

Effects of Film Morphology on Ambipolar Transport of Solution-Processed Top-gate-Type Organic Field-Effect Transistors Utilizing Blended Fluorene Derivatives

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1. Introduction

Fluorene-type polymer has emerged as an important class of conducting polymers due to their efficient emission, relatively high mobility and high stabilities. Fluorene-type polymer also has the potential to be in full color emission via energy transfer to longer wavelength emitters in blends with other emitters.

Carrier mobility depends on the microstructure and morphology of the organic layer. Moreover, the surface morphology of the first few layers, where charge transport occurs, can strongly influence the mobility. The effects of film morphology on the electrical properties of p-channel polymer field-effect transistors are mostly investigated.

It is well known in OFETs that charge carriers run a few nm around the interface/semiconductor interface. For the top-gate type structure, whose device has a gate electrode on the gate insulating layer, the channel can be considered to be formed near the surface of the film. Then, top-gate structure was employed for OFETs in this study. We investigated the effects of the film morphology on ambipolar transport in solution-processed top-gate-type OFETs utilizing blended fluorene derivatives.

2. Experimental Procedure

Poly(9,9-dioctylfluorene) (F8), which contains only fluorene backbone, polyfluorene based block copolymer, poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-{2,1',3'-thiadiazole})] (F8BT) with an electron-withdrawing group, and blended F8:F8BT were used as the active semiconducting layers. The substrate was degreased with solvents and cleaned in a UV ozone chamber. Semiconducting layer was formed by spin coating method onto patterned ITO electrodes, which serve as source and drain electrodes, and baked. The channel length and width were 0.1 and 2 mm, respectively. Then, poly(methyl methacrylate) (PMMA) was used as gate insulator. PMMA solution was spun onto a patterned ITO-coated glass substrate and baked above 150 °C. The typical thicknesses of the semiconducting layer and the gate insulator were approximately 60-80 and 500-600 nm, respectively. The gate electrode of Ag with a 50 nm thickness was vacuum evaporated at a background pressure of about 10^{-4} Pa onto the polymer gate insulating layer which was formed on the polyfluorene semiconducting layer. The deposition rate and the thickness of the deposited electrode were monitored using a quartz crystal oscillator.

The measurements of electrical characteristics of OFETs were carried out at room temperature in a vacuum chamber at a background pressure of about 10^{-4} Pa. Differential scanning calorimetry (DSC) scans were taken with a thermo plus EVO II (Rigaku) under nitrogen flow. The heating and cooling rates were +20 and -20 °C/min, respectively.

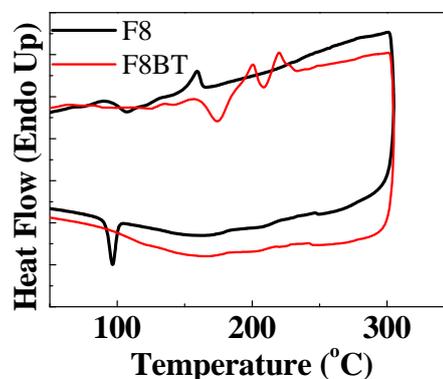


Fig. 1. DSC curves of F8 and F8BT

3. Results and Discussion

Film morphologies depend strongly on the annealing temperature. Figure 1 shows the DSC curves of F8 and F8BT used in our experiments. Phase changes were accompanied by the release or intake of thermal energy, represented by peaks and dips in the DSC curve. Both crystallization and melting processes were observed. From the DSC heating scan, the glass transition temperature, T_g , the crystallization temperature, T_c and the liquid crystal transition temperature, T_m of F8 (F8BT) used in our experiments were estimated to be approximately 70 (160), 110 (170) and 160 (220) °C, respectively. Therefore, the F8 films annealed at both 200 and 290 °C were held in the mesophase. While, the F8BT films annealed at 200 and 290 °C were held in the crystallized phase and mesophase, respectively.

Carrier transport occurs not only along chains but also between neighboring chains. It is considered that intermolecular transport occurs via a hopping or tunneling mechanism. Carrier transport is strongly dependent on the packing of both the polymer chains and the grain boundary. For the top-gate type structure, the channel can be considered to be formed near the surface of the film because the transistor channel is formed in a few nanometer-thick layers at the insulator interface. Therefore, the surface morphologies of F8:F8BT films are of crucial importance for the OFET de-

vice performance. We observed the difference in the thin film morphologies in the topographic images of the F8:F8BT films using a scanning force microscope. Figure 2 shows topographic images of F8:F8BT films baked at different annealing temperature of 200 and 290 °C. For both the 25 mol% F8BT blended films annealed at 200 and 290 °C, a lot of small grains with 200-300 nm-size were observed on the surface. The morphology changed markedly with the F8BT blend ratio. For 50 mol% F8BT blended film, the phase-separated morphology of surface was observed. The mesh-like structure was formed over the surface when the F8BT and F8 annealed at 200 °C were held in the crystallized phase and mesophase, respectively. On the other hand, for F8:F8BT film annealed at 290 °C, the surface structure showed the isolated island-like domains of approximately 2 μm in diameter protruding out of the surface.

