

Molecular orientation analysis of C₈-BTBT thin films

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Abstract

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 [1]benzothieno[3,2-b]benzothiophene (C₈-BTBT) thin films grown under a temperature gradient, has been evaluated by x-ray absorption fine structure measurements. It is considered that the C₈-BTBT has a molecular orientation with standing up on the substrate, and, is aligned to the temperature gradient direction.

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 due to the sulfur atom in the 5-membered ring [Fig. 1(a)], and researches on various applications are proceeding. The previous study has revealed that a herringbone structure of C_8 -BTBT, i.e. the π stacking results in high charge carrier mobility [1]. Furthermore, oriented growth of highly ordered organic thin films has been reported to influence on the carrier mobility [2-4]. Grazing incidence X-ray diffraction and X-ray absorption fine structure (XAFS) measurements have indicated that the packing structure and the molecular orientation of C_8 -BTBT are modified by controlling the growth direction [4]. Therefore, the oriented growth affects the molecular orientation, then it would lead to high charge carrier mobility.

Another method to control the growth direction is usage of an external temperature gradient in a substrate during drop-casting [5]. This method follows the procedures; pouring a droplet on a Si substrate carried on a temperature gradient Al plate, then evaporating the droplet and making a thin film [Fig. 1(b)]. 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 films has been evaluated by a polarization-dependent XAFS measurement.

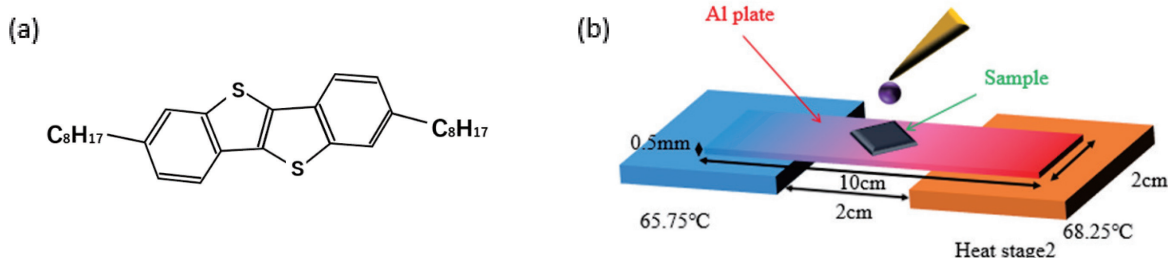


Fig. 1 (a) Molecular structure of C_8 -BTBT. (b) Schematic view of a drop-casting method on a temperature gradient substrate. Since the direction of solvent evaporation is determined by the temperature gradient, the molecular orientation is expected to be similarly aligned to the temperature gradient [3].

2. Experimental

Sample preparation

We generated an external temperature gradient as follows [5]. Two heat stages were kept at different temperatures and a 0.5mm-thick aluminum plate (10 cm \times 2 cm) bridged them. We placed a 1.2 cm-square heavily-doped Si substrate with a 200 nm-thick thermal oxide layer on this Al plate. A solution of 0.2 wt% C_8 -BTBT (Sigma-Aldrich) in chlorobenzene was drop-

casted on the substrate. As a contrast experiment, we prepared C₈-BTBT thin films by spin coating without an external temperature gradient.

A polarization-dependent XAFS

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 -150 V. The measurements were performed at room temperature under ultrahigh vacuum of $\sim 1 \times 10^{-7}$ Pa. In order to see the molecular orientation of the C₈-BTBT thin films, the polarization vector of the incident X-ray was changed, that is, the incidence angle with respect to the substrate normal was varied from 60 ° to -60 ° at intervals of 30°. Furthermore, C₈-BTBT thin films was azimuthally rotated around the substrate normal to see the in-plane molecular orientation. Especially, the polarization vector of the incident X-ray and the temperature gradient direction of the thin film were set to either parallel or perpendicular. These two geometries were called as the parallel or the perpendicular geometries, respectively.

