Analysis of Molecular Aggregation States in Pentacene Thin Films Prepared from Soluble Precursor

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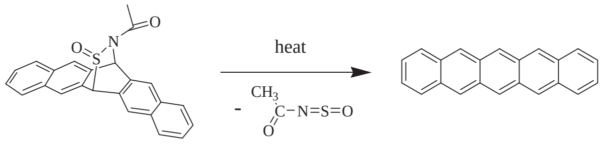
Molecular packing structure in pentacene films prepared from the Afzali's precursor soluble in general organic solvents was characterized by in-plane grazing-incidence X-ray diffraction (GIXD) measurements. The crystallographic *ab* plane of pentacene was parallel to the surface of a Si substrate. Crystal structure of pentacene near the substrate was identified as the thin-film phase.

Past decade, the research of organic semiconductors has become very popular. The printing of organic semiconductor-inks can realize low-cost fabrication.[1] However, most of soluble organic semiconductor shows low-semiconducting properties. On the other hand, some of insoluble organic semiconductors show high-semiconducting properties. Especially, pentacene films show semiconducting properties as high as amorphous silicon, reproducibly.[2]

Recently, the method using the pentacene precursor is examined as the strategy which realizes solubility and high mobility. In 1999, Müllen and Herwig reported a soluble pentacene precursor which has tetrabromobenzene moiety as a leaving group.[3] In 2002, Afzali et al. reported a convenient manufacturing method of the soluble pentacene precursor which has *N*-sulfinylacetamide moiety as a leaving group through retro Diels–Alder reaction.[4] The Afzali's precursor is soluble in chloroform, dichloromethane, THF, and dioxane, and it transforms to pentacene by heating at 393–473 K under nitrogen atmosphere (Scheme 1). In addition, it was reported that pentacene precursors which can be soluble in alcohols and be patterned by UV light were synthesized with the other types of *N*-sulfinylalkylamides.[5,6] Although crystal structure in the film sate is very important for semiconductor performance, molecular aggregation structure of pentacene has not been revealed yet for its films prepared from these soluble precursors. Grazing incidence X-ray diffraction (GIXD) measurement is a powerful technique to investigate molecular packing structure in the near-surface region of organic materials.[7,8] In this paper, the authors investigated molecular packing structure and morphology of pentacene films prepared from the Afzali's soluble precursor by using GIXD measurements and field emission scanning electron microscopic (FE-SEM) observation, respectively.



Scheme 1.

A precursor of pentacene was synthesized as reported by Afzali et al.[4] The obtained precursor was dissolved in chloroform and spin-coated on Si substrates at 2000 rpm. The precursor was converted to pentacene in the film state with heating at 423 K for 30 min under nitrogen atmosphere. Bulk structure was investigated for powder samples by wide-angle X-ray diffraction (WAXD) measurements with a large Debye–Scherrer camera and an imaging plate detector at BL02B2 beamline of JASRI/SPring-8. The wavelength, λ, of incident X-rays was 0.100 nm, and exposure time was 300 s. In order to investigate molecular packing state in the parallel direction to the substrate surface, in-plane GIXD measurements were carried out for films with a six-axis diffractometer and a scintillation detector at BL13XU beamline of JASRI/SPring-8. The λ of incident X-rays was 0.128 nm. The incident angle of the X-rays to the sample surface was 0.1 deg which was lower than the critical angle of the samples and Si substrate.

Figure 1 shows WAXD profiles for bulk samples of a pentacene precursor and pentacene obtained by completion of retro Diels–Alder reaction for the precursor. The magnitude of scattering vector q is defined as $q = 4\pi \sin\theta/\lambda$, where θ is Bragg angle. Weak reflections from the precursor which was not detected with laboratory instruments were detected in excellent S/N ratio by synchrotron WAXD measurements. With increasing in temperature, reflections from the precursor crystal decreased in intensity, and those from pentacene crystal increased because of elimination of *N*-sulfinylacetamide from the precusors by retro Diels–Alder reaction. Crystal structure of pentacence precursor was difficult to obtain owing to difficulty in preparation of a large single crystal and low stability. According to ref 9, some distinct diffraction peaks observed for pentacene at $q < 10\,\text{nm}^{-1}$

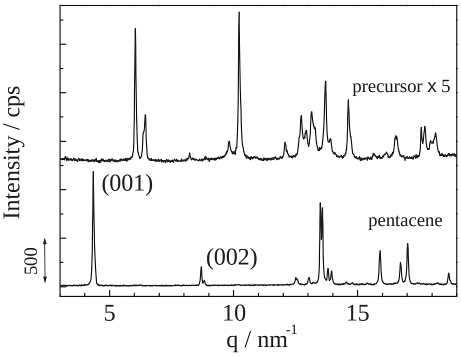


Figure 1. WAXD profiles measured for powder samples of a pentacene precursor (top) and pentacene (bottom) obtained by completion of retro Diels–Alder reaction for the precursor.

