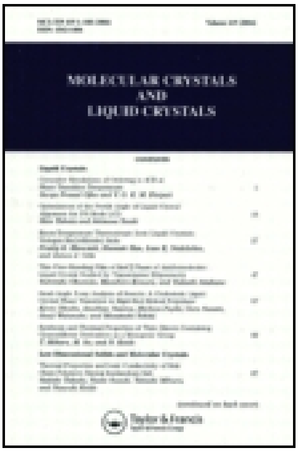

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Two Dimensional Grazing Incidence X-Ray Diffraction of TIPS-Pentacene Thin Films

R. Kamiya [a], T. Hosokai [a], T. Watanabe [a], T. Koganezawa [b], M. Kikuchi [a] & N. Yoshimoto [a]

[a] Graduate School of Engineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate, Japan

[b] Japan Synchrotron Radiation Research Institute, 1-1-1 kouto, Sayo, Hyogo, Japan

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Two Dimensional Grazing Incidence X-Ray Diffraction of TIPS-Pentacene Thin Films

R. KAMIYA,[1] T. HOSOKAI,[1] T. WATANABE,[1]
T. KOGANEZAWA,[2] M. KIKUCHI,[1] AND N. YOSHIMOTO[1,*]

[1]Graduate School of Engineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate, Japan
[2]Japan Synchrotron Radiation Research Institute, 1-1-1 kouto, Sayo, Hyogo, Japan

We report crystal structure of TIPS-pentacene thin films studied by two dimensional grazing incidence x-ray diffraction (2D-GIXD). Thin films were fabricated by dry and wet processes, and precisely compared the crystal structures of the fabricated films. Slight differences in the unit cell parameters are found in the films. Furthermore, a new polymorph is identified in the film fabricated at sufficiently low substrate temperature, −166°C. The unit cell parameters of the new polymorph are determined by analyzing the 2D-GIXD pattern.

Keywords Organic semiconductors; TIPS-pentacene; X-ray diffraction; 2D-GIXD; polymorph

1. Introduction

In recent years, organic thin-film transistors (OTFTs) have attracted great attention, and their performance has continually improved [1]. OTFTs have many advantages in terms of a low-cost, low-temperature process, and compatibility with flexible substrates. In comparison to transistors made from conventional inorganic semiconductors such as amorphous silicon, however, the stability and uniformity of OTFTs require improvements. Because the crystal structure significantly affects the charge transport properties in OTFTs, investigation of crystal structure of organic semiconductors is important. Two-dimensional grazing incidence x-ray diffraction (2D-GIXD) is one of the suitable methods to solve the crystal structure of organic thin films. A combination of high-brilliance synchrotron radiation and a high-sensitive two-dimensional X-ray detector has made possible to study crystal structures of organic thin films. To clarify the dependence of fabrication methods on crystal structure, we compared the films fabricated by dry and wet processes. We employed 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene; Fig. 1) [2] as the sample, which is known as a promising material for use in OTFTs because of its high career mobility, air-stability, and solubility to organic solvents [3, 4]. In this study, crystal structures of TIPS-pentacene thin films fabricated by physical vapor deposition and drop-cast are investigated by 2D-GIXD.

*Address correspondence to N. Yoshimoto, Graduate School of Engineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan. E-mail: yoshimoto@iwate-u.ac.jp

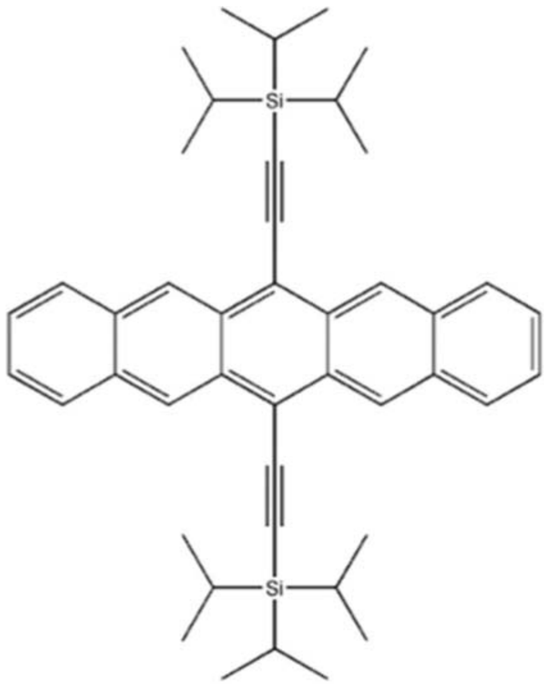

Figure 1. Molecular structure of TIPS-pentacene.

