Polymer Field Effect Transistors of F8T2 Prepared by Evaporative Spray Deposition using Ultradilute Solution Technique

Koji Sagane¹, Masato Shakutsui¹, Tetsuo Tsutsui¹,², and Katsuhiko Fujita¹,²*  

¹Department of Applied Science for Electronics and Materials, Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga Koen, Kasuga, Fukuoka 816-8580, Japan  
²Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga Koen, Kasuga, Fukuoka 816-8580, Japan

The evaporative spray deposition using ultradilute solution (ESDUS) technique enables layer-by-layer and pixel-by-pixel deposition of polymer semiconductors. In this study we prepared thin films of diocylfluorene-co-bithiophene) alternating copolymer, F8T2, by ESDUS and by a conventional spin-coat. These films were made into fabricated field effect transistors to investigate carrier transportation properties. Since the organic films were formed by deposition of aerosol particles in ESDUS, the carrier transportation properties in ESDUS films had been expected lower than those in spin-coat films, which are formed through spread polymer solution. However, the device performance was almost identical, indicating that the polymer deposited as particles undergoes rearrangement process on the substrate.  

Keywords: spray deposition, organic field effect transistor, polymer light-emitting diodes, polymer thin film, conjugated polymer

1. Introduction

The evaporative spray deposition using ultradilute solution (ESDUS) technique is a polymer thin film preparation method having significant four advantageous features: 1) non-vacuum process, 2) pixel size deposition with simple shadow masks, 3) device fabrication of polymers showing very low solubility, 4) layer-by-layer deposition of polymers soluble to a same solvent. Recently we demonstrated that polymer light-emitting diodes (PLEDs) with a polymer stacking layered structure were fabricated by ESDUS, resulting drastic improvement in the device performance [1-3].

The ESDUS apparatus is schematically illustrated in Fig. 1. The sample solution of a concentration around 1 ppm is nebulized into air and made into an aerosol with the particle size of around 10μm. The aerosol is transported by nitrogen carrier gas from the first chamber to a nozzle facing a substrate in the second chamber. During the transportation, the solution particles shrink with the evaporation of the solvent. The substrate is held on a ceramic heater with a thermocouple settled on an x-y positioner stage. The particles containing the appropriate amount of the solvent are deposited onto the substrate while keeping the distance from the nozzle constant for homogeneous deposition. The flatness or thickness of the resulted films can be controlled by the spraying rate, chamber temperature and substrate temperature.

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The organic films prepared by ESDUS are formed by the deposition of the particles. Therefore, the growth process of the films should be very different from those by conventional methods such as spin-coat. Although PLEDs and photovoltaic cells prepared by ESDUS showed better or almost identical device performance compared with those by spin-coat, those devices are sandwiched structure, i.e. 100 nm of short and vertical carrier transportation. It is worth to compare ESDUS films with spin-coat films in a device with long and horizontal carrier transportation. In the present study, the organic field effect transistors (OFETs) prepared by ESDUS and by spin-coat were compared.

2. Experimental

We prepared a polymer film of dioctylfluorene-co-bithiophene alternating copolymer, F8T2 (Fig. 2, Sumitomo,Chem.). The spin-coated films were formed on a glass substrate or a Si/SiO$_2$ using 0.4 wt% chloroform solution, followed by annealing at 150 and 280 °C for 1 min in air. The ESDUS films were deposited onto precleaned glass or Si/SiO$_2$ substrates using THF solution of F8T2 at the concentration of 4×10$^{-4}$ wt% with the substrate temperature of 120 °C, followed by annealing at 150 and 280 °C for 1 min in air. The films on glass substrates were used for spectroscopic investigation. Gold source-drain electrodes (channel width W=5mm, length L=75μm) were vacuum-deposited on Si/SiO$_2$/F8T2 to fabricate FET with bottom gate-top contact geometry. The surface morphology and the film thickness were determined by atomic force microscopy (AFM) (Nanopics 100, SII).

3. Results and discussion

F8T2 is widely investigated as an active layer of OFETs.[4] Thermotropic transitions were investigated using differential scanning calorimetry (DSC, TA Instruments Q100). Fig. 3 shows the DSC profile of F8T2 in heating scan at the rate of 10 °C/min in N$_2$. An exothermic peak around 103 °C should be attributed to a glass transition. An endothermic peaks around 246 °C, 273 °C and 330 °C are corresponding to a solid-mesophase transition, a mesophase-mesophase transition and a mesophase-isotropic transition, respectively.[5]

The optical properties of F8T2 films on glass substrates prepared by ESDUS and by spin-coat with annealing at various temperatures. The absorption spectra (Fig. 4) show that the absorbance is significantly decreased when the films are annealed at high temperature. It should be caused by the change of the molecular orientation when the molecules become mobile at the liquid crystal phase.
The surface morphology of the F8T2 films was observed using AFM (Fig. 5). In the comparison of the films without annealing [Fig. 5 (a) and (d)], the ESDUS film gave undulated surface, probably aggregated, while the spin-coat film gave smooth surface. On the other hand, surface morphology
was quite similar in ESDUS films and spin-coat films [Fig. 5 (b), (c), (e), (f)]. Small domains appeared as the temperature increased. This tendency is almost identical to the previously reported results.[5]

The output characteristics of the F8T2 OFETs prepared by ESDUS and spin-coat without annealing were shown in Figure 6. In the saturation regime, drain current is modeled with the standard FET equation [6]. The field effect hole mobility and threshold voltage were summarized in Table 1.

The field effect hole mobility shows decrease tendency when the annealing temperature increases. The device characteristics were almost compatible within experimental error in both methods. In ESDUS, the substrates were heated at 120 °C during the deposition to prevent condensation of the solvent.

<table>
<thead>
<tr>
<th>Anneal</th>
<th>Method</th>
<th>Mobility ($\times 10^{-3}$cm$^2$/Vs)</th>
<th>Threshold (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>without</td>
<td>ESDUS</td>
<td>1.1 ± 0.6</td>
<td>-18</td>
</tr>
<tr>
<td></td>
<td>Spin-coat</td>
<td>2.3 ± 0.3</td>
<td>-13</td>
</tr>
<tr>
<td>150 °C</td>
<td>ESDUS</td>
<td>1.2 ± 0.1</td>
<td>-13</td>
</tr>
<tr>
<td></td>
<td>Spin-coat</td>
<td>1.7 ± 0.7</td>
<td>-15</td>
</tr>
<tr>
<td>280 °C</td>
<td>ESDUS</td>
<td>0.6 ± 0.4</td>
<td>-11</td>
</tr>
<tr>
<td></td>
<td>Spin-coat</td>
<td>1.4 ± 0.5</td>
<td>-18</td>
</tr>
</tbody>
</table>

Average of three individual devices

It can be understood in terms of the temperature during the deposition that absorbance of the ESDUS film without annealing is almost identical to that at 150 °C while that of spin-coat film is different (Figure 4) The field effect hole mobility of ESDUS film without annealing is very close to that with annealing at 150 °C. The molecular arrangement in ESDUS film without annealing should be very close to that with annealing at 150 °C.

ESDUS films are formed by deposition of aerosol particles. We thought that the molecular arrangement or entanglement might be very different from those in the films prepared by spin-coat. However, the films of F8T2 showed almost compatible optical and electronic properties. Polymers having mobile nature, low glass transition temperature or liquid crystal, should be rearranged on the substrate during the deposition after they are deposited as particles. It should be required to investigate properties of less mobile polymers in ESDUS films

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**References**