

Morphological characterization of pentacene single crystals grown by physical vapor transport

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Abstract

Pentacene single crystals were grown by physical vapor growth. It was found that large-sized pentacene single crystals can be grown under 1 atm argon either in a closed tube or in an opened tube. The morphology of surface and transect of pentacene crystals was characterized by optical microscope, atomic force microscope and scanning electron microscope. Pentacene monolayers and layer-like structures are observed on the surface and in the interior of single crystals, respectively. The array of large straight steps is also observed on the surface of pentacene single crystals. All results indicate that the growth mechanism of pentacene single crystals is a two-dimensional nucleation–elementary steps–large straight steps–layer-by-layer periods growth.

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Keywords: Pentacene; Single crystal; Morphology; Physical vapor transport; Growth mechanism

1. Introduction

Compared with organic thin film transistors (OTFTs), organic single crystal transistor (OSCTs) can be used to study the intrinsic electronic transport properties of organic semiconductor and physical limitations on the performance of organic field-effect transistors (OFETs) [1]. Therefore, the research of OSCTs has attracted much attention in recent years [1,2].

Organic semiconductors are the key component of OSCTs and always grown by physical vapor growth (PVT) [3,4]. However, there are few reports about the surface morphology, structure defects of organic semiconductor crystals [5,6]. It is obvious that the surface morphology and defects of organic semiconductor single crystals have important effects on the performance of OSCTs, since the conductive channel exists on the surface of organic semiconductor single crystals and the surface morphology will influence the interface between the organic semiconductor single crystals and the dielectric layers.

Pentacene is the most promising organic semiconductor applied in organic electronic devices. There have already been many reports about the study of OTFTs based on pentacene [7]. It has been found that the morphology and defects of pentacene thin films both have important effects on the performance of OTFTs [8,9]. And there have already been many reports about the morphology and growth of pentacene films [10–12]. The study of OSCTs based on pentacene single crystals has been reported in recent 2 or 3 years [13–15]. Up to now, we have not found reports about the surface morphology and structural defects of pentacene single crystals grown by PVT.

In this paper, pentacene single crystals were grown under 1 atm argon either in a closed tube or in an opened tube. And the crystal plane orientation, surface morphology and macroscopic defects are discussed.

2. Experiments

The crystal growth apparatus is similar to the one reported by Laudise et al. [4]. The source temperature and the deposition temperature are 285–295 and 220–260 °C, respectively. Two types of experiments were conducted: physical vapor deposition in a closed system at 1 atm argon and in an opened system at 1 atm argon. The flowing rate of argon is 5–30 ml/min. It was

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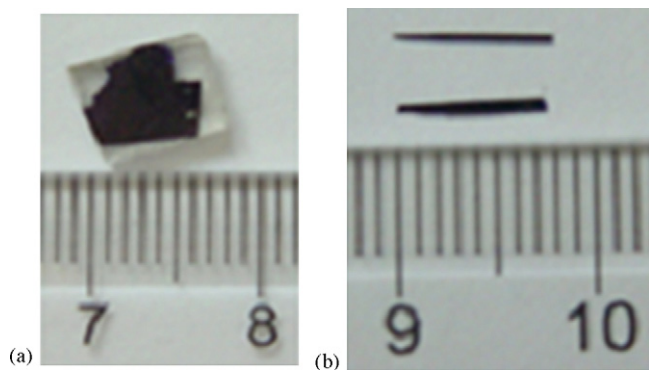


Fig. 1. Pentacene single crystals grown in a closed system at 1 atm argon: (a) 6 mm \times 7 mm plate-like crystal positioned on a glass; (b) 1 mm \times 7 mm needle-like crystals.

found that large-sized pentacene single crystals can be grown under both conditions. The pentacene single crystals exhibit plate-like and needle-like shapes. Fig. 1 shows the single crystals grown in a closed system at 1 atm argon.

X-ray diffraction (XRD) experiments were conducted by a RIGAKU D/max-B X-ray diffractometer. The surface of crystals was characterized by a Nanoscope IV (Veeco company) atomic force microscope (AFM) and an optical microscope. The transect of needle-like pentacene single crystals was observed by a S-4500-type scanning electron microscope (SEM).

