Crystal Structure at the Initial Growth Stage of Organic Semiconducting Thin Films Studied by GIXD

Recently, organic semiconductors have attracted great attention because of their notable functions as materials used in organic electronic devices such as organic thin-film transistors (OTFTs), solar cells and organic light-emitting diodes (OLEDs). The organic devices have many advantages in terms of a low-cost, low-temperature process, compatibility with flexible substrates, and a large variety of composite materials. A number of novel organic semiconductors have been synthesized, and the performance has continuously progressed. Reported values of the carrier mobility in OTFTs exceed that in amorphous silicon, which is used as the material for TFTs in liquid crystal displays. However, the stability and uniformity of OTFTs require improvements. Control of the crystal growth of semiconducting molecules is an effective method to increase device performance and stability, because the physical properties of organic semiconductors show significant anisotropy. Furthermore, control of the crystallinity of the films is required to decrease their carrier scattering at grain boundaries. Therefore, investigation of the crystal structure of ultrathin films is demanded to improve device performance of OTFTs.

Distyryl-oligothiophenes, one of the organic semiconductors, have been used in OTFTs as a promising material. We have so far demonstrated that the OTFTs based on distyryl-oligothiophenes show remarkable stability in air [1-5], and the high field-effect mobility (up to 0.1 cm/Vs) was unchanged for more than 300 days. However, the details of the film structure have not been investigated. Because the charge carriers move on the interface between the organic semiconductor layer and dielectric surface in the OTFTs, the structure of organic semiconductors at the initial stage of crystal growth is important to understand its remarkable transport properties. In this study, the in-plane structures of ultrathin films based of distyryl-oligothiophenes (Fig. 1) on SiO_2 substrates were investigated by grazing incidence X-ray diffractometry (GIXD). The effects of film thickness and end-cap groups on the in-plane structure were examined.

Distyryl-oligothiophenes were synthesized and sublimated from a k-cell-type crucible onto SiO_2 substrates under a base pressure of 2×10^{-4} Pa. The film thicknesses were 0.2 to 100 nm and were monitored using a quartz crystal microbalance during the deposition process, and calibrated using cross-sectional height profiles, area and coverage of islands observed by atomic force microscopy (AFM) after deposition. Characterization of the films was carried out using multi axes X-ray diffractometer at beamlines **BL13XU** and **BL46XU**. In-plane diffractions were measured at grazing incidence condition.

Figure 2 shows AFM images of deposited films of distyryl-oligothiophenes. The size and number density of the islands changed with the nature of the end-cap groups. The number density of the islands increases with increasing volume of the end-cap group. This is due to the fact that the frequency of nucleation on the substrate depends on the surface energy of clusters, which decreases with the packing density of molecules in the crystals. The decrease in the number density of nuclei causes the increase in the grain size in thick films. The X-ray diffraction patterns in the conventional $\theta/2\theta$ mode of DS-4T, DFS-4T and Py-4T deposited on SiO_2 substrates with the film thickness of 100 nm show that the *ab*-planes of the grains orient parallel to the substrate surfaces. The obtained d_{001} spacings of DS-4T, DFS-4T and Py-4T were 2.802, 3.220 and 3.110 nm, respectively, which are comparable to their molecular lengths. Figure 3 shows the thickness dependence of the in-plane GIXD patterns of thin films of distyryl-oligothiophenes. Depending on the thickness, slight peak shifts are observed in 020 of DS-4T and 110 of DFS-4T. The peak shift of 020 of DS-4T is due to the occurrence of another polymorph with increasing thickness. As to the slight peak shift observed in 110 of DFS-4T, it could be due to changes in the molecular packing between ultrathin films and thicker ones.

From the GIXD data, it is clarified that the volume of end-cap groups causes the decrease in crystallinity in this series of compounds. This could be due to the decrease in the molecular interaction caused by the steric hindrance. Because a smaller molecular interaction results in a smaller surface energy of the

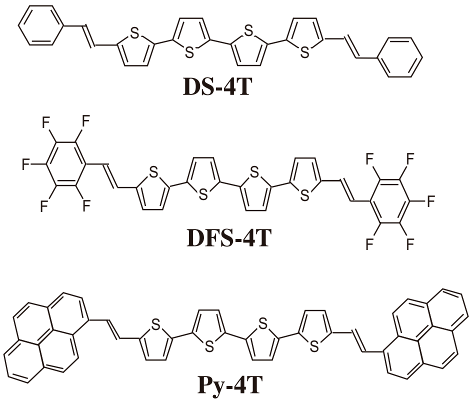

Fig.1. Molecular structures of end-capped oligothiophenes DS-4T, DFS-4T and Py-4T.

