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

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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 adsors as CH₃OH, CH₃O and CH₃ (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.

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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