3. Results and Discussions

C *K*-edge XAFS spectra were shown in Fig. 2. The peaks around 310 eV is attributed to the C 1*s* → σ^* transition for aromatic rings. The peaks around 285 eV is attributed to the C 1*s* → π^* (C=C) transitions for aromatic rings. The peaks around 287 eV is attributed to the C 1*s* → σ^* (C-H) and C 1*s* → π^* (C=C) transitions. Since the peak around 287 eV could not be distinguishable, we discuss about the peak around 285 eV. The peak intensity of the C₈-BTBT thin films fabricated by both the drop-casting and the spin-coating methods decrease with increasing the incident angles. From these results, it can be seen that the C₈-BTBT molecule inside the thin films has a standing up structure with respect to the substrate. The peak intensities (285.5 eV) were different between the parallel and the perpendicular geometries. From this result, the molecular orientation of C₈-BTBT showed anisotropy as for the temperature gradient direction.

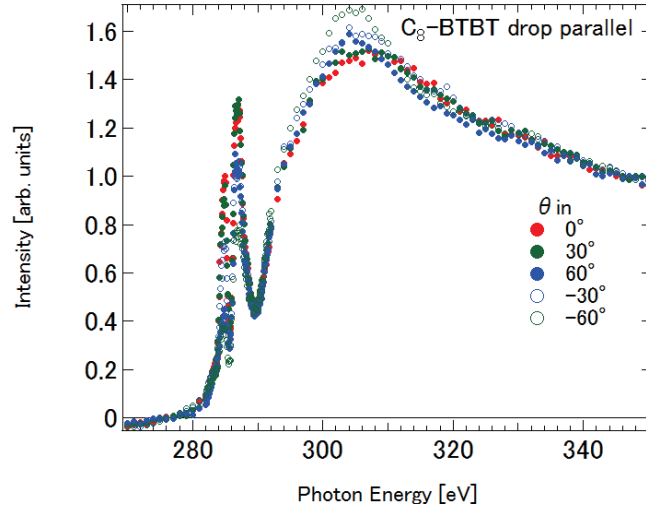


Fig. 2 C *K*-edge XAFS spectra of C₈-BTBT (drop-casted, parallel geometry). The peaks around 285eV is attributed to the C 1s → π* (C=C) transitions for aromatic rings. The peaks around 310eV is attributed to the C 1s → σ* transition for aromatic rings.

Although domain structures were observed in the C₈-BTBT thin film prepared by the drop-casting method, as shown in Fig. 4, the angular dependence in Fig. 3 was measured within the one domain. In-plane anisotropy was not observed in C₈-BTBT produced by the spin-coated method in Fig. 5. Fitting was performed on the results obtained from angular dependence measurement, following the literature [6]. As shown in Fig. 6, C₈-BTBT fabricated by drop-casting has twofold substrate symmetry, and for parallel ones, fitting can be done by

$$I_{\pi^*} = A(\sin^2\theta\sin^2\alpha + \cos^2\theta\cos^2\alpha\sin^2\Phi).$$

Also, for perpendicular ones, fitting can be done by

$$I_{\pi^*} = A(\sin^2\theta\sin^2\alpha + \cos^2\theta\cos^2\alpha\cos^2\Phi).$$

As shown in Fig. 7, C₈-BTBT fabricated by spin-coating methods has isotropy, and fitting can be done by

$$I_{\pi^*} = A(\sin^2\theta\sin^2\alpha + \frac{1}{2}\cos^2\theta\cos^2\alpha).$$

θ indicates the angle between the substrate normal and the incident X-ray. The parameters of α and Φ are defined from the coordinate system in Fig. 8.

The orientation angle of C₈-BTBT inside the thin film was obtained (Table 1). From the obtained parameters, it was found that C₈-BTBT produced by the drop-casting method had the polar angle from the substrate normal is $\alpha = 11 \pm 4^\circ$. Also, it was found that C₈-BTBT produced by the drop-casting method had the azimuth angle from the growth direction is Φ

$= 50 \pm 3^\circ$. Moreover, it was found that C_8 -BTBT produced by the spin-coated method had the polar angle from the substrate normal is $\alpha = 17 \pm 3^\circ$. C_8 -BTBT fabricated by the drop-casting method showed much more standing up structure, as compared with the C_8 -BTBT produced by the spin-coating method.

