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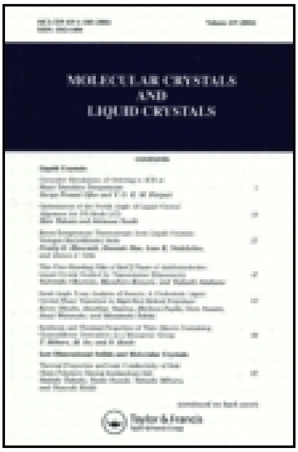

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Growth and Structure of Picene Thin Films on SiO_2

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Growth and structure of picene thin films on SiO_2 surface were studied from ultrathin film to thick film regimes (nominal film thickness upto 100 nm) by using X-ray diffraction and atomic force microscopy. We found that from initial film growth picene form crystalline grains with a certain multilayer height, in which their crystalline ab-plane orients parallel to the substrate surface. With increasing the film thickness the number of the grains increases with keeping the grain height until the substrate surface is fully covered. These results indicate that picene films exhibit island growth mode on SiO_2 surface.

Keywords Organic semiconductor; structural analysis; thin film growth; X-ray diffraction

Introduction

For recent years there has been growing an interest for new organic semiconductor picene (Fig. 1) owing to observation of its superconductivity in single crystals and high hole carrier mobility as well as O_2 gas sensing ability in organic field-effect transistors (FETs) [1,2]. These intriguing properties stimulated many of researchers for several fundamental studies of picene, such as electronic structure and film structure [3–5]. Previously we reported the details of film structure of picene (nominal film thickness (δ) = 35.6 nm) grown on SiO_2 surface by using X-ray scattering techniques [6]. In this paper, we studied the film growth and structure of picene on SiO_2 in a wide δ range till 100 nm using a combination of X-ray diffraction (XRD) and atomic force microscopy (AFM).

Experimental

Picene purchased from NARD Co Ltd, (purity: 99.9%) was thermally deposited on silicon wafer coated with native SiO_2 at room temperature under high vacuum conditions of 2×10^{-4} Pa prepared using a diffusion pump. Before film growth, the substrates were cleaned ultrasonically with acenton, isopropanol and ultrapure water, followed by heating in air to remove residue water. The growth rate of 0.01~0.03 nm/s chosen here was monitored by a quartz crystal microbalance. Thin films were then removed to atmosphere, and were characterized by using out-of-plane XRD (Rigaku Co., ATX-G) [7] and AFM (Seiko

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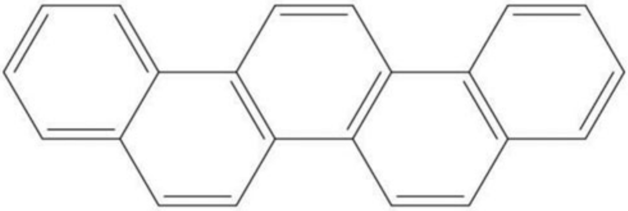

Figure 1. Chemical structure of picene ($C_{22}H_{14}$).

Instruments Inc., NanoNaviReal). AFM images were taken in tapping mode and were analyzed with Gwyddion software [8].

Results and Discussion

Figure 2 shows the out-of-plane XRD of picene films grown on SiO_2 as a function of δ. The vertical axes indicate diffraction intensity represented by a logarithmic scale, while the lateral axes are 2θ (θ is an incident angle). For all the δ, the reflections derived from (00*l*) plane of picene crystallites are observed, indicating that the molecules orient with their longer molecular axis parallel to substrate normal [3,6]. The lattice constant of the (00*l*) plane calculated by *Bragg*'s law is 1.35 nm, which is consistent with the reported one for single crystals [9] and thin films [3,6].

