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Liquid crystalline thin films as a precursor for polycrystalline thin films aimed at field effect transistors

Hiroaki Iino and Jun-ichi Hanna^{a)}

Imaging Science and Engineering Laboratory, Tokyo Institute of Technology, J1-2, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan and Japan Science and Technology Agency (JST), Core Research for Evolutional Science and Technology (CREST), 4-1-8 Hon-cho, Kawaguchi 332-0012, Japan

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We have investigated the availability of liquid crystalline thin films as a precursor of quality polycrystalline thin films for organic field effect transistors (OFETs) by solution process. The experiments of spin-coating at various temperatures proved that the morphology of resulting polycrystalline thin films at room temperature strongly depend on what the films immediately after spin-coating and solvent evaporation at those temperatures were, i.e., crystal, liquid crystal, or isotropic liquid. The polycrystalline films spin-coated at the temperatures for crystal and isotropic liquid phases were much roughened owing to many small crystal flakes and droplets. On the other hand, the thin films spin-coated at liquid crystal temperatures were very uniform in a whole area and showed high FET mobility having a small variation from device to device. © 2011 American Institute of Physics. [doi:10.1063/1.3563586]

I. INTRODUCTION

Because of high mobility comparable to that of amorphous silicon thin films, organic polycrystalline thin films have attracted high attention for organic field effect transistors (OFETs). Many organic materials have been synthesized and investigated in order to develop the OFET materials that meet various requirements for practical applications of OFETs such as high FET mobility, good electrical contacts with source and drain electrode materials, good processability for film fabrication, and good stability in ambient atmosphere.

In recent years, a considerable attention has been paid to wet-processable materials, which have to have high solubility in common organic solvents: in fact, organic materials having an extended π -conjugated system suitable for high mobility such as polyacenes and oligomers of aromatic heterocycles exhibit poor solubility in common organic solvents because of strong π - π interaction of the extended π -conjugated system. Several trials to improve the poor solubility in OFET materials have been carried out, which includes the utilization of polymer materials, soluble precursor, and bulky-moiety substituted materials.¹⁻⁵ The most popular strategy to improve the poor solubility of OFET materials is chemical modification of the extended π -conjugated system with long alkyl chains. Such the extended π -conjugated systems chemically modified with long alkyl chains often exhibit liquid crystalline phases, which is not surprising because it is the same strategy as the molecular design of liquid crystalline materials for enhancing the molecular anisotropy in molecular shape and suppressing easy crystallization. In fact, the soluble OFET materials such as diaklyl benzo[thienobenzothiophene] (BTBT), pentacene, and oligothiophene derivatives, show some liquid crystal phases in certain

temperature ranges.⁶⁻⁹ However, the liquid crystallinity in these materials has hardly been paid any attention to.

In this report, we have investigated the importance of liquid crystal phases in fabrication of very uniform thin film by solution process. In order to show it in general, we used a well-known and one of the most popular liquid crystalline materials, terthiophene derivative, 5,5'-dioctylterthiophene (8-TTP-8) (Ref. 10), as a model liquid crystal; furthermore, we used a new material recently reported to show high mobility, 2,7-didecyl-benzothienobenzothiophene derivative (10-BTBT-10) (Ref. 6), which shows a liquid crystal phase.¹¹

II. EXPERIMENTAL

8-TTP-8 and 10-BTBT-10, whose chemical structures are shown in Fig. 1, were synthesized as reported elsewhere in detail.^{10,11} 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) in cooling process. 10-BTBT-10 shows a low ordered phase, smectic A (SmA: 122-95 °C), in cooling process. The 8-TTP-8 and 10-BTBT-10 were purified by column chromatography and recrystallization from *n*-hexane. The concentration of electrically active impurities in these materials was confirmed to be less than 1 ppm by time-of-flight (TOF) technique.¹²

We spin-coated their solutions onto thermally oxidized Si-wafer (300nm-SiO₂/p⁺-Si), which had a size of ca. 20 mm square and was untreated with any surface modification agents, at 3000 rpm for fifteen seconds and given temperatures in an oven, and then cooled them to a room temperature in order to make them crystallized. In order to avoid ambiguity of spin-coating temperature, we set a spin-coater in an oven kept at a given temperature and monitored substrate and solution temperatures using an infrared temperature sensor. The film morphology was evaluated by optical microscopes in reflection mode (OLYMPUS or Nikon ECLIPSE

^{a)}Electronic mail: hanna@isl.titech.ac.jp.

