

Acridine Orange Base as an Electron Donor on the ZnO Surfaces

K. Ozawa^{1,*}, M. Suzuki², R. Tochikubo², H. Kato², and K. Mase³¹Tokyo Institute of Technology, Tokyo 152-8551, Japan²Hirosaki University, Hirosaki 036-8560, Japan³Institute of Materials Structure Science, Tsukuba 305-0801, Japan

1 Introduction

ZnO is a wide-band-gap n-type semiconductor with the Fermi level (E_F) lying just below the conduction band minimum (CBM). Electron-doping of the surface by hydrogen (H) adsorption leads to significant downward band bending so that the CBM is lowered below E_F , and surface metallization by forming two-dimensional electron gas is realized [1-3]. Metallization of the ZnO surfaces is also achieved by adsorption of water and methanol, both of which adsorb dissociatively to form adsorbed H which acts as an electron donor [1]. In search of organic molecules that bring oxide surfaces the metallic nature, we first examined tetrathiafulvalene (TTF) [4], a prototype of an electron donor molecule in organic charge-transfer salts. However, TTF is found not to donate electrons to ZnO but to withdraw them from ZnO [4]. In the present study, we have investigated the interaction between ZnO and acridine orange base (AOB, Fig. 1) by photoelectron spectroscopy (PES).

2 Experiment

AOB was purified once by vacuum sublimation by heating the sample at 120°C. Deposition of AOB on the ZnO surfaces was done at 120°C by using a home-build evaporator in the ultrahigh vacuum chamber. The PES measurements were carried out at beamlines 3B and 13A.

3 Results and Discussion

The measurements of the valence band spectra reveal that AOB induces downward bending of the ZnO band on both the Zn-terminated (0001) and O-terminated (000-1) surfaces, while the position of the band is almost intact on the (10-10) surface (Fig. 2). This means that AOB acts as an electron donor on the (0001) and (000-1) surfaces, whereas charge transfer between AOB and the (10-10) surface is not operative. The valence band maximum (VBM) positions on the clean surfaces are 3.0 eV, 2.9 eV, and 2.4 eV on the (0001), (10-10) and (000-1) surfaces, respectively, and they are shifted to 3.5 eV and 3.0 eV on the (0001) and (000-1) surfaces, respectively, by AOB adsorption. Considering the band gap of ZnO is 3.37 eV, the CBM on the (0001) surface covered with AOB should

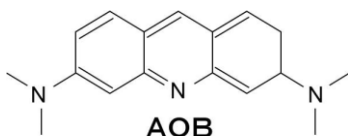


Fig. 1 Molecular formula of acridine orange base (AOB).

be located at 0.1 eV below E_F , whereas those on the other two surfaces remain above E_F .

One of the criteria for metallization is that the CBM of the substrate surface should be lowered below E_F . Therefore, the AOB-adsorbed ZnO(0001) surface is possibly in a metallic nature. Although a direct evidence for surface metallization is still unavailable, AOB is the first organic molecule which may induce metallization of the oxide surface.

References

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

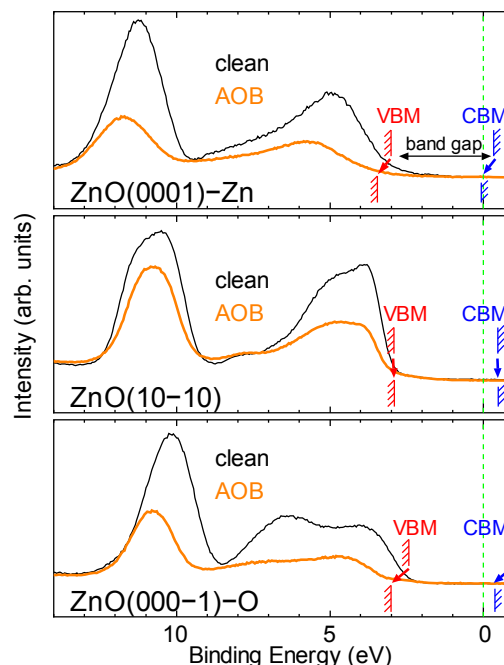


Fig. 2 Normal-emission valence band spectra of AOB-covered ZnO surfaces. Positions of the VBM and CBM before and after AOB adsorption are indicated.