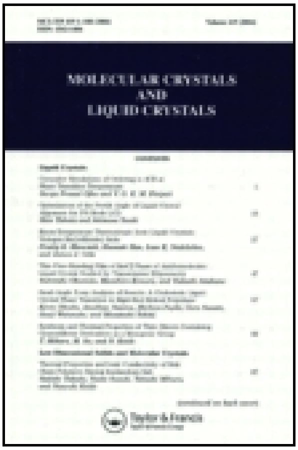

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Polycrystalline Organic TFT Fabricated by Solution Process Using Liquid Crystalline Material

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Polycrystalline Organic TFT Fabricated by Solution Process Using Liquid Crystalline Material

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We have fabricated polycrystalline thin film transistors (TFTs) with a liquid crystalline material i.e., ω,ω′-dihexylquaterthipohene by solution process. The TFTs exhibited p-*channel performance and its mobility was determined to be 0.04 cm*^{2}*/Vs, which was comparable to that determined by time-of-flight experiments. We discuss that how "liquid crystallinity" helps fabricating uniform thin films on substrates by spin-coating and controlling grain boundaries not to across the conduction channels formed by self-aligned π-conjugated aromatic cores in liquid crystalline molecules, and conclude that liquid crystalline material is a good candidate for quality polycrystalline thin films for organic TFTs.*

Keywords: grain boundaries; liquid crystal; mobility; polycrystal; spin-coat; thin film transistor (TFT)

INTRODUCTION

In fabrication of organic thin film transistors (TFTs), polycrystalline thin films of π-conjugated aromatic compounds such as Pentacene and Oligothiophenes are used because of the high field effect transistor (FET) mobility up to 1 cm^2/Vs[1]. The reason why these materials are so attractive is that less defective polycrystalline thin films that need to achieve a high mobility are easily fabricated by vacuum

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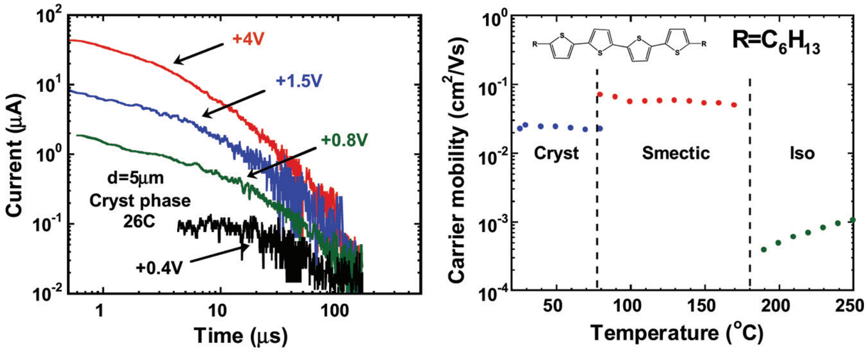
evaporation because of their anisotropic molecular structures, which enhanced anisotropic crystal growth such as "layer-by-layer" [2]. However, because of their low solubility in common organic solvents, it is very difficult to prepare polycrystalline thin films by wet processes such as spin-coating and solution cast techniques, which is very attractive for low-cost production of devices. Thus, in resent material researches for organic TFTs, π-conjugated aromatic systems modified by long alkyl chains are paid attention [3–7]. In this type of materials, "liquid crystallinity" often appears and it becomes recognized little by little that "liquid crystallinity" plays important role in fabricating uniform and less defective polycrystalline thin films, as we demonstrated previously [8].

Since the discovery of electronic conduction in discotic and calamitic mesophases in 1990s [9–11], liquid crystalline materials have attracted a new attention as a new type of organic semiconductors exhibiting self-organization and high mobility up to $\sim 1\,\mathrm{cm^2/Vs}$ [12–15]. Liquid crystalline materials are very unique among various organic materials, because it is easy to control the molecular alignment by surface treatment, in addition to a high solubility in common organic solvents. Furthermore, more importantly, liquid crystalline materials exhibit mesophases, which form ordered molecular alignment in self-organizing manner, i.e., the structural relaxation proceeds from isotropic liquid to crystal step-wisely *via* mesophases. It is quite beneficial to control grain boundaries when we fabricate polycrystalline thin films in solution process. Therefore, we can utilize the liquid crystals as an organic semiconductor not only in mesophase but also in crystal phase [8].