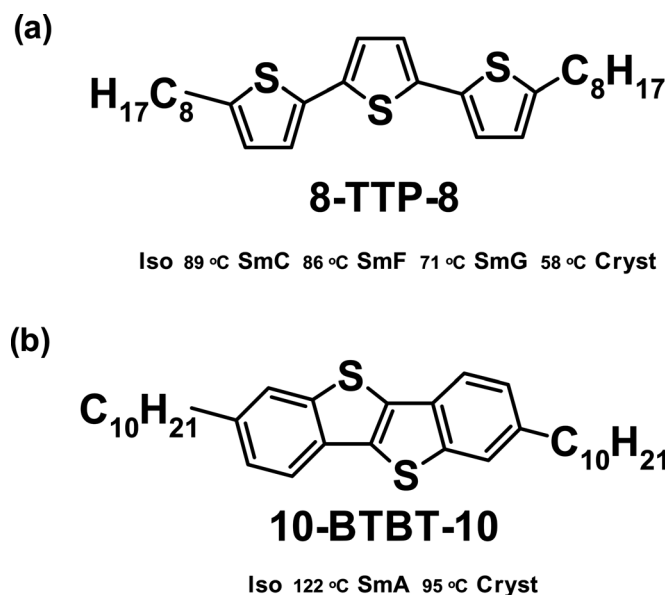


FIG. 1. The chemical structures and phase transition temperatures of (a) 8-TTP-8 and (b) 10-BTBT-10.

LV100). The thickness of thin films was evaluated by a confocal laser scanning microscopy (CLSM: Keyence VK-9710), which used a violet light laser ($\lambda = 408$ nm) and the resolution for height is one nm. For CLSM observation of the thin films, we used quartz substrates because we could not obtain correct information about the films on 300 nm SiO₂ on Si wafer.

In FET fabrication, gold for source and drain electrodes was deposited onto the resulting polycrystalline films by thermal evaporation through a metal mask at 2×10^{-6} Torr, whose thickness was 30 nm and 90 nm for 8-TTP-8 and 10-

BTBT-10, respectively. The FET characteristics were measured by using two source measurement units (ADCMT 8252) under ambient atmosphere and at room temperature. The FET mobility was estimated from transfer characteristics in saturation region.

III. RESULTS AND DISCUSSION

In order to spin-coat the liquid crystal solution at high temperatures including their liquid crystal and isotropic phases, i.e., up to 115 °C, we choose diethylbenzene as solvent because of a high boiling point of 182 °C, rather than common organic solvents such as toluene and xylene. As we discuss later on, the concentration of liquid crystals in spin-coating solution is one of important factors to have good surface morphology of the resulting films. We selected a concentration of 1 wt% for 8-TTP-8 and spin-coated it at various room temperatures including temperatures for crystal phase, liquid crystal SmG and SmF phases, and isotropic phase.

The films spin-coated at room temperature, 42 °C, and 50 °C for crystal phase were very inhomogeneous and just aggregation of small crystal flakes as shown in Figs. 2(a)–2(c), respectively. Furthermore, the films were not covered the whole area of substrates, which suggests that FET characteristics would have a big variation from device to device due to the inhomogeneity of these films. On the contrast to the films spin-coated at crystal phase temperatures, the films spin-coated at 60, 68, 72, and 85 °C for liquid crystal phases were very uniform and covered the whole area of substrates as shown in Figs. 2(d)–2(g), respectively: above all, the films spin-coated in SmF phase at 72 and 85 °C were quite uniform as shown in Figs. 2(f) and 2(g), respectively; the thin films spin-coated at 60 and 68 °C for SmG phase

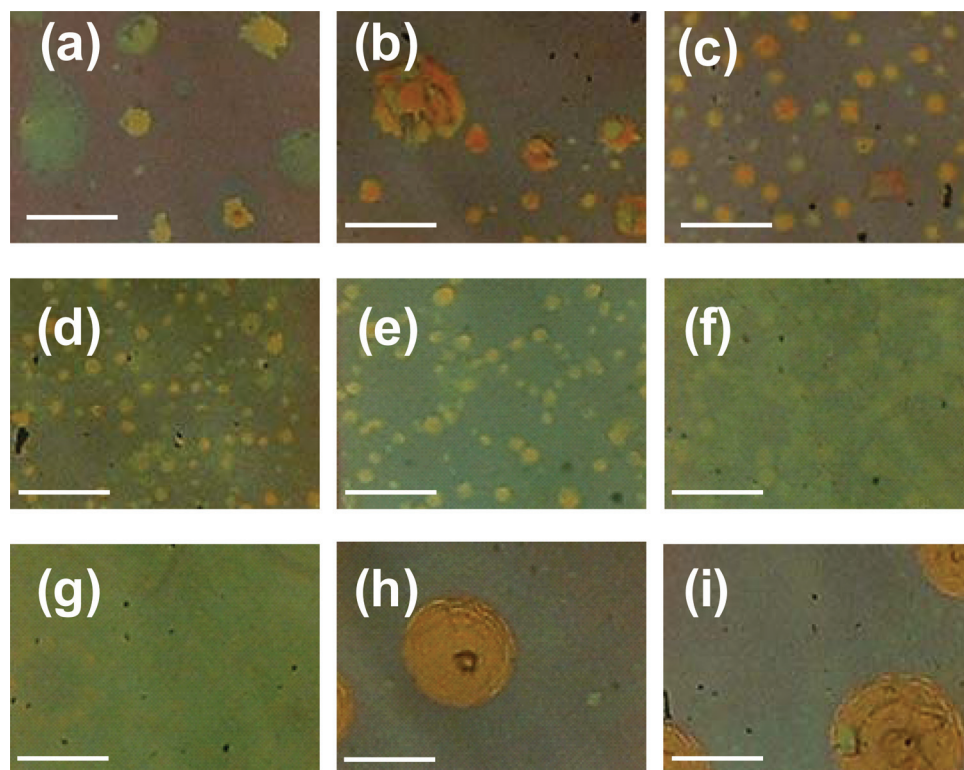


FIG. 2. (Color online) Optical microscopy textures of 8-TTP-8 polycrystalline thin films fabricated from diethylbenzene solution 1 wt% at several temperatures, in crystal phase at (a) room temperature, (b) 42 °C, and (c) 50 °C, in SmG phase at (d) 60 °C and (e) 68 °C, in SmF phase at (f) 72 °C and (g) 85 °C, and in isotropic phase at (h) 100 °C and (i) 115 °C. White bars indicate 25 μ m in length.

contained some small crystal grains in the uniform texture as shown in Figs. 2(d) and 2(e); the thin films spin-coated at 72 and 85 °C for SmF phase, which is a lower ordered phase, contained few small crystal grains as shown in Figs. 2(f) and 2(g). The thickness of thin films was ca. 50 nm. The good uniformity and surface morphology in the polycrystalline thin films spin-coated at liquid crystal temperatures come from the viscous and soft nature in liquid crystal phases, which prevent dewetting on the substrate surface and make the film morphology uniform. The films spin-coated in the isotropic phase at 100 and 115 °C were quite inhomogeneous and just like some crystal droplets on substrates, as is similar to the films spin-coated at crystal phase temperatures. These crystal droplets probably resulted from the dewetting of 8-TTP-8 from substrates immediately after solvent evaporation because of smaller viscosity of its isotropic phase. These uniform crystalline thin films could be fabricated not only from diethylbenzene solution in the present result, but also from *p*-xylene solution¹³ when these were spin-coated at liquid crystalline temperature. Judging from these facts, the uniform crystalline films spin-coated at liquid crystalline temperature result not from an optimal condition with a particular solution but from the nature of liquid crystal phase.

