallel to the [1 $\bar{2}$ 1 0] direction. The lower panels are the grayscale band maps, which are constructed by plotting the BE of the spectra against the surface parallel component of the wave number vector $k_\parallel$; $k_\parallel = \sqrt{2m_e E_{kin}/\hbar^2}\sin\theta_d$, where m_e, θ_d and E_{kin} are the mass of the electron, the detection angle of the photoelectrons and the kinetic energy, respectively. At 3.0 ML, the Cu 3d state forms a dispersing band with a 14.5-nm^{-1} periodicity (the dispersion width is 0.16 eV). The emission intensity also exhibits the periodic modulation. When Θ_{Cu} is decreased to 1.35 ML, the Cu 3d band bears a similar feature to that at 3.0 ML. On the other hand, the periodic structures are absent for the Cu 3d band at 0.45 ML, though the band shows a clear dispersion.

From the results shown in Fig. 2, two important conclusions are deduced. First, since the Cu 3d band depends on $k_\parallel$ at any Θ_{Cu} investigated, the Cu clusters formed on ZnO(1 0 $\bar{1}$ 0) are crystalline and these crystals are azimuthally oriented to a certain direction with respect to the substrate surface. Second, the Cu 3d band of the Cu clusters changes greatly when Θ_{Cu} increases from 0.45 to 1.35 ML, whereas the clusters at 1.35 and 3.0 ML possess a similar band structure. We consider that the change in the electronic structure between 0.45 and 1.35 ML is associated with the 2D-to-3D transition of the electronic structure. The 3D band of the Cu cluster at higher Θ_{Cu} is