

# Crystal Structure Analyses of Organic Semiconductor Thin Films with Variable-Temperature Two-Dimensional Grazing Incidence X-ray Diffraction

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## Abstract

Crystal structures of organic semiconducting materials in those thin-film states are important to understand their physical properties, especially carrier transport. In this study, crystal structures of organic semiconducting thin films have been investigated using two-dimensional grazing incidence X-ray diffraction with changing the temperature in order to reveal temperature dependence of the crystal structure. Herein the dependence of lattice parameters of the DNTT thin film on temperature is reported. The structural phase transition of DNTT thin film is revealed at 320–330 K.

## 1. Introduction

Physical properties of organic semiconducting material are generally originated from the molecular shape and packing structure. Their physical properties, especially those related to carrier transport, are strongly related to the crystallographic parameters. They are easily changed by temperature to affect the electrical characteristics. Hence, it is necessary to investigate the crystal structures of organic semiconducting materials and their temperature dependence in order to predict the electrical characteristics.

Recently, the structure analysis of organic thin film using the two-dimensional grazing incidence X-ray diffraction (2D-GIXD) has been established<sup>[1–4]</sup>, and the relationship between carrier mobility and crystal structure is often discussed<sup>[5]</sup>.

In semiconductor thin films of organic small molecules, the crystal structure is easily modulated by the temperature due to the weakness of the van der Waals interactions between neighbor molecules. As a result, carrier transport property is largely changed because overlap of  $\pi$ -orbitals changes between the molecules. Although the temperature-modulation of the structure in thin films is, in many cases, different from that in single crystals because of the stress induced by the substrates. The X-ray diffraction reciprocal space mapping technique<sup>[6]</sup> is therefore desired to be applied even to thin films to exactly understand the crystal structure. In this study, the lattice parameters of organic thin films are evaluated by the variable-temperature 2D-GIXD method using a synchrotron X-ray source and the crystallographic parameters are evaluated through the

mathematical analysis.

## 2. Experimental Method

The glass substrate was cleaned by the sonication in acetone for 5 minutes, rinsed in heated acetone, and UV/O<sub>3</sub> treatment just before loading into a vacuum chamber. The organic semiconducting materials were deposited onto the glass substrates at room temperature in a vacuum ( $1 \times 10^{-6}$  Pa). The deposition rate was maintained to 0.1 Å/s and the film thickness to *ca.* 500 nm which was confirmed using stylus profilometer.

The 2D-GIXD measurement system was made by combined a multi-axes diffractometer and highly sensitive large-area two-dimensional detector (PILATUS 300K) at BL19B2 beamline in SPring-8. The geometry of 2D-GIXD measurement is depicted in Fig.1. A heating-cooling stage was set on the goniometer and diffraction patterns were recorded through the beryllium windows by exposure time of 30 seconds under steady temperature. X-ray energy was set to 12.40 keV and incidence angle ( $\omega$ ) to 0.12° which satisfies the total reflection condition at organic/substrate interface.

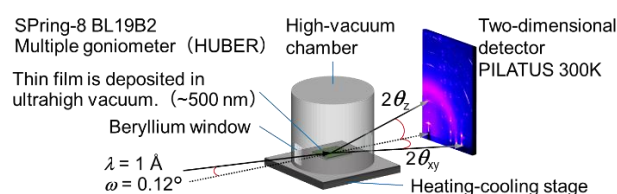


Fig.1 Schematic diagram of the variable-temperature 2D-GIXD measurement system used in this work.

## 3. Results and Discussion

Figure 2 shows a two dimensional diffraction pattern from a dinaphtho[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]thiophene (DNTT) thin film at 280 K. Many spots with large intensity are observed {Fig.2(a)}. From the position of those spots, it is found that the  $c^*$ -axis of the unit cell is oriented vertically to the substrate surface, although the in-plane orientation is random in the polycrystalline film. Similar patterns are obtained with thin films of various semiconductor small molecules.

The position of major diffraction spots in Fig.2(a) are

plotted by circles in Fig.2(b) The Miller indices ( $h k l$ ) of the spots are identified according to a reported structure of single crystals<sup>[7]</sup>. Lattice parameters ( $a, b, c, \alpha, \beta, \gamma$ ) are then estimated by the X-ray diffraction reciprocal space mapping method<sup>[6]</sup>.