FET transfer characteristics strongly depended on temperatures in spin-coating 8-TTP-8 solution as shown in Fig. 3(a). As shown in Fig. 3(a), the transfer characteristics show high threshold voltage and small on-current in FETs fabricated with the films spin-coated in the crystal and liquid phases, whose FET mobility obtained from transfer characteristics in saturation region were small and less than 10^{-3} cm²/Vs, which is the same small value as reported recently, 5×10^{-5} cm²/Vs (Ref. 14). On the other hand, transfer characteristics show a low threshold voltage and a high on-current in FETs fabricated with the uniform films spin-coated in liquid crystal phases, whose FET mobility was over 0.1 cm²/Vs. This superior performance hardly depended on the spin-coat temperature at liquid crystal phases, i.e., SmF and SmG phases. Figure 3(b) shows FET mobility as a function of spin-coat temperature for fabrication of polycrystalline thin films. FET mobility of the films fabricated in liquid crystal phases was 0.05–0.1 cm²/Vs and had a small variation from device to device. On the other hand, the FET mobility of the films fabricated in crystal and isotropic phases were very small, 10^{-3} – 10^{-5} cm²/Vs, and had a large variation from device to device. These results indicate that liquid crystalline thin films are a good precursor for fabrication of uniform and quality polycrystalline thin films. In general, the FET mobility was determined by not only the intrinsic mobility of OFET materials but also extrinsic factors such as the contact resistance between organic materials and source/drain electrodes, and interface trap density between organic materials and gate insulators, and so on. The FET mobility of 8-TTP-8 films spin-coated at liquid crystal phases is almost the same value as the bulk mobility of 8-TTP-8 polycrystalline film, 0.3 cm²/Vs, determined by TOF experiments.¹⁵ This fact indicates that the FET mobility hardly depended on the extrinsic factors such as the contact resistance and interface traps. In fact, the contact resistance of 8-TTP-8 and gold

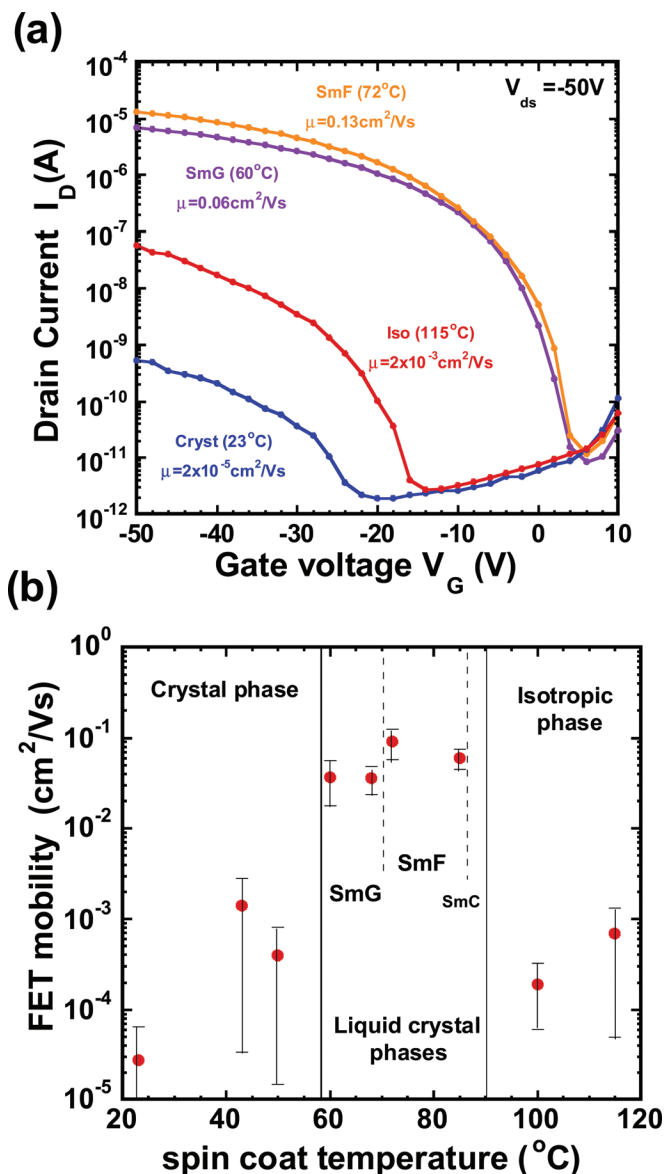


FIG. 3. (Color online) FET characteristics of the polycrystalline thin films of 8-TTP-8 at various spin-coat temperatures. (a) Transfer characteristics and (b) FET mobility. Channel length and width are 20 μ m and 200 μ m, respectively.

electrodes in the FET devices estimated using transfer line method was ca. 0.3 M Ω mm, which was two orders of magnitude smaller than that of the polycrystalline films of 8-TTP-8 in the recent report.¹⁴ Furthermore, this small contact resistance of 8-TTP-8 FETs was the almost same value as that of FETs fabricated with vacuum deposition polycrystalline film of a dialkylated quaterthiophene derivative,^{16,17} regardless of the smaller core moiety of terthiophene.