Figure 3(a) shows a comparison of (001) reflections normalized at the peak top intensity. It is seen that the width of each curve is comparable until $\delta = 20$ nm, while the curves become significantly sharper above the δ. To understand this quantitatively, Fig. 3(b)

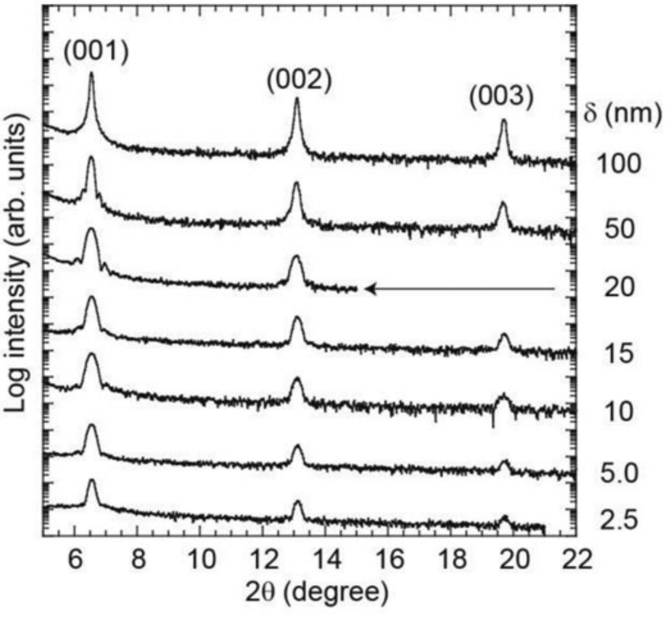

Figure 2. δ dependence of out-of-plane XRD of picene/SiO_2 systems.

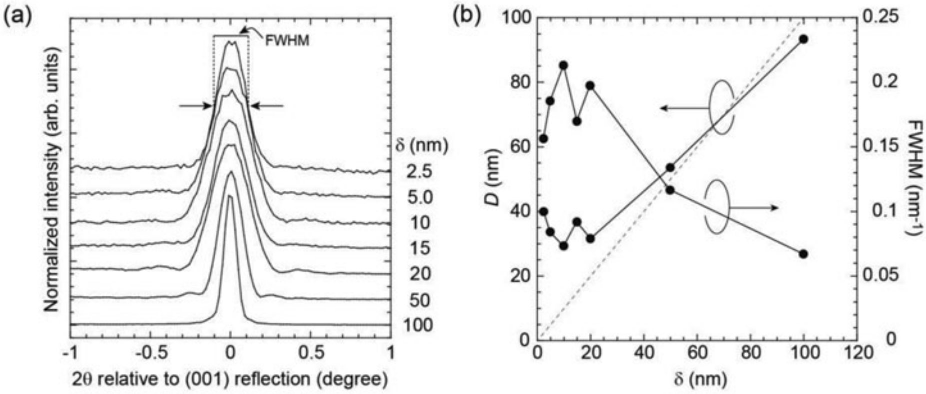

Figure 3. (a) Progress of (001) reflection with δ. The vertical axes are represented by a linear scale. (b) FWHM of (001) reflection and D of picene thin films. The broken line represents a linear 1:1 relationship between δ and D.

(right axis) shows the full width half maximum (FWHM) of the (001) reflections as a function of δ. Here the unit of FWHM is shown as a scattering vector $q(= 4\pi^*\sin\theta/\lambda : \lambda$ is wavelength of X-ray light source and here is 0.1542 nm) for the following calculation. In Fig. 3(b), FWHM is estimated to be $0.184 \pm 0.028\ \mathrm{nm}^{-1}$ until $\delta = 20$ nm, and is clearly smaller above the δ, $0.116\ \mathrm{nm}^{-1}$ for $\delta = 50$ nm and $0.067\ \mathrm{nm}^{-1}$ for $\delta = 100$ nm. By adopting those FWHM to Scherrer formula [10], lower limits of coherent out-of-plane length $D\ (= 2\pi/(\mathrm{FWHM}^*0.9394^*K\mathrm{s})$, where $K\mathrm{s} = 1.0747$ is the Scherrer constant for spherical grains) of crystalline grains can be estimated. Fig. 3(b) (left axis) shows the result of δ dependent-D. It is obvious that D of picene crystallites shows similar values of 35 ± 5 nm until $\delta = 20$ nm, but increases clearly above the δ. D is 55 nm at $\delta = 50$ nm and is 90 nm at $\delta = 100$ nm, a very close value of each corresponding D and δ. This result indicates that the films are almost coherently ordered above $\delta = 20$ nm, as similarly found before for the same system with $\delta = 35.6$ nm [6].

