

Mixed valence state of TNAP on Bi(001)

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1 Introduction

Charge transfer complexes, which are known to show various properties depending on the amount of charge transfer [1], are one of the most notable systems regarding the mixed valence states of organic materials. In the case of organic thin film, charge transfer is a key point to determine the strength of the organic molecule-substrate interaction [2].

11,11,12,12, -tetracyanonaphtho-2,6-quinodimethane (TNAP, Fig.1) is a strong acceptor type molecule and is known to show interesting phenomena [3]. For example, different molecule-substrate interactions were reported for TNAP on noble metals, such as weak interaction on Au, an ionic interaction with charge transfer on Ag, and diffusion of atoms on Cu. The difference in interactions was proposed to have a correlation with the work functions of the substrates (Au: 5.3eV, Ag: 4.7eV, Cu: 4.9eV) [3]. That is, a substrate with smaller work function was supposed to have a stronger interaction. However, despite of its small work function (4.22 eV), Bismuth (001) was considered to be inert against organic molecule [4].

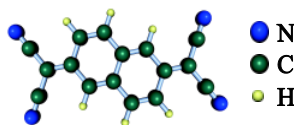


Fig. 1: TNAP

Here, we report the electronic structure of TNAP/Bi(001) obtained with X-ray photoemission spectroscopy (XPS). Mixed valence state of neutral and anionic TNAP was observed for the first monomolecular layer (ML).

2 Experimental

Samples were prepared by depositing TNAP (Tokyo Chemical Co., Ltd.) on a Bi (001) film grown on Si(111) in an ultra high vacuum (UHV) chamber. XPS measurement was performed in the UHV chamber (2.8×10^{-10} Torr) in normal emission at BL-13A. The reliability of the spectra was checked by the time dependence of the beam damage and reproducibility. All measurements were carried out at ~ 295 K.

3 Results and Discussion

Figure 2 shows the N1s spectra obtained at different TNAP thickness. At a thickness of 0.075 nm, whose value corresponds to a coverage of approximately 1/4 ML, a peak is clearly observed at a binding energy of 397.7eV. At 0.3 nm (1ML), two more peaks appear at binding energies of 400.0eV and 398.8 eV. Taking the previous

report of tetrafluoro- tetracyanoquinodimethane (F4-TCNQ) adsorbed on graphene [5] into account, we assign the origins of the two peaks at 397.7 eV and 400.0 eV to the anionic and neutral nitrogen, respectively. This indicates that TNAP is anionic at 1/4 ML and mixed valence state of anionic and neutral nitrogen is present at 1ML. Furthermore, the peak of anion shifts slightly to higher binding energy by increasing the thickness. This indicates that anionic TNAP is not strongly hybridized to Bi(001). The result about the hybridization has been confirmed by the Metastable atom electron spectroscopy (MAES) spectra, in which a density of states (DOS) is observed just below the Fermi energy (in the case of strong hybridization, the DOS of the single occupied molecular orbital would not appear just below the E_F like the case of TNAP/Ag or Cu). In order to obtain information about the film growth mode, we have measured the cut-off of secondary electron in ultraviolet photoelectron spectroscopy (UPS) that showed a large shift up to 1 ML and a small shift at higher coverage. This change in cut-off indicates that the film does not grow as islands. Regarding the peak at 398.8 eV, its origin might be anionic TNAP

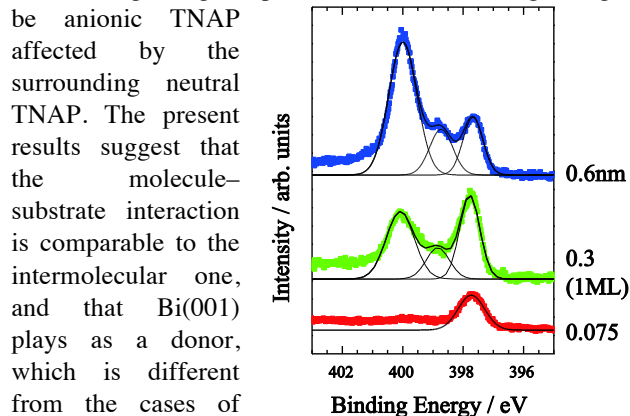


Fig. 2: N1s spectra

affected by the surrounding neutral TNAP. The present results suggest that the molecule-substrate interaction is comparable to the intermolecular one, and that Bi(001) plays as a donor, which is different from the cases of other organic molecule systems.

References

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