

Growth of Alkyl-Monosubstituted Thiophene/Phenylene Co-Oligomer Crystals and Their Device Application

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Abstract

We grew crystals of a small molecule organic semiconductor by using several solution techniques. The material is soluble in organic solvents at room temperature under normal pressure. We applied the crystals to the field-effect transistors (FETs). The device with a single crystal prepared by slow solvent evaporation exhibited the carrier mobility of 0.2 cm²/Vs.

1. Introduction

Carrier transport characteristic in organic semiconductors highly depends on their forms. Single crystal devices generally exhibit more excellent carrier transport characteristic than polycrystal ones due to less carrier scattering at grain boundaries of polycrystalline domains. Therefore, expansion in size of the polycrystalline domains improves the device performance.

We have investigated electrical and optical properties of small molecule organic semiconductors, thiophene/phenylene co-oligomers (TPCOs), and applied them to optoelectronic devices [1,2]. Single crystals of unsubstituted TPCOs can be grown in vapor phases [3,4] because of their high crystallinity. However, these TPCOs are poorly-soluble and a few methods are available for liquid phase crystal growth [5]. Recently, soluble TPCOs were designed and synthesized by introducing alkyl substituents to one molecular terminal, and their crystal device characteristics were reported [6]. In this study, we grew crystals of another alkyl-monosubstituted TPCO and investigated the device characteristics.

2. Experimental Procedure

Crystal growth

We prepared a monochlorobenzene or trichlorobenzene solution of the alkyl-monosubstituted TPCO, 1P3T-10Hx (see the inset of Fig. 1), and grew its crystals according to the following procedures. All crystal growths were carried out at room temperature under normal pressure.

Procedure A: We used the drop-casting for preparing the crystal films on a substrate. To reduce the solvent evaporation

speed, we put the substrate in a polystyrene box, and inserted a paraffin film between the box and its lid.

Procedure B: After the drop-casting, we put quietly a glass cylinder on the solution droplet to control the crystal growth orientation [7].

Procedure C: We put the solution in a screw vial and covered it with the lid to reduce the solvent evaporation speed. The most of the solvent was evaporated over one month (slow solvent evaporation). Floating crystals were formed at the surface of the remaining solution and the inside wall surface of the vial.

We carried out the X-ray diffractometry (XRD) measurement of these crystals.

FET device fabrication and measurements

We used silicon substrates covered with a silicon dioxide film (Si/SiO₂). On the substrates, comb-shaped electrodes were preliminarily made of chromium (Cr)-gold (Au). Some substrates were treated with phenyltrichlorosilane (PTS) to form a self-assembled monolayer (SAM) on their surface. Using the above procedures, we grew crystals on the substrates (Devices 1, 2, 3, and 5) and stuck them on the substrates (Device 6). These FETs had a bottom-contact configuration.

We also grew crystals on the PTS treated Si/SiO₂ substrate, and vacuum-deposited Au as electrodes to fabricate the FETs with a top-contact configuration (Device 4). For comparison, we fabricated the bottom contact FET by vacuum-depositing 1P3T-10Hx on the substrate with the comb-shaped electrodes (Device 7). Table 1 shows the summary of device fabrication.

Current-voltage characteristics were measured in vacuum and carrier mobility was calculated from the characteristics.

3. Results and Discussion

Figure 1 shows the relationship between the domain size and carrier mobility. The figure includes polarizing micrographs of the crystals. While the domain size varied depending on the crystal growth methods, all the XRD patterns of the crystals had the first- and higher-order diffraction peaks

Table 1. Crystal growth conditions and carrier mobility of FET devices.

Device	Process	Solvent	Concentration (wt%)	SAM	Device configuration	Carrier mobility (cm ² /Vs)
1	Cast	Chlorobenzene	0.40	No	Bottom-contact	3.37×10 ⁻⁴
2	Cast	Chlorobenzene	0.40	Yes	Bottom-contact	1.83×10 ⁻³
3	Cast ^a	1,2,4-Trichlorobenzene	0.21	No	Bottom-contact	1.19×10 ⁻³
4	Cast ^a	1,2,4-Trichlorobenzene	0.40	Yes	Top-contact	2.98×10 ⁻²
5	Cast ^b	Chlorobenzene	0.40	Yes	Bottom-contact	1.48×10 ⁻³
6	Slow solvent evaporation ^c	Chlorobenzene	0.30	—	Bottom-contact	2.06×10 ⁻¹
7	Vacuum-depositing	—	—	—	Bottom-contact	1.41×10 ⁻³

^a Procedure A was used. ^b Procedure B was used. ^c Procedure C was used.

at the same diffraction angles, showing the same diffraction spacing of 4.0 nm (not shown in the figure). This suggests that the crystallographic structure was identical among the crystals grown by different methods. Figures 2 and 3 show polarizing micrographs and current–voltage characteristic of Device 6, respectively. This device showed the highest carrier mobility (0.206 cm²/Vs, see Table 1). When the crystal image of this device rotated under crossed Nicols, the image disappeared. This indicates that the crystal of the device was a single crystal.

4. Conclusion

We grew single crystals of an alkyl-monosubstituted TPCO by using several solution techniques at room temperature under normal pressure. We fabricated FETs using the grown crystals. The device with the crystal grown by the slow solvent evaporation showed high carrier mobility of 0.2 cm²/Vs. The present solution process readily produces large single crystals and is applicable to high-performance optoelectronic devices.

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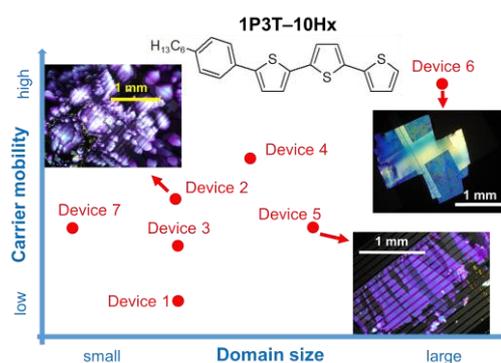


Fig. 1. The relationship between the domain size and carrier mobility. The insets are polarizing micrographs of some devices.

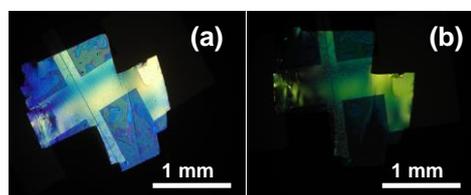


Fig. 2. Polarizing micrographs of Device 6. These are taken under the (a) diagonal and (b) extinction positions.

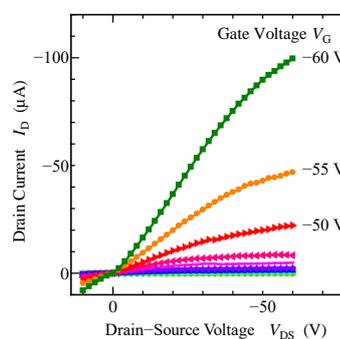


Fig. 3. Current–voltage characteristics of Device 6.

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