In this report, we fabricated TFTs with a liquid crystalline oligothiophene derivative by solution process, i.e., spin-coating technique, and evaluated the FET performance. We discuss the device performance with reference to "liquid crystallinity" and demonstrate how promising the liquid crystalline materials are for TFT applications.

EXPERIMENTAL

As quarterthiophene derivative, i.e., ω,ω'-dihexylquaterthiophene (6-QTP-6) whose chemical structure is shown the inset of Figure 1(b) was selected for a model liquid crystalline material for organic TFTs, because it has good electrical contact with a gold electrode. 6-QTP-6 was synthesized by Ni-catalyzed coupling reaction of 5,5′-dibrom-2,2′-bithiophene and 2-bromo-5-hexylthiophene. The isolated crude material was purified repeatedly by recrystallization with distilled



(a) (b)

FIGURE 1 (a) Typical transient photocurrents of polycrystalline films of 6-QTP-6 and (b) its positive carrier mobility as a function of temperature. Applied electric fields were 6×10^3, 2×10^4, and 1×10^5 V/cm in crystal, smectic, and isotropic phases, respectively. Inset of (b) is chemical structure of 6-QTP-6.

hexane. 6-QTP-6 exhibited a smectic mesophases in the temperature range from 179 to 56°C in cooling process as reported elsewhere [3].

We fabricated liquid crystal cells capillary-filling 6-QTP-6 at its isotropic temperature of about 200°C for evaluating its charge carrier transport properties in the bulk by time-of-flight (TOF) technique. The cell thickness was about 5 μm. The TOF set-up used in the experiments is described in detail elsewhere [16]. The transit time of carriers, which means that the fastest carriers reach the counter electrode, was determined from a shoulder in the transient photocurrent and used to calculate mobility.

The polycrystalline thin films of 6-QTP-6 were fabricated by spin-coating its 1 wt% *p*-xylene solution at a speed of about 3000 rpm onto the SiO_2 thermally grown on n^+ silicon wafer, which was used as gate insulator and electrode. In order to fabricate the thin film at a given temperature, the 6-QTP-6 solution is spin-coated on the substrate in an oven thermally equilibrated at the temperature. As-fabricated thin films were examined by optical microscopy (OLYMPUS) and atomic force microscopy (SEIKO SPA 300) in tapping mode. Gold for source and drain electrodes was deposited onto the polycrystalline films by thermal evaporation through a metal mask under 2×10^{-6} Torr, whose thickness was 90 nm. The channel width, W and length, L were 1200 μm and 20 μm, respectively. The FET characteristics were measured using a source measurement unit (HP4140B) under ambient atmosphere. All measurements were carried out at a room temperature.

RESULT AND DISCUSSION

In order to evaluate the charge carrier transport property in the polycrystalline thin films of 6-QTP-6, we measured the transient photocurrents in the polycrystals of 6-QTP-6 crystallized in the liquid crystal cells, in which 6-QTP-6 was cooled from mesophase temperature. We confirmed that 6-QTP-6 molecules were homogenously aligned, i.e., in planer direction for the electrode in the liquid crystal cells by texture observation under polarized optical microscope. Therefore, charge carrier transport takes place perpendicular to the substrate, i.e., through the quaterthiophene moieties of 6-QTP-6 molecules stacked parallel to electrodes. In liquid crystalline and isotropic phases, the transient photocurrent exhibited a well-defined transit and a shoulder indicating a transit time, and the mobility was determined to be 6×10^{-2} and $5 \times 10^{-4}\,\mathrm{cm}^2/\mathrm{Vs}$ at 130 and 200°C, respectively. In the polycrystalline phase, transient photocurrents did not have well-defined transit in a linear plot, but we could find the transit time in double logarithm plot as shown in Figure. 1(a), indicating that the photo-generated carriers are dispersed, which means a variation of velocity. This mobility of $0.03\,\mathrm{cm}^2/\mathrm{Vs}$ in the polycrystal phase was smaller than that of liquid crystal phase. Both mobility (0.03 and $0.06\,\mathrm{cm}^2/\mathrm{Vs}$) in crystal and liquid crystal phases hardly depended on temperature as shown in Figure 1(b).

