Polymorphism in pentacene thin films on SiO₂ substrate

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The polymorphism of pentacene thin films on SiO₂ substrate was investigated by grazing incidence x-ray diffractometry (GIXD). The in-plane GIXD patterns were obtained from vacuum deposited ultrathin films. By comparing the in-plane structures with thicker films, it was elucidated that ultrathin films have the same lattice constants as that of films of 100 nm thick. Consistency of determined interplanar d_{11} spacings of the two polymorphs suggests the epitaxial growth that bulk phase grows onto thin-film phase. Considering the obtained unit cell parameters, the mechanism of the transformation between polymorphs was discussed in terms of equilibrium shapes during nucleation process. © 2007 American Institute of Physics. [DOI: 10.1063/1.2709516]

In recent years, organic thin-film transistors (OTFTs) have attracted great attention, and their performance has continually improved.^{1,2} OTFTs have many advantages in terms of a low-cost, low-temperature process, compatibility with flexible substrates, and a large variety of composite materials. Pentacene is a representative organic semiconductor that shows promise for use in OTFTs.²⁻⁸ At least four different polymorphic modifications of pentacene have been identified so far, which are characterized by interplanar d_{001} spacings of 1.41, 1.45, 1.51, and 1.54 nm.⁹⁻¹¹ The vacuum deposition process generally yields two of the polymorphs, a thin-film phase and a bulk phase, in vapor-deposited thin films.^{10,11} Although the bulk phase is supposed to be the stable phase at around room temperature,⁹ generally the thin-film phase preferentially occurs in vapor-deposited process. The appearance of polymorphs depends on the growth conditions such as substrate temperature and film thickness.¹²⁻¹⁴ Because carrier transport properties of organic thin films depend on π -orbital overlap that is sensitive to the molecular packing in the crystal, difference in polymorphs brings different conducting properties.^{15,16} Therefore, investigation and control of the polymorphism and film structures are demanded to improve device performance of OTFTs. Several studies on the structure and the growth mechanism of pentacene films have been carried out;¹⁷⁻²⁴ however, the mechanism of the transformation from the thin-film phase to the bulk phase is not fully clarified.

In this study, the structure and polymorphism of pentacene thin films on SiO₂ substrates were investigated by grazing incidence x-ray diffractometry (GIXD). Two-dimensional lattice constants of the polymorphs were determined from observed GIXD patterns, and the consistency of determined interplanar d_{11} spacings of the polymorphs was found. Furthermore, the equilibrium shapes were deduced from the lattice constants and reported surface energy values.^{25,26} Finally, the mechanism of the transformation between the polymorphs of pentacene was discussed using the classical nucleation theory.

Pentacene powder (98%, Tokyo Kasei Co.) was sublimated from *K*-cell-type crucible. The substrates used were silicon wafers having a 300 nm insulating layer of thermally grown silicon dioxide on the top. The substrate temperatures (T_s) and the deposition rate were 20 or 50 °C and 0.01 nm/s, respectively. Final film thicknesses and the base pressure were 0.6–100 nm and 1×10^{-4} Pa, respectively. Final thicknesses were monitored by a quartz crystal microbalance during the deposition process and calibrated by cross-sectional height profiles, area, and coverage of pentacene islands observed by using atomic force microscopy after deposition. Hereafter, we will describe the film thicknesses as the mean thickness value. To examine the thermodynamical stability of the polymorphs, the deposited thin films were thermally treated at 100 °C for 24 h under a pressure of 1×10^{-4} Pa. Characterization of the films was performed by using x-ray diffractometers (Rigaku Co., ATX-G and synchrotron radiation at the BL13XU ATX-GSOR in SPring-8), which were specially designed for

FIG. 1. Temperature and thickness dependence of $\theta/2\theta$ mode x-ray diffraction patterns of deposited pentacene films on SiO₂ substrates. Substrate temperature (a) $T_s=20$ °C and (b) $T_s=50$ °C. The indices $(00l)_T$ and $(00l)_B$ denote the reflections from thin-film and bulk phases, respectively.

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FIG. 2. Temperature and thickness dependence of in-plane GIXD patterns of deposited pentacene films on SiO₂ substrates. Substrate temperature (a) $T_s=20\text{ }^{\circ}\text{C}$ and (b) $T_s=50\text{ }^{\circ}\text{C}$.

characterization of thin films. Both in-plane and out-of-plane diffractions could be measured, because the goniometers have not only conventional $\omega/2\theta$ axes but also in-plane $\phi/2\theta\chi$ axes.

Figure 1 shows the x-ray diffraction patterns in conventional $\theta/2\theta$ mode of pentacene films deposited on SiO₂ substrates. By comparison with crystal structures reported in the literature,^{10,11} the peaks observed in Fig. 1 can be indexed as (001) and higher orders of the bulk and thin-film phases. This means that the (001) planes of the grains of pentacene polymorphs orient parallel to the substrate surfaces. In terms of polymorphism, the ratio of the two phases changed with substrate temperature and film thickness. At $T_s=20\text{ }^{\circ}\text{C}$, the thin-film phase occurred preferentially, and the proportion of the bulk phase increased with increasing thickness to 100 nm. The thicknesses that the bulk phase appeared were 50 nm thick at 20 °C, but it decreased to 10 nm with increasing temperature to 50 °C.

