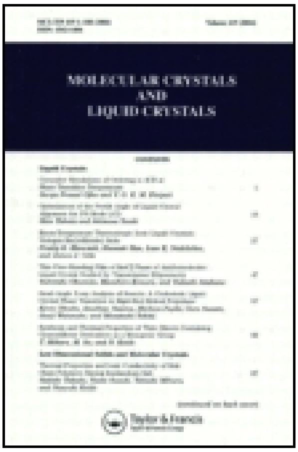

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In Situ Real-Time X-Ray Diffraction During Thin Film Growth of Pentacene

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In Situ Real-Time X-Ray Diffraction During Thin Film Growth of Pentacene

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In situ *and real-time observation of 2-dimensional grazing incidence x-ray diffraction (2D-GIXD) during growth of pentacene thin films were carried out using a newly home-built portable vacuum deposition chamber using synchrotron radiation at SPring-8. Crystal growth and successive polymorphic transformation from thin film phase to bulk phase are clearly observed at room temperature and 75°C. A distinct orientation of bulk phase characterized by tilted (001) plane is found in the grown thin films at room temperature.*

Keywords X-ray diffraction; Thin film growth; Organic semiconductor; Structural analysis; 2D-GIXD

Introduction

Observation of crystal structures at initial growth stage of organic thin films gives us valuable information about the mechanism of crystal growth of organic molecules on substrates. Because crystal structures affect the charge transport properties in organic devices such as organic thin-film transistors, control of crystal growth at the initial stage is necessary for the progress of device performances. We have so far studied the initial growth stage of organic thin film by using grazing incidence x-ray diffraction (GIXD) using synchrotron radiation at SPring-8 [1]. According to the recent progress in a high-sensitive two-dimensional x-ray detector (pixel apparatus for the Swiss Light Source: PILATUS), real-time study on growth of organic thin films by means of 2-dimensional GIXD (2D-GIXD) measurements has become realistic.

Pentacene is a representative organic semiconductor that shows high field effect mobility. A lot of studies have been done on the thin film growth and structural analysis of pentacene thin-films. Meyer zu Heringdorf et al. have observed thin film growth of pentacene by real-time imaging of photoelectron emission microscopy [2]. Ruiz *et al*. have reported about the growth mechanism with experimental data of atomic force microscopy and X-ray reflectivity [3]. However, there have been a limited number of reports that

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mention the in-plane microstructures in pentacene thin films, even though they must be important for carrier transport in a TFT. Recently, Kim et al. reported thin film structure of pentacene measured by means of 2D-GIXD [4], and Guo et al. reported temperature dependence of the growth of pentacene thin films investigated with GIXD [5]. However, *in situ* and real-time measurements for the growth of pentacene thin films using 2D-GIXD have not been reported.

In this paper, we report the first demonstration of *in situ* and real-time 2D-GIXD measurements during the growth of pentacene thin films using a home-build deposition chamber combined with PILATUS detector.

Experimental

Pentacene (Sigma Aldrich, triple-sublimed grade 99.995% purity) was deposited on silicon wafer coated with native oxide (SiO_2) under high vacuum conditions of 2×10^{-4} Pa. The substrate temperature (T_s) during deposition was room temperature (R.T.) or 75°C. The growth rate of 0.01∼0.1 nm/s was monitored by a quartz crystal microbalance (QCM). 2D-GIXD measurements were carried out at the BL19B2 in SPring-8. The used growth chamber and measurement set-up are schematically shown in Figure 1(a) and (b). X-ray beam irradiates on the substrate surface with a grazing angle of 0.12°, which is less than the critical angle of total external reflection of the substrate. The diffracted x-ray from the sample surface was detected by PILATUS 100K. PILATUS detector is capable of providing a large reciprocal space mapping data with very short reading time. During the real-time measurements the positions of the sample and detector have been fixed, and the x-ray exposure and the deposition of molecules were continuously performed. Integration time for photon counting on the x-ray detector was 30 sec for each image, and the total number of the acquired images was 150 frames for each measurement.

Results and Discussion

Figures 2 (a), (b) and (c) show the 2D-GIXD patterns of pentacene films grown at R.T. The figures are selected from the series of the collected images of *in situ* and real-time 2D-GIXD measurements. The background signal of the detector has been subtracted by using the image data from bare substrate. At the beginning of deposition (Fig. 2(a)), 001 and 002 diffractions are observed along q_z axis, and 11L, 02L and 12L diffraction streaks in the in-plane direction are also observed. Each diffraction spot of the 2D-GIXD diffractions

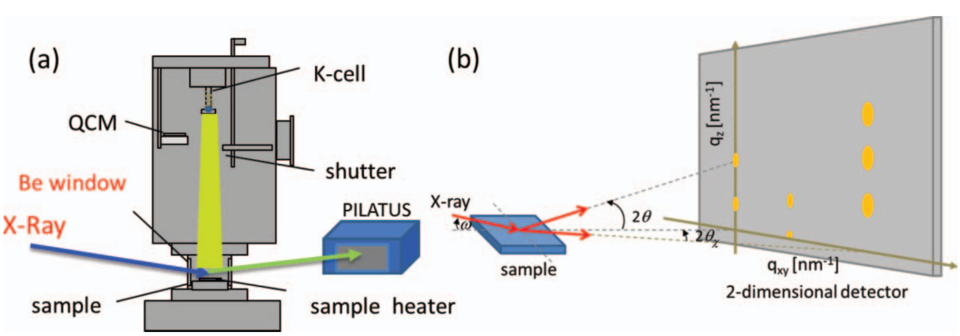

Figure 1. (a) A sketch of home-built vacuum deposition chamber equipped with beryllium windows. (b) Geometry of the 2D-GIXD measurements.

