

Controllable *n*- to *p*-type doping of MEH-PPV films by evaporative spray deposition using ultra-dilute solution method

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Abstract

Evaporative spray deposition using ultra-dilute solution (ESDUS) technique enables polymer film preparation using diluted solution at ppm level and layer by layer deposition of organic semiconductors with out damaging bottom layers. We used this method to prepare *p*-type and *n*-type doping in identical polymer semiconductors. The device characteristics indicated drastic improvement of the conductivity with the electron mobility.

1. Introduction

Organic semiconductors such organic light-emitting diodes or solar cells are almost used in the non-doped state. Therefore, the loss due to resistance of the semiconductor inside the low carrier density is large. One method to solve this problem is a carrier doping, dispersing donor or acceptor molecules in the organic semiconductor. The carrier density of the organic semiconductor by carrier doping increases, the conductivity can be greatly improved. However, the known dopants are hardly soluble in organic solvent which can dissolve the semiconductor materials and are also unstable in the air. This is main reason that the fabrication of organic semiconductor devices by wet process makes more difficult.

Recently, we have developed a polymer thin film preparation method, Evaporative Spray Deposition using Ultra-dilute Solution (ESDUS) [1], which enables preparing polymer semiconductor films using highly diluted solution at several ppm. In a previous report, taking advantage of enabling the film preparation of polymer semiconductors using ultra-dilute solution, we have tried to prepare *n*-type doped polymer semiconductor thin films with Cs_2CO_3 which is known as effective *n*-type dopant and low solubility in organic solvent. As the result, the conductivity was significantly improved with high doping efficiency. Furthermore, we have also tried preparing and evaluation of the pn junction by laminating *n*-type doped polymer semiconductor film on the

p-type doped polymer semiconductor film. Interestingly, it became clear that depletion layer was present and the theory of inorganic semiconductor was applicable [2].

In the current study, to extend the possibility of polymer semiconductors, we attempted *p*- and *n*-type doping in the similar polymer semiconductor. One of most versatile conductive polymer, MEH-PPV (LUMO: 3.1 eV [3], HOMO: 5.2 eV [3]) was chosen as the host polymer semiconductors, a *p*-type dopant FeCl_3 (WF: 5.52 eV [4]) and a *n*-type dopant Cs_2CO_3 (WF: 2.96 eV [4]) were introduced in the MEH-PPV films by ESDUS method respectively.

2. Experimental

A schematic diagram of ESDUS method is shown in Fig.1. MEH-PPV was dissolved at 10 ppm in THF. By the optimization of temperature of the 1st chamber (aerosol produced room) and the 2nd chamber (film deposition chamber), substrate temperature, carrier gas flow rate, and the liquid feed flow rate, a 20 nm-thick thin film with homogeneous and continuous was obtained (1 scan: 2 minutes deposition). After 2 scans deposition, there weren't almost damage to underlayer (confirmed by UV-vis measurement).

Dopants were dissolved in dehydrate ethanol at the concentration of 3 mg/ml by stirring overnight at 50°C in a glove box. After that, these dopant solutions were added to 10 ppm THF solution of MEH-PPV at desired ratio (0-2 wt% against polymer) respectively.

(Current-voltage (I-V) characterization) Current-voltage (I-V) characteristics were measured by Keithley 238 source meter. Carrier current increase due to donor molecule doping was evaluated by the fabrication of electro-only-device (EOD): Al/MEH-PPV (5 scans, 100 nm)/Ca. Hole current increase due to acceptor molecule doping was evaluated by the fabrication of hole-only-device (HOD): ITO/MEH-PPV (3 scans, 60 nm)/Al. Hole and carrier density of the non-doped MEH-PPV and these mobility were calculated from the I-V characteristics.

(Surface (Kelvin) potential measurements) Hole and carrier density of doped MEH-PPV films were estimated from surface potential (Keivin probe, FAC-1, Riken Keiki) measurements of comparison between non-doped and doped MEH-PPV film (5 scans, 100 nm on the Al electrode) with respect to the Au standard (5.03 eV).

3. Result and discussion

The I-V characteristics of EODs with Cs_2CO_3 and HODs with FeCl_3 at various ratios, 0-2 wt% was described in Fig.2. The current was increased as the doping concentration got higher. The non-doped MEH-PPV devices showed typical space charge limited current behavior (slope 2) and ohmic behavior (slope 1) in the low-bias regions. Since inflection voltage (V_T) from ohmic behavior can be seen, the carrier and hole density of the non-doped

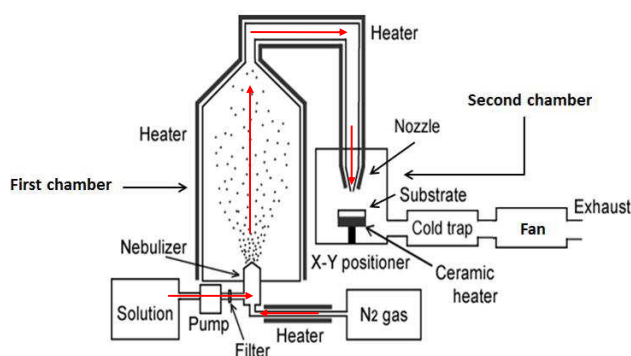


Fig. 1 Schematic illustration of ESDUS apparatus.