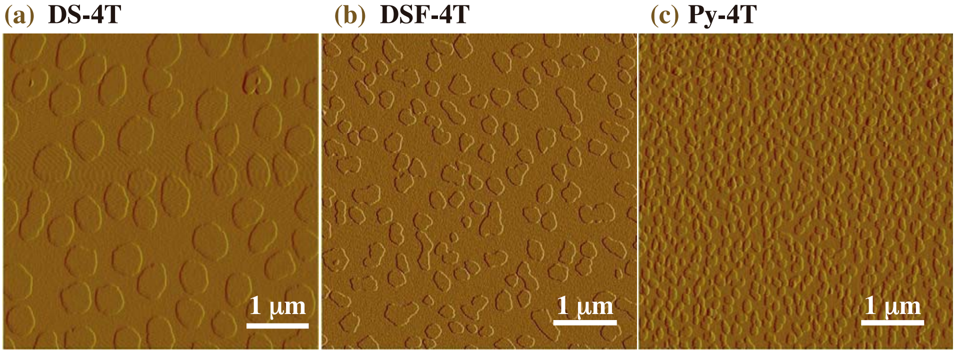

Fig. 2. AFM images of ultrathin films DS-4T, DFS-4T and Py-4T. The average thickness was 1 nm and the islands were composed of monolayers.

nuclei during the crystal growth, the difference in the number density of the island shown in Fig. 2 can be attributed to the difference in the molecular packing. This difference could be related to the transport properties in OTFTs. Since the π-orbital in the molecules extends to the *ab*-axis direction, the difference in the area of the *ab*-plane should be essential to the difference in the charge mobility among the derivatives. The area of the *ab*-plane of DS-4T is smaller than that of DFS-4T. Therefore, introducing end-cap groups with increasing volume into oligothiophene molecules seems to result in the decrease in grain size and the decrease in the conductivities in each grain.

The present results have proved that GIXD is an effective tool for characterizing the crystal structure of organic ultrathin films for OTFTs with the thickness covering 0.2 ~ 100 nm.

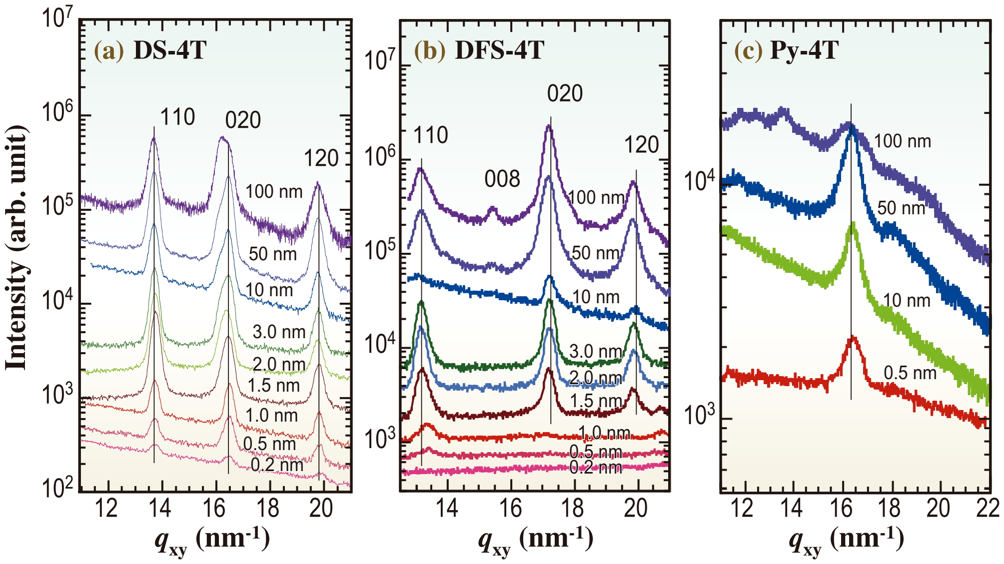

Fig. 3. Thickness dependence of in-plane GIXD patterns of DS-4T, DFS-4T and Py-4T films deposited on SiO_2.

Noriyuki Yoshimoto

Department of Materials Science and Engineering,
Iwate University

E-mail: yoshimoto@iwate-u.ac.jp

References

[1] C. Videlot-Ackermann *et al.*: J. Am. Chem. Soc. **127** (2005) 16346.
[2] C. Videlot-Ackermann *et al.*: Organic Electronics **7** (2006) 465.
[3] Y. Didane *et al.*: J. Am. Chem. Soc. **103** (2008) 17681.
[4] N. Yoshimoto *et al.*: Cryst. Res. Tech. **42** (2007) 1228.
[5] *N. Yoshimoto, W.Y. Li, K. Omote, J. Ackermann, C. Videlot-Ackermann, H. Brisset and F. Fages: J. Phys.: Conf. Ser.* ***83*** *(2007) 012026.*