Molecular Orientation Analysis of a C$_8$-BTBT Thin Film Grown under an External Temperature Gradient

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Organic semiconductors with a high carrier mobility can be realized by controlling a growth direction of the thin film. A new method to control the growth direction is using a temperature gradient. Molecular orientation strongly influences on the carrier mobility. Therefore, the molecular orientation of 2,7-dioctyl benzothieno benzothiophene (C$_8$-BTBT) thin films grown under a temperature gradient, has been evaluated by X-ray absorption fine structure measurements. It is considered that the C$_8$-BTBT has a molecular orientation with standing up on the substrate and is aligned to the temperature gradient direction. [DOI: 10.1380/ejssnt.2018.79]

Keywords: Carbon; Near edge extended X-ray absorption fine structure (NEXAFS); X-ray absorption spectroscopy; Semiconductor films

1. INTRODUCTION

An organic molecule 2,7-dioctyl[1]benzothieno[3,2-b]benzothiophene (C$_8$-BTBT) has attracted much attention as an organic semiconductor material with high carrier mobility. C$_8$-BTBT is superior to conventional organic molecules in atmospheric stability, and research on various applications is proceeding. The previous study has revealed that a herringbone structure of C$_8$-BTBT, i.e., the $\pi$ stacking results in high charge carrier mobility [1]. The herringbone structure of C$_8$-BTBT is unique among the molecular packing motifs and has been reported to exhibit a layered-herringbone (LHB) structure which is known to be very suitable for obtaining high-performance organic thin-film transistors (TFTs) [2–4]. The crystallinity of the LHB structure enables efficient two-dimensional carrier transport to realize a high performance organic TFT. Moreover, the calculated carrier transport properties indicate that the difference in the type of contact in the LHB structure, i.e., T-shaped (core-to-edge) and slipped parallel (core-to-core) contacts between adjacent planar $\pi$-electron skeletons that are taken place of glide and translational symmetric arrangement, respectively, results in anisotropy in carrier transport [2].

In addition, it is reported that a difference in mobility is observed due to a difference in preparation method [5–7]. Differences in preparation methods may lead to molecular orientation differences. Since the molecular orientation can strongly influence on the carrier mobility [6], it is important to quantitatively determine the molecular orientation of C$_8$-BTBT. Growth direction of C$_8$-BTBT thin films can be controlled by an external temperature gradient in a substrate during drop-casting [8]. This temperature-gradient method is the following procedure; pouring a droplet on a Si substrate carried on a temperature gradient Al plate, then evaporating the droplet and making a thin film. It is expected to align the molecular orientation to some extent by controlling the growth direction of the thin film. In this study, the molecular orientation of the C$_8$-BTBT thin film has been evaluated by polarization-dependent X-ray absorption fine structure (XAFS) measurements.

II. EXPERIMENTAL

A. Sample preparation by the temperature-gradient method

An external temperature gradient was generated as follows [8]. Two heat stages were kept at different temperatures and a 0.5 mm-thick aluminum plate (10 cm $\times$ 2 cm) bridged them. A 1.2 cm-square heavily-doped Si substrate with a 200 nm-thick thermal oxide layer was placed on this Al plate. A solution of 0.2 wt% C$_8$-BTBT (Sigma-Aldrich) in chlorobenzene was drop-casted on the substrate with the temperature gradient of $\approx$ 2.5$^\circ$C (65.75–68.25$^\circ$C). A thin film of 7 mm in the direction along the temperature gradient and 4 mm in the direction perpendicular to the temperature gradient direction was prepared. The film thickness was approximately 20–50 nm estimated by an atomic force microscopy (AFM) image.

As a contrast experiment, C$_8$-BTBT thin films by spin coating without an external temperature gradient were prepared. A solution of 0.4 wt% C$_8$-BTBT in chlorobenzene was used. And the Si substrate was placed on the center of the spin-coater. The spinning speed was set to 1000 rpm for the first 5 s, then 3000 rpm for 25 s.