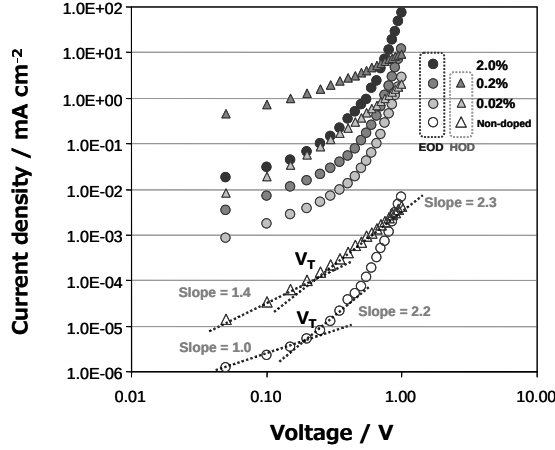


Fig. 2 I-V characteristics of EODs and HODs with Cs_2CO_3 and FeCl_3 at doping concentration at 0, 0.02, 0.2, 2% respectively.

MEH-PPV were determined by using following equation (1) which is defined by Blom et al [5].

$$N = \frac{9}{8} \cdot \frac{\epsilon_0 \epsilon_r}{q} \cdot \frac{V_T}{d^2} \quad (1)$$

The carrier density (N_{Di}) and hole density (N_{Ai}) could be estimated to be $5.9 \times 10^{21} \text{ m}^{-3}$ and $1.2 \times 10^{22} \text{ m}^{-3}$ respectively. Since the slopes for the doped devices were approximately 1 indicated the Ohmic behavior, the carrier and hole density of the doped MEH-PPV were determined by using following equation (2,3) and surface potential measurements of comparison between non-doped(E_i) and doped(E_F) MEH-PPV layer.

$$N_D = N_{Di} \cdot \exp\left(\frac{E_F - E_i}{\kappa_B T}\right) \quad (2)$$

$$N_A = N_{Ai} \cdot \exp\left(\frac{E_i - E_F}{\kappa_B T}\right) \quad (3)$$

Cs_2CO_3 could be introduced at high concentration to the host polymer without reducing the MEH-PPV film's quality. On the other hand, FeCl_3 doping reduced the film's quality remarkably from beyond 0.5 wt%. It seems to be originated from the aggregation of dopants and reflected the difference in solubility of the dopants to THF. The doping efficiency was determined from the ratios of the increased carrier and hole density and the molecular density of introduced Cs_2CO_3 and FeCl_3 , as shown in Table I. While the doping efficiency of FeCl_3 (the solubility to THF decreased with the concentration increase) decreased, the doping efficiency of Cs_2CO_3 only slightly decreased. Nonetheless, high doping efficiency of over 10%, significant increase in hole and carrier density was found to be realized. At the present stage, we believe that high dispersion of the dopants in ultra-dilute solution lead to good doping efficiency and high charge separation with the host polymer.

Furthermore, the electron mobility and hole mobility of MEH-PPV film was increased with doping level increase (Fig.3). This result indicates that carrier or hole transport in the non-doped MEH-PPV is dominated by carrier or hole trapping, enable to

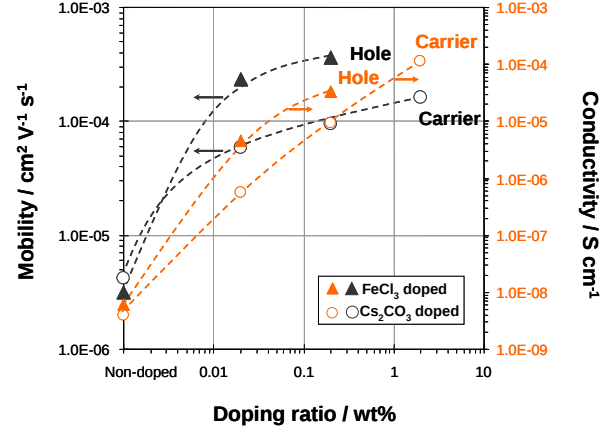


Fig. 3 Carrier & Hole mobility and conductivity of MEH-PPV films with Cs_2CO_3 and FeCl_3 at doping concentration at 0, 0.02, 0.2, 2%.

increase the mobility by the doping. The conductivity was also enhanced by the improvement of mobility.

Table I Carrier(N_D) and hole(N_A) density, were estimated from surface potential measurement (Kelvin probe)

Doping ratio (wt%)	$N_A \text{ (m}^{-3}\text{)}$ (Doping efficiency)	$N_D \text{ (m}^{-3}\text{)}$ (Doping efficiency)	$E_f \text{ (eV)}$
undoped	1.2×10^{22}	5.9×10^{21}	4.35
0.02	1.2×10^{23} (14.9%)	6.0×10^{22} (14.7%)	4.41 / 4.29
0.2	5.8×10^{23} (7.9%)	6.2×10^{23} (16.5%)	4.45 / 4.23
2	—	4.3×10^{24} (11.5%)	— / 4.18

3. Conclusions

We demonstrated the preparation of laminated-able and controllable n- to p-type doping of MEH-PPV films by ESDUS method. ESDUS method is also capable to deposit with high fineness, can be expected to be applied to the print devices such as transistors in the future.

Acknowledgements

We thank Shuzi Hayase and Yuhei Ogomi (Kyushu Institute of Technology University, Japan) for Kelvin probe measurement.

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