SmE Liquid Crystals for High Performance Solution-processed Polycrystalline Organic Field Effect Transistors

Jun-ichi Hanna, Hiroaki Iino, and Masafumi Kunii

Imaging Science and Engineering Research Center, Tokyo Institute of Technology, 4249 Ngatsuta, Midori-ku, Yokohama, Kanagawa, 226-8503, Japan Phone: +81-45-924-5188 E-mail: hanna@isl.titech.ac.jp

Abstract

We propose SmE liquid crystals for high performance OFETs, which can solve a dilemma between solubility and thermal durability of crystalline films, and film uniformity and morphology remained to be solved in soluble small molecule OFET materials. We demonstrated high mobility of over 10 cm²/Vs, high thermal durability up to 200°C, and high tolerance to bias stress in bottom-gate and bottom-contact FETs fabricated with solution-processed polycrystalline thin films of a SmE liquid crystal of Ph-BTBT-10. These results promise a technology basis of the organic semiconductor for practical applications in the future.

1. Introduction

Since high mobility competing with that of amorphous silicon (a-Si:H) was reported in field effect transistors (FETs) fabricated with crystalline thin films of pentacene [1], organic FETs (OFETs) have attracted high attention as a potential candidate for solution-processed transistors required in printed electronics. In fact, soluble OFET materials have been explored for high mobility, and small molecules and polymeric OFET materials exhibiting high mobility of over a few cm²/Vs have been proposed so far, which include TIPS-pentacene [2], C8-BTBT [3], bent-heteropolyacenes V-shaped and N-shaped [4], [5], and do-nor-acceptor type of π -conjugated main-chain polymers [6], [7].

As for the small molecule OFET materials, there is a dilemma between solubility for solution-processes and melting point that determines thermal durability of FETs, so that it is not easy to find an appropriate material for practical applications. On the other hand, polymer OFET materials need to establish an practical technique to fabricate a properly aligned and high crystallinity film, in addition to reliable materials synthesis and purification lot by lot.

For this challenge, we prose a new strategy utilizing SmE liquid crystallinity to solve the dilemma and problems in the small molecules: a crystalline film of SmE liquid crystals can maintain a film form even if the film temperature goes at a SmE temperature thanks to solid-like nature of the SmE film, while it keeps advantages of liquid crystals such as solution-processability and easy formation of uniform and molecularly flat films [8], [9], [10]. In addition, a herringbone structure of crystalline films is promised when

SmE films are crystallized. Furthermore, mono-alkyl OFETs materials may cause a bilayer structure in a crystalline film, which enhances carrier transport due to molecular interaction among the molecules aligned in head-to-head alignment, as shown in Fig. 1.



Fig. 1 Schematic diagram of mono-layered and bilayed configuration of a mono-alkyl small molecule OFET material

In this study, we demonstrate high performance of OFETs fabricated with polycrystalline thin films of 2-decyl-7-phenyl-[1]benzothieno[3,2-b][1]benzothiophene of a SmE liquid crystal, Ph-BTBT-10 [10].

2. Material and fabrication of polycrystalline thin films

Ph-BTBT-10, whose chemical structure is illustrated in Fig. 2, exhibited two smectic mesophases, i.e., SmE phase from 142° C to 210° C and SmA phase from 210° C to 232° C in heating process.



Fig. 2 Chemical structure of Ph-BTBT-10

Polycrystalline thin films of Ph-BTBT-10 were easily fabricated by spin-coating its solution on to a substrate at a SmE temperature of around 100°C and cooling down to room temperature. The resulting films of 50 nm were polycrystalline and consisted of crystal grains of 20 μ m in size. Judging from X-ray diffraction study and the surface profile studied by AFM before and after thermal annealing, as-coated crystalline films exhibited a mono-layered structure and transformed into a bilayered structure, when thermally annealed at a temperature of over 70°C.

3.Fabrication of FETs and their performance

Bottom-gate FETs were fabricated with polycrystalline thin films fabricated by spin-coating a toluene solution of Ph-BTBT-10 at the elevated temperature on SiO₂/Si substrate in both top and bottom-contact configurations.

Fig. 3 shows a typical transfer characteristics of as-fabricated bottom-contact FETs. Average FET mobility for 30 FETs was 3.3 cm²/Vs, while it was increased up to $11.2 \text{ cm}^2/\text{Vs}$ for 49 FETs after the thermal annealing at 120°C for 5 min.[11]



Fig. 3 Transfer and out-put characteristics of as- fabricated and thermally annealed bottom-gate and bottom-contact FETs of Ph-BTBT-10

We compared the thermal durability of FETs of fabricated with polycrystalline thin films of C_{10} -BTBT and Ph-BTBT-10 exhibiting the SmA and the SmE phase at a temperature region next to that of the crystal phase, respectively. Fig. 4 shows FET mobility at room temperature after a thermal stress test at a given temperature for 5 min. The FET mobility in FETs fabricated with Ph-BTBT-10 was not changed at all when the FET was thermally stressed up to 140°C, and kept a high mobility as high as 3 cm²/Vs, even when stressed at 200°C for 5 min, while the FETs fabricated with C₁₀-BTBT was degraded, when stressed at SmA temperatures, as shown in Fig. 4.



Fig. 4 Thermal durability of FETs fabricated with polycrystalline thin films of BTBT derivatives of C_{10} -BTBT and Ph-BTBT-10.

Furthermore, FET performance at a low operation voltage was investigated, and it was found that the saturation mobility was $4.9 \text{ cm}^2/\text{Vs}$ with a high on/off ratio of 10^7 , and the subthreshold swing was 76mV/decay, which is far better than that of inorganic counterparts including a-Si:H and poly-Si FETs and oxide FETs [12].

In addition, stability of the FET devices under a bias-stress conduction, i.e., at $V_{GS}=V_{DS}=20V$ for 15000s, was investigated in order to demonstrate the superior stability of the OFETs against the bias stress. The current was not reduced much and maintained $20\mu A$ even after 15000s, which was 70% of the initial current [13].

4. Conclusions

We have proposed a SmE liquid crystalline OFET material of Ph-BTBT-10 in order to solve the problems remained in soluble small molecule OFET materials. We demonstrated high mobility of over 10 cm²/Vs comparable to those of single crystal OFETs [4],[5],[14], high thermal durability up to 200°C, and high tolerance to bias stress in bottom-gate and bottom-contact FETs solution-processed. These results are not achieved by conventional inorganic counterparts including a-Si:H and Oxide FET materials, and encourage further study of organic semiconductors for practical applications in the future.

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