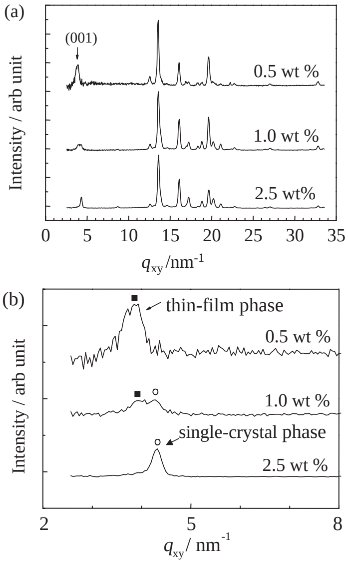


Figure 2. (a) In-plane GIXD profiles of pentacene films prepared from precursor. Precursor films were spin-coated from 0.5, 1.0, and 2.5 wt % chloroform solutions at 2000 rpm for 30 s. Figure 2b is enlarged view of Figure 2a ($2\,\mathrm{nm}^{-1} < q < 8\,\mathrm{nm}^{-1}$).

and at $q > 13\,\mathrm{nm}^{-1}$ corresponded to the (001) and (002) reflections and the reflections from the π–π stacking structure of fused aromatic rings of single-crystal phase, respectively.

Figure 2a shows in-plane GIXD profiles of the pentacene films transformed by heating from spin-coated films with 0.5, 1.0, and 2.5 wt % chloroform solutions of the precursor. The magnitude of in-plane component of scattering vector is defined as q_{xy}. In comparison with the WAXD profile of the pentacene powder, the reflections corresponding to the intermolecular distance of fused aromatic rings showed relatively strong intensity against the (001) reflection in these GIXD profiles for the pentacene films. This result suggested that the crystallographic *ab* plane of pentacene in the film was parallel to the substrate surface and that *c* axis was slightly tilted from the surface normal as reported for the thin films of pentacene.[9] Figure 2b shows in-plane GIXD profiles for the pentacene films in a range of ca. $2.0 < q_{xy} < 8.0\,\mathrm{nm}^{-1}$ of Figure 2a. The (001) reflection shifted to the lower q range with decreasing in concentration of the precursor in chloroform solutions. GIXD profiles revealed a presence of two phases, which are single-crystal and thin-film phases. Single-crystal phase, where peak is observed at $q =$ ca. $4.3\,\mathrm{nm}^{-1}$, is a thermodynamically stable polymorph (white circle). Thin-film phase, where peak is observed at $q =$ ca. $4.0\,\mathrm{nm}^{-1}$, is a metastable polymorph (black square), as already reported in vacuum deposition process.[10] It is known that thin-film phase is stable near the substrate in vacuum deposited pentacene. On the basis of the relative intensity of these two phases in in-plane GIXD profiles, it can be concluded that the fraction of single-crystal phase increased with concentration of precursor solution.

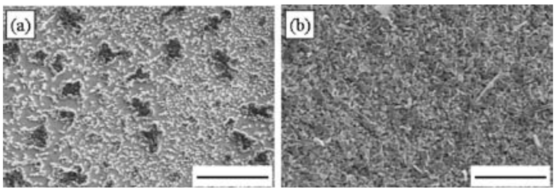


Figure 3. FE-SEM images of pentacene films prepared from precursor. Precursor films were spin-coated from (a) 1.0 and (b) 2.5 wt % chloroform solutions at 2000 rpm 30 s. The length of scale bar is 10 μm.

In order to examine the morphology of the films, FE-SEM observation was carried out. FE-SEM images of pentacene films prepared from 1.0 and 2.5 wt % chloroform solutions are shown in Figure 3. The film both consisting of the thin-film phase and the single-crystal phase shows isolated submicrometer-sized grains and some aggregated grains (dark part) (Figure 3a). The film consisting of only the single-crystal phase shows an aggregate of submicrometer-sized grains (Figure 3b). These results suggested that pentacene crystal near the Si-wafer substrate interface grew as the thin-film phase. The absence of thin-film phase in the GIXD profile of the film prepared from 2.5 wt % solution suggested that the pentacene single-crystal phase was grown on the thin-film phase. This result in precursor method is almost similar to the previous report in vacuum deposition process.[11]

In summary, crystal structure of pentacene films prepared from soluble precursor was characterized by in-plane GIXD. The *ab* plane of these films was parallel to the Si-wafer substrate. The structure of crystalline state near the substrate was identified as the thin-film phase.

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