

# Influence on Molecular Orientation of DNTT Film on Copper by Diamine Molecular Adhesion Layers

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## 1 Introduction

There is a report that charge injection efficiency and mobility are improved by adsorbing a self-assembled monolayer (SAM) on an insulating layer and an electrode of an organic thin film transistor (OTFT). [1] [2] However, since different SAMs have to be used for the insulation layer and the electrodes, there would be some drawbacks such as 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 SiO<sub>2</sub>. 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  $\pi$ - $\pi$  interaction of the planar  $\pi$ -conjugated molecule such as DNTT. The purpose of this study is to clarify the effect on the molecular orientation of dinaphtho[2,3-b:2',3'-f]thieno[3,2-b] thiophene (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

Two samples were prepared in this experiment. (1) Pre-annealing treatment (30 min), Ar sputtering treatment (15 min) and post-annealing treatment (30 min) were applied to Cu substrate in ultra-high vacuum, then exposing the cleaned Cu substrate in the atmosphere (10min), and DNTT was deposited (6.0 nm) in ultra-high vacuum. (2) Cleaned Cu substrates were dipped in a-TES solution (10 min) in the atmosphere, and then DNTT was deposited (6.0 nm) in ultra-high vacuum. All processes were performed at room temperature. Measurement of NEXAFS was performed using PF BL 27 A with the total electron yield method, changing the incidence angle ( $\alpha$ ) from 0 to 60° at intervals of 10°. ( $\alpha = 0^\circ$ : normal incidence)

## 3 Results and discussion

Fig.1 (a) and (b) show Sulfur K-edge NEXAFS of DNTT (6.0 nm) / Cu and DNTT(6.0 nm) /a-TES/Cu. Peak A appearing around  $h\nu$  of 2472 eV shows that the transition intensity increases as the incident angle  $\alpha$  increases (from normal incidence to grazing incidence). From DFT calculations, peak A was attributed to S1s  $\rightarrow \sigma^*$  (a transition moment locates mainly in the molecule plane and the direction is parallel to the long axis of DNTT molecule).

From the previous study [3], DNTT molecules on CuO

as well as a-TES/CuO are oriented with the long axis standing. So we assume that DNTT molecules on Cu and a-TES/Cu stand on the long axis. The calculated transition intensity with a function of the incidence angle ( $\alpha$ ) at various molecular tilt angle ( $\beta$ ) are shown in the Fig.2. This shows that at a tilt angle ( $\beta$ ) of 40 degrees or more, the transition intensity increases as the incidence angle increases. Experimental results as shown in Fig.1 (a) and (b) (a-TES regardless of whether or not) show that the transition intensity increases as the incident angle increases. So we found DNTT molecules have stand-up orientation with molecular tilt angle ( $\beta$ ) of 40 degrees or more on the Cu substrate as well as a-TES absorbed Cu substrate.

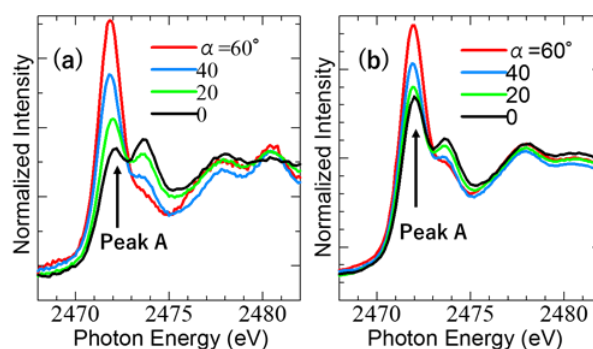


Figure. 1 (a)DNTT/Cu (b)DNTT/a-TES/Cu Sulfur K-edge NEXAFS measurement

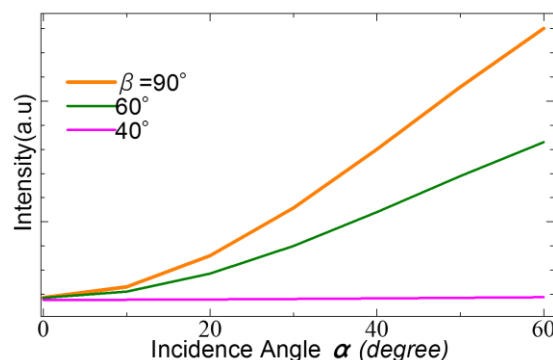


Figure.2 Transition intensity against incidence angle from calculation. It showed a result with an inclination angle of 40°, 60° and 90°.

Furthermore, by detail analysis of calculated transition intensities as shown in Fig.2, the change of the transition intensity as a function of incidence angle ( $\alpha$ ) become small with small molecular tilt angle ( $\beta$ ). In observed NEXAFS spectra as shown in Fig.1 (a) and (b), the intensity of the peak A for DNTT/a-TES/Cu shows smaller change from

incidence angle ( $\alpha$ ) of 0 to 60 degree than that for DNTT/Cu. It is found that DNTT molecules on a-TES/Cu substrate have a smaller tilt angle ( $\beta$ ) than that on Cu substrate. It is indicated that by inserting the a-TES layer, the inclination angle of DNTT is reduced. DNTT has a  $\pi$  conjugate plane. If DNTT molecules orient with small molecular tilt angle on the substrate, it is expected that the overlap between the substrate and the  $\pi$  orbital of DNTT becomes large and then the carrier injection efficiency for Cu substrate to DNTT molecules would increase.

#### References

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