2. Experimental

Three types of TIPS-pentacene (Sigma-Aldrich purity $\geq$ 99%) thin films were fabricated, vacuum deposition at R.T. (VR), drop-cast (DC) and vacuum deposition at low temperature (VL). VR thin film was fabricated by vacuum-deposition on native SiO_2/Si wafers at

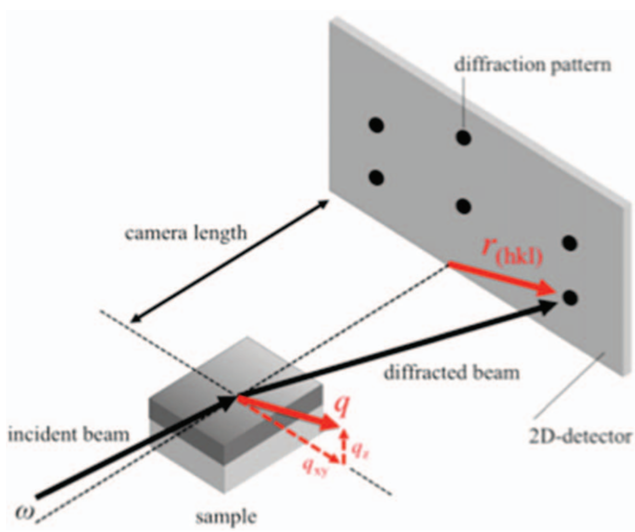

Figure 2. Schematic of 2D-GIXD setup using synchrotron radiation.

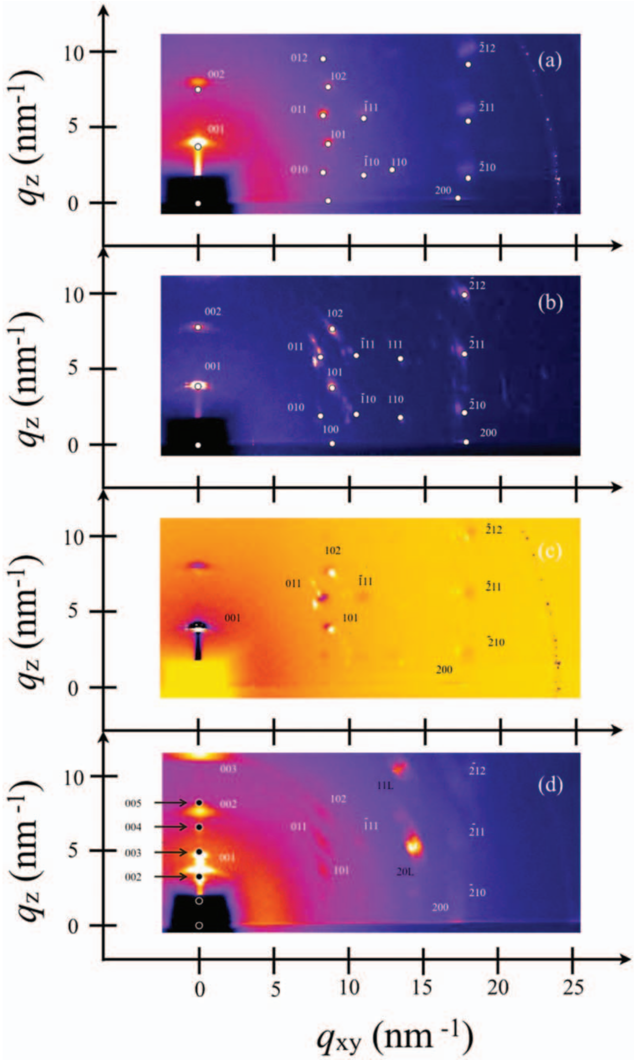

Figure 3. 2D-GIXD patterns of differently prepared TIPS-pentacene films. (a): fabricated by physical vapor deposition at R.T. (VR), (b): drop-casting (DC), (c) difference of (a) and (b), and (d): physical vapor deposition at −166°C (VL).