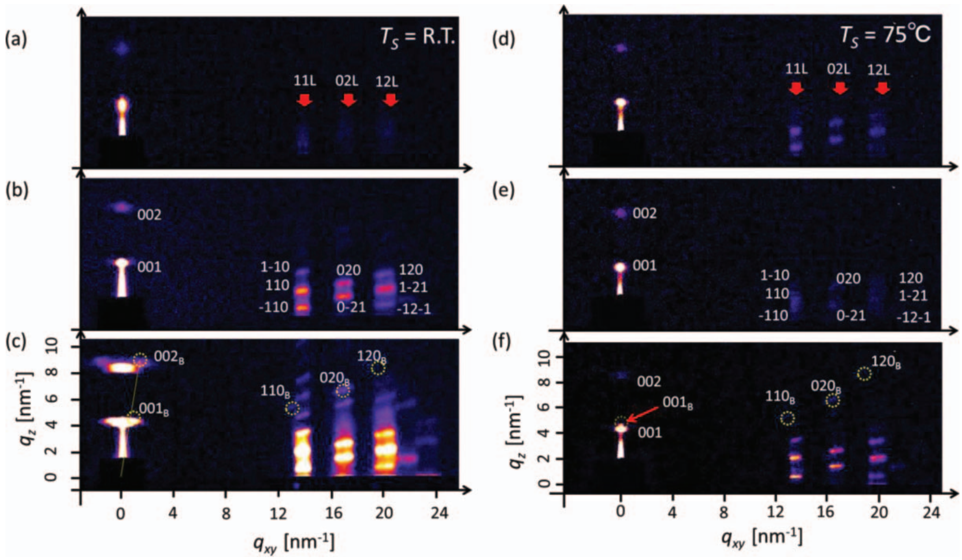

Figure 2. 2D-GIXD patterns of vacuum-deposited thin-film of pentacene on SiO_2 fabricated at T_s = R.T: (a)-(c), and at T_s = 75°C: (d)-(f). The thickness is, (a): 1.0 nm, (b): 2.0 nm and (c): 10 nm at T_s = R.T., and (d):1.0 nm, (e): 2.0 nm and (f): 10 nm at T_s = 75°C.

observed in the experiments were indexed by simulating the diffraction patterns using the crystal structural data of thin film phase and bulk phase reported by Yoshida *et al.* [6, 7]. With increasing film thickness to 2.0 nm, the in-plane diffraction streaks changed to spot-like shape as shown in Fig. 2(b). These results imply the changed in the growth mechanism of pentacene thin films from layer growth to 3D island growth. The 2D-GIXD pattern shown in Fig. 2(b) indicates the formation of thin film phase as Yoshida et al. reported previously [7]. As shown in Fig. 2(c), intensity of diffraction spots of thin film phase increased with increasing thickness to 10 nm, and other diffraction spots appeared simultaneously as marked by broken circles in the figure. The appeared spots are assigned to bulk phase structure [6]. It is worth noting that a series of 00*L* diffractions of bulk-phase denoting "$(00L)_B$" in Fig. 2(c) appeared not on the q_z axis but on a distinct scattering vector indicated by the yellow broken line in the figure. This indicates that (001) plane of bulk phase is tilted from the substrate surface with a certain angle.

Fig. 2 (d), (e) and (f) show the *in situ* and real-time 2D-GIXD patterns of the pentacene films grown at 75°C, and the nominal thickness was 1.0, 2.0 and 10 nm, respectively. The same tendency in growth was observed compared with that grown at R.T. Namely, thin film phase occurred in the beginning and subsequently bulk phase appeared with increasing thickness. It is notable that 001_B diffraction of bulk-phase appeared with a sharp spot-shape just on the q_z axis as indicating by an arrow in Fig. 2 (f). This suggests that (001) plane of bulk-phase grown at 75°C is oriented parallel to the substrate surface [8,9].

Summary

In summary, a portable vacuum deposition chamber for use at a bright synchrotron x-ray source at SPring-8 has been fabricated, and real-time and *in situ* characterization during thin film growth of pentacene was performed. *In situ* and real-time 2D-GIXD measurements clarified the initial growth stages of pentacene thin films on SiO_2 substrates. Additionally, polymorphic transformations from thin film phase to bulk phase has been observed at R.T. and 75°C, and a characteristic tiled orientation of bulk phase was found at the later stage of the growth.

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