However, Fig. 3(b) remains a question for the D below $\delta = 20$ nm, i.e. $D = 35 \pm 5$ nm is obviously larger than each δ in the δ regime. To solve the question we conducted AFM measurements of the picene/SiO_2 systems. Figure 4 shows the results of the AFM measurements at selected δs$(= 2.5, 5.0, 15, 20, 50, \text{and } 100\ \text{nm})$. For $\delta = 2.5$ nm (a) a number of grains with polygonal shape having different contrasts, which originate from different heights, are observed. The other regime (colored by black) exhibits a high flatness, implying a bare surface regime of the substrate. The number of grains increases with increasing δ, but the substrate surface is still visible even at $\delta = 15$ nm. Above $\delta = 20$ nm the surface is almost fully covered. These results strongly indicate the island growth mode of picene thin films on SiO_2. Indeed, the numerical analysis of the AFM image results in the average grain height of 45 nm at $\delta = 2.5$ nm close to D $(= 40$ nm) at the δ. This supports the formation of picene crystallites with the large grain height from initial film thickness.

Accordingly, the growth scenario of picene thin films could be proposed as follow; (i) picene molecules deposited on SiO_2 do not easily wet on the SiO_2 surface, instead they prefer to form crystallites with (average) height of 35 ± 5 nm until a certain δ (here δ is 20 nm). (ii) Above $\delta = 20$ nm the crystallites finally cover the substrate surface and can start to grow vertically again to show larger D. Such a growth behavior is considered to be 3D to 2D-like growth mode transition, and is indeed also reported in very recent published

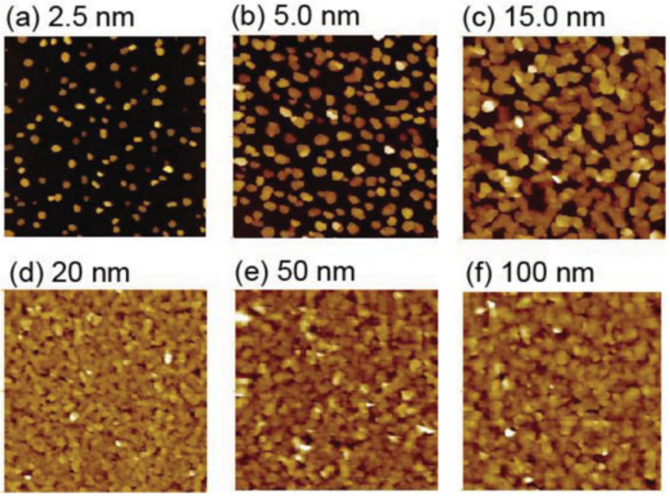

Figure 4. (a)–(f) AFM images (10 × 10 μm) of picene/SiO_2 systems at different δ depicted above each image.

paper by Gottaradi et al, in spite of uses of other deposition technique [11]. On the other hand, *in situ* real-time X-ray reflectivity measurement during conducting molecular beam deposition of picene on SiO_2 under ultrahigh vacuum condition (10^{-7} Pa) also exhibits the behavior of initial island growth [12]. Therefore, based on these facts it is concluded that the 3D to 2D-like growth mode transition observed for picene/SiO_2 system is independent of the growth condition and is a characteristic for picene thin films.

Summary

We studied growth and structure of picene films on SiO_2. We observed that picene exhibits island growth on the surface with keeping a certain grain height from initial depositions. When the surface is fully covered, picene crystallites can restart to grow vertically to show larger grain height. This result may be of benefit to understand the growth mechanism of picene thin films on different practical substrates used in organic electronic devices, such as insulating polymers or metal electrodes.

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