This difference of mobility in crystal and liquid crystal phases is very curious because both of the shorter molecular distance and less disordered molecular alignment in the crystalline lattice favor a high mobility compared with the mesophase, suggesting a relatively high density of shallow traps at the grain boundaries. According to our accumulated results on charge carrier transport properties of polycrystals in the liquid crystalline materials, the carrier transport is affected very much by how the crystal growth takes place: the transient photocurrent becomes devastating, if the molecular alignment in the mesophase is much changed much in crystal phase when the sample is cooled to lower temperatures than a phase transition temperature from mesophase to crystal phase, for example, from "homogeneous alignment" to "homeotropic alignment". We do not have any clear answers about how the molecular alignment in the mesophase was preserved at the phase transition in this case. In fact, the cracks in texture pattern of the crystals in the liquid crystal cell was different from the co-circular or parallel pattern observed in the polycrystalline film of 8-TTP-8 [8], which indicates that grain boundaries are formed parallel to the molecular layers perpendicular to the substrate. Therefore, we attribute this low mobility in the crystal

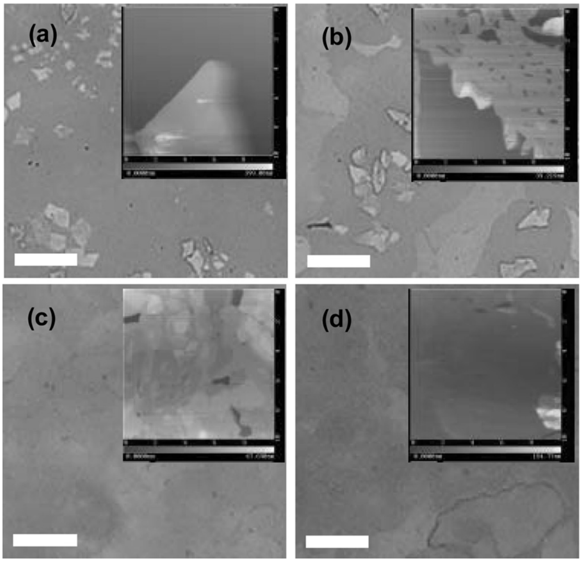


FIGURE 2 Textures of polycrystalline thin films of 6-QTP-6 observed by an optical microscope. The polycrystalline thin films are fabricated by spin-coating technique at (a) 26°C, (b) 50°C, (c) 75°C, and (d) 100°C. White bar indicates 10 μm. Inset figures are topographical images by AFM measurements.

phase to a relatively high density of grain boundaries responsible for shallow traps, which may come from the molecular alignment of the resulting polycrystals.

We prepared thin polycrystalline thin films of 6-QTP-6 on the glass substrates by spin-coating from a 1 wt% solution in *p*-xylene, in which we expected to have a "homeotropic alignment" of 6-QTP-6 molecules to the substrate. Figures 2(a)–(d) show the optical microscopic textures of the samples by spin-coating at different temperatures, i.e., at 26, 50, 75, and 100°C. In a film spin-coated at 26°C, the film was not continuous, but we saw many small crystals whose size was about 5 μm as shown in Figure 2(a). According to an AFM image shown in the inset of Figure 2(a), thickness of the film was about 400 nm. In the films spin-coated at 50°C as shown in Figure 2(b), the texture showed both film-like structures of 30 nm as shown in the inset of Figure 2(b) and small crystals described above. In the films coated at 75 and 100°C, the films are uniform as shown in Figure 2(c) and (d). The AFM image of the films showed that the films are continuous and the film thickness is about 40 nm as shown in the inset of Figure 2(c) and (d). According to these results, at the temperatures lower than 57°C, 6-QTP-6 is recrystallized on the substrate, as the solvent is evaporated, resulting in small crystals on the substrate. At a liquid crystalline temperature of 70°C, however, 6-QTP-6 is liquid-crystallized on the substrate when the solvent is evaporated. This gives a uniform liquid crystalline film first, and then give rise to a uniform polycrystalline film when cooled down to the crystalline temperature. This is thanks to the "liquid crystallinity", which makes the viscosity high and helps the film uniformly coated on the substrate. These results strongly indicate that spin-coating at a liquid crystalline temperature is quite beneficial to fabricate a uniform polycrystalline thin film on the substrate.