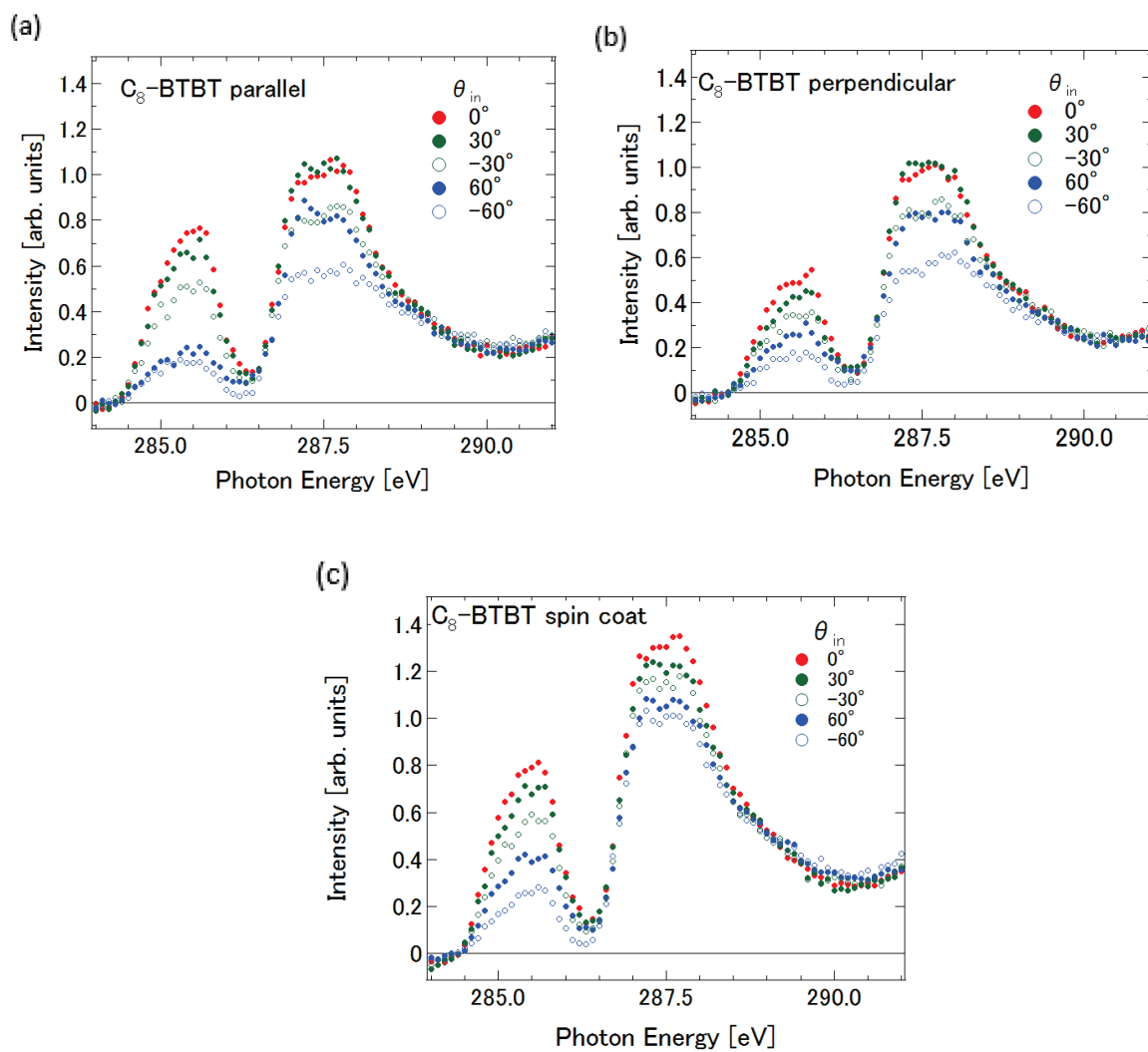


Fig. 3 (a) Incident angle dependence π^* orbital spectra of C_8 -BTBT (drop-casted, parallel geometry). (b) π^* orbital spectra of C_8 -BTBT (drop-casted, perpendicular geometry). (c) π^* orbital spectra of C_8 -BTBT (spin-coated).

