

Photoemission study of a possibility of forming small metal clusters : IV. Cr on TiO₂(001)

Yasuo Sakisaka*, Nobuo Nakajima, Hiroo Kato

Faculty of Science and Technology, Hirosaki University, Hirosaki 036-8561, Japan

Introduction

Rutile titanium dioxide (TiO₂) is representative of easily-reducible *d*-type nonmagnetic metal oxides and its surface has evolved as one of the most important model systems for metal oxide surfaces.

It has been found that the reduced Ti³⁺ (*3d*¹) states at the interface is also formed by metal deposition on TiO₂ surface, and extensive research has been devoted to the study of the electronic properties and growth modes of vapor-deposited metal overlayers on TiO₂ surfaces so far.

The morphology and growth mode of the metal adsorption on TiO₂ has been intensively studied, however, the electronic structure created in the in-gap region by metal adsorption was less examined.

We have studied the electronic properties of Cr/TiO₂(001) system by means of photoemission spectroscopy. Cr is believed to be a more reactive metal than Fe, and therefore a stronger interaction between the Cr overlayer and the TiO₂ substrate is expected. Our main findings are that (1) two defect states of Ti *3d* character and of Cr *3d* character appear in the bulk band-gap of TiO₂ and (2) the Cr overlayer is non-metallic up to 2 ML thickness probably due to the nature of a small cluster.

Experiment

The experiments using synchrotron radiation were performed at BL-3B. The details of experimental conditions (ARPES measurement system, cleaning and reducing procedure of TiO₂, control of deposition) were the same as is described in the preceding paper (I. Cu on TiO₂(110)). Cr (5N) was deposited on a TiO₂(001) surface at room temperature.

Results, Discussion and Conclusion

We investigated the evolution of the electronic structure in the band-gap region. Figure 1 shows the details of Cr-deposition dependence of the two emissions in the band-gap region measured at $h\nu = 40$ eV up to 1.3 ML. Here, Cr was deposited on a stoichiometric TiO₂(001) surface, where no in-gap emission was observed. At the initial deposition, two in-gap emissions A and B appear at about 1.1 eV and 2.9 eV below E_F and both grow without movement in energy up to 0.3 ML. Upon further deposition up to 1.3 ML, the emissions A and B gradually shift to about 0.6-0.7 eV and ~2.3 eV, respectively. It should be remarked that a Fermi edge is not formed up to 1.3 ML.

All the results including *3p-3d* resonant photoemission indicate that as increasing Cr deposition, the in-gap

emission grows and increases intensity. At higher coverages between 1 ML and 2 ML (not shown here), the in-gap emission is developed into the 2-peak-structure emission of Cr *3d* character. The corresponding state is considered to be of metallic nature from the viewpoint of the high ability of oxygen adsorption, but has no Fermi edge, indicating a possibility of forming small Cr clusters on TiO₂(001) at this stage. We think that the electronic structure of the Cr cluster is size-dependent, *i.e.*, the small cluster is non-metallic and the cluster is expected to become metallic as the size increases.

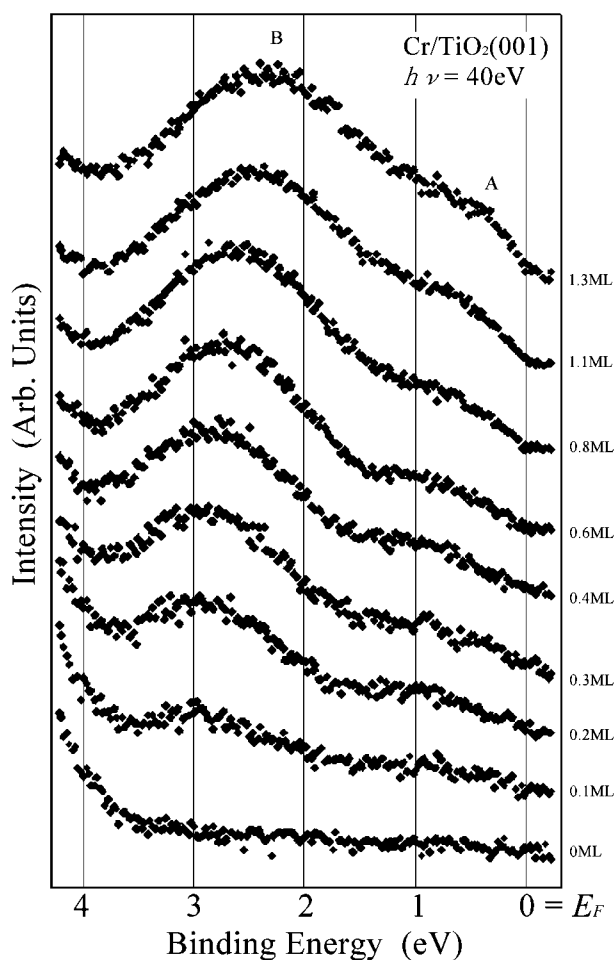


Fig. 1 Details of Cr-deposition dependence of the two emissions in the band-gap region measured at $h\nu=40$ eV up to 1.3 ML.

* sakisaka@cc.hirosaki-u.ac.jp