Organic Thin Film Transistors Having High Mobility Fabricated by High-Speed Solution Process Using Liquid Crystalline Organic Semiconductors

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ABSTRACT

Organic transistors are fabricated by high-speed blade coating and dip coting using liquid crystalline organic semiconductors. The polycrystalline thin films fabricated by high-speed blade coating at 140 mm/s, the mobility shows about 5 cm^2/Vs and small variation, which is attributed to precursor films of uniform and flat liquid crystalline films, even though high speed solution process.

1 Introduction

Organic thin film transistors (OTFTs) have attracted high attention because of the high expectation of the possible development of solution-processed TFTs. Soluble TFT materials make it possible to fabricate TFTs by solution-processes such as coating and various printing techniques. Various soluble OTFT materials including small molecule and polymer materials have been developed extensively, so that high mobility of over 5 cm^2/Vs were achieved in some of the materials developed so far.

In TFT application of crystalline materials, a small variation of TFT performance from device to device is quite important for active-matrix display. Therefore, the variation of crystallinity and film morphology of crystalline films for each TFT have to be minimized, so that control of nucleation and crystal growth processes are keys for fabrication of crystalline thin films for OTFTs. In solution process with soluble OTFT material, nucleation takes place randomly on the substrate during solvent evaporation, so that the uniformity and morphology of the resulting film become quite poor. In order to control them, edge cast technique and meniscus coating techniques are proposed. Random nucleation on a substrate is suppressed in these techniques and directional growth of crystals is promoted to achieve single crystalline thin films on the substrate, so that the resulting films show high mobility, often of over 10 cm^2/Vs [1,2]. However, these techniques are not practical because of a slow process speed about several mm/min. TFTs for active-matrix display required the high-speed coating.

The organic semiconductor having liquid crystal phase and it is easy fabricate uniform thin film by solution process using liquid crystallinity. In this study, I reported uniform thin film fabricated by spin coating technique using liquid crystallinity and evaluated the performance of the OTFTs with uniform thin films. Furthermore, uniform thin films fabricated by high-speed solution process and the OTFT performance are reported.

2 Liquid crystalline organic semiconductors

2.1 Uniform thin films fabricated by solution process using liquid crystallinity

Molecules of liquid crystalline materials are oriented and ordered in self-aggregation properties in liquid crystal phases. Liquid crystalline thin films are very uniform and flat films by conventional solution process because of the fluidity of liquid crystal properties and the resulting crystalline thin films fabricated with precursor of uniform liquid crystalline films by just cooled down to room temperature. This idea can produce highly crystalline thin films with aligned molecular orientation, high flatness, and high crystallinity in short time by conventional solution process.

In fact, the liquid crystalline films of the liquid crystalline materials such as dialkyl-terthiophene and dialkyl-beozothienobeozothiophene (BTBT) derivatives are very uniform and flat [3,4]. And then the uniform liquid crystal films are just cooled down to room temperature and crystallized, so the resulting polycrystalline thin films are uniform and flat by the conventional spin-coating technique. In fact, atomic force microscopy (AFM) of these polycrystalline thin films shows the molecular level flat, X-ray diffraction (XRD) measurements also show that highly crystalline thin films can be fabricated, and transistors with the polycrystalline thin films shows high mobility and low variation. Thus, it is easy to fabricate polycrystalline thin films which have uniformity, high crystallinity, and high mobility by a conventional solution process using liquid crystalline properties that is low energy consumption and highly productive.

2.2 Suitable liquid crystalline materials for organic transistor, Ph-BTBT-10

Taking account of the merits of liquid crystals [5,6], especially highly ordered smectic liquid crystals, a new type of liquid crystalline organic semiconductor, i.e., decyl-phenyl-benzothienobenzothiophene, Ph-BTBT-10, was designed on the basis of molecular design strategy for highly ordered smectic liquid crystals as shown in Fig. 1(a). In molecular design of this molecule, one side chain of decyl group is attached to Ph-BTBT core in order to induce asymmetric phase transition behavior in heating and cooling processes as shown in a differential scanning calorimetry (DSC) chart as shown in Fig. 1(b). This asymmetric phase transition behavior allows us to fabricate the film at a lower temperature of 93 °C for Smectic E (SmE) phase, and to keep crystalline phase up to 143 °C in principle [7].

