

Analysis of Interfacial Nanostructure of Organic Nanoelectronics Materials

The molecular aggregation structure of organic thin films has received much attention because of their applications to various electronic devices such as light-emitting diodes, field-effect transistors (FET) and photovoltaic cells. A central concern with respect to the performance of organic electronic devices such as FET is that their switching speed is generally too low owing to the low mobility of the charge carriers. One of the factors influencing the magnitude of carrier mobility may be the surface and interfacial molecular aggregation structures of the organic thin films. Grazing incidence X-ray diffraction (GIXD) using evanescent X-rays is an excellent method for characterizing the surface and interfacial molecular aggregation structures of organic polymer thin films [1,2]. In this study, the surface nanostructure of poly(3-hexylthiophene) (P3HT) and pentacene thin films was investigated by means of GIXD.

Pentacene and P3HT were used as samples in this study. GIXD measurements were carried out at beamline **BL13XU**. When the incident angle to the surface of a sample (α_i) is below the critical angle (α_c) in the GIXD measurements, X-rays undergo total external reflection and penetrate into the sample as evanescent waves. Under this condition, diffractions

from the ultrathin films are sufficiently strong in intensity to be detected as peaks. The GIXD measurements of pentacene and P3HT thin films were carried out at a α_i smaller than the value of α_c . Bragg diffractions from the crystallographic planes normal to the sample surface were measured in the in-plane direction by a scintillation counter. The scattering vector parallel to the sample surface is defined as $q_{xy} (= 2\pi/d = 4\pi \sin\theta/\lambda)$ where d , θ , and λ are the d -spacing, the Bragg angle, and the wavelength of incident X-rays, respectively.

In order to develop polymer semiconductors, the crystal structure of polyalkylthiophene has been studied extensively. P3HT thin films prepared on Si substrates by spin-coating and a P3HT powder sample were annealed at 473 K for 30 min. **Figure 1** shows the $2\theta/\theta$ symmetric reflection and in-plane GIXD profiles of the annealed P3HT films, and a powder diffraction profile of the annealed P3HT. On each profile for the films and the powder sample, the effect of annealing was apparent due to sharpening of the diffraction peaks, the appearance of higher order peaks and a decrease in intensity of the amorphous scattering. The powder diffraction profile showed the (100) reflection and its higher order reflections corresponding to the side-chain lamellar stacking distance ($d_{110} = 1.60$ nm) as well as the (010) reflection ($d_{010} = 0.38$ nm) corresponding to the π - π stacking of the thiophene ring in the main chain. In the symmetric reflection profile, the relative intensity of the (100) reflection and its higher order reflections up to the

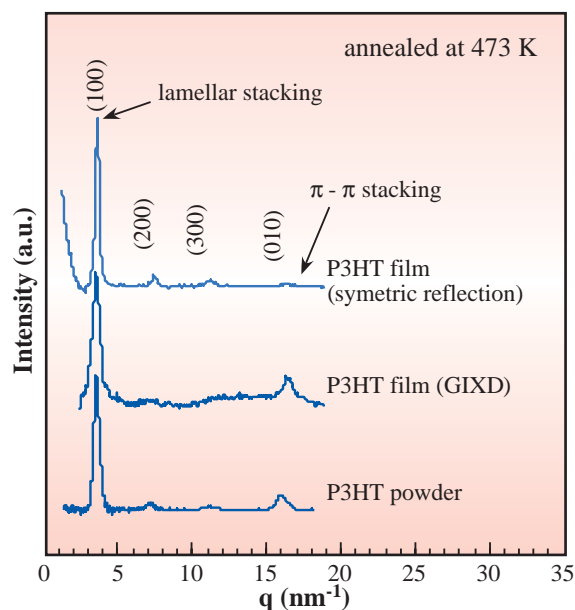


Fig. 1. $2\theta/\theta$ symmetric reflection and in-plane grazing incidence X-ray diffraction (GIXD) profiles of the annealed poly(3-hexylthiophene) (P3HT) films, and a powder diffraction profile of the annealed P3HT.

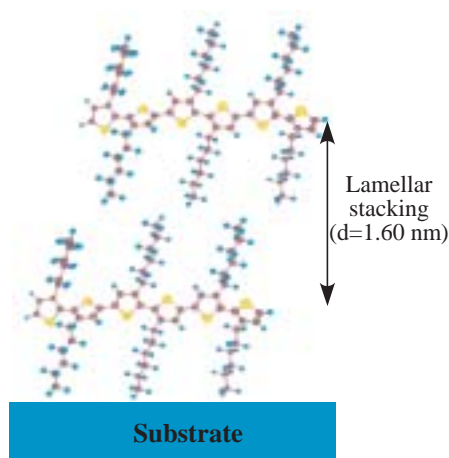


Fig. 2. Schematic representation of the chain orientation in P3HT film.