Crosses in Fig.2(b) show fitting results by the reciprocal space mapping. Reliability of the calculated position of diffraction spots is then checked by a reliability factor (R-factor) given by,

$$R\text{-factor} = \frac{\sum \sqrt{\frac{(2\theta_{z\_Exp.} - 2\theta_{z\_Calc.})^2}{\sigma_{z\_Exp.}^2} + \frac{(2\theta_{xy\_Exp.} - 2\theta_{xy\_Calc.})^2}{\sigma_{xy\_Exp.}^2}}}{\sum \sqrt{\frac{2\theta_{z\_Exp.}^2}{\sigma_{z\_Exp.}^2} + \frac{2\theta_{xy\_Exp.}^2}{\sigma_{xy\_Exp.}^2}}}, \quad (1.1)$$

where  $\sigma_z$  and  $\sigma_{xy}$  are the standard deviation of the experimental spots and used as a weight in the R-factor<sup>[8,9]</sup>. R-factor of the fitting results in Fig.2(b) was 0.66 %, which is small enough to discuss the small change of lattice parameters by temperature.

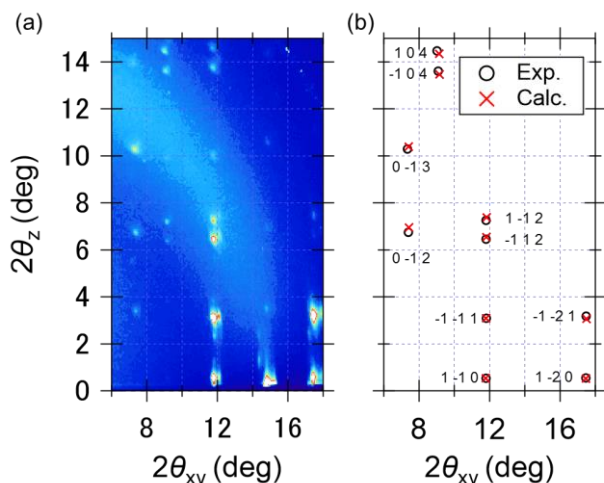


Fig.2 (a) 2D-GIXD patten obtained with a DNTT thin film at 280 K. (b) positions of representative diffraction spots from the experiment and those obtained by X-ray reciprocal space mapping.

Figure 3 shows dependence of the lattice parameters on temperature the DNTT thin film. The filled marks are those reported for a single crystal ( $a = 6.187 \text{ \AA}$ ,  $b = 7.662 \text{ \AA}$ ,  $c = 16.208 \text{ \AA}$ ,  $\alpha = 90^\circ$   $\beta = 92.49^\circ$   $\gamma = 90^\circ$ )<sup>[7]</sup>. The  $c$ -axis of the thin film is longer than those of the single crystal, and it is indicated that the effect by oriented molecules in the substrate. As increasing temperature,  $a$  and  $b$ -axis slightly decreases by  $0.06 \text{ \AA}$  and  $c$ -axis decreases  $0.20 \text{ \AA}$ . The variation of the lattice angles indicates that the crystal system changes from monoclinic to triclinic at  $320\text{--}330 \text{ K}$ . This structure phase transition is considered to be caused by slight changes of the van der Waals interactions between neighbor molecules.

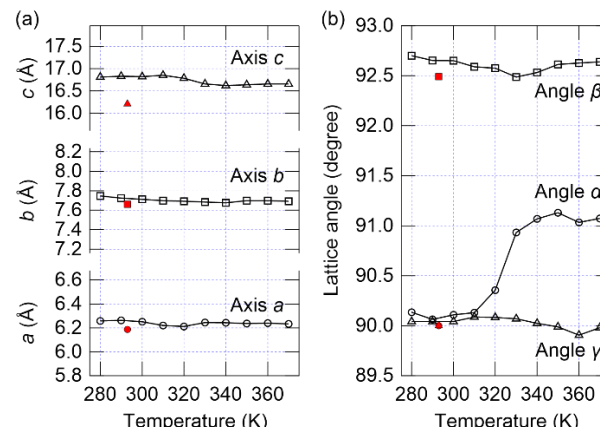


Fig.3 Temperature dependence of the lattice parameters (open circle, square, and triangle) and these reported for a single crystal (Filled circle, square, and triangle)<sup>[7]</sup>.

#### 4. Conclusion

Structural change of organic semiconducting materials is observed using the variable-temperature 2D-GIXD technique. Unreported phase transition is suggested for DNTT thin film. Structural change of organic semiconducting materials was observed using the variable-temperature 2D-GIXD technique. The results shown in this abstract revealed an unknown phase transition of a DNTT thin film. In the presentation, analyses for other semiconducting small-molecule thin films will be also reported.

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