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

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Introduction

Metal oxide surfaces with adsorbed metal atoms have received much attention in recent years. In the initial stage of adsorption, charge transfer from the metal adsorbate to the oxide occurs resulting in oxidation of the adsorbed metal atoms and reduction of the oxide cations at the interface. The properties of oxide surfaces are always dependent on the stoichiometry and some novel features may appear when reduction takes place. Therefore, an understanding of the modification of the electronic properties of metal/oxide interfaces due to metal-oxide interactions is important for the design of devices and other composite materials.

We report the results of angle-resolved and resonant photoemission of Fe/TiO_2(110). Our main findings are that (1) Fe grows in a Stranski-Krastanov mode and (2) the electronic structure of the Fe cluster is cluster size-dependent, *i.e.*, the small cluster is non-metallic and the cluster becomes metallic as the size increases.

Experiment

The experiments using synchrotron radiation were performed at BL-3B. The details of experimental conditions (ARPES measurement system, cleaning and reducing procedure of TiO_2, control of deposition) were the same as is described in the preceding paper (I. Cu on TiO_2(110)). Fe (5N) was deposited on the TiO_2(110) surface at room temperature.

Results, Discussion and Conclusion

We investigated the details of evolution of the electronic structure in the band-gap region. Figure 1 shows the details of Fe-deposition dependence of the emission in the band-gap region measured at $h\nu$ =50 eV up to 3.4 ML. The $h\nu$ was so chosen as to emphasize the behavior of Ti 3*d* character. At the initial deposition, an in-gap emission appears at about 1.3 eV (see the 0.2 ML- and the 0.4 ML-spectra). The figure shows that this 1.3-eV in-gap emission is gradually shifted to about 0.9 eV between 0.6 ML and 1.0 ML. Upon further Fe deposition above 2 ML, the in-gap emission is evolved to a three-structure bulk Fe spectrum with forming no Fermi edge up to 3.4 ML. It should be remarked that a sharp Fermi edge is not formed between 2 ML and 3.2 ML, though the overall shape of the emission closely resembles the metallic Fe spectrum. The Fermi edge starts to form at 3.4 ML.

Summarizing all the results including also the uptake curves and 3*p*-3*d* resonant photoemission, the small Fe clusters (< a few nm size) of non-metallic nature are formed on TiO_2(110) between 1 ML and 3.2 ML, and then the clusters grow and become metallic above 3.4 ML, revealing a sharp Fermi edge.

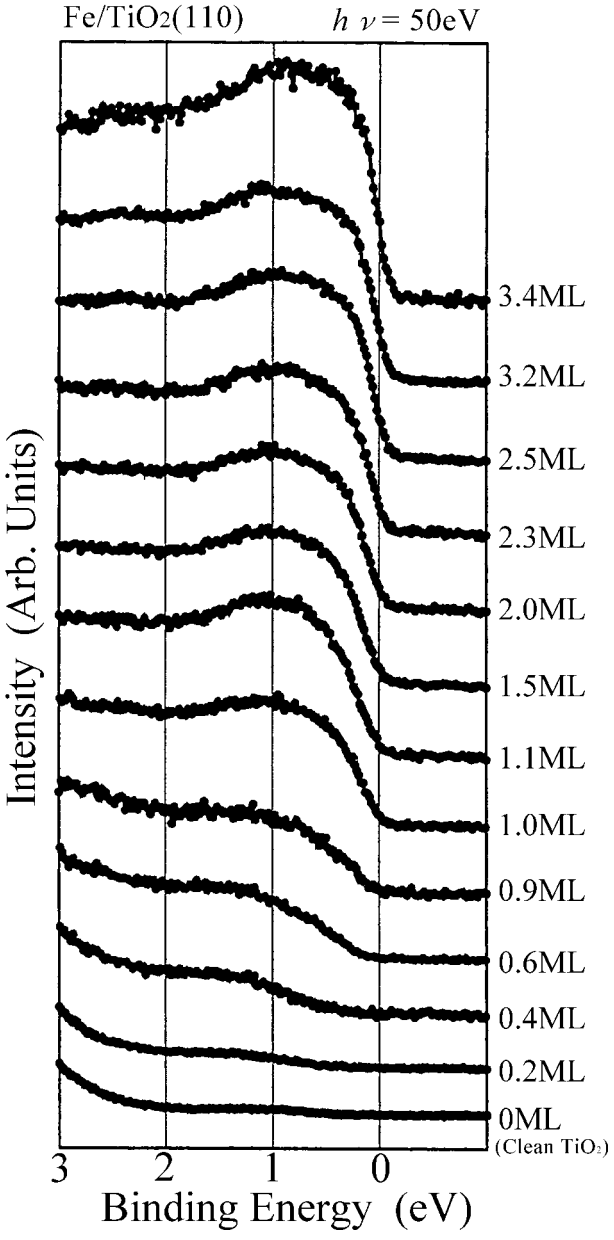

Fig. 1 Details of Fe-deposition dependence of the emission in the band-gap region measured at hν=50 eV up to 3.4 ML.

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