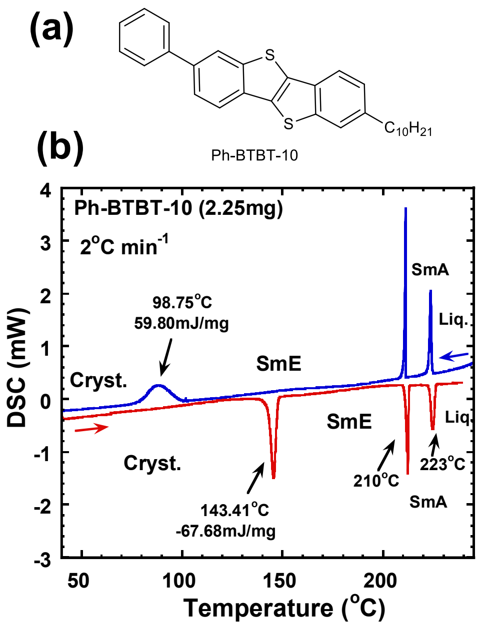

Fig.1 Ph-BTBT-10 thermal behavior. (a) Chemical structure and (b) DSC charts.

2.3 Polycrystalline thin films of Ph-BTBT-10

The polycrystalline thin film of Ph-BTBT-10 fabricated by spin coating technique at a temperature of supercooled liquid crystal phase, about 110 °C, shows no inhomogeneous microcrystalline aggregate structure accompanying crystallization as shown in Fig. 2(a). The cross-sectional profile of this polycrystalline thin films was observed by confocal laser scanning microscopy, and it was found that the film thickness was 50 nm and the surface roughness was small as shown in Fig. 2(b). Furthermore, the AFM images of the surface of the polycrystalline thin films revealed the presence of terrace and step structures (2.8 nm) extending over 10 μm. This step corresponds to the molecular length, corresponding to the (001) peak that appears in the low-angle region observed by out-of-plane XRD measurements of Ph-BTBT-10 crystalline thin film, and the (110), (020), and (120) peaks are observed in the wide-angle region of in-plane XRD measurements, which also confirm that molecules in the thin film is oriented perpendicular to the substrate.

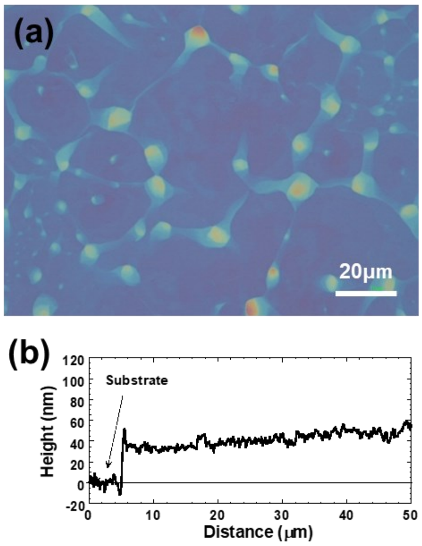

Fig.2 Film morphology of polycrystalline thin films of Ph-BTBT-10. The textures of (a) optical microscope and (b) confocal laser scanning microscope.

2.4 Performance of Ph-BTBT-10 OTFTs

The mobility in a bottom-gate and top-contact type of transistors with the polycrystalline thin film of Ph-BTBT-10 shows about 2 cm²/Vs as shown in Fig.3. Interestingly, the TFT mobility is increased up to of over 10 cm²/Vs by thermal annealing at 120 °C in spite of spin-coated polycrystalline thin films as shown in Fig. 3. It was found that this enhanced TFT mobility is accompanied by the change of crystal structure from monolayered to bilayered crystal structures, as indicated by small angle XRD measurement for the polycrystalline thin film, as shown in Fig. 3. One of the reasons why the crystal structure change causes such the enhanced TFT mobility is due to not only improvement of crystallinity but also enhanced carrier transport path between molecular layers within a bilayer.

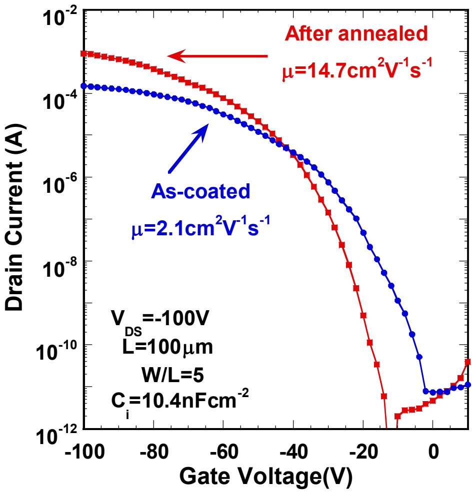

Fig.3 Transfer characteristics of Ph-BTBT-10 OTFTs before and after thermal annealing at 120 °C for 5 min.