Figure 2 shows in-plane GIXD patterns of the pentacene thin films. The peaks observed in Fig. 2 can be indexed as shown in the figure. As to the polymorphism, the same tendency as shown in Fig. 1 was observed. Namely, the thin-film phase occurred preferentially, and the proportion of the bulk phase increased with increasing temperature and thickness. Furthermore, it is worth noting that ultrathin films of 0.6 nm thick have the same two-dimensional lattice constants as that of films of 100 nm thick. The obtained values of two-dimensional lattice constants of the thin-film phase and the bulk phase were summarized in Table I with the comparable reported values.^{10,11,17,18} The d_{11} lattice spacing of the bulk phase is well consistent with that of the thin-film

TABLE I. Two-dimensional lattice constants obtained from in-plane GIXD patterns with that of reported in the literature.

		a (nm)	b (nm)	γ (deg)	d_{11} (nm)
Thin-film phase	This work	0.754	0.594	89.5	0.465
	Ref. 11	0.76	0.61	89.5	
	Ref. 17	0.759	0.592	89.95	
Bulk phase	This work	0.780	0.609	85.8	0.463
	Ref. 10	0.79	0.606	85.8	
	Ref. 18	0.79	0.608	85.7

FIG. 3. Schematic illustration of the lattice spacing d_{11} of polymorphs. (a) The thin-film phase and (b) the bulk phase.

phase. From this consistency, the possibility of an epitaxial growth that the bulk phase grows onto the thin-film phase can be suggested. The d_{11} lattice spacing of polymorphs is shown in Fig. 3, with one of the benzene rings in pentacene molecules depicted as black circles within the two-dimensional lattice on the a - b plane, shown by quadrangles divided by straight lines. The positions of pentacene molecules in the unit cell of the thin-film phase were speculated from that of the bulk phase.

To explain the mechanism of the thickness-dependent transformation from the thin-film phase to the bulk phase, we examined the thermodynamical stabilities for the polymorphs at room temperature. The area of (001) and the unit cell volume of the thin-film phase and that of the bulk phase were summarized in Table II. The density of the bulk phase is estimated slightly higher than that of the thin-film phase, which was deduced from the unit cell volumes. Thus, the bulk phase should be the more stable phase at lower temperatures, because generally the enthalpy term in Gibbs's free energy is favorable for the polymorphs having high density.²⁵ Figure 4 shows x-ray diffraction pattern of $\theta/2\theta$ mode of as-deposited pentacene films compared with a film annealed at 100 °C for 24 h. The ratio of the thin-film phase to the bulk phase reduced after thermal treatment. This indicates that the bulk phase is more stable in comparison with the thin-film phase. Furthermore, to explain the polymorphism, the crystallographic equilibrium shapes for each polymorph were examined. If the number of molecules in a unit cell is the same for both polymorphs, the surface density in (001) of the thin-film phase should be 6% higher than that of the bulk phase, because the two dimensional unit cell of the thin-film phase is smaller than the bulk phase, as shown in Table II. On the other hand, the surface density of lateral planes of the bulk phase is higher than that of the thin-film phase. Hence, the equilibrium shape of thin-film phase should be more anisotropic in comparison with the bulk phase, as shown in Fig. 5, because the surface energy of the (001) plane has the lowest value than any other planes.^{26,27}

TABLE II. Area of (001) and the unit cell volume of the thin-film phase and that of the bulk phase obtained from the XRD data.

	Area of the a - b plane (nm ²)	d_{001} (nm)	Volume of the unit cell (nm ³)
Thin-film phase	0.448	1.54	0.690
Bulk phase	0.474	1.45	0.687

FIG. 4. Effects of thermal treatment on $\theta/2\theta$ mode x-ray diffraction patterns of pentacene thin films on SiO_2 substrates. The dashed line and solid line denote the data of as-deposited pentacene film and the annealed film, respectively.

The activation energy for heterogeneous nucleation on substrates (ΔG^*) can be expressed as

$$\Delta G^* = \frac{f\gamma_c^2\Delta\gamma\nu^2}{\Delta\mu^2}, \quad (1)$$

where f , γ_c , ν , and $\Delta\mu$ are geometrical factors of the nucleus, the surface free energy, molecular volume of nucleus, and the difference in chemical potential between the crystal and gas phase, respectively.²⁸ $\Delta\gamma$ is the difference in surface energy by the contribution of interface, which is expressed as

$$\Delta\gamma = \gamma_c + \gamma_i - \gamma_s, \quad (2)$$

where γ_i and γ_s are the interface energy and surface free energy of the substrate, respectively. During the heterogeneous nucleation process, the thin-film phase can preferentially nucleate assisted by advantages in the favorable equilibrium shape through surface energy term. Once the bulk phase nucleates onto the thin-film phase, then the growth of the bulk phase becomes more dominant. The consistency of d_{11} spacings facilitates the nucleation of the bulk phase when the bulk phase grows epitaxial on the thin-film phase.

In summary, the polymorphism of pentacene thin films on SiO_2 substrate depends on film thickness and substrate temperature was investigated by GIXD. It was clarified that ultrathin films have the same lattice constants as that of films

FIG. 5. Schematic illustration of the deduced equilibrium shape and the unit cell of pentacene polymorphs.

of 100 nm thick. The two-dimensional lattice constants of the polymorphs were determined from observed GIXD patterns. Considering the obtained lattice constants, we could explain the mechanism of the transformation using the classical nucleation theory.

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