Charge Transfer at Chemisorption Interfaces Between Air-Stable Dye Molecule and Oxide Surfaces

K. Ozawa1,*, Y. Kimura2, Y. Mimori2, H. Kato3, and K. Mase3
1Tokyo Institute of Technology, Tokyo 152-8551, Japan
2Hirosaki University, Hirosaki 036-8560, Japan
3Institute of Materials Structure Science, Tsukuba 305-0801, Japan

Organic-oxide composite materials are important as key components in organic-based semiconductor devices such as organic solar cells and organic light emitting diodes. In these organic devices, properties of carrier transport across the organic/oxide interface determine the device performance. Therefore, it is crucial to understand formation mechanisms of interface dipole moment and carrier injection barriers at the interface.

Acridine orange base (AOB) is an air-stable dye molecule. It shows a good electron donating character on Au, ZnO and SrTiO3 surfaces [1,2]. Utilizing this feature, AOB can be used as an insertion layer between a Au electrode and a Cs film to decrease the electron injection barrier from the electrode to the Cs film [1]. Unlike organic molecules with a strong hole donating nature such as tetracyanoquinodimethane (TCNQ) and its derivatives, only a few electron donating molecules are available. Although tetraphiafulvalene (TTF) exhibits an electron donating character to some materials [3], it is one of the promising molecules as an electron dopant for a wide range of materials.

In the present study, we have investigated the interface electronic structure between AOB on the ZnO(10-10) and SrTiO3(001) surfaces by photoelectron spectroscopy (PES) to obtain a detailed picture of the charge transfer across the interface. Here, the oxide surfaces were chemically modified to tune the work functions, and AOB was deposited on the surfaces. The PES measurements were carried out at BL-3B and BL-13A. PES spectra in the valence band region and the secondary electron cut-off region were measured to follow AOB-induced band bending (BB) and the work function change. First, we have examined the interaction type, i.e., a weak or strong interaction, between AOB and Cs-modified oxide surfaces. The interaction type can be distinguished by the relation between the work functions of the AOB-adsorbed Cs-modified surfaces (ΦAOB/sub) and those of the AOB-free Cs-modified surfaces (Φsub). Fig. 1 shows the ΦAOB/sub versus Φsub dependences for the two adsorption systems. Both gives linear relations with slopes of 0.31 and 0.75. If the AOB-substrate interaction is so weak that the integer charge-transfer model [5] is applied, the slop should been 1.0. A deviation from 1.0 implies the involvement of the orbital hybridization between the molecular orbitals of AOB and the surface wave functions.

From the shift of the valence band of the substrate upon AOB adsorption, it is found that AOB induces both downward and upward band bending (BB) of the substrate bands depending on the Φsub values. Fig. 2 shows plots of AOB-induced BB against Φsub. On both surfaces, the bands bend downwardly upon AOB adsorption on the surfaces having the Φsub values larger than ~3.5 eV, while vice versa at Φsub < 3.5 eV. Thus, AOB acts as either an electron donor or a hole donor depending on Φsub of the substrate surfaces with the threshold Φsub value of ~3.5 eV irrespective of the substrates.

References

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

Fig. 1 Dependences of ΦAOB/sub on Φsub for two adsorption system.

Fig. 2 The AOB-induced BB values are plotted against Φsub. Positive and negative values of BB mean that AOB-induced BB is downwardly and upwardly, respectively.