

Mixed valence state of TNAP on Bi(001)

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Introduction

The correlation between molecular-substrate interaction and intermolecular interaction is one of the fundamental interests in organic thin film. In most cases, the molecular-substrate interaction is much stronger than the intermolecular interaction on metal substrates, and the interactions are comparable in the case of an inert substrate.

11,11,12,12, -tetracyanonaphtho-2,6-quinodimethane (TNAP, Fig. 1), a strong acceptor type molecule, is known to show interesting phenomena. On noble metals, weak molecular-substrate interaction has been reported 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) [1]. 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), Bi (001) was considered to be inert [2].

In this paper, 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 at the first monomolecular layer (ML).

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. The nominal growth rates, 0.025 nm min⁻¹, was obtained by measuring the quartz-crystal thickness monitor. The quality of the Si(111)-7×7 reconstruction was checked by low energy electron diffraction after annealing at 1520 K. The thickness of Bi deposited on the Si(111) substrate was 10 bi-layers. The surface cleanliness was checked by XPS. 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.

Results and Discussion

Figure 2 shows the N1s spectra obtained at different TNAP thickness. At 0.075 nm, whose value corresponds to approximately 1/4 ML, a peak is clearly observed at 397.7eV. At 0.3 nm (1ML), two more peaks appear at

400.0eV and 398.8 eV. Taking the previous report of tetrafluoro- tetracyanoquinodimethane (F4-TCNQ)/graphene [3] into account, we assign the origins of the peaks at 397.7 eV and 400.0 eV to be anionic and neutral nitrogen, respectively. This indicates that TNAP is anionic at 1/4 ML and mixed valence state of anionic and neutral appears at 1ML. Regarding the peak at 398.8 eV, its origin might be anionic TNAP affected by surrounding neutral TNAP, since the intensity of the anionic nitrogen peak decreases when the intensity of the neutral nitrogen and the 398.8 eV peaks increase at coverages from 0.3 nm to 0.6 nm. This type of peak intensity variation is not observed at F4-TCNQ/graphene case, and therefore this result suggests the presence of stronger intermolecular interaction between anionic and neutral TNAP.

References

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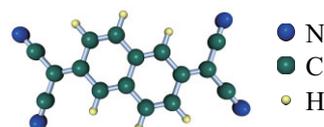


Fig.1. TNAP

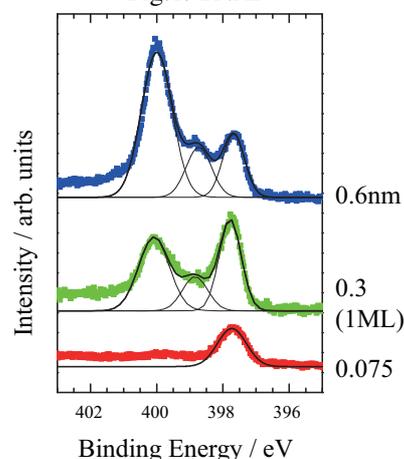


Fig.2. Thickness dependence of N1s spectra

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