(010) reflection was very strong. This result indicated that the main chains had a tendency to orient parallel to the film surface (Fig. 2). On the other hand, the in-plane GIXD profile exhibited the (010) reflection corresponding to the π - π stacking of the thiophene ring, as well as the (100) reflection. A comparison between the symmetric reflection and GIXD profiles revealed that the degree of side-chain lamellar orientation was relatively low in the near-surface region. The control of orientation of the conjugated lamellae is expected to control the anisotropic carrier mobility.

Pentacene is a candidate molecule for the semiconducting layer in organic FET. Since pentacene is not soluble in a conventional organic solvent, most thin films of pentacene have been prepared by vapor phase deposition or molecular beam deposition. Breem *et al.* reported that the introduction of the polar group to pentacene by a Diels-Alder reaction (Fig. 3) enhanced the solubility of pentacene in organic solvents [3]. In this study, the thus-prepared pentacene precursor was spin-coated onto Si substrates and annealed at 453 K for 60 min. The powder diffraction profile for the precursor changed under annealing, due to the elimination of N-sulfinylacetamide from the precursor by a retro Diels-Alder reaction. Annealing treatment for the spin-coated films of the precursor also yielded crystalline thin films of pentacene. Figure 4 shows the $2\theta/\theta$ symmetric reflection and GIXD profiles of pentacene thin films, and a powder diffraction profile of pentacene prepared using a soluble pentacene precursor. The (00 l) reflections were only observed in the symmetric

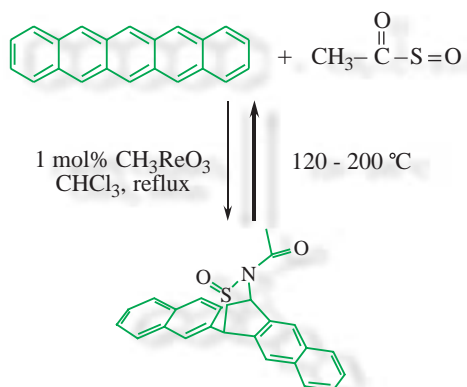


Fig. 3. Diels-Alder and retro Diels-Alder reactions of pentacene. Pentacene was reacted with excess N-sulfinylacetamide in the presence of a catalytic amount of methyltrioxorhenium to give the Diels-Alder adducts (pentacene precursor). The Diels-Alder adducts then undergoes a retro-Diels Alder reaction starting at 398 K to yield pentacene.

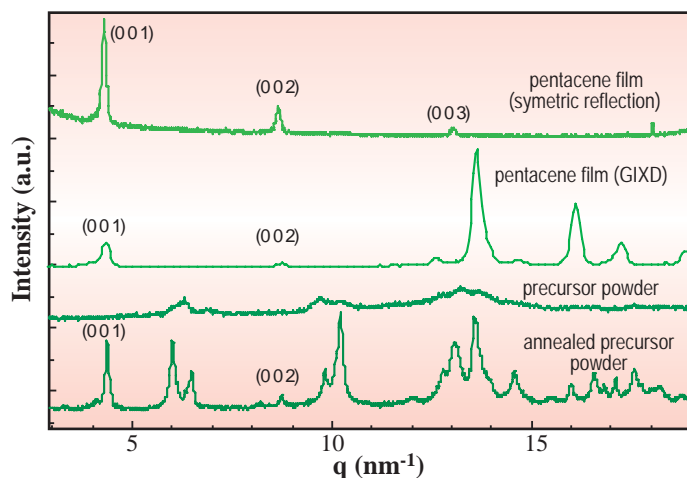


Fig. 4. $2\theta/\theta$ symmetric reflection and in-plane grazing incidence X-ray diffraction (GIXD) profiles of the pentacene films, and powder diffraction profiles of the pentacene precursor and pentacene. Pentacene was prepared from the pentacene precursor through retro Diels-Alder reaction.

reflection profile. This indicates the possibility of a perpendicular orientation of the c axis to the film surface. Also, the GIXD profile showed a strong diffraction that would relate to regular interchain packing between the aromatic rings in the in-plane direction. These results suggest that the pentacene molecules were oriented almost perpendicular to the film surface.

In this study, it was revealed that the synchrotron-sourced GIXD measurement is a powerful method for characterizing the state of molecular orientation in organic electronics materials. Further study is now in progress in order to clarify the relationships between semiconductor performance and molecular aggregation states at the surfaces and interfaces.

Atsushi Takahara^a, Masamichi Morita^b and Sono Sasaki^{b,c}

(a) Institute for Materials Chemistry and Engineering, Kyushu University

(b) Graduate School of Engineering, Kyushu University

(c) Present address: SPring-8/JASRI

E-mail: takahara@cstf.kyushu-u.ac.jp

References

- [1] T. Koga, M. Morita, H. Ishida, H. Yakabe, S. Sasaki, O. Sakata and A. Takahara: *Trans. Mater. Res. Soc. Jpn.* **28** (2003) 85.
- [2] H. Yakabe *et al.*: *Macromolecules* **36** (2003) 5905.
- [3] A. Afzail *et al.*: *J. Am. Chem. Soc.* **124** (2002) 8812.