Figure 3 shows the out-of-plane x-ray diffraction (XRD) pattern of polycrystalline thin films fabricated by spin-coating at a liquid crystal temperature of 60°C. The XRD peak at 3.250° corresponds to a spacing of 27.16 Å, which shows a good agreement with a molecular length of 6-QTP-6, 31 Å. The AFM image of the uniform polycrystalline thin film fabricated at liquid crystal temperature has terrace structure having step heights from 24 to 29 Å as shown in the inset of Figure 2(c). These results proved that 6-QTP-6 molecules sat vertical to the substrate. The sharp and strong reflection peaks up to the 8th order indicate a high

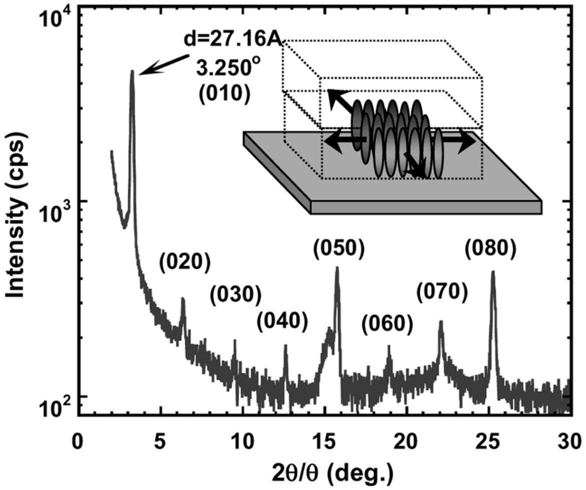
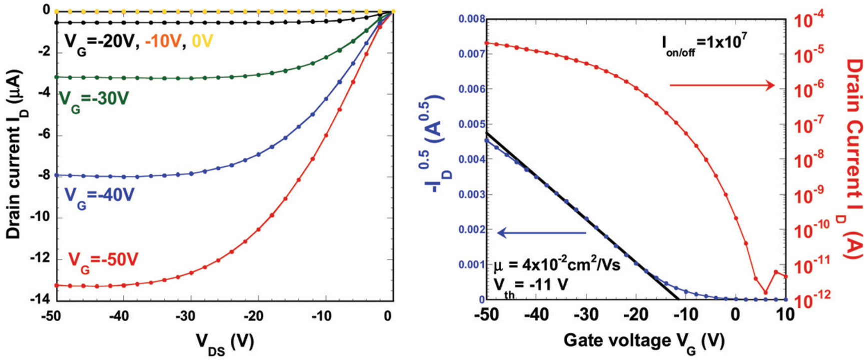


FIGURE 3 The x-ray diffraction patterns of the polycrystalline thin films of 6-QTP-6 fabricated by spin-coated at liquid crystalline temperature about 60°C. Inset is schematic illustrations of vertical molecular alignment.



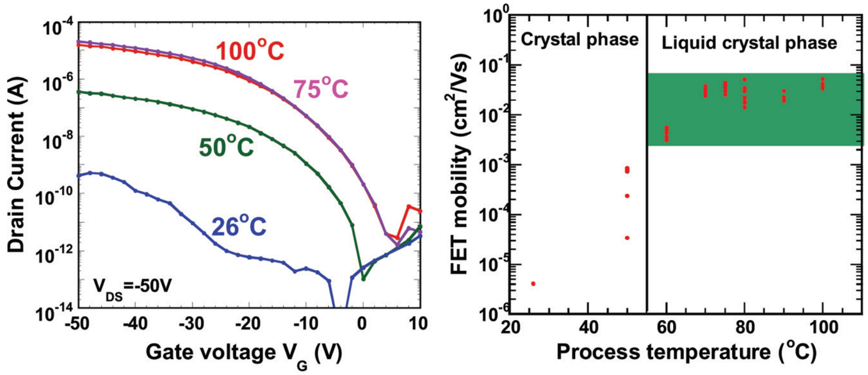
(a) (b)

FIGURE 4 Output and transfer characteristics in the TFTs fabricated with polycrystalline thin film of 6-QTP-6. (a) Output and (b) transfer characteristics at applied drain voltage, −50 V. The polycrystalline thin film of 6-QTP-6 was fabricated by spin-coating at 75°C. The channel length and channel width were 20 and 1200 μm, respectively.

crystallinity of the films, despite of as-fabricated films. This molecular alignment promises good carrier transport along the molecular layer parallel to the substrate, i.e., in the planar direction.

