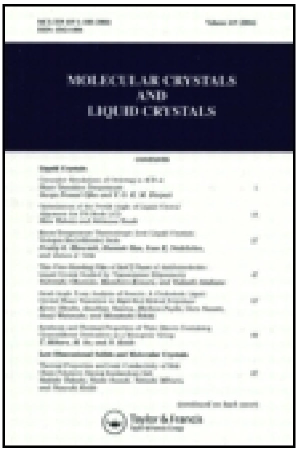

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Liquid Crystalline Materials for Organic Polycrystalline Field Effect Transistors

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We have investigated features of liquid crystalline materials *for organic polycrystalline field effect transistors (OFETs) with a model liquid crystalline material of 5,5″-dioctylterthiophene (8-TTP-8). Bulk mobility in polycrystalline thin films of 8-TTP-8* via *its liquid crystalline phase was easily determined by time-of-flight experiments. Furthermore, we could evaluate impurity contamination that caused electrically active trap states in the films by analysis of transient photocurrents in liquid crystal phase. We could fabricate uniform and less defective polycrystalline thin films for OFETs by spin-coating its solution at liquid crystal temperatures, with which we fabricated OFET exhibited high mobility of* $0.18\,cm^2/Vs$.

Keywords Bulk mobility; field effect transistor; liquid crystallinity; polycrystalline film; purity of materials; time-of-flight method

1. Introduction

Polycrystalline thin films of organic materials having an extended π-conjugated system such as pentacene and oligothiophenes have attracted high attention for organic field effect transistors (OFETs) because of high FET mobility comparable to that of hydrogenated amorphous silicon thin films. Taking advantage of organic materials for FET applications, the recent materials research is focused on organic materials that allow us to fabricate polycrystalline thin films by solution processes instead of costly vacuum evaporation. Because of strong π-π interaction of extended π-conjugated system in OFET materials, they show poor solubility in common organic solvents. The most popular strategy to improve the poor solubility is chemical modification of the π-conjugated system with long alkyl chains, as was demonstrated in oligothiophenes and more recently in pentacene and benzothienobenzothiophene (BTBT) [1–4]. The resulting materials chemically modified with long alkyl chains often show the liquid crystal phases because of the same strategy

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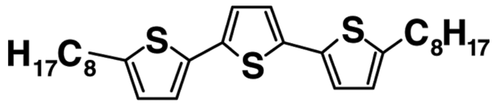

8-TTP-8

Iso 89 °C SmC 86 °C SmF 71°C SmG 58°C Cryst

Figure 1. The chemical structure and phase transition temperatures of 8-TTP-8.

of molecular design for liquid crystalline materials. However, the importance of liquid crystallinity in the OFET materials has not fully recognized yet.

In this paper, we have investigated the features of *liquid crystalline materials* for organic polycrystalline field effect transistors (OFETs) with a model liquid crystalline material of 5,5″-dioctylterthiophene (8-TTP-8), whose chemical structure is shown in Figure 1. And we discuss its availability as OFET materials in terms of materials purity, the intrinsic properties of the bulk, and the processability for polycrystalline thin films.

2. Experimental

8-TTP-8 was synthesized as reported elsewhere in detail [5]. 8-TTP-8 shows three liquid crystalline phases, i.e., smectic C (SmC: 89–86°C), smectic F (SmF: 86–71°C), and smectic G (SmG: 71–58°C) phases on cooling process. 8-TTP-8 was capillary-filled into liquid crystal cells, which was consisting of two ITO-coated glass plates spaced by silica particles, at its isotropic temperature of about 110°C. In order to evaluate its charge carrier transport properties in the bulk, the transient photocurrents were measured by the conventional time-of-flight (TOF) set-up equipped with a nitrogen laser ($\lambda = 337$ nm, pulse duration = 600 ps), recorded by a digital oscilloscope (Nicolet Pro92) and applied bias to the cells by a power supply unit (Keithley 237). The cell thickness was ca. 15 μm, where the one charge carrier condition in TOF measurements was well established due to a short penetration depth of 1.5 μm in 8-TTP-8 for 337 nm excitation light. The transit time of carriers, which indicated a travel time across the cell to the counter electrode for the fastest carriers reach the counter electrode, was determined from an inflection point of the transient photocurrent in a double logarithmic plot for convenience. The mobility was obtained from the transit time, sample thickness, and applied electric field.