B. XAFS analysis

The XAFS measurements were carried out at the BL-8 of SR Center, Ritsumeikan University. C $K$-edge XAFS spectra were obtained by the partial electron yield method with retarding voltage of $\approx$ 150 V. The measurements were performed at room temperature under ultrahigh vacuum of $\approx$ 1 $\times$ 10$^{-7}$ Pa. In order to see the molecular orientation of the C$_8$-BTBT thin films, the incidence angle with respect to the substrate normal was varied. Furthermore, in order to see the in-plane anisotropy of the C$_8$-BTBT thin films, the samples were azimuthally rotated around the substrate normal. Although the film thickness was
III. RESULTS AND DISCUSSION

C K-edge XAFS spectra are shown in Fig. 1. The structure around 293 eV is attributed to the C 1s → σ* (C-C) transition for both the aromatic rings and the alkyl chain [9, 10]. The structure around 285 eV is attributed to the C 1s → π*(C=C) transitions for aromatic rings [9, 10]. The structure around 287 eV is attributed to the C 1s → σ*(C-H) and C 1s → π*(C=C) transitions. Since the peak around 287 eV could not be distinguishable, we discuss about the structure around 285 eV. The peak intensity of the C8-BTBT thin films fabricated by both the temperature-gradient and the spin-coated methods decrease with increasing the incident angles. From these results combined with the observed step height of ~2.6 nm by AFM [8], which corresponds to the length of a C8-BTBT molecule, it can be seen that the C8-BTBT molecule in the thin films has a standing up structure with respect to the substrate.

For C8-BTBT prepared by the temperature-gradient method, the incidence-angle dependences of the peak intensities around 285 eV were different when the sample was azimuthally rotated (Fig. 2). That is, the polarization dependence of the intensities with the in-plane polarization parallel to the temperature-gradient direction [Fig. 2(a)] was stronger than that with the in-plane polarization perpendicular to the temperature-gradient direction [Fig. 2(c)]. This result indicates that the π* orbital of the C8-BTBT molecule preferentially aligns to the temperature-gradient direction. Note that the tilt direction of the π* orbital is irrelevant to the hotter/cooler sides of the temperature-gradient direction since the similar incidence-angle dependences were observed for the opposite grazing incidence (not shown). For C8-BTBT prepared by the spin-coated method, on the other hand, the incidence-angle dependences of the peak intensities around 285 eV were almost the same even when the sample was azimuthally rotated (Fig. 3), indicating the isotropic C8-BTBT molecular orientation.

In order to evaluate the molecular orientation, fitting was performed on the results obtained from the angular dependence measurements, following the literature [9]. Since in-plane anisotropy was observed for C8-BTBT prepared by the temperature-gradient method.
FIG. 3. Incident angle dependence $\pi^*$ orbital spectra of C$_8$-BTBT prepared by the spin-coated method. The azimuthal angle was varied to be 0° (a), 45° (b), and 90° (c).

(Fig. 2), the directions of the $\pi^*$ orbitals with respect to the temperature-gradient direction are assumed to be $\pm \Phi$. Considering the four molecular orbitals shown in Fig. 4(b), fitting can be done by

$$I_{\pi^*} \propto P \left[ \sin^2 \theta \cos^2 \alpha + \cos^2 \theta \sin^2 \alpha \left( \frac{\cos^2 (\Phi + \beta) + \cos^2 (\Phi - \beta)}{2} \right) \right] + (1 - P) \left[ \sin^2 \alpha \left( \frac{\sin^2 (\Phi + \beta) + \sin^2 (\Phi - \beta)}{2} \right) \right]$$

(1)

for each geometry. Here, $P$ is the degree of polarization, $\theta$ is the angle between the substrate normal and the incident X-ray, $\alpha$ and $\Phi$ are a polar and an azimuthal angles of the molecular orbital, $\beta$ is the angle between the temperature gradient direction and the projected electric field vector (Fig. 4). We have assumed the degree of polarization $P = 0.85$, which is typical for a bending magnet source [9].