3. Results and discussion

3.1. The orientation of crystal plane of the pentacene single crystals

As shown in Fig. 2, the baseline of the XRD pattern is very straight and the diffraction peaks are very sharp, indicating that the crystalline of pentacene single crystal is very good. The strong diffraction peak at 6.238° corresponds to that of (0 0 1), and other equivalent periodic peaks, (0 0 2), (0 0 3), (0 0 4), (0 0 5), (0 0 6), and (0 0 7) can be observed. The d_{001} is nearly equivalent to 1.41 nm and well corresponds with the one of the

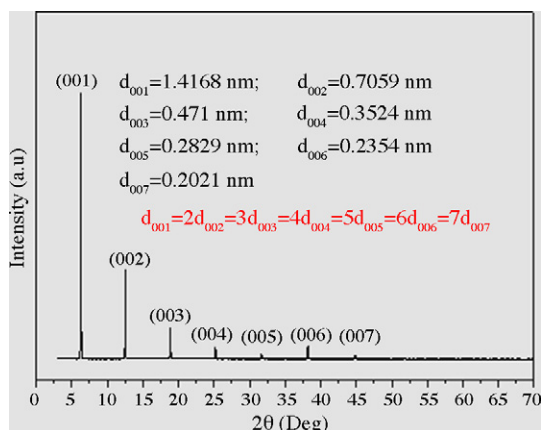


Fig. 2. The XRD pattern of pentacene single crystals grown by PVT.

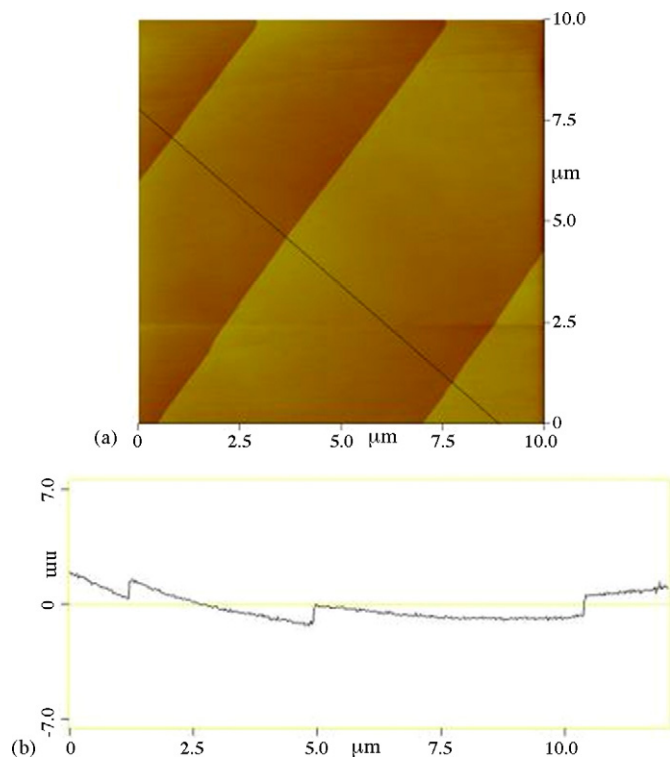


Fig. 3. (a) AFM image of 10 μm \times 10 μm area of pentacene crystal surface; (b) cross-section curve indicated by the line in (a).

vapor-grown pentacene single crystal [16,17]. For pentacene single crystals, there are two kinds of polymorphs: the d_{001} of one polymorph is 1.41 nm and the single crystals are always grown from vapor phase; the d_{001} of the other polymorph is 1.45 nm and the single crystals are always grown from solution. For exception, the polymorph corresponding to 1.45 nm can also be grown from vapor phase [18]. Obviously, the polymorph corresponding to 1.41 nm is denser than the polymorph corresponding to 1.45 nm.

