Determination of the charge transfer path from TCNQ to SrTiO$_3$(001)

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1 INTRODUCTION

Controlling interface charge transfer between organic films and metal oxide semiconductors is essential to realize high performance organic-inorganic hybrid devices. Hole-injection and electron-injection barrier heights are key parameters to access the feasibility of the interface charge transfer. Actually, they have been proved to be good indicators in the systems with a weak interface interaction between an organic molecule and a substrate surface. However, it is not obvious to say so if chemical bonds are formed between the molecule and the surface, since the chemical bonds are expected to facilitate the transfer of the holes and electrons which reside at bonding and anti-bonding states, respectively.

In the present study, a core hole clock technique has been utilized to determine the transfer time of photoexcited electrons from organic molecules to the oxide substrate. It is found that the excited electrons in an unoccupied state, whose molecular orbital extends towards the substrate surface, are found to be transferred to the substrate in a femtosecond order.

2 EXPERIMENTAL

The experiment was performed at beamlines (BLs) 3B and 13B. Photoelectron spectroscopy (PES) and X-ray absorption spectroscopy (XAS) measurements were carried out to examine the adsorption state and the adsorption geometry of TCNQ (tetracyanoquino-dimethane) on SrTiO$_3$(001). The charge transfer time was estimated by the core hole clock method. Change in the PES intensity of the HOMO state of TCNQ was measured as a function of the photon energy ($h\nu$) in the N K-edge absorption region and an $h\nu$-intensity profile was obtained. This profile was, then, compared with the N K-edge XAS spectrum to estimate the transfer time by the peak intensity analysis [1].

The SrTiO$_3$(001) surface was cleaned by Ar$^+$ sputtering and annealing at 950 K in O$_2$ atmosphere. TCNQ was deposited on the surface at room temperature using a home-made evaporator.

3 RESULTS AND DISCUSSION

The PES and XAS measurements reveal that TCNQ adsorbs molecularly with its molecular plane nearly parallel to the SrTiO$_3$(001) surface. This interaction scheme is reasonable because TCNQ tends to interact with solid surfaces through its four cyano groups.

Fig. 1a shows PES spectra of TCNQ/SrTiO$_3$(001). A structure between 3 and 9 eV is a valence band of the oxide substrate. The HOMO peak of TCNQ is seen at the lower-binding-energy side of the valence band (indicated by an arrow). The peak intensity variation as a function of $h\nu$ is seen with an enhancement at ~401 eV. The $h\nu$-intensity profile (an upper part of Fig. 1b) resembles the N K-edge XAS spectrum (a lower part); both curves are composed of three peaks with a slightly different intensity ratios. Three peaks are associated with unoccupied levels (LUMO, LUMO+1, and LUMO+2) of TCNQ (Fig. 1c). In the $h\nu$-intensity profile, the intensity of the LUMO+1 peak is diminished in comparison with the other two. This implies that the electrons in the LUMO+1 level are transferred to the substrate faster than those in the LUMO and LUMO+2 levels. Assuming that the N 1s core-hole lifetime is 6 fs [1], the intensity analysis allows us to estimate the charge transfer time between 1 fs and 4 fs.

The molecular orbital of the LUMO+1 level extends vertically with respect to the molecular plane, while the spatial extent of the LUMO and LUMO+2 orbitals are within the molecular plane. Thus, the LUMO+1 level is highly probable to interact with substrate orbitals to form chemical bonds. The present results indicate that the faster electron transfer occurs through the chemical bond.

Reference
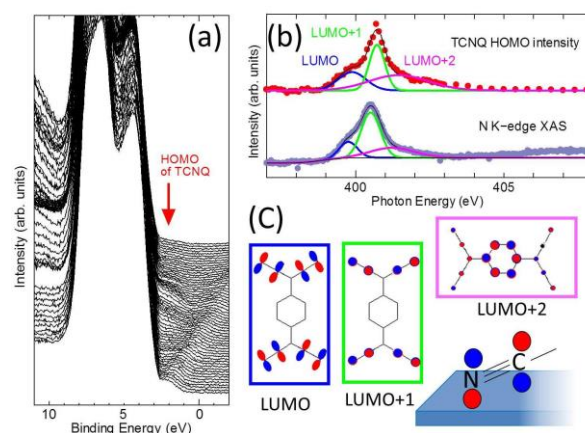[1] P.A. Bruhwiler et al., *Rev. Modern Phys.* **74**, 703 (2002).

Fig. 1 (a) Valence band PES of TCNQ/SrTiO$_3$(001) measured from 397 and 403 eV by 0.1 eV intervals. (b) The $h\nu$-HOMO-intensity profile (upper) and the N K-edge XAS spectrum (lower). (c) Unoccupied molecular orbitals of TCNQ from LUMO to LUMO+2.

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