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Effects of film morphology on ambipolar transport in top-gate-type organic field-effect transistors using poly(9,9-dioctylfluorene-co-bithiophene)

Kyohei Koiwai, Hirotake Kajii*, Yutaka Ohmori

Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

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ABSTRACT

The effects of film morphology on ambipolar transport in solution-processed top-gate-type organic field-effect transistors (OFETs) utilizing poly(9,9-dioctylfluorene-co-bithiophene) (F8T2) films were investigated. All the F8T2 OFETs without toluene-vapor treatment showed ambipolar characteristics. In contrast, for toluene-vapor-treated F8T2 films at below 250 °C, which were observed to have a small fibrillar structure and a large number of grain boundaries, electron conduction decreased remarkably. Structure ordering in F8T2 films has a strong influence on ambipolar charge transport in OFETs. With an increase in the annealing temperature, the electron transport characteristics were improved. Improving the interface geometry of the F8T2 film, which is related with the decrease of grain boundaries, led to an increase in mobility, and the appearance of ambipolar characteristics. These results suggest that the appearance of electron conduction results not only from the increase in grain size but also from improvements in the connections between grain boundaries in F8T2. Ambipolar F8T2 OFETs exhibited yellow EL emissions, hole and electron field-effect mobilities of approximately 10^{-3} cm^2 V^{-1} s^{-1}, and maximum external quantum efficiency of approximately 0.2%.

1. Introduction

Organic semiconductors have attracted considerable attention, due to their simple and low-cost processing, as well as their potential for electronic and optoelectronic applications. In particular, the possibility of electronic and optoelectronic devices fabricated by solution processing for large-area and flexible devices has been demonstrated. For this reason, organic field-effect transistors (OFETs) have been studied extensively [1–9]. These investigations have yielded high performance of OFETs fabricated using highly crystalline organic materials; however, solution processing is attractive from the viewpoint of a simple fabrication process for large area devices. OFETs with various device structures have been reported to show ambipolar characteristics and light emission [8–18]. In particular, ambipolar materials are useful for fabricating OFETs, because they can be used either as a p-channel or an n-channel by changing the polarity of the gate voltage.

Fluorene-type polymers have emerged as an important class of conducting polymers due to their efficient emission, high stability and relatively high mobility [8,19–21]. Polyfluorene derivatives, the characteristics of which can be modified by copolymerization of fluorene units with various functional groups, can be also applied as a solution-processable buffer layer to modify the surface free energy at the insulator to active layer interface [22]. For OFET application, organic film with crystalline domains can be utilized to facilitate high carrier mobility. The characteristics of devices utilizing polymer films modified by thermal and solvent-vapor treatments are strongly dependent on the self-organized structure. It is known that poly(9,9-dioctylfluorene) (F8), which contains only a fluorene backbone, changes from an amorphous phase to the β phase by toluene-vapor treatment [23], and the β phase F8 shows improved carrier transport and optical characteristics. Polyfluorene-based block copolymers of poly(9,9-dioctylfluorene-co-bithiophene) (F8T2) with the thiophene group as the hole transporter is a promising conducting polymer with high hole mobility and environmental stability. The effects of film morphology on the electrical properties of p-channel polymer field-effect transistors are mostly investigated [24,25]. On the other hand, the ambipolar transport and light-emitting properties of F8T2 devices have been less studied. To investigate the ambipolar properties and the light-emitting characteristics of F8T2 films with crystal domains, it is important to examine the OFET characteristics utilizing polymer films modified by thermal and solvent-vapor treatments further.

In this study, we investigated the effects of the film morphology on ambipolar transport in solution processed top-gate-type OFETs utilizing F8T2 films modified by thermal and solvent-vapor treatments. We also discuss properties of light-emitting field effect transistors by varying the gate voltage.

* Corresponding author.
E-mail address: kajii@oled.eei.eng.osaka-u.ac.jp (H. Kajii).

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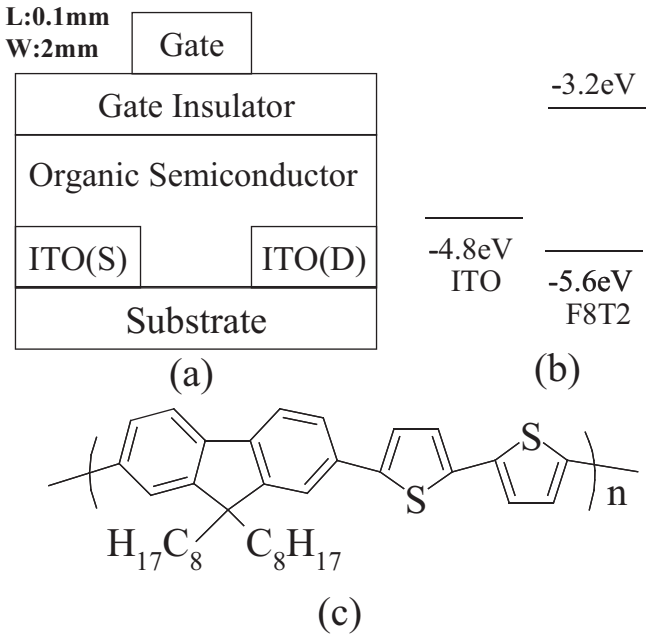

Fig. 1. (a) Device configuration, and (b) energy diagram and (c) molecular structure of F8T2.