Tapping mode of AFM was used to scan the 10 μm \times 10 μm area of the crystal surface. As shown in Fig. 3(a) and (b), step-like structure was observed. Fig. 3(b) shows the cross-section curve corresponding to Fig. 3(a). The average height of steps is about 1.23 nm, which approaches to $d_{(001)}$ of pentacene single crystal. The AFM results correspond well with the XRD pattern as shown in Fig. 2. Therefore, it can be further concluded that the surface of pentacene single crystal corresponds to (0 0 1) crystal plane. Obviously, these steps are pentacene monolayers and we conclude that they are elementary steps [23], that is the steps have a height of one pentacene monolayer. The width of these steps is about 2–5 μm .

3.2. Surface morphology of pentacene single crystals

As shown in Fig. 4, the array of large straight steps can be observed on the surface of both the plate-like crystal and the needle-like crystal. Surprisingly, the array of large straight steps covers the whole surface of needle-like crystals. Here, the scanned area as shown in Fig. 4 is very typical. Although the large straight steps are parallel with each other, the width of

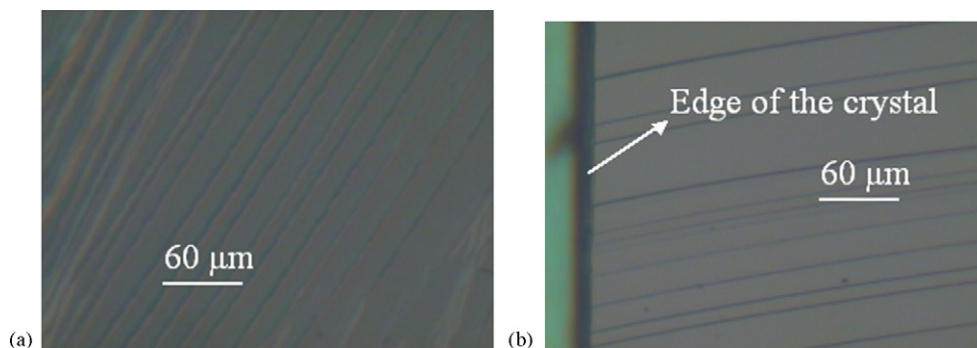


Fig. 4. Surface morphology of pentacene single crystals observed with optical microscope: (a) surface morphology of plate-like crystal; (b) surface morphology of needle-like crystal.

steps is varied. The contact mode of AFM has been used to measure the height and width of large straight steps.

As shown in Fig. 5(a), a very clear morphology of steps on the surface of plate-like crystal can be seen. The height of steps is ranged from 174 to 370 nm and the width of steps is from 10 to 20 μm . Similar results can be obtained through measuring the surface of needle-like crystals. It should be noticed that the height and width of these steps are far larger than those of elementary steps as shown in Fig. 3.

3.3. Transect morphology of pentacene single crystals

As shown in Fig. 6(a), the thickness of pentacene single crystal is about 55 μm and a large layer-like hole is observed. It is well known that organic molecular crystals are formed via the Van der Waals force. Therefore, we think pentacene layers should be easily peeled off when the crystal is broken. As shown in Fig. 6(b), some pores are observed. The larger pores are about 1 μm in diameter and the smaller pores are

about 0.1–0.5 μm in diameter. The formation of these pores is possibly due to the presence of 1 atm argon in the growth tube. A little argon gas may be enwrapped into the pentacene single crystals in the crystal growth process. Therefore, some small pores are formed in the crystals as shown in Fig. 6(b). Similar phenomenon has also been observed in inorganic crystals [19].

As shown in Fig. 6(c) and (d), layer-like structures are obviously observed and parallel to the surface of the crystal. The width of these layers is about 2–5 μm and very close to the width of elementary steps as shown in Fig. 3. Because the height of the layers cannot be measured by our SEM, we cannot sure if these layers are pentacene monolayers or not.

3.4. The formation mechanism of large straight steps on the surface of pentacene crystals and the growth mechanism of pentacene crystals grown by PVT

In principle, there are two kinds of viewpoints about the formation mechanism of the large steps on the surface of crystals. One is that the large spiral steps are grown from spiral dislocation. Such spiral steps can be observed on the surface of SiC crystal [20] and CdI_2 crystal [21]. It is obvious that the straight steps on the surface of pentacene single crystals as shown in Fig. 4 are not grown from spiral dislocation as no spiral steps and spiral dislocation are found.

