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

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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 SrTiO<sub>3</sub> surfaces [1,2]. Utilizing this feature, AOB can be used as an insertion layer between a Au electrode and a C<sub>60</sub> film to decrease the electron injection barrier from the electrode to the C<sub>60</sub> 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. Althugh tetrathiafulvalene (TTF) exibits an electron donating character to some materials [3], it withdraws charge from the ZnO surfaces [4]. Thus, AOB is one of the promising molecules as an electron dopant for a wide range of materials.

In the present study, we have investigate the interface electronic structure between AOB on the ZnO(10-10) and  $SrTiO_3(001)$  surfaces by photoelectron spectroscopy (PES) to a obtain 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 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



Fig. 1 Dependences of  $\Phi_{AOB/sub}$  on  $\Phi_{sub}$  for two adsorption system.

distinguished by the relation between the work functions of the AOB-adsorbed Cs-modified surfaces ( $\Phi_{AOB/sub}$ ) and those of the AOB-free Cs-modified surfaces ( $\Phi_{sub}$ ). Fig. 1 shows the  $\Phi_{AOB/sub}$  verusu  $\Phi_{sub}$  dependences for the two adsorption systems. Both gives linear relations with slops 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  $\Phi_{sub}$  values. Fig. 2 shows plots of AOB-induced BB against  $\Phi_{sub}$ . On both surfaces, the bands bend downwardly upon AOB adsorption on the surfaces having the  $\Phi_{sub}$  values larger than ~3.5 eV, while vice versa at  $\Phi_{sub} < 3.5$  eV. Thus, AOB acts as either an electron donor or a hole donor depending on  $\Phi_{sub}$  of the substrate surfaces with the threshold  $\Phi_{sub}$  value of ~3.5 eV irrespective of the substrates.

## **References**

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Fig. 2 The AOB-induced BB values are plotted against  $\Phi_{sub}$ . Positive and negative values of BB mean that AOB-induced BB is downwardly and upwardly, respectively.