We fabricated TFTs with polycrystalline films spin-coated on the SiO_2/Si-susbtrsates at 75°C by evaporating a set of gold thin films of 90 nm for source and drain electrodes. Figures 4(a) and (b) show a typical output and transfer characteristics of as-fabricated TFT, respectively. On and off currents were 10^{-5} and 10^{-12} A at the gate voltage of -50 V, respectively. The On/Off ratio is as high as 10^7. The FET mobility was estimated to 0.04 cm^2/Vs from the transfer characteristics and the general field effect transistor equation in the saturation region. This mobility of 0.04 cm^2/Vs was almost same as the bulk mobility of 0.03 cm^2/Vs determined by TOF experiments described above.

Figure 5(a) shows a summary of transfer characteristics of the TFTs fabricated with the polycrystalline thin films spin-coated at various temperatures. Few TFTs were operated, when TFTs were fabricated with the films spin-coated at the temperatures lower than the phase-transition temperature of 57°C, i.e., 26 and 50°C: on-currents were smaller than 10^{-6} A even in active samples. On the other hand, the TFTs fabricated with the films spin-coated at liquid crystalline temperatures, i.e., 75 and 100°C were operated well, and the



(a) (b)

FIGURE 5 Transfer characteristics and FET mobility in the TFTs fabricated with polycrystalline films of 6-QTP-6 at various process (spin-coating) temperatures. (a) Transfer characteristics (b) FET mobility as a function of process temperature.

on-currents were higher than 10^{-5} A. In addition, the transfer characteristics hardly depended on the process temperature as clearly shown in Figure 5(a). We made 9 TFT devices in each film spin-coated on the substrates (area size: about 16×25 mm) and evaluated all of the TFTs. The FET mobility of each TFT was plotted in Figure 5(b). It should be noted that the variation of each FET mobility, is small and from 2×10^{-2} to 6×10^{-2} cm^2/Vs, for the TFTs fabricated with the polycrystalline films spin-coated at liquid crystalline temperatures.

In this study, TFT devices exhibiting a good performance, e.g., FET mobility of 0.04 cm^2/Vs and a high on-off ration of 10^7 by spin-coating technique at elevated temperatures higher than the phase-transition temperature from liquid crystal to crystal phases. The FET mobility was almost the same as the TOF mobility of 0.03 cm^2/Vs, for which the fast carriers in a carrier packet to reach the counter electrode are responsible. This fact indicates that neither the contact resistance between the electrodes and 6-QTP-6 nor the space charges at the channel region attributed to deep states are decisive for the source-drain current, which probably determined by a relatively high shallow trap density at the grain boundaries across the electric field between source and drain electrodes. We need to study more in order to clarify the exact reason why the mobility in polycrystalline phase is lower than that of the mesophase.

CONCLUSION

We fabricated polycrystalline thin films of a rod-like liquid crystal of 6-QTP-6 by spin-coating technique at various temperatures. And we found that not only the uniform films could be prepared when the films were spin-coated at the liquid crystalline temperatures, but also the deep states density in the resulting polycrystalline thin film was lowered enough to observe the charge carrier transport across the bulk of the film. The TFTs fabricated with the poly crystalline films exhibited a small variation of FET performance and their FET mobility was 0.04 cm^2/Vs. All these results are thanks to the "liquid crystallinity" of 6-QTP-6, which we can utilize to fabricate opto-electronic devices and distinguish from the conventional "non-liquid" crystalline organic semiconductors. Therefore, we conclude that liquid crystalline material is a good candidate for quality polycrystalline thin films for organic TFTs.

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