On the other hand, C$_8$-BTBT fabricated by spin-coated methods has isotropic molecular orientation, and fitting can be done by

$$I_{\pi^*} \propto P \left( \sin^2 \theta \cos^2 \alpha + \frac{\cos^2 \alpha}{2} \right) + (1 - P) \frac{\sin^2 \alpha}{2}$$

(2)

Note that the vector equations in Ref. [9] are applicable because the BTBT core is considered to be rigid, that is, because all the $\pi^*$ orbitals on the rigid BTBT core align to the same direction.

The fitting results for the C$_8$-BTBT produced by the temperature-gradient and spin-coated methods are shown in Fig. 5 and Fig. 6, respectively. From the obtained parameters, it is found that the tilt angle of a C$_8$-BTBT

| Method              | Tilt angle | Azimuth angle$^a$ |
|---------------------|------------|-------------------|
| Temperature-gradient| $20 \pm 2^\circ$ | $52 \pm 2^\circ$ |
| Spin-coated         | $21 \pm 2^\circ$ | - (isotropy) |
| Off-center spin-coated [7]$^b$ | $\sim 13^\circ$ | $\sim 55^\circ$ |

$^a$ Note that the angles for the off-center spin-coating method from Ref. [7] are re-estimated by using Eq. (1).

$^b$ Angle between the molecular plane and the growth direction.
molecule is $20\pm2^\circ$ and that the angle between the molecular plane and the temperature-gradient direction is $52\pm2^\circ$ for the temperature-gradient method (Fig. 5). Note that the molecular orientation angles are different from the molecular orbital direction ($\alpha$ and $\Phi$) by $\pi/2$. It was found that the C$_8$-BTBT produced by the spin-coated method also had the tilt angle of $21\pm2^\circ$ (Fig. 6). As shown in Fig. 5(a, b) and Fig. 6, other values of $\alpha$, e.g., $80^\circ$ and $60^\circ$, do not reproduce well the experimental data. Note that Eq. (1) for $\beta = 45^\circ$ does not depend on $\Phi$ [Fig. 5(b)]. For $\beta = 0^\circ$, it does depend on $\Phi$ so that the simulation curves of $\alpha = 80^\circ$ and $60^\circ$ with the optimal $\Phi$ of $38^\circ$ are shown in Fig. 5(a). With the optimal $\alpha$ of $70^\circ$, other values of $\Phi$, e.g., $50^\circ$ and $30^\circ$, do not reproduce well the experimental data [Fig. 5(c)]. The molecular orientation angles of C$_8$-BTBT inside the thin films were summarized in Table I.

Previous study controlling the growth direction by off-center spin-coating method has also shown the anisotropic molecular packing [7]. Re-estimating the molecular orientation by Eq. (1), the tilt angle is $\sim 13^\circ$ and the angle between the molecular plane and the growth direction is $\sim 55^\circ$. As summarized in Table I, these molecular angles are different from the above mentioned angles by the temperature-gradient method though both methods lead to the anisotropic molecular packing. Considering the herringbone angles, which correspond to the angle between the two molecules, are $\sim 55^\circ$ and $\sim 125^\circ$ in the direction to the $a$-axis and $b$-axis of the C$_8$-BTBT crystal, respectively [2], the temperature-gradient direction is thought to lead to the preferential $b$-axis growth. Similarly, the preferred growth direction of the off-center spin-coated film was reported to be along the (010) direction of the C$_8$-BTBT crystal [7].

IV. CONCLUSION

We have performed polarization-dependent X-ray absorption spectroscopy measurements on C$_8$-BTBT films. It was found that the $\pi^*$ intensity of the thin films decreases with grazing incidence and has an anisotropy with respect to the temperature gradient. From these results, it is found that the C$_8$-BTBT thin film has a standing-up structure and that the molecules are aligned in the direction of temperature gradient. Furthermore, C$_8$-BTBT thin films fabricated by the temperature-gradient method have similar standing up structure, as compared with the C$_8$-BTBT produced by the spin-coated method.

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