

## Structural characterizations of organic semiconductor thin films investigated by two-dimensional grazing incidence X-ray diffraction

Organic thin-film transistors (OTFTs) have attracted much attention, and their performances have been continuously improved. It is well known that the structural properties, such as crystallinity, grain size, crystal orientation and polymorphism determine the carrier transport properties in OTFTs [1]. Hence, crystallographic characterization of thin organic films is necessary to further improve the performances of OTFTs.

Grazing incidence X-ray diffraction (GIXD) has been used in the structural analysis of organic thin films. To date, the structure of organic thin films has yet to be thoroughly characterized; only the lattice parameters of the thin films have been compared to the bulk by assuming that they have similar structures. However, the crystal structures of some organic thin films differ from the bulk structures, as observed in the polymorphs of pentacene [2]. Because the crystal structure of organic semiconductors affects the carrier transport properties, a method to analyze crystal structures of thin-film organic semiconductors is necessary to understand the physical properties of OTFTs. In this paper we report the crystal structure of vacuum deposited organic thin films by two-dimensional GIXD (2D-GIXD) using a synchrotron X-ray source and a high-sensitivity area detector (PILATUS 300K) [3].

The 2D-GIXD measurements were carried out using a multi-axes diffractometer combined with PILATUS 300K at **BL46XU** beamline. The geometry of 2D-GIXD measurement is depicted in Fig. 1.  $\alpha$ , $\omega$  - Hexyl-distyrylbithiophene (DH-DS2T, see the molecular structure in Fig. 2(a)), a p-type organic semiconductor, was chosen as the sample [4]. The crystal structure of DH-DS2T has not yet been clarified since it is difficult to grow a



Fig. 1. Geometry of the 2D-GIXD measurement setup. i, j, and k are defined as the unit vector. Element of i vector is parallel to the incident beam. [3]

single crystal. DH-DS2T was vacuum deposited onto a silicon wafer coated with native oxide  $(SiO_2)$  at room temperature.

The 2D-GIXD pattern from the polycrystalline DH-DS2T thin film is shown in Fig. 2(b), where  $2\theta_z$  on the vertical axis and  $2\theta_{xy}$  on the horizontal one denote the takeoff and horizontal component of the scattering angle, respectively. A number of diffraction spots were successfully observed owing to the combination of a sensitive 2D-detector and a high-brightness synchrotron X-ray source. The observed pattern indicates that the sample is a highly oriented polycrystalline film along the surface normal.

As the primary step for structure analysis of the 2D-GIXD pattern, the unit cell parameters and crystalline orientation were determined from the diffraction positions. Figure 2(b) shows the comparison of experimental and calculated (marked by open circle) 2D-GIXD patterns. All the observed diffractions can be indexed by a monoclinic unit cell with the following lattice parameters: a = 0.58 nm, b = 0.78 nm, c = 3.43nm,  $\alpha = \gamma = 90.0^{\circ}$ , and  $\beta = 94.3^{\circ}$ . It was found that the c\*-axis of the unit cell is oriented perpendicular to the substrate surface, although the azimuthal orientation is random in the polycrystalline film. Some of the main diffractions are indexed and labeled in the figure. The c value of DH-DS2T is larger than that of the DS2T thin film, which lack alkyl chains (a = 0.77 nm, b = 0.56 nm, c = 2.08 nm, and  $\beta = 95.3^{\circ}$ ) [5]. Moreover, parameters a and b of DH-DS2T are similar to the exchanged parameters b and a of DS2T, indicating that the tilting direction of *c*-axis against the *a-b* plane is changed from long axis to short axis upon attaching alkyl chains.

As the second step for structural analysis, the inner structure of the DH-DS2T unit cell was considered by comparing the observed intensities with the calculated ones. As a model for calculation, the DH-DS2T molecule was divided into two parts: DS2T and alkyl parts, as shown in Fig. 2(a). Three rotation angles ( $\theta_t$ ,  $\varphi_t$  and  $\phi_t$ ), which were used to define better configurations of the molecules in the unit cell, can describe suitable atomic positions  $(r_i)$ . The molecular structure factor of the DH-DS2T crystal in a thin film is calculated using these rotation angles and the space group. The calculated and observed intensities agree well, and the extinction rules at  $\theta_t = 25^{\circ}$  correspond well. Figure 3 shows the three-dimensional crystal structure of the DH-DS2T thin film obtained from the best-fit of  $r_i$ . Our calculation elucidates that the overall DH-DS2T molecule in the unit cell tilts about 25° against the substrate normal.



Fig. 2. (a) Molecular structure of DH-DS2T. DH-DS2T molecule was divided into two parts for the calculation: DS2T and the alkyl parts. (b) 2D-GIXD pattern image of a DH-DS2T thin film on SiO<sub>2</sub>. Black square on the bottom-left corner is the shadow image of the direct-beam stopper. Open circles show the results of simulated diffractions. [3]

This means that the inner structure of the DH-DS2T unit cell is partly similar to that of DS2T.

A number of the X-ray diffraction spots from the highly oriented DH-DS2T thin film were simultaneously observed using a combination of the sensitive 2D-detector and the high-brightness synchrotron X-ray source. The method developed in the present study can be widely applied to other highly oriented crystalline organic materials and will contribute to clarify their crystal structures. The method is especially vital for materials that form extrinsic structures in thin films or cannot be grown into bulk single crystals.



Fig. 3. Three-dimensional crystal structure of the DH-DS2T thin film determined by 2D-GIXD pattern. [3]

Takeshi Watanabe

SPring-8/JASRI

E-mail: t5511001@spring8.or.jp

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