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Surface Metallization by Chemical Modification: Adsorption of Methanol and Ethanethiol on Single Crystal Surfaces of ZnO

Kenichi OZAWA[*, 1], Masato EMORI[2], Mari SUGITA[2], Hiroshi SAKAMA[2], Kazuhiko MASE[3]
[1]Department of Chemistry and Materials Science, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8551, Japan
[2]Department of Physics, Sophia University, Chiyoda-ku, Tokyo 102-8554, Japan
[3]Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba 305-0801, Japan

Introduction

Hydrogenation of some n-type semi-conductor surfaces has been known to induce surface metallization [1-3]. H adatoms on these surfaces act as electron donors, and cationization of H induces downward bending of the substrate bands. Transferred charge, then, occupies the quantized states in the potential well at the surface to realize the two-dimensional electron gases (2DEGs). ZnO, a wide-band-gap n-type semiconductor, is one of the examples [3]. Of the single crystal ZnO surfaces, the (10-10) and (000-1) surfaces are metallized by H adsorption, whereas the H-adsorbed (0001) surface remains semiconducting. Here, we show, using photoelectron spectroscopy (PES), that methanol and ethanethiol also induce insulator-metal transition of the ZnO surfaces with (10-10) and (000-1) orientation.

Experimental

The PES measurements were carried out at beamlines 11D and 13A of the Photon Factory, KEK. The electronic structure of single-crystal ZnO surfaces with (10-10), (000-1), and (0001) orientation were examined by using an SES200 analyzer (VG-SCIENTA). Methanol and ethanethiol were exposed to the surfaces at room temperature. Adsorption structure of these molecules was determined by C 1s and S 2p core-level lineshapes, and the insulator-metal transition was judged by the density of states (DOS) at the Fermi level (E_F).

Results and Discussion

Methanol and ethanethiol adsorbs molecularly as well as dissociatively on three ZnO surfaces at room temperature. Methanol adsorbs as CH_3OH, CH_3O and CH_x (x = 1-3) (Fig. 1a) with different ratio depending on the surface termination. Although no metallic feature is developed on ZnO(0001) upon methanol adsorption, metallization is realized on ZnO(10-10) and (000-1) surfaces, as evident from the DOS at E_F (Fig. 1b). The metallic states form free-electron-like parabolic bands (Fig. 1c). This, together with the fact that surface metallization is accompanied by downward bending of the ZnO band, 2DEGs are formed at the ZnO surfaces by methanol adsorption.

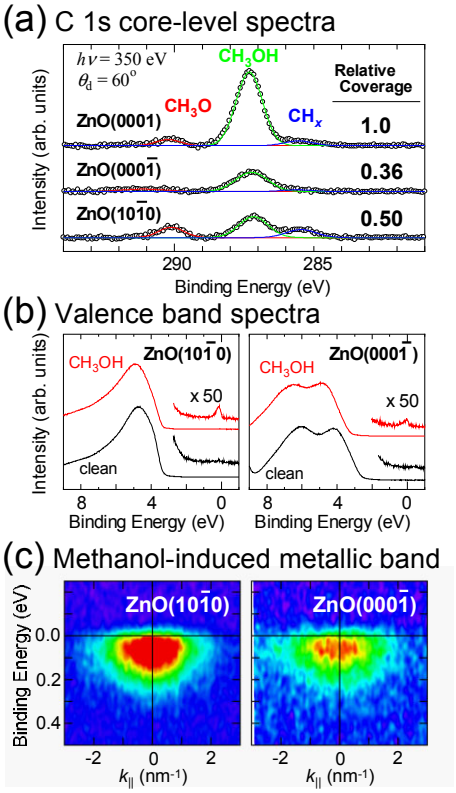

Fig. 1. (a) C 1s core-level spectra for methanol-saturated ZnO surfaces. (b) Valence band spectra of ZnO(10-10) and (000-1) before and after methanol adsorption. (c) Two-dimensional intensity distribution of the methanol-induced metallic states.

Essentially the same metallization mechanism is realized when ethanethiol adsorbs on ZnO(10-10) and (000-1), but with much weaker metallic DOS in comparison with the methanol adsorption systems.

References

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*ozawa.k.ab@m.titech.ac.jp