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P-type and N-type Doping for Polymer Semiconductor by Wet Process

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Abstract

Evaporative spray deposition using ultra-dilute solution (ESDUS) technique enables polymer film preparation using diluted solution at ppm level. We used this method to prepare p- and n-type doping in poly(2-methoxy-5-(2'-methyl-hexyloxy)-p-phenylenevinylene) (MEH-PPV) which is a bipolar-transport polymer semiconductor. The device characteristics indicated drastic improvement of the conductivity with the carrier mobility. Moreover, doping efficiency was beyond 15% in both p- and n-type doping due to the high dopant dispersion realized by the ESDUS technique.

1. Introduction

Non-doped organic semiconductors are used usually in organic devices such as organic light-emitting diodes (OLEDs) and solar cells, though inorganic semiconductor devices are realized by doped semiconductors. Carrier doping have been attempted with dispersing donor or acceptor molecules in some organic semiconductors. [1,2] The conductivity can be improved significantly. On the other hand, high doping efficiency in polymer semiconductors have not been realized yet, because there are some problems in n-type molecular dopants. The representative dopants used in co-evaporation such as Cs_2CO_3, $FeCