Search of Optimum Conditions for Sublimation Growth of Thiophene/Phenylene Co-Oligomer Crystals

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Summary: Optimum crystal growth conditions of thiophene/phenylene co-oligomers (TPCOs) have been studied by means of sublimation recrystallization method with changing both gas flow rate and gas pressure. The largest flaky crystal, more than 10 mm^2, was produced at the gas flow rate ~50 ml/min and reduced pressure ~0.05 Mpa, while no crystals were obtained at pressure less than 0.01 MPa. Excess supply of N_2 gas or reduced pressure for accelerating sublimation might obstruct the crystal growth of TPCOs.

Keywords: crystallization; growth; orientation; self-organization; thiophene/phenylene co-oligomers

Introduction

Organic field effect transistors (OFETs) are expected to have a high mobility if one uses thin crystal films in which high molecular alignment is achieved. One method of producing organic crystals is vapor phase growth in an open system.[1,2] Another method utilizes a closed system by using tightly sealed furnace including inactive gas.[3] Thiophene/phenylene co-oligomers (TPCOs) have good sublimation characteristic and a distinct melting point as well as the excellent optical and electrical properties. Plate crystals of TPCOs can be grown by the sublimation method. High mobility OFETs[4,5], the spectrally narrowed emission (SNE)[3] and the photo-pumped lasing[6] have been evidenced with those crystals. These will tempt one to make large crystals of TPCOs. How to grow TPCO crystals in the open system, especially using the gas-flow furnace method, however, has not yet been optimized to date.

In this study, the optimum conditions for crystal growth of TPCO materials were explored with the gas-flow furnace method based on the sublimation recrystallization by changing gas flow rates and pressures. As a result large plate crystals of high quality have been reproducibly obtained. Both size and orientation of the resulting crystals were examined.

Experiment

A TPCO material, 1,4-Bis(5′-phenylthiophen-2′-yl)benzene (AC5), was selected because of possible availability for future optical application by its excellent optical properties. Structural formula of AC5 is shown in Figure 1. The melting point of AC5 is confirmed to be 306.8 °C by thermal measurements.

An apparatus have been constructed for the TPCO crystal growth with a slight modification of the method already reported.[7] The apparatus is schematically shown in Figure 2. This consists of a metal part and inner and outer glass tubes. The outer tube, which is a test tube of 25 mm

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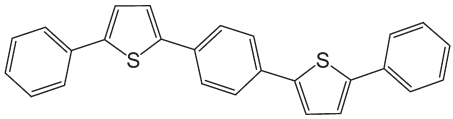

Figure 1.
Structural Formulas for 1,4-Bis(5′-phenylthiophen-2′-yl)benzene (AC5).

diameter, is exchangeable for each crystal growth. The powder sample is placed at the bottom of the outer tube, and heated up by an electric heater (band type) until sublimation starts. Growth temperature is typically set about 10–20 °C higher than the material melting point. With keeping this constant temperature, many crystals were grown on the both glass tubes at the upper end of the heater after several hours. During crystal growth, nitrogen gas flows in the furnace through the inner tube for preventing material degradation.

In this study, AC5 crystals were grown in changing N_2 gas flow rate and growth pressure for searching optimum conditions for TPCO materials, keeping sublimation temperature at 320 °C which is ~15 °C higher than the melting point of AC5. The N_2 flow rate was controlled by a flow meter from 15 to 150 ml/min at the ambient pressure. A needle valve and a rotary pump regulated the pressure in the furnace.

Results and Discussion

Under reduced pressure less than 0.01 MPa, almost no crystals were grown except when the gas flow rate is over 50 ml/min at which condition the crystal sizes were less than 2 mm^2. On the other hand, we could find many crystals of more than 2 mm^2 in size under ambient pressure with gas flow rate from 5 to 150 ml/min. The largest crystal in those conditions is 7 mm^2 at the gas flow rate of 50ml/min. The grown-up crystal was confirmed to be an almost single crystal by polarization microscope observation (Figure 3).

We could see large grown-up crystals at the N_2 gas flow rate around 50ml/min in the both ambient and reduced pressure conditions. The optimum condition is likely to be located midway between these two pressures at N_2 flow ~50ml/min.