In order to confirm the availability and generality of these results, we investigated them with a different liquid crystalline material of BTBT derivatives, i.e., 10-BTBT-10, which have attracted a high attention for FET materials because of high FET mobility over 1 cm²/Vs (Ref. 6). We fabricated those polycrystalline thin films in both crystal and liquid crystal phases in the same manner as described above. The spin-coating solvent was also diethylbenzene and its concentration was 1 wt%. It was quite inhomogeneous, the

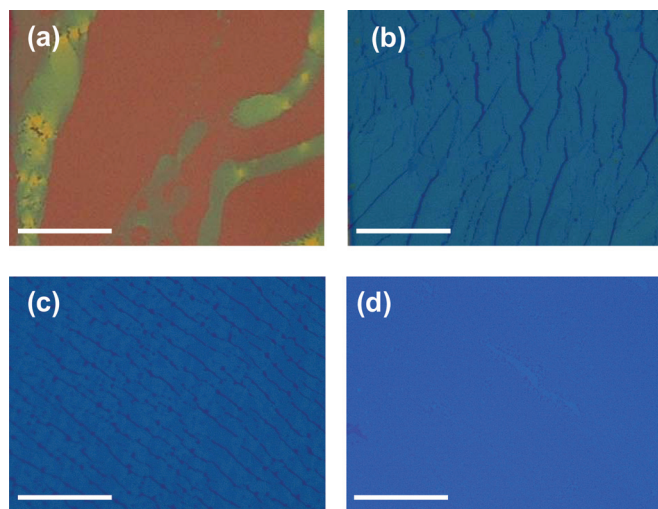


FIG. 4. (Color online) Optical microscopy textures of polycrystalline thin films of 10-BTBT-10 fabricated by spin-coating its 1 wt% diethylbenzene solution (a) at room temperature for crystal phase and (b) at 105 °C for SmA phase, and (c) its 0.5 wt% diethylbenzene solution at 108 °C and (d) its 0.25 wt% diethylbenzene solution at 107 °C for SmA phase. White bars indicate 25 μm in length.

polycrystalline thin films spin-coated at temperatures for crystal phase, which the whole area of substrates was not covered with, as shown in Fig. 4(a). This was very similar to the results on the films of 8-TTP-8 at those temperatures. On the other hand, the polycrystalline thin films spin-coated in the liquid crystal (SmA) phase at 105 °C was as uniform as the films of 8-TTP-8 spin-coated at its liquid crystal phases, as we expected. The thickness of the thin film was 58 ± 2 nm. However, the films had some cracks as shown in Fig. 4(b). It is very plausible that the cracks are due to rather thick films of ca. 60 nm, in addition to a big change of densities from SmA phase into crystal phase. We tried to improve this problem by making thinner films with 10-BTBT-10 solutions of lower concentrations for spin-coat. In fact, the polycrystalline film spin-coated in the SmA phase of 108 °C from a solution of 0.5 wt% exhibited less cracks than the films from 1 wt% solution as shown in Fig. 4(c). Furthermore, the polycrystalline film in the SmA phase of 107 °C from a solution of 0.25 wt% did not show any cracks as shown in Fig. 4(d). The thickness of thin films were 28 ± 3 nm and 13 ± 2 nm for the solutions of 0.5 wt% and 0.25 wt%, respectively. As is clear from these results, the cracks in the films, which are caused by the shrinkage of bulk film from liquid crystal to crystal phases, can be fairly suppressed by making a balance of the compressive stress in the bulk of the film and the adhesive force on the surface of substrates. On the contrary, it was very interesting that the morphology of the 8-TTP-8 polycrystalline films fabricated at liquid crystal SmF phase did not have any cracks even thick film, ca. 50 nm, as shown in Fig. 2(g).

