

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

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Introduction

When an oxide surface is reduced, excess electrons can occupy a variety of states, such as surface *F*-centers (also called surface color centers) in alkaline-earth oxides (MgO, CaO, and SrO) or reduced Ti³⁺ (*3d*¹) states in TiO₂. At the electron rich surface of TiO₂ with oxygen vacancies, the excess electrons occupy Ti *3d*-states localized on the Ti ions near to the vacancy. The resulting Ti³⁺ (*3d*¹) states lie in the bulk band gap of TiO₂. The same Ti³⁺ (*3d*¹) in-gap states are produced also by transition-metal adsorption on TiO₂ surfaces.

The following two mechanisms are generally thought to play an important role for the initial stage of transition-metal adsorption on TiO₂ surfaces: (1) Chemisorption caused by charge transfer from the transition-metal adsorbate into unoccupied Ti *3d* states of TiO₂, leading to oxidation of the transition-metal atom and reduction of the Ti-cation, *i.e.*, a Ti³⁺ (*3d*¹) in-gap state is created, and (2) Hybridization of the O *2p*-orbitals of the oxide anions with the *s*- and/or *d*-valence orbitals of the transition-metal adsorbate.

The electronic states of the Ni overlayers on TiO₂(001) surfaces were studied by angle-resolved (ARPES) and resonant photoemission spectroscopy using synchrotron radiation. Compared with Cu, much stronger interaction of Ni with TiO₂ is expected.

We found that the Ni overlayer is non-metallic up to 2 ML thickness

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)). Ni (5N) was deposited on the TiO₂(001) surface at room temperature.

Results, Discussion and Conclusion

We investigated the details of evolution of the electronic structure in the band-gap region of the Ni/TiO₂(001) system. Details of the normal-emission spectra in the in-gap region measured at $h\nu = 22$ eV for the various Ni depositions are shown in Fig. 1. The in-gap emission probably from the reduced Ti³⁺ *3d*¹ state appears at around 1.2 eV below E_F for the initial Ni deposition of 0.2 ML. Upon further Ni deposition, the Ni-induced in-gap emission grows and is gradually shifted to about 0.9

eV up to 0.8 ML, and then start to be split into two structures. The in-gap state at this stage is considered to become of Ni *3d*-like. Finally, at above 1.2 ML, the emission is evolved to a spectrum which is very similar to that of Ni metal. The bulk Ni valence-band spectrum measured at $h\nu \sim 22$ eV has typically two structures at about 0.5 eV and 1.2 eV below E_F as seen in the present 1.6- and 2.0-ML spectra. Note that the 1.6- and 2.0-ML spectra show no Fermi edge characteristic of metal, however. From all the results obtained, we can conclude that the non-metallic nature may be attributed to the formation of small Ni clusters on TiO₂(001).

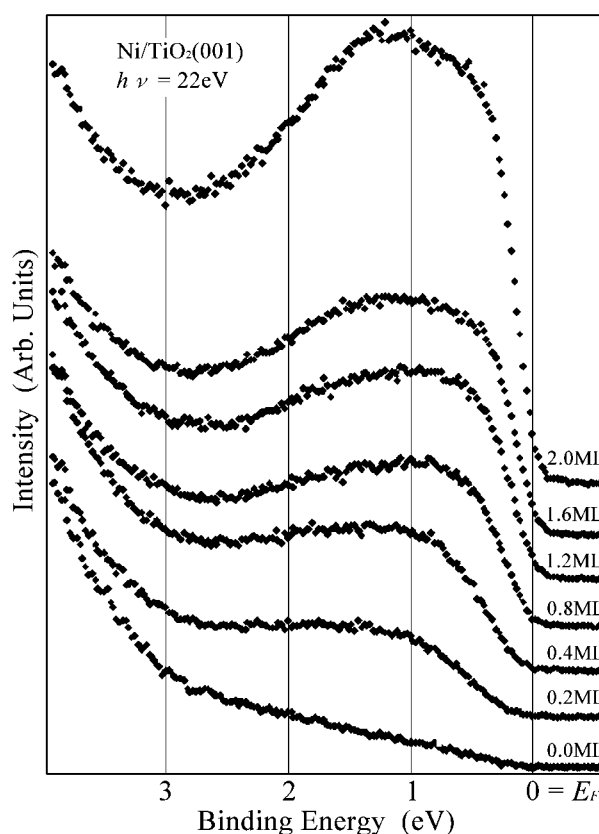


Fig. 1 Details of the normal-emission spectra in the in-gap region measured at $h\nu = 22$ eV for the various Ni depositions from 0.2 ML to 2.0 ML.

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