The other formation mechanism of steps is that the large straight steps are grown from two-dimensional nucleation. Malkin et al. studied the growth of protein and virus crystals and found that most of these crystals grew principally on steps generated by two-dimensional nucleation on surfaces [22]. On the surface of $\text{Hg}(\text{C}_4\text{H}_8\text{N}_2\text{S})_3\text{Br}_2$ (abbreviated as ATMB) crystal, arrays of large straight steps were also observed [23]. In the case of ATMB, the moving direction of straight steps is vertical to the arrays of themselves, and the crystal plane was grown from the moving of straight steps [23]. In other words, on the crystal plane, each large step is regarded as the result of the piling of elementary steps (of a height of one ATMB unit cell parameter), and the crystal grows by tangential movement of step trains and layer-by-layer deposition [23]. From the macroscopic point of view, all layers pile along the direction vertical to the crystal surface [23].

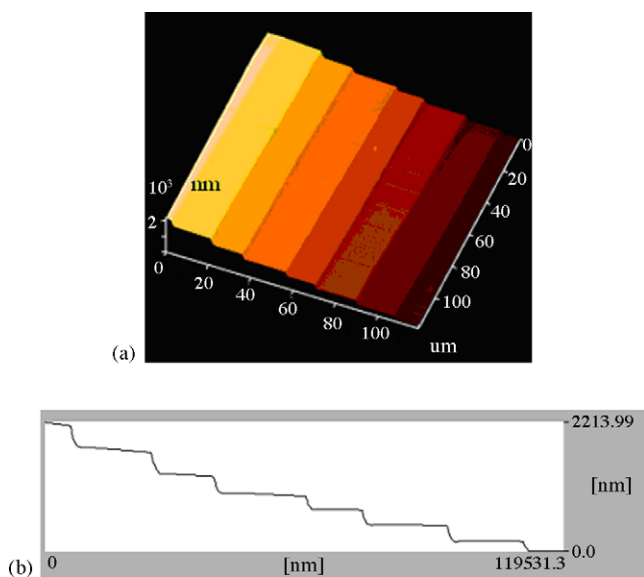


Fig. 5. Morphology of large straight steps measured with contact mode of AFM: (a) three-dimensional image of large straight steps; (b) cross-section curve of image (a).

