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Characterization of pentacene crystals grown from liquid naphthalene solution

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Abstract

We report crystal growth and characterization of pentacene crystals grown from liquid naphthalene solution. Plate-shaped crystals with ~ 1cm^2 area was obtained. From the X-ray diffraction pole figure, it was found that the crystal consists of microtwins with two orientatons.

1. Introduction

Organic semiconductors are important materials for the application to flexible, light-weight and printable electronic circuits. It is necessary to design and synthesize molecules with high performance for the applications. There are still some "missing links" connecting molecular structures and the physical properties of organic semiconductors as solid state materials. Important properties include carrier mobilities, exciton binding energies and lifetimes and so on. It is highly desirable to make single crystals of organic semiconductors and study crystal structures and various physical properties experimentally to find the way to connect the molecular structures and the important physical properties as semiconductors. In this paper, we focused on the crystal growth of pentacene by newly developed "flux evaporation method" and characterization of the product.

Unfortunately, pentacene decomposes beyond the melting point, and the melt growth technique cannot be applied. Physical vapor transport (PVT) technique has mainly been used for the single crystal growth of pentacene[1]. The solubility of pentacene to ordinary organic solvents are poor. 1,2,4-trichlorobenzene solution at 140 ºC was used to grow pentacnee thin film crystals to make transitors[2], but the size of the crystals were far inferior to the PVT.

We develop a new technique for the organic single crystal growth using solid state aromatic molecule as flux[3]. The principle of this method is to control the concentration of pentacene solution by controlling the vapor pressure of naphthalene.

2. Experiment

Since the materials are air sensitive at elevated temperatures and naphthalene is highly volatile, the growth process was performed in a vacuum-sealed H-shaped glass tube. The schematics of the growth process is shown in Fig.1.

First, pentacene and napthalene was put into the left side of the H-shaped glass tube. Next, the glass tube was evacuated to vacuum and sealed by flame. Then the H-shaped glass tube was put into a aluminum heater block, in which the temperature of the left side and right side can be controlled separately. First, the right side was heated, and then the left side was heated to the same temperature, and the temperature of the right side was cooled down. The left side was cooled at the same time, but the temperature was kept slightly higher than the right side. The pentacene crystal was formed in the left leg of the H-shaped glass tube. All the naphthalene was collected to the right side. Pentacene crystals were obtained in the left side. Typical maximum temperature in the profile was 280oC and the time from 280 ºC to 88 ºC (melting point of naphthalene) was 16 hours.

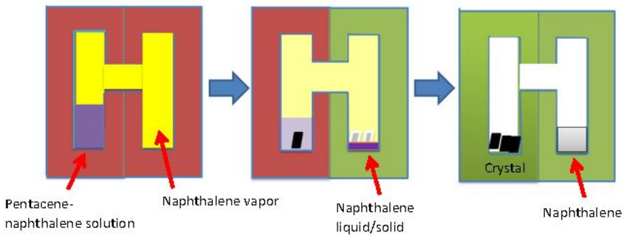

Fig. 1: Crystal growth procedure

After the crystal growth, the pentacene crystals were collected and was characterized by optical microscope, laser microscope (KEYENCE VK-8700), X-ray diffraction with out-of-plane and pole figure configuration (Rigaku Smart Lab).

3. Results and Discussion

Figure 2 shows an optical microscope image of a pentacene crystal obtained by the experiment. The ruler scale is 1mm. Figure 3 shows a height profile of another crystal measured by laser microscope. The thickness of the crystal was uniform and was 14 μm.

In order to examine the crystallinity, X-ray diffraction was measured. Figure 4 shows θ-2θ diffraction pattern of a plate like crystal. It shows 00n diffractions. It shows periodic peaks corresponding to the layered stacking of herringbone lattice of pentacene. There are more than 10 types of polytypes of pentacene reported so far, which are basically classified into three types. Bulk type reported by Campbell, single crystal type, and thin film type. [3] We can rule out the possibility of thin film phase because the 001 diffraction appeares below 2θ = 6.0º.[12]

Fig. 2: Optical image of a crystal

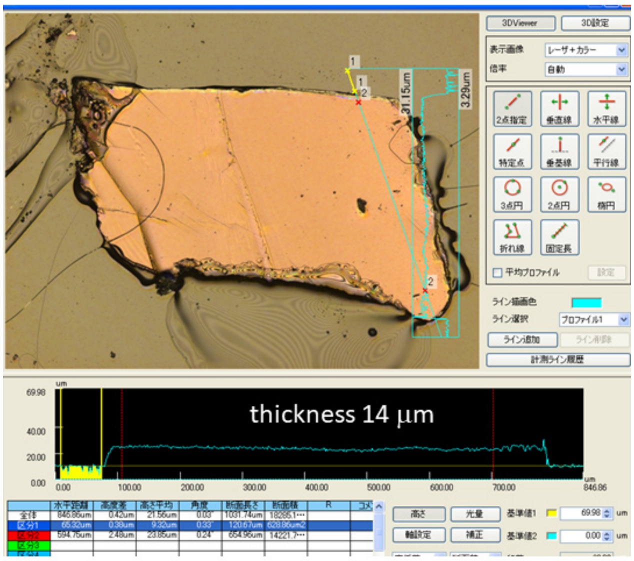

Fig.3: Laser microscope image and thickness profile of a crystal.

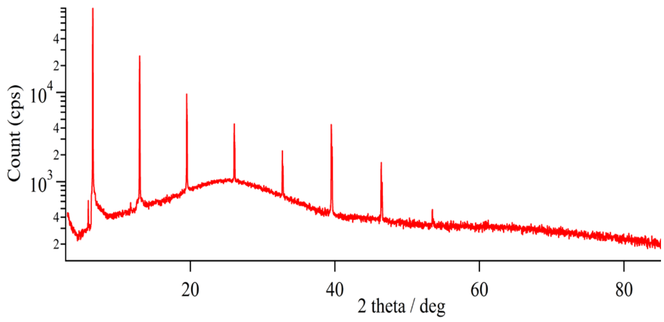

Fig. 4. Out-of-plane X-ray diffraction of a pentacene plate-like crystal

In order to determine the crystal structure and the crystallinity, we measured in-plane pole figure as shown in Fig. 5. 2θ was set to 17.7º, which correspond to 111 diffraction of "single crystal type" and 1 0 -3 diffraction of "bulk type". From the pole figure shown in Fig. 5(a), There are 4 spots on a circle of a=16o. It corresponds to 1 0 -3 of bulk type. The existence of 4 spots, as shown in Fig. 5(b), indicates the crystal was made of two different orientations. In the real space, the orientations are as shown in Fig. 5(c), which have very similar shape in a-b plane. The existence of these micro twins is rather reasonable considering possible stacking faults.

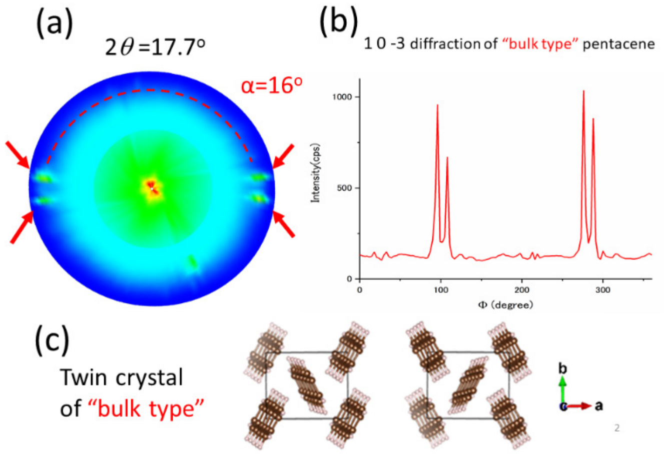

Fig. 5: X-ray pole figure of a plate like pentacene crystal. (a) Pole figure. (b) Diffraction intensity profile as a function of in-plane rotation at 2θ=17.7 º and α=16 º. (c) Real space structure of micro twining.

4. Conclusions

We have grown pentacene crystals with ~1cm size from melted napthalene solution, and characterized them. The crystal was "bulk-type" structure and made of micro twins.

Acknowledgment

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