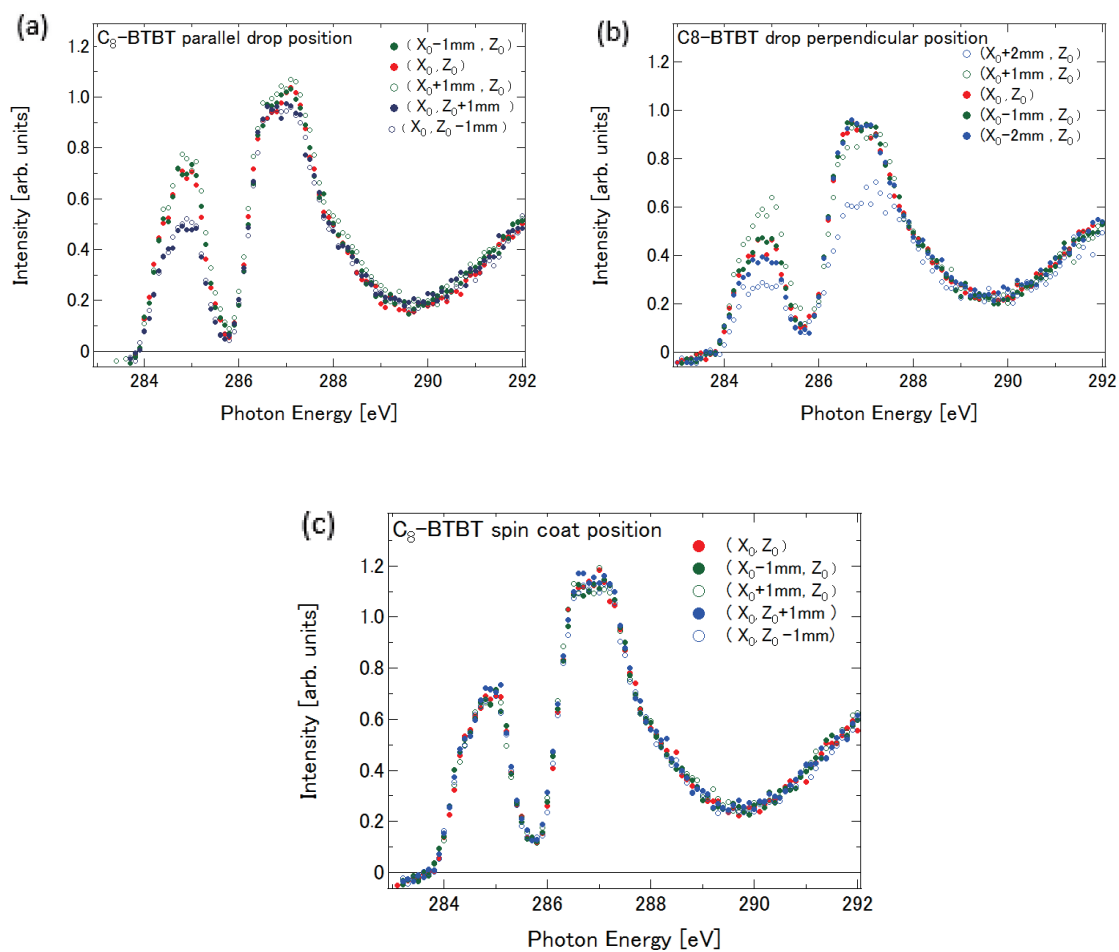


Fig. 4 (a) Position dependence π^* orbital spectra of C_8 -BTBT (parallel geometry). (b) Position dependence π^* orbital spectra of C_8 -BTBT (perpendicular geometry). (c) Position dependence π^* orbital spectra of C_8 -BTBT (spin-coated).