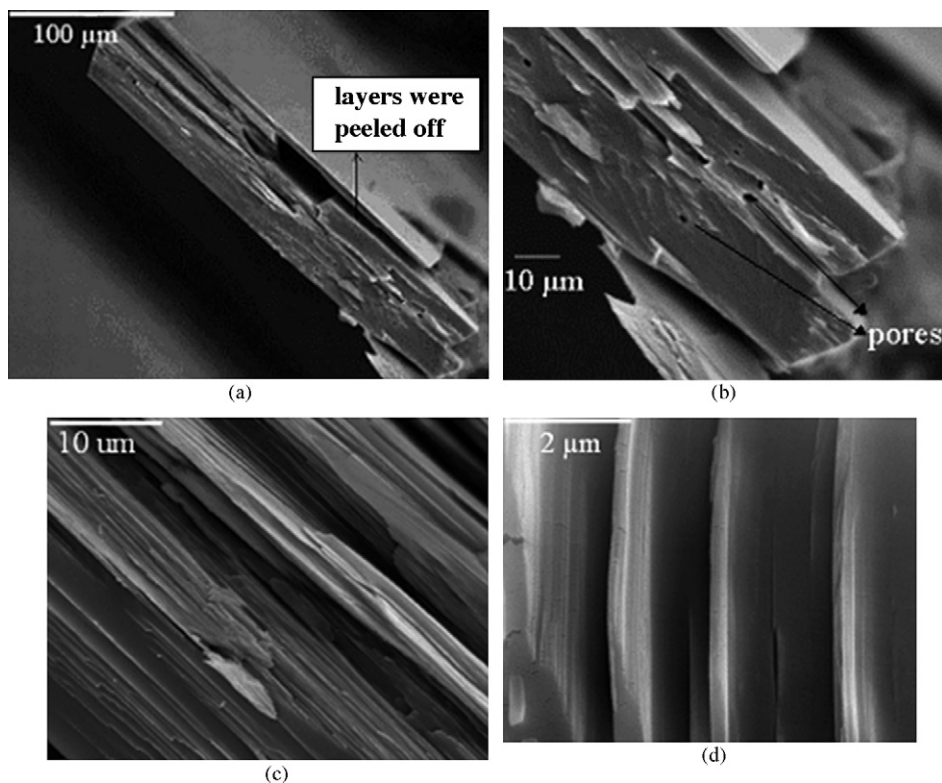


Fig. 6. SEM photographs of the transect of pentacene single crystal: (a) overall morphology of the transect of pentacene single crystal; (b) right bottom of the transect of pentacene single crystal in (a); (c) left top of the transect of pentacene single crystal in (a); (d) left bottom of (c).

As to our experiments, we think that the array of large straight steps on the surface of pentacene crystals as shown in Fig. 4 is grown from two-dimensional nucleation.

For pentacene thin films, its morphology and growth dynamics have been well studied [10–12]. Although the pentacene films are always grown far away from thermodynamic equilibrium when the growth methods are PVD and MBE [24], the growth mechanism and dynamics of pentacene films can be applied to explain the growth of pentacene single crystals.

In the growth process of organic thin films, only physisorption occurs because no chemical bonds are formed between the molecules. As a result, the growth process is governed by the Van der Waals force [24]. Meyer zu Heringdorf et al. studied the growth dynamics of pentacene thin films by in situ monitoring the evolution of pentacene thin films [12]. During the initial stages of growth, stable two-dimensional islands nucleate on the substrate surface. The nucleation density depends on the deposition rate and is related to the preparation of the substrate. In deed, layer-by-layer growth was observed [12].

In our experiments, it is observed that the pentacene single crystals grow on the inner surface of glass tube, and the crystals extend to the center of the glass tube. Similar to the growth of pentacene thin films, the growth process is also governed by the Van der Waals force [24] and two-dimensional islands nucleate on the inner surface of glass tube. Different from the cases of PVD and MBE methods, in our experiments, pentacene single crystals are grown at thermodynamic equilibrium. Therefore, high crystalline quality has been achieved. As shown in Figs. 3

and 6, pentacene monolayers and layer-like structure are observed on the surface and in the interior of single crystals, respectively. And they are all parallel with the (0 0 1) crystal plane. So, it can be concluded that pentacene single crystals are also grown by layer-by-layer growth. These pentacene monolayers can be considered as elementary steps as shown in Fig. 3. It is also noticed that the large straight steps as shown in Fig. 4 are parallel with the (0 0 1) crystal plane and the elementary steps as shown in Fig. 3. Therefore, it can be concluded that each large step is formed from the piling of elementary steps.

It is reasonable to think that there is also two-dimensional nucleation process on the surface of the pentacene single crystals since two-dimensional nucleation occurs on the inner surface of the glass tube in our experiments. Then two-dimensional “islands” [12] with one pentacene monolayer height should be observed on the surface of pentacene single crystals. Here, we regard that the elementary steps as shown in Fig. 3, in deed, are two-dimensional “islands”. There are two reasons: first, the height of the elementary steps is nearly equal to the height of the pentacene monolayers; second, previous works indicate that nucleation on (0 0 1) crystal plane is not easy according to PBC theory and the elementary straight steps will be quickly formed from the nucleus after the two-dimensional nucleus are formed on (0 0 1) crystal plane [25].

According to the above discussions, we conclude that the growth mechanism of pentacene crystals grown by PVT is a two-dimensional nucleation–elementary steps–large straight steps–layer-by-layer periods growth.

4. Conclusions

The observation by XRD and AFM (tapping-mode) indicates that the surface of pentacene single crystal corresponds to (0 0 1) crystal plane. The experiments with AFM (contact-mode) and SEM indicate that the array of large straight steps on the surface of pentacene crystals is grown from two-dimensional nucleation and the growth mechanism of pentacene crystals grown by PVT is a two-dimensional nucleation–elementary steps–large straight steps–layer-by-layer periods growth. We think these results will be useful for the study of the growth mechanism of organic single crystals.

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