2. Experimental procedure

A top-gate-type structure, whose device has a gate electrode on the gate insulating layer, was employed for the OFETs based on F8T2. The fluorene copolymers of F8T2 with different molecular weights (No.1: Mw 41k, No.2: unknown) were supplied by Sumitomo Chemical Co., Ltd. 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 shows the device structure, as well as the schematic energy level diagram and the molecular structure of an amorphous F8T2 film. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of F8T2 were obtained from previously published work [26]. Polished ITO precoated on a glass substrate, and obtained commercially, was used for the source and drain electrodes. Surface morphologies were observed using atomic force microscopy (AFM; JEOL, JSPM-5200). The average surface roughness of the ITO was estimated to be about 0.5 nm, from AFM images. The channel length and width in the device were 0.1 and 2 mm, respectively. The substrate was degreased with solvents and cleaned in a UV ozone chamber. A semiconducting layer was formed by spin coating from a xylene solution onto patterned ITO electrodes, which served as source and drain electrodes, in air and then baked at 80 °C for 10 min. For toluene-vapor treatment, the thin film was exposed to toluene vapor over 40 h at room temperature in a dark place. The typical thickness of the semiconducting layer was approximately 50–80 nm. The F8T2 films with and without toluene-vapor treatment were annealed at various temperatures for 20 min, and subsequent quenching to room temperature was performed in a dry nitrogen glove box.

It is well known in OFETs that charge carriers run a few nm around the insulator/semiconductor interface [27,28]. The OH groups at the interface between the polymer gate insulator and the organic active layer interfere with n-type carrier transport [8,9,15,18,21,29]. Poly(methyl methacrylate) (PMMA), which does not contain electron trapping groups, such as OH, was used as the gate insulator in this study. Using anhydrous n-butyl acetate as a solvent, a PMMA solution was spun onto an active layer and annealed at 80 °C (only F8T2 film annealed at 80 °C) or 150 °C for 20 min. PMMA gate insulator was formed on the active layer without intermixing. The typical thickness of the gate insulator was approximately 600 nm. An Au or Ag gate electrode with a 30 or 50 nm thickness was vacuum-evaporated at a background pressure of about 10^{-4} Pa onto the polymer gate insulating layer formed on the polyfluorene semiconducting layer. The deposition rate and thickness of the deposited electrode were monitored using a quartz crystal oscillator.

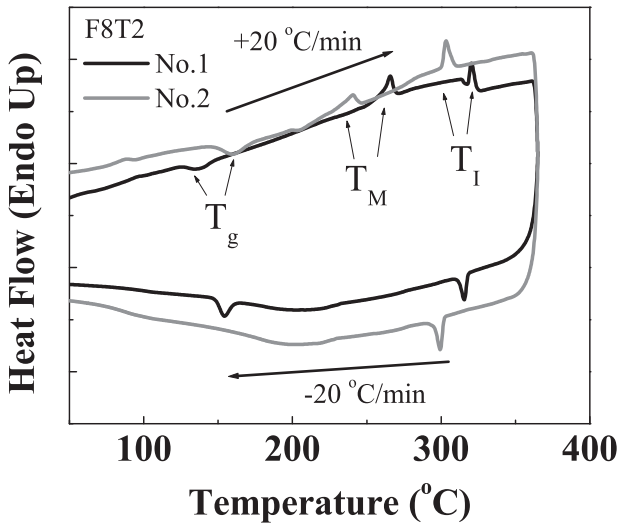

Fig. 2. DSC curves for the F8T2 (No.1, No.2) films.

After the deposition of the Au or Ag gate electrode, devices were exposed to air. Then, measurements of electrical and optical characteristics of the OFETs were carried out at room temperature in a vacuum chamber with a background pressure of about 10^{-4} Pa after evacuation for more than 6 h. The current–voltage characteristics were obtained using 2400 and 6517A source meters (Keithley). The electroluminescence (EL) output was measured using a S1337 or S2281 silicon photodiode (Hamamatsu Photonics). The EL spectra were measured using a photonic multichannel spectral analyzer (Hamamatsu Photonics PMA-11). For the measurement of EL spectra, the devices were covered with a glass plate and encapsulated by epoxy resin in an argon gas atmosphere to prevent oxidation of the electrode and the organic layer. External quantum efficiency was calculated from the conventionally measured parameters: EL output, EL spectrum and current [30].

3. Results and discussion

Film morphologies depend strongly on the annealing temperature. Fig. 2 shows the DSC curves of F8T2 (No.1, No.2) films 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 liquid crystal transition temperature, T_M, and isotropic transition temperature, T_I, of the F8T2 films used in our experiments were estimated to be approximately 135 (160), 265 (240), and 320 (300) °C, respectively, for F8T2 (No.1) (F8T2 (No.2)). These temperatures are in good agreement with those previously reported [24,25]. Therefore, the F8T2 films annealed at 80 °C, 250 °C for No.1 (or 220 °C for No.2), 290 °C and 350 °C were held in the amorphous phase, crystallized phase, mesophase and isotropic phase, respectively.

Carrier transport occurs not only along chains but also between neighboring chains. It is considered that intermolecular transport