The FET characteristic of polycrystalline thin film fabricated in SmA phase of 105 °C from a solution of 1 wt% has lower threshold and high on-current than that fabricated in crystal phase as shown in Fig. 5. The FET mobility obtained from the transfer characteristics in saturation region show 0.03 and 1.5 cm^2/Vs for films fabricated in crystal and SmA

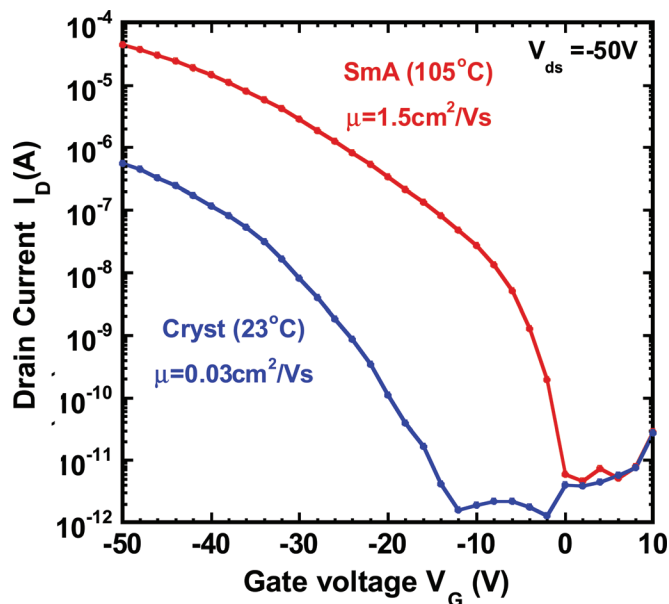


FIG. 5. (Color online) Transfer characteristics of 10-BTBT-10 FETs fabricated with polycrystalline thin films spin-coated 1 wt% diethylbenzene solution at room temperature for crystal phase and 105 °C for SmA phase. Channel length and width are 100 μm and 1000 μm , respectively. FET performance was measured at room temperature.

phases, respectively. The FETs fabricated with the films of 10-BTBT-10 spin-coated at the temperatures for SmA phase showed a threshold voltage of -28 V and a high on-current on the order of 10^{-5} A, and gave high mobility of 1.5 cm^2/Vs , while the FET fabricated with the films spin-coated at room temperature showed low mobility of 0.03 cm^2/Vs . This mobility is far better than 0.28 – 0.86 cm^2/Vs in the FETs previously reported, in which the films were spin-coated at room temperature and successively annealed at 80 °C for 60 mins.⁶

Interestingly, the high FET mobility in the thick films, ca. 60 nm, fabricated at SmA phase temperatures from a solution of 1 wt% were not affected at all irrespective of whether the films had cracks in the film or not. Judging from a fact that the channel region in the OFETs are formed within a few molecular layers of the OFET material from the interface of gate insulator, this is probably because the crystal films are electrically well connected within a few molecular layers on the gate insulator of SiO_2 even in the films having the cracks, which does not cause a serious problem on the carrier transport in the channel on the gate insulator. In fact, the high FET mobility was almost same in these films fabricated from 0.5 wt% and 0.25 wt% diethylbenzene solutions. It is very interesting to note that the thickness of a thin film fabricated with 0.25 wt% solution, whose thickness is ca. 13 nm, corresponds to four layers of 10-BTBT-10 molecules vertically aligned on the substrate. These results support that the channel in the FET is formed in a few monolayers at the interface of the gate insulator and an organic semiconductor film as reported in oligothiophene and pentacene FETs previously.^{18–20}

All of these results support an idea that a liquid crystal thin film is a good precursor for its polycrystalline thin films suitable for OFETs. We attribute the less defective nature of polycrystalline thin films fabricated by spin-coating at liquid

crystal phases to a fully relaxed crystal structure through step-wise structural relaxation of molecular alignment from the liquid crystal phase to crystal phase, which the soft nature of the liquid crystal phase is very helpful.

IV. CONCLUSION

We have investigated fabrication of polycrystalline thin films of liquid crystalline terthiophene and BTBT derivatives by a spin-coating technique and their application to FETs. We found that uniform and less defective polycrystalline thin films were fabricated by spin-coating their solutions at liquid crystal phase temperatures, and they gave high FET mobility up to 0.1 and 1.5 cm²/Vs for 8-TTP-8 and 10-BTBT-10, respectively. We conclude that the liquid crystallinity in OFET materials is available to fabricate uniform and less defective polycrystalline thin films, for which the liquid crystalline thin films are a good precursor.

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¹Z. Bao, A. Dodabalapur, and A. J. Lovinger, *Appl. Phys. Lett.* **69**, 4108 (1996).

²H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, and D. M. de Leeuw, *Nature (London)* **401**, 685 (1999).

³I. McCulloch, M. Heeney, C. Bailey, K. Genevicius, I. MacDonald, M. Shkunov, D. Sparrowe, S. Tierney, R. Wagner, W. Zhang, M. L. Chabinyc, R. J. Kline, M. D. McGehee, and M. F. Toney, *Nature Mater.* **5**, 328 (2006).

⁴A. Afzali, C. D. Dimitrakopoulos, and T. L. Breen, *J. Am. Chem. Soc.* **124**, 8812 (2002).

⁵M. M. Payne, S. R. Parkin, J. E. Anthony, C.-C. Kuo, and T. N. Jackson, *J. Am. Chem. Soc.* **127**, 4986 (2005).

⁶H. Ebata, T. Izawa, E. Miyazaki, K. Takimiya, M. Ikeda, H. Kuwabara, and T. Yui, *J. Am. Chem. Soc.* **129**, 15732 (2007).

⁷K. Okamoto, T. Kawamura, M. Sone, and K. Ogino, *Liq. Cryst.* **34**, 1001 (2007).

⁸H. E. Katz, J. G. Laquindanum, and A. J. Lovinger, *Chem. Mater.* **10**, 633 (1998).

⁹F. Garnier, R. Hajlaoui, A. El Kassmi, G. Horowitz, L. Laigre, W. Porzio, M. Armanini, and F. Provasoli, *Chem. Mater.* **10**, 3334 (1998).

¹⁰M. Fuhnanashi and J. Hanna, *Appl. Phys. Lett.* **76**, 2574 (2000).

¹¹B. Kosata, V. Kozmik, J. Svoboda, V. Novotna, P. Vanek, and M. Glogarova, *Liq. Cryst.* **30**, 603 (2003).

¹²H. Iino and J. Hanna, "Liquid crystalline materials for organic polycrystalline field effect transistors," *Mol. Cryst. Liq. Cryst.* (in press).

¹³H. Iino and J. Hanna, "Availability of liquid Crystallinity in Solution Processing for Polycrystalline Thin Films," *Adv. Mater.* (in press).

¹⁴V. Lemaire, S. Bouzakraoui, Y. Olivier, P. Brocorens, C. Burhin, J. El Beghdadi, A. Martin-Hoyas, A. M. Jonas, D. A. Serban, A. Vlad, N. Boucher, J. Leroy, M. Sferrazza, P.-O. Mouthuy, S. Melinte, S. Sergeev, Y. Geerts, R. Lazzaroni, J. Cornil, and B. Nysten, *J. Phys. Chem. C* **114**, 4617 (2010).

¹⁵H. Iino and J. Hanna, *Jpn. J. Appl. Phys.* **45**, L867 (2006).

¹⁶A. Hoppe, J. Seekamp, T. Balster, G. Gotz, P. Bauerle, and V. Wagner, *Appl. Phys. Lett.* **91**, 132115 (2007).

¹⁷M. Leufgen, U. Bass, T. Muck, T. Borzenko, G. Schmidt, J. Geurts, V. Wagner, and L. W. Molenkamp, *Synth. Met.* **146**, 341 (2004).

¹⁸A. Dodabalapur, L. Torsi, and H. E. Katz, *Science* **268**, 270 (1995).

¹⁹F. Dinelli, M. Murgia, P. Levy, M. Cavallini, F. Biscarini, and D. M. D. Leeuw, *Phys. Rev. Lett.* **92**, 116802 (2004).

²⁰Kiguchi, M. Nakayama, K. Fujiwara, K. Ueno, T. Shimada, and K. Saiki, *Jpn. J. Appl. Phys.* **42**, L1408 (2003).