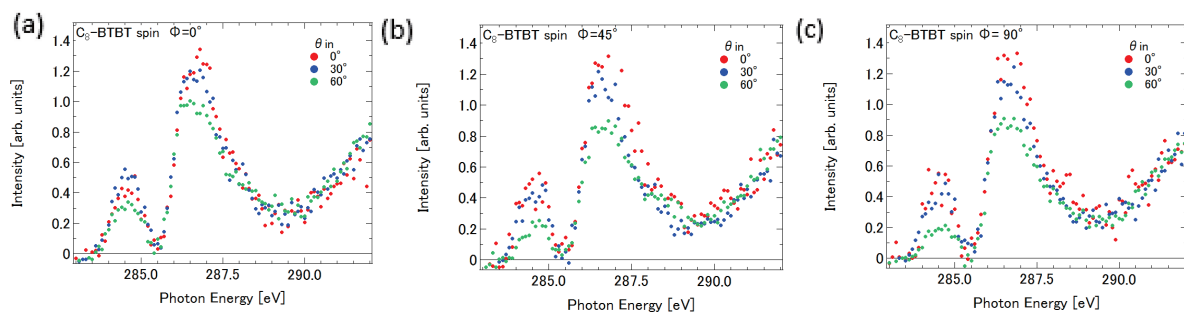


Fig. 5 In-plane anisotropy dependence π^* orbital spectra of C_8 -BTBT. From the left, indicates azimuthal angle $\Phi=0^\circ$ (a), $\Phi=45^\circ$ (b) and $\Phi=90^\circ$ (c), respectively.

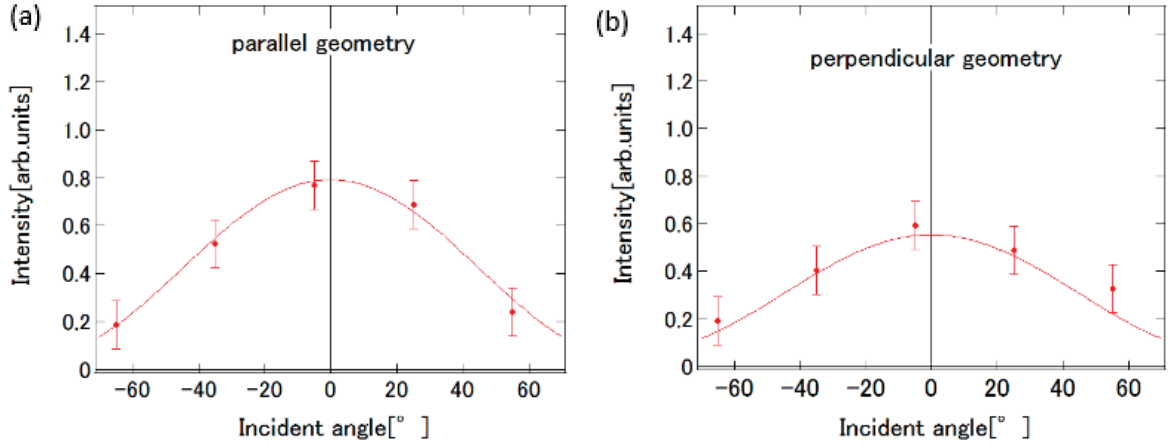


Fig. 6 As a result of plotting the peak intensity of 285.5 eV at each incident angle and performing fitting. The points indicate experimental values, and the curves in Fig.6 (a) indicates the spectrum from $I_{\pi^*}=A(\sin^2\theta\sin^2\alpha+\cos^2\theta\cos^2\alpha\sin^2\Phi)$. Also, the curves in Fig.6 (b) indicates the spectrum from $I_{\pi^*}=A(\sin^2\theta\sin^2\alpha+\cos^2\theta\cos^2\alpha\cos^2\Phi)$. These equations were for the case of twofold substrate symmetry.