We spin-coated 8-TTP-8 chloroform or *p*-xylene solutions onto thermally oxidized Si-wafer (300 nm-SiO_2/p^+-Si) untreated with any surface modification agent at 3000 rpm for 15 seconds. Gold for source and drain electrodes were deposited onto the polycrystalline films by thermal evaporation through a metal mask at 2×10^{-6} Torr, whose thickness was 30 nm. The channel width and length were 20 and 200 μm, respectively. The FET characteristics were measured using two source measurement units (ADCMT 8252) under ambient atmosphere and at room temperature.

3. Result and Discussion

After the discovery of electronic conduction in liquid crystals in 1990s [6–8], it was clarified that the ionic conduction that was often observed in liquid crystals was caused by trace amounts of not only ionic impurities but also non-ionic impurities responsible for charge trap states in liquid crystals [9,10], and that the microphase-separated structure of liquid crystal phases are very much concerned with the easy drift of ionized impurity molecules in liquid crystalline phases [11]. According to the previous report on the impurity effect on the charge carrier transport in liquid crystal phases, the electronic conduction in less ordered phases such as SmA and SmC phases is easily degraded into the ionic conduction when the concentration of the non-ionic impurities is relatively high, e.g., over 1 ppm [9,10]. Because of a big difference of mobility and its temperature and field dependences for ions and electronic charges in the liquid crystal phase, it is not difficult to judge which conduction is governed, ionic or electronic conduction in a particular liquid crystal. In fact, there are both ionic and electronic photocurrents in the different time range in a transient photocurrent obtained by TOF experiments when the concentration of non-ionic impurities is very low, e.g., less than tens ppm. Therefore, we can estimate the relative contribution of ionic and electronic charges to the photocurrent in that case by analyzing the transient photocurrent. Figure 2(a) shows the transient photocurrents of 8-TTP-8 in SmC phase. The transient photocurrents have a clear shoulder in a time range of 10 μs for hole conduction in SmC phase, but do not any shoulders and tails in a long time range of milli-second, which is corresponded to ionic transport. Therefore, we can judge that the concentration of the electrically active impurities should be less than 1 ppm or less in the present 8-TTP-8 sample. In non-liquid crystalline materials, however, we cannot estimate a concentration of electrically active impurities because there is no way to detect such a low concentration of the impurities. This is a big advantage of the liquid crystalline materials over the conventional non-liquid crystalline OFET materials.

In general, FET mobility is determined from transfer characteristics of FETs fabricated and the characteristics depend on not only bulk mobility of the materials but also other external factors such as electrical contact with electrode materials for source and drain, traps at the interface sites between organic semiconductor and gate insulator, and traps in the bulk of gate insulator. Therefore, there is no way to

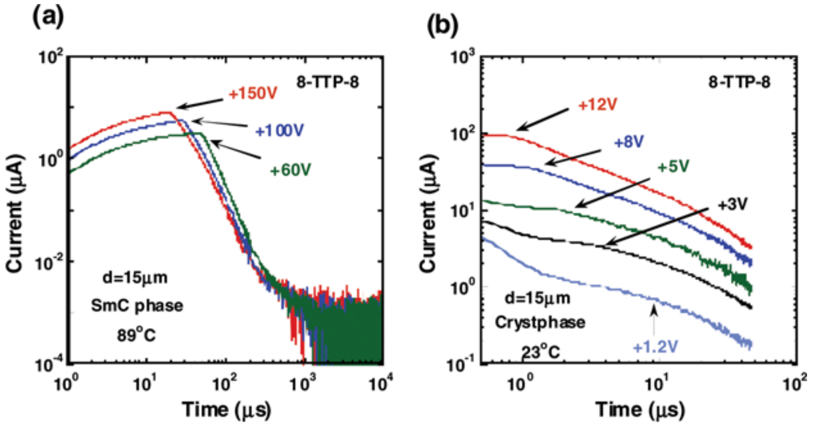

Figure 2. Typical transient photocurrents of 8-TTP-8 in SmC phase at 89°C (a) and in crystal phase at 23°C (b) for positive carrier. Sample thickness and area are ca. 15 μm and 16 mm^2, respectively. (Figure appears in color online.)

estimate any FET mobility expected in a particular material if we do not have any information about the bulk mobility in that material. In fact, it is quite difficult to estimate the bulk mobility in a polycrystalline thin film of a non-liquid crystalline material; for example, we cannot determine the mobility in the polycrystalline thin film by TOF experiment because the photocurrent always shows a decay curve owing to many defect states in it. In contrast to the non-liquid crystalline materials, we can determine the bulk mobility of a liquid crystalline material crystallized *via* a liquid crystalline phase in a liquid crystal cell [12]. In fact, by TOF experiments, we could measure the hole mobility to as high as 0.25 $\mathrm{cm^2/Vs}$ at room temperature in a range of 10^3 to 10^4 V/cm for a polycrystalline thin film formed in a liquid crystal cell of ca. 15 μm, as shown in Figure 2(b). Here, it should be noted that the electric field range described above is comparable to that in FET operation. Thus, we can have a goal of FET mobility after process and device optimization in FET fabrication, even though the TOF mobility is not always an intrinsic bulk mobility of the material.