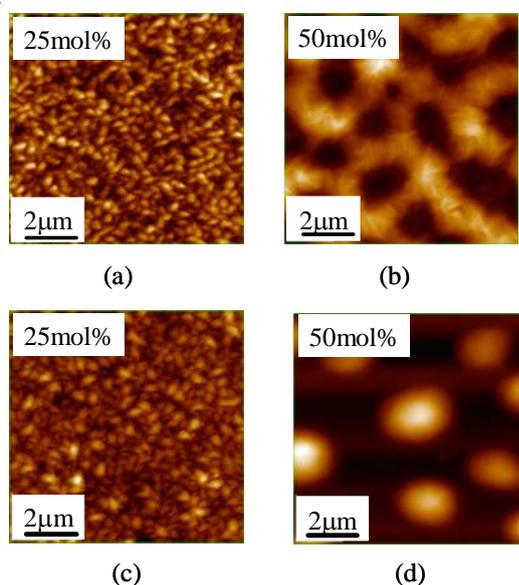


Fig. 2. AFM images of films annealed at (a) (b) 200 and (c) (d) 290 °C utilizing 25 mol % and 50mol % F8BT blended with F8.

The value of work function of ITO electrode exists in the approximately middle between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of F8 and F8BT. Therefore, for top-gate type OFETs with F8 and F8BT as active layers, both holes and electrons from ITO drain/source electrodes into the HOMO and LUMO levels of F8 and F8BT can be expected to be injected by applying voltage. [1] The HOMO level of F8BT is almost the same at that of F8. The LUMO level of F8BT is lower than that of F8. The OFET based on F8 or F8BT films annealed at 200 and 290 °C as the active layer exhibited the ambipolar characteristics with both hole and electron field-effect mobilities of approximately $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ as shown in Fig. 3.

Figure 3 shows F8BT mole ratio dependence of hole and electron field-effect mobilities in the OFETs with F8:F8BT films annealed at 200 and 290 °C. For the OFETs with F8:F8BT films annealed at both 200 and 290 °C, the

hole field-effect mobilities were almost independent on F8BT mole ratio. This is because hole can easily transfer between F8 and F8BT owing to the narrow gap between F8 and F8BT HOMO levels. On the other hand, it is obvious that for both devices, the electron field-effect mobility is dependent markedly on the F8BT mole ratio. The electron field-effect mobilities decreased with increasing the F8BT mole ratio below approximately 25 and 75 mol% for the OFETs with F8:F8BT films annealed at 200 and 290 °C, respectively. This is because F8BT molecules in F8 act as electron trap site owing to the wide gap between F8 and F8BT LUMO levels.

The electron mobility of OFET with F8:F8BT (50 mol%) film annealed at 200 °C is higher than that at 290 °C, and almost the same as that with the F8BT device. From these results, for F8:F8BT(50 mol%) film annealed at 200 °C, the mesh-like structure, as shown in Fig. 2(b), was identified as the F8BT-rich parts. Therefore, above 50 mol% F8BT blended films, the transfer characteristics from F8BT dominated. The difference of F8BT mole ratio dependence of electron mobilities in the OFETs with F8:F8BT films annealed at 200 and 290 °C resulted from the major morphological differences of surface structure that the channel can be considered to be formed.

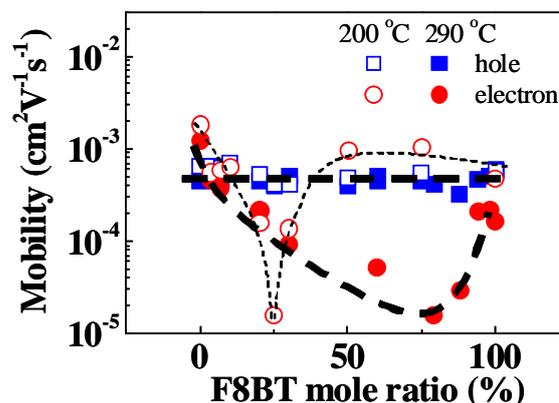


Fig. 3. F8BT mole ratio dependence of hole and electron field-effect mobilities in the OFETs with F8:F8BT films annealed at 200 and 290 °C.

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References

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