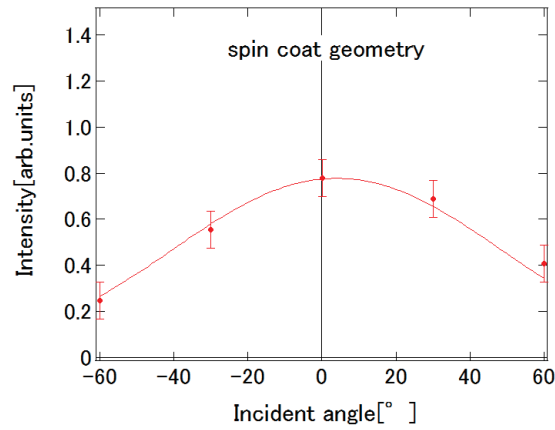


Fig. 7 As a result of plotting the peak intensity of 285.5 eV at each incident angle and performing fitting. The points indicate experimental values, and the curves in Fig.7 indicates the spectrum from $I_{\pi^*}=A(\sin^2\theta\sin^2\alpha+\frac{1}{2}\cos^2\theta\cos^2\alpha)$. This equation was for the case of threefold substrate symmetry.

Table 1 Parameters obtained by fitting

| | $\alpha / ^\circ$ (polar angle) | $\Phi / ^\circ$ (azimuthal angle) |
|-------------|---------------------------------|-----------------------------------|
| Drop-casted | $11 \pm 4^\circ$ | $50 \pm 3^\circ$ |
| Spin-coated | $17 \pm 3^\circ$ | - (isotropic) |

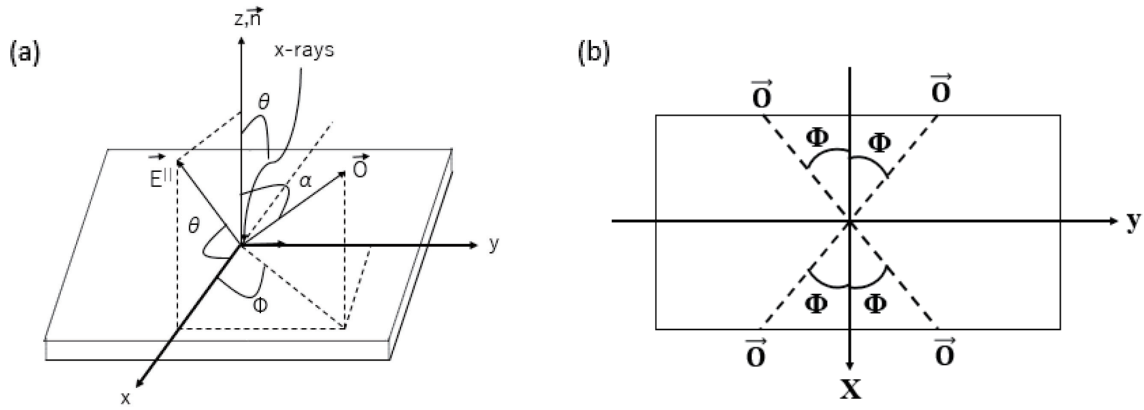


Figure 8. (a) Coordinate system defining the geometry of a π^* vector orbital on the surface. The orientation of the orbital, i.e., of the vector \vec{O} , is characterized by a polar angle α and an azimuthal angle Φ . The X-rays are incident in (x, z) orbit plane of storage ring which contains the major electric field vector component E^{\parallel} . The X-ray incidence angle θ , which is also the polar angle of E^{\parallel} , is changed by rotating the substructure about the y -axis. The z -axis is the surface normal and the azimuthal rotation axis of the substructure [6]. In this study, the parallel geometry is defined as the temperature gradient being along with the x -axis, while the perpendicular geometry is the temperature gradient being along with the y -axis. (b) Analysis geometry of the \vec{O} vector directions due to the symmetry.

4. Conclusion

We have performed polarization-dependent X-ray absorption fine structure measurements on C₈-BTBT thin films. It was found that the π^* 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 C₈-BTBT thin film has a standing-up structure and that the molecules are aligned in the direction of temperature gradient. Furthermore, C₈-BTBT fabricated by the drop-casting method showed much more standing up structure, as compared with the C₈-BTBT produced by the spin-coated method.

References

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