Furthermore, there is another advantage of the liquid crystalline material for fabrication of polycrystalline thin films: it is not easy to fabricate the uniform films for non-liquid crystalline small molecules by solution process such as spin-coat, because the recrystallization always takes place on the substrate during solvent evaporation; therefore, we must do time-consuming optimization of process condition before getting uniform polycrystalline film in a certain area. In fact, we could not obtain uniform polycrystalline thin films by spin-coating of 8-TTP-8 chloroform solution of 0.5 wt% at room temperature, which consisted of many small crystal flakes as shown in Figure 3(a). The bottom gate and top contact FETs fabricated with the polycrystalline thin film showed typical *p*-channel operation. However, the transfer characteristics, on-current, and threshold voltage were relatively poor as shown in Figure 4(a). The mobility, on-current, and threshold voltage were determined to be 0.02 $\mathrm{cm^2/Vs}$, 10^{-6} A and −20 V, respectively. This FET mobility is one order magnitude smaller than that estimated to be 0.25 $\mathrm{cm^2/Vs}$ for the bulk mobility of polycrystalline thin films of 8-TTP-8. This film morphology was improved as shown in Figure 3(b) and (c) after thermal annealing for 1hour in SmF phase at 80 and SmC phase at 88°C, respectively, while the films were hardly changed by thermal annealing below 70°C for crystal phase and highly ordered SmG phase. The thermal annealing in the isotropic phase of 100°C for 1 hour degraded film uniformity and formed some thick crystalline droplets as shown in Figure 3(d).

The FET performance was improved up to 0.04 $\mathrm{cm^2/Vs}$ after thermal annealing at the temperature of SmF and SmC phases, while it was much degraded after the annealing at high temperature of 100°C: the transfer characteristics did not have any turn-on in the annealed FET at 100°C.

As we reported previously, we could fabricate very uniform polycrystalline films when we spin-coated the dialkylquaterthiophene (6-QTP-6) diethylbenzene solution of 1 wt% in liquid crystal phases given temperatures in an oven, and then cooled them to a room temperature in order to make them crystallized [13]. Interestingly, we could obtain a uniform film even when we spin-coated it at 65°C for SmG phase in this technique as shown in Figure 5(a). This polycrystalline film showed high FET mobility of 0.18 $\mathrm{cm^2/Vs}$ in as-fabricated FET as shown in Figure 5(b). This result indicates that the polycrystalline film fabricated as described above was less defective and fully relaxed in as-fabricated. In fact, FET mobility was not improved further after annealing in SmC phase at 88°C for 1 hour, but it was degraded to be 0.021 $\mathrm{cm^2/Vs}$.

