

Effect on Orientation of DNTT on Cu by Triazine-based Molecular Adhesion

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1 Introduction

Organic device such as organic thin film transistors (OTFTs) and organic photovoltaics (OPVs) is a highly active research field because of the relative ease of fabrication, and the very attractive ecological advantages. It is well known that self-assembled monolayers (SAMs) are an effective way of controlling the surface properties of metal electrodes such as Au. Furthermore, for the case of OTFT, SAMs have been used very successfully to change the surface properties of gate dielectric (insulating layer) such as SiO₂, to achieve the high mobility. [1] [2] By considering practical use of bottom-gate type OTFT, where the substrate is composed of not only the metal electrode but also gate dielectric, it is necessary to use two types of SAM, one is available to bond to metal surface another to dielectric insulator. However, since different SAMs have to be used for the insulation layer and the electrodes, there would be some drawbacks such as

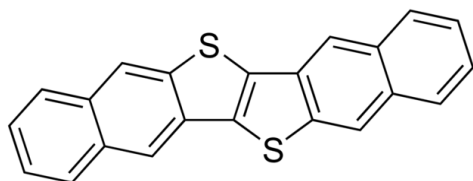


Fig.1 Molecular structure of DNTT

adverse action of the mutual SAMs, complication of the fabrication process, and increase in costs. Therefore, we focused on triazine-based molecular adhesion material (a-TES), which is expected to bond to both metal and an insulator such as SiO₂. Improvement of the charge mobility of OTFT by insertion of SAM and the like, is affected not only by electronic at the interface the so-called energy alignment but also by a change in molecular orientation due to the strong relationship between the direction of charge transfer and the π - π interaction of the planar π -conjugated molecule such as dinaphtho[2,3-b:2',3'-f]thieno[3,2-b] thiophene (DNTT) (Fig.1). DNTT have shown the best p-channel organic semiconductors for OFET applications in terms of high mobility, air stability, and good reproducibility. [3]

The purpose of this study is to clarify the effect on the molecular orientation of DNTT thin film by insertion of a-TES layer on Cu substrate by X-ray absorption fine structure near the absorption edge (NEXAFS).

2 Experiment

Cu substrates were obtained by plating Cu layer was on Si wafer. Cu substrates were cleaned by pre-annealing treatment (30 min), Ar sputtering treatment (15 min) and post-annealing treatment (30 min) in ultra-high vacuum.

Before depositing DNTT (6.0nm) in ultra-high vacuum exposing the cleaned Cu substrate in the atmosphere (10min), (DNTT(6nm)/Cu) and Cleaned Cu substrates were dipped in a-TES solution (10 min) in the atmosphere (DNTT(6nm)/a-TES/Cu). All processes were performed at room temperature. Measurement of NEXAFS was performed using PF BL 13A, changing the incidence angle (α) from 0 to 60° at intervals of 20°. ($\alpha = 0^\circ$: normal incidence). NEXAFS were obtained indirectly by measuring the electron current at the sample (drain current) in the total electron yield (TEY) mode simultaneously with a photon flux monitor (Au mesh).

3 Results and discussion

Figure 2 (a) and (b) show polarization dependence of C

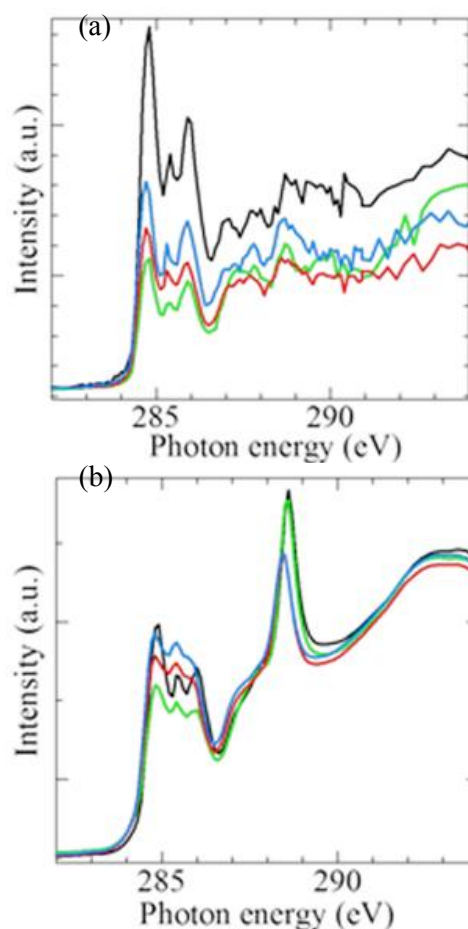


Fig.2 Polarization dependence of C K-edge NEXAFS of (a) DNTT(6nm)/Cu (b) DNTT(6nm)/a-TES/Cu. Black, blue, red and green lines indicate NEXAFS at incidence angle (α) = 0°, 20°, 40°, and 60°, respectively.

K-edge NEXAFS of DNTT (6.0 nm)/Cu and DNTT(6.0 nm)/a-TES/Cu, respectively. In the C K-edge NEXAFS of both DNTT(6nm)/Cu and DNTT(6nm)/a-TES/Cu, three peaks appear around $h\nu$ of 285 eV. By a close analysis, for DNTT(6nm)/Cu, three peaks shows same polarization dependence, where the transition intensities of these peaks become large as the incidence angle decrease. These peaks could be assigned to $C\ 1s \rightarrow \pi^*$. [4] We found that DNTT molecules show stand-up orientation on Cu substrate. In generally, the planar π -conjugated molecules such as pentacene, phthtlocyaine, and DNTT would have small tilt angle or random orientation on active surface such as clean metal substrate. The Cu substrate in this experiment was exposed to atmosphere about 10min. before DNTT deposition, which is mimic to the active process. Since the activity of the surface of Cu substrate would become lower, it is considered that DNTT molecules have stand-up molecular orientation.

In C K-edge NEXAFS of DNTT(6nm)/a-TES/Cu, three peaks at about 285eV show smaller polarization dependence than those of DNTT(6nm)/Cu. It means that DNTT molecules rather randomly orient by insertion of a-TES layer. It means that there are more DNTT molecules at small tilt angle on a-TES/Cu substrate than that on Cu substrate. At the interface between the electrode and the organic semiconductor layer, it is considered that molecules having π conjugated systems close to lying orientation become larger in overlap of the electrode and the π orbit, which is advantageous for injection. In fact, it has been reported that, on the insulating layer, when the molecule having π conjugation is close to standing orientations, the overlap of π orbitals between the molecules becomes larger, and the mobility is improved. [5] We conclude that the insertion of a-TES layer may be favor of the OTFT with high mobility. In the future, we will investigate on the detail structure of a-TES layer to clarify the origin of the change of molecular orientation by insertion of a-TES layer.

References

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