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Photoemission study of a possibility of forming small metal clusters : I. Cu on TiO_2(110)

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Introduction

Metal adsorption on the metal oxide surfaces can modify the electronic and atomic structures of the supporting metal oxide surfaces. We study the electronic states of Cu/TiO_2(110) by angle-resolved (ARPES) and resonant photoemission spectroscopy. Strong interactions of Ni, Fe, and Cr with TiO_2 involving significant charge transfer between the adsorbed metals and the substrate are expected, but much weaker interaction for Cu.

Experiment

The photoemission experiments were performed at BL-3B using a VSW analyzer with an acceptance of ±1°. The single crystal rutile TiO_2(110) samples of 1mm thick were polished, etched, and then reduced by heating them to 1100 K for 120 h in ultrahigh vacuum (UHV). Such heat treatment was found to lead to the saturation concentration of surface O vacancies. The stoichiometric TiO_2(110) surface was restored by 20 min annealing at 1100 K in $3x10^{-6}$ Torr of O_2 and cooling down to 470 K in the same oxygen atmosphere. Cu (5N) were deposited on the TiO_2(110) surface using a K-cell evaporator and/or an electron beam evaporator. The cleanliness of all the surfaces was carefully monitored by Auger electron spectroscopy throughout the course of the experiments.

Results, Discussion and Conclusion

We investigated the details of evolution of the electronic structure of the Cu/TiO_2(110) system in the band-gap region near E_F. Details in the in-gap region measured are shown in Fig. 1. At the initial deposition, the Ti^{3+} $3d^1$ in-gap emission appears at about 0.8 eV below E_F. As increasing Cu deposition up to 0.75 ML, this emission grows and increases intensity. Note that no Fermi edge is seen at this stage. Upon further Cu deposition, the spectrum is abruptly changed between 0.75 ML and 1.0 ML and thereafter evolved to the typical 4*s* band emission spectrum of Cu metal. It should be remarked that a poor and imperfect Fermi edge is seen between 1.0 ML and 1.2 ML. However, a clear and perfect Fermi edge is observed above 3.0 ML.

From all the results obtained, we can conclude that (1) Cu grows in a Stranski-Krastanov mode, (2) for Cu adsorption, a defect state of Ti 3*d* character appears below 0.75 ML thickness and therefore there is a sign of reduction of the Ti ion on the surface at low coverages, and (3) the Cu overlayer is non-metallic up to 1 ML thickness and then soon becomes metallic above 2 ML thickness.

A poor and imperfect Fermi edge is seen between 1.0 ML and 1.2 ML. A clear and perfect Fermi edge is observed for Cu coverages more than 3.0 ML. Such delayed completion of the Fermi edge may be explained by finite cluster size effects. That is, we think that after the completion of a monolayer, the growth of three-dimensional clusters of Cu is followed: the small Cu clusters (< a few nm size) of non-metallic nature are formed on TiO_2(110) between 1 ML and 2 ML, and then the clusters grow and become metallic above 3 ML.

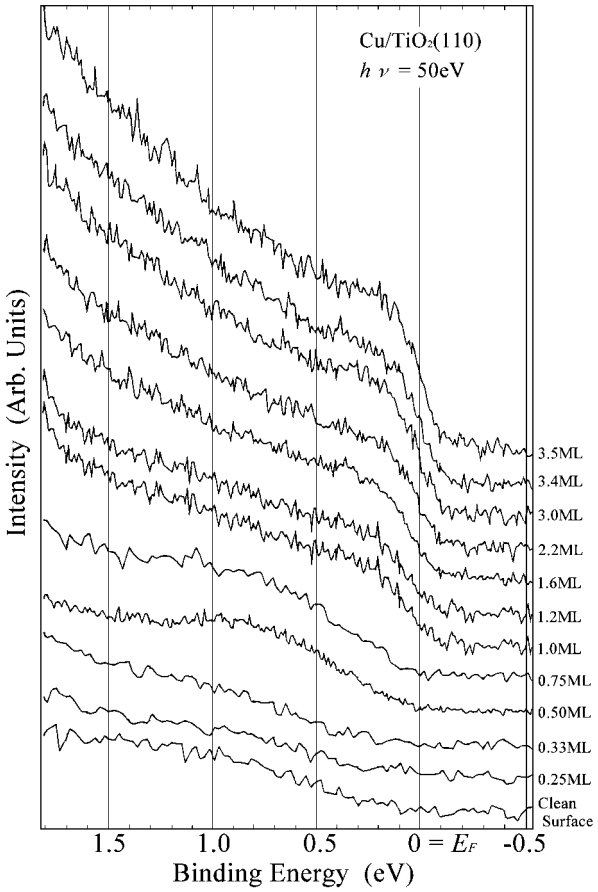

Fig. 1 Details of the Cu-deposition dependence of the normal-emission spectra in the in-gap region measured at $h\nu$= 50 eV for the various Cu depositions from 0.25 ML to 3.5 ML.

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