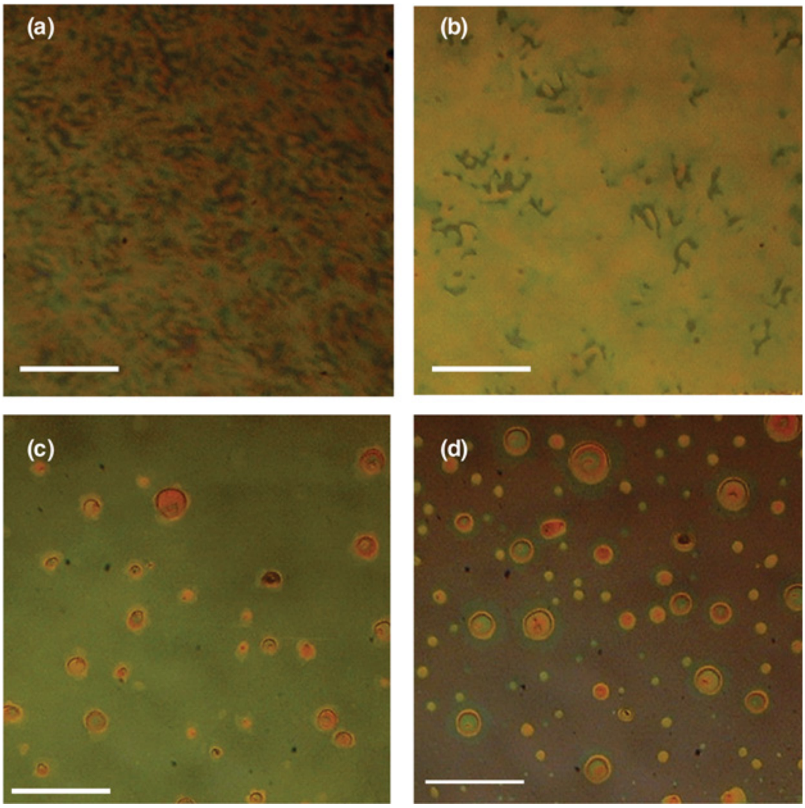

Figure 3. Optical microscopy textures of 8-TTP-8 polycrystalline thin films fabricated from chloroform 0.5 wt% solution at room temperature as-fabricated (a), after anneal at 80°C for 1 hour (b), after anneal at 88°C for 1 hour (c), and after anneal at 100°C for 1 hour (d). White bars indicate 50 μm in length. (Figure appears in color online.)

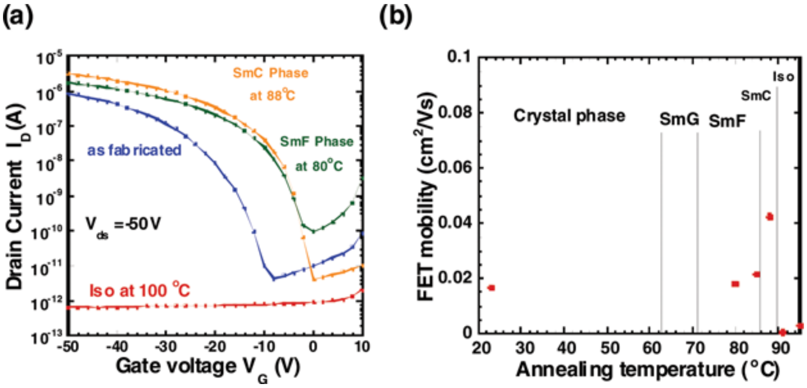

Figure 4. FET characteristics of the polycrystalline thin film of 8-TTP-8 at various annealing temperature. Transfer characteristics (a) and FET mobility (b). Channel length and width are 20 μm and 200 μm, respectively. (Figure appears in color online.)

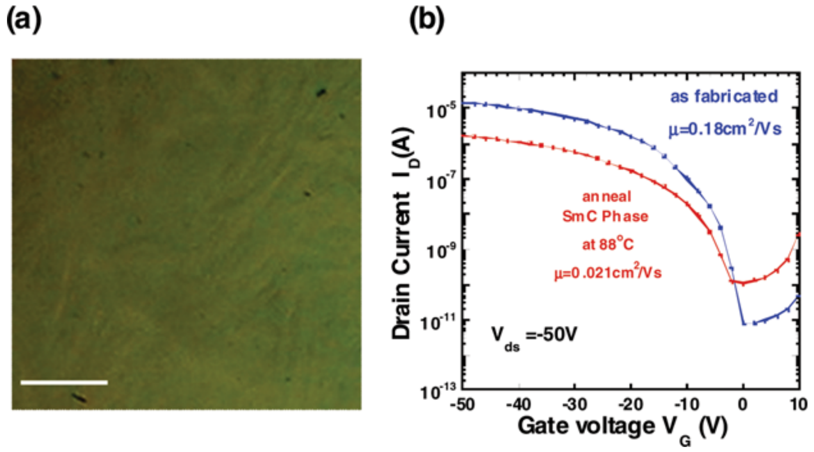

Figure 5. Optical microscopy textures of 8-TTP-8 polycrystalline thin films fabricated from *p*-xylene 1 wt% solution in SmG phase at 65°C. White bars indicate 25 μm in length (a). Transfer characteristics of the polycrystalline thin film of 8-TTP-8 before and after annealing in SmC phase at 88°C for 1 hour (b). Channel length and width are 20 μm and 200 μm, respectively. (Figure appears in color online.)

4. Conclusion

We have investigated some features of *liquid crystalline materials* for organic polycrystalline field effect transistors (OFETs) with a model liquid crystal of a terthiophene derivative, 8-TTP-8. The polycrystalline thin films spin-coated at liquid crystal phases exhibited high FET mobility of 0.18 cm^2/Vs, which was comparable to the bulk mobility of 0.25 cm^2/Vs determined by TOF experiments. According to the present results, we conclude that the liquid crystalline materials have several advantages over non-liquid crystalline materials for OFETs, which include guarantee of materials purity, easy fabrication of uniform films by spin-coating, good morphology, and less defects in the films *via* liquid crystal phase.

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