R.T. under a base pressure of 4×10^{-4} Pa. A deposition rate was 0.01 nm/s and final thickness was 40 nm. DC was fabricated by drop-cast method on SiO_2/Si wafers at R.T. under an air pressure. As-grown film was heated at 170°C after drop-casting to remove the solvent. Monochlorobenzene was used as solvent, and the concentration of solution was 17 mg/ml. VL thin film was vacuum-deposited on SiO_2/Si wafers at −166°C under a base pressure of 2×10^{-4} Pa. The deposition rate was 1 nm/s and final thickness was 50 nm. 2D-GIXD measurements were performed at the BL19B2 in SPring-8 using bright synchrotron radiation with a wavelength of 0.1 nm. Figure 2 shows the schematic illustration of measurement set-up of 2D-GIXD. A high-sensitive two-dimensional X-ray detector (pixel apparatus for the Swiss Light Source: PILATUS) was used and operated in single photo counting mode.

3. Results and Discussion

Figure 3 shows the 2D-GIXD patterns of TIPS-pentacene films of VR, DC and VL. The horizontal and vertical axes in this figure indicate magnitude of scattering vector q in xy and z directions, respectively. A number of diffraction spots are observed for each film, and are indexed as show in the figures. The diffraction spots on the line of $q_{\mathrm{xy}} = 0$ are sorted into $00l$ series, and the interval of the spots correspond to inter-lamella distance $d_{(001)}$. The other spots in the area from $q_{\mathrm{xy}} = 7$ to 20 correspond to diffractions from in-plane structure. From the diffraction patterns, it is obvious that the film is c^*-oriented polycrystalline. The diffraction patterns of VR (Fig. 3(a)) and DC (Fig. 3(b)) show a typical triclinic crystal system, and the crystal structure is confirmed as same as that reported by Anthony *et al.* [2]. Figure 3 (c) depicts the numerical difference of diffraction intensity of Fig. 3 (a) and (b). Slight differences in the position of diffraction spots are clearly observed. This means that the unit cell parameters of VR and DC slightly differ depending on the fabrication methods of the films. The position of 011 spot from DC film shifted toward lower q_{xy} values comparing with that of VR film. While 101 and 102 spots shifted to the opposite direction. These suggest that the inter-planer distance in the crystal structure of DC film spread toward b axis direction, and shrank the distance of a axis. This could be due to the inclusion of solvent molecules into the lattice of TIPS-pentane crystal in the case of solution grows such as DC.

Figure 3(d) shows the 2D-GIXD pattern of VL fabricated at low temperature. In this figure, diffraction spots are distinguished into two groups. Namely, two kinds of polymorphs coexist in VL films. One is the same crystal structure observed in VR and DC films, but the other one is a polymorph that have not seen in the previous reports. The diffraction spots at $q_{\mathrm{z}} = 3$ to 8, $q_{\mathrm{xy}} = 13$ to 14 correspond to the diffraction from new polymorph. The unit cell parameters of $a = 0.88$, $b = 0.56$ and $d_{001} = 3.85$ nm are determined by analyzing the 2D-GIXD patterns. The almost twice value of d_{001} observed in the new polymorph could suggest the existence of dimer structure in periodicity in c axis. In Fig. 4, a predicting dimer structure is presented.

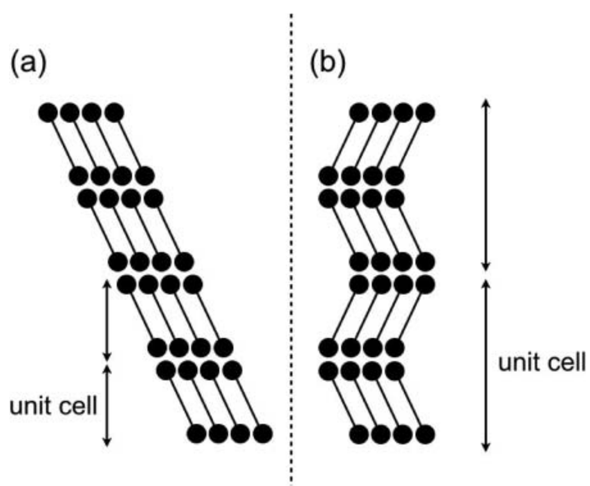

Figure 4. Schematic of crystal structure of predicting (b) dimer structure comparing with (a) monomer structure.

In summary, we report crystal structures of TIPS-pentacene thin films studied by 2D-GIXD. The thin films were fabricated by dry and wet processes, and precisely compared the 2D-GIXD patterns. Slight differences in the position of diffraction spots are found. Furthermore a new polymorph having unit cell parameters of $a = 0.88$, $b = 0.56$ and $d_{001} = 3.85$ nm is identified in a film fabricated at low temperature.

Acknowledgments

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