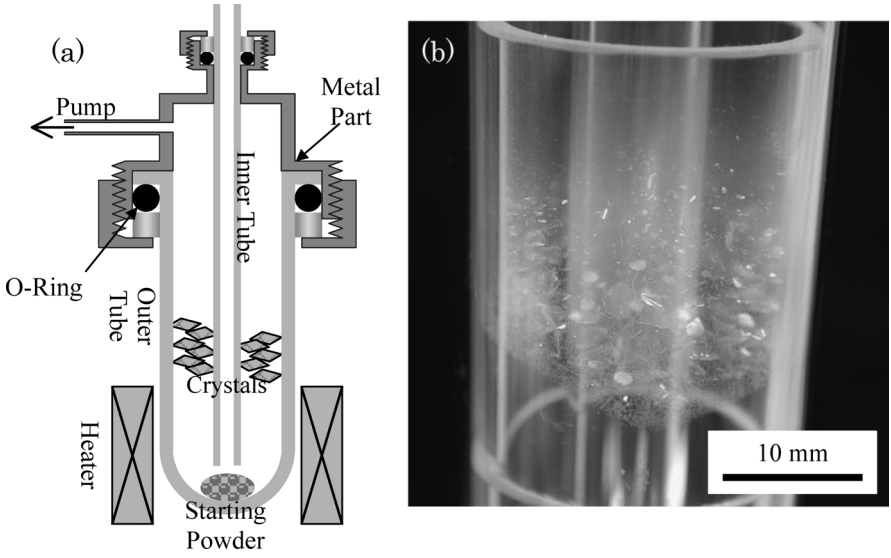

Figure 2.
(a) Schematic diagram of the present gas-flow furnace for sublimation recrystallization. (b) Photograph image of grown crystals in the furnace.

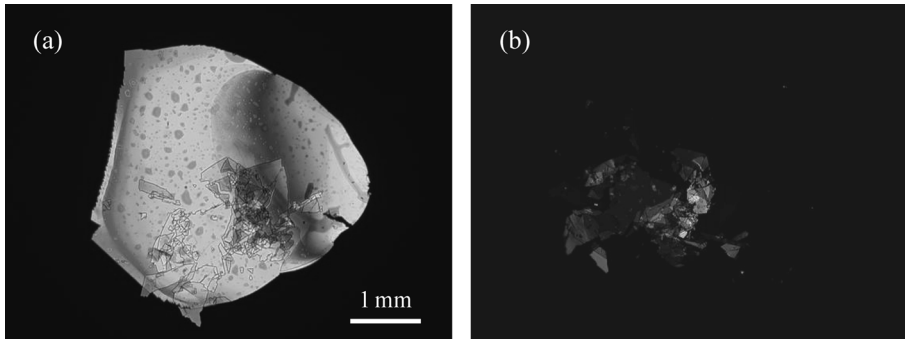

Figure 3.
Polarization microscope images for a sublimed AC5 crystal with Crossed Nicols condition at (a) Diagonal position and (b) extinction position.

The crystal growth was, then, performed under medium pressure (0.05 MPa) with N_2 gas flow rate of 50 ml/min. Under the condition, we could see the largest crystals, more than 10 mm^2, in the present study. One example of AC5 crystals is shown in Figure 4. Crossed Nicols microscope images confirm that the individual flaky crystals comprise a large monodomain with small crystallites interspersed.

Typical crystal sizes at every growth conditions in the present study are summarized in Table 1.

From the table, the most suitable condition with gas-flow sublimation was found around 0.05 MPa with N_2 flow ~50 ml/min for crystal growth of TPCOs materials in the present study.

The thickness of the crystal sample was measured to be around 2 μm by surface profiler after it was attached on oxide silicon substrate by ultrapure water. It was also confirmed that the long axis direction of this crystal is almost perpendicular to the substrate surface by X-ray diffraction measurement.

On the basis of the above observations we infer that the suitable N_2 flow rate and relatively high pressure are responsible for both removing impurities and suppress violent sublimation of the materials, enabling us to grow large crystals of high quality.

Conclusion

In this study, the AC5 crystals of more than 10 mm^2 in size were produced at N_2 gas flow rate of 50ml/min, pressure of 0.05 MPa and temperature of 320 °C by the sublimation recrystallization method with a gas flow type furnace. Optimizing the gas flow rate and pressure turned out effective in yielding large crystals. We have applied the optimized condition to the crystal growth of other TPCO materials and confirmed that large plate crystals of high purity are again available.

Table 1.
Summary of typical crystal sizes (mm^2).

N_2 gas flow rate (mL/min)	Pressure (Mpa)		
	<0.01	0.05	0.1
0	N.G.		
15	N.G.		2.6
50	1.8	10.6	7.7
150	0.7		6.5

"N.G." denotes "Not Grown" in the condition.

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