3 High-speed fabrication process by blade coating

One of high-speed thin film fabrication process using the liquid crystallinity is blade-coating technique, which is often used in the roll-to-roll process. The film fabrication speed of the blade-coating technique was 140 mm/s [8]. In the film fabrication at room temperature of 30 °C, which is the temperature of the crystal phase, crystal nuclei and crystal growth are randomly generated and occurred, respectively, and the resulting crystalline thin film did not cover the whole substrate surface and had big roughness as shown in Fig. 4(a). This is due to recrystallization on the substrate when organic solvent is evaporated. On the other hand, when the crystalline thin films were formed at 80 °C, which is the supercooled liquid crystal phase temperature, uniform and flat crystalline thin films were fabricated as in Fig. 4(b). This is because no recrystallization occurred when the thin films was fabricated at the supercooled liquid crystal phase temperature, and crystallization occurred during the cooling process to room temperature after the uniform and flat liquid crystal thin films was fabricated.

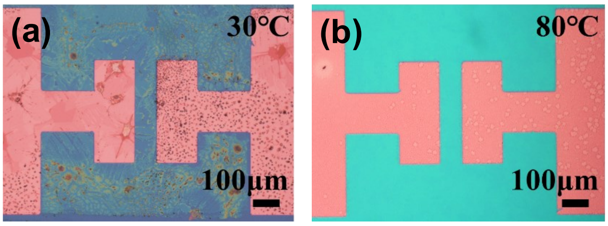

Fig.4 Optical microscopy textures of polycrystalline thin film of Ph-BTBT-10 fabricated by high-speed blade coating at (a) 30 °C and (b) 80 °C.

When organic transistors with bottom-gate-bottom-contact structure were fabricated with these polycrystalline thin films, the average mobility was as low as 0.24 cm^2/Vs due to the inhomogeneity of the polycrystalline thin films fabricated at room temperature, and the variation of transfer characteristics was extremely large as shown in Fig. 5(a). On the other hand, the organic transistor of polycrystalline thin films fabricated at the temperature of liquid crystal phase showed an average mobility of 4.8 cm^2/Vs and a small coefficient of variation of 7.3 %, which is the standard deviation of mobility divided by average mobility as shown in Fig. 5(b).

Especially, in OTFTs with Ph-BTBT-10 polycrystalline thin films fabricated at the temperature of liquid crystalline phase, the threshold voltage was also within the range of 1 V or less, suggesting that the transistors can be used in transistor arrays for active-matrix display and logic integrated circuits.

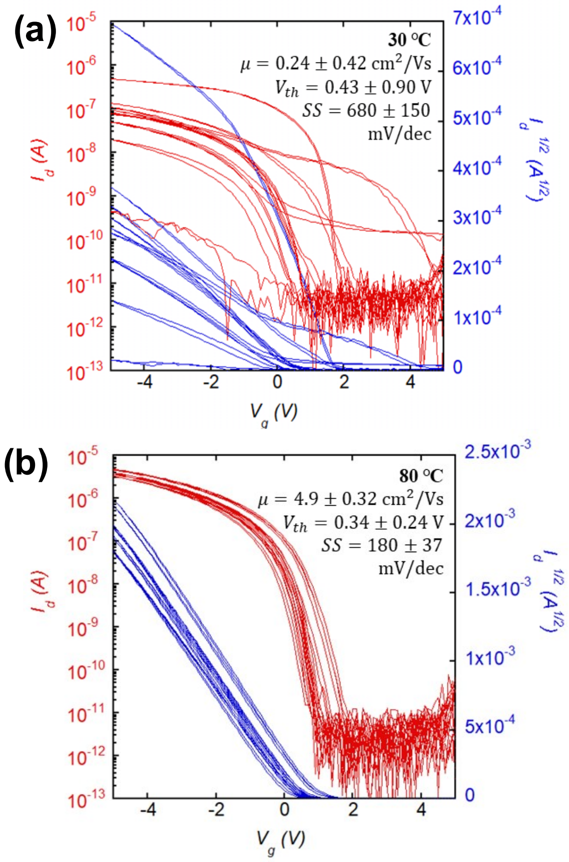

Fig.5 TFT performance of Ph-BTBT-10 polycrystalline thin films fabricated by blade coating at (a) 30 °C and (b) 80 °C.

4 High-speed fabrication process by dip coating

In the dip-coating technique, the uniform and flat polycrystalline thin films can be fabricated using the precursor of uniform liquid crystalline thin films by solution heated on the hot plate at 130 °C [9]. Even at high dip-coating speed of 40 mm/s, uniform and flat crystalline thin films can be realized on the whole surface of about 1-inch square substrate as shown in Fig. 6(a).

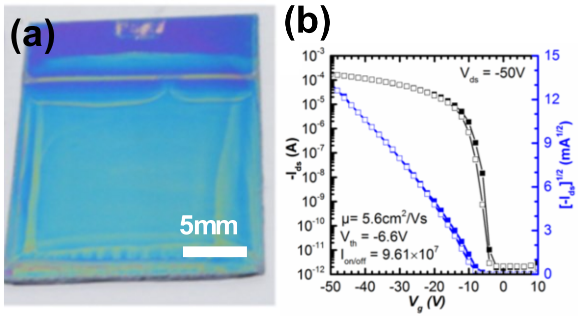

Fig.6 Polycrystalline thin films of Ph-BTBT-10 fabricated by dip coating (40 mm/s). (a) Photographic image and (b) transfer characteristics of OTFTs of polycrystalline thin films.

In the slow dip-coating speed of 5 mm/s, the polycrystalline thin films with large crystal grains oriented in coating direction are formed as shown in Fig. 7(a). On the other hand, polycrystalline thin films fabricated by fast dip coating speed of 40 mm/s has mosaic-like textures which indicates the polycrystalline thin films consist of non-oriented crystal grains as shown in Fig. 7(b). Polycrystalline thin films with no crystal grain orientation have big benefit for practical applications because the transistor performance is independent of coating direction and the design for integrated circuit is not limitation for coating directions. In fact, when bottom-gate bottom-contact transistors were fabricated using these polycrystalline thin films and the electrical characteristics were compared, the polycrystalline film with mosaic-like texture fabricated by high dip coating speed of 40 mm/s exhibits a high mobility of 5.6 cm^2/Vs as shown in Fig. 6(b), furthermore, the standard deviation of the mobility of more than 25 transistors divided by the average mobility is less than 20%, which indicates that the polycrystalline thin films are suitable for active matrix display and integrate circuit.

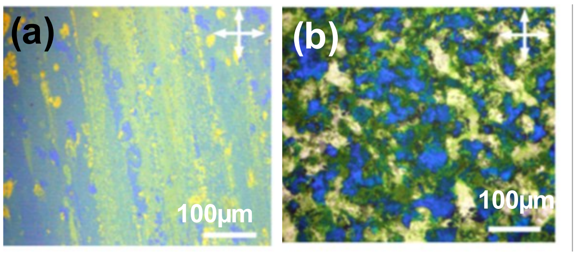

Fig.7 Textures of polycrystalline thin films fabricated by dip coating at (a) 5 mm/s and (b) 40 mm/s.

In order to investigate the scalability of high-speed dip coating technique for large-area substrates, polycrystalline thin films are fabricated not only on 1-inch substrates, but also on 2-inch and even 4-inch substrates. Uniform and flat polycrystalline thin films were achieved regardless of substrate size, and the polycrystalline thin films are consisted of the mosaic-like crystal structure. Bottom-gate bottom-contact transistors (more than 200 transistors) were fabricated with the polycrystalline thin films on large 4-inch square substrate and the transistors exhibited high average mobility about 4 cm^2/Vs and small variation of mobility. These results of dip coating technique indicate that the dip-coating technique using liquid crystallinity is scalable and applicable to the fabrication of high-quality organic semiconductor thin films.

5 Conclusion

Liquid crystalline organic semiconductors are good materials for OTFT applications. It is easy to fabricate the uniform thin film by fast speed solution process. In organic semiconductor materials, liquid crystals are best materials because the liquid crystalline molecules are oriented and ordered by self-aggregation properties, which help the fabrication of uniform and flat crystalline thin film by common solution process. Especially, uniform and flat crystalline thin films are fabricated by blade coating and dip coating with very fast coating speed such as 140 mm/s using liquid crystallinity and the crystalline thin films show high mobility over 4 cm^2/Vs and small variation of transistor performance. Therefore, I concluded that liquid crystals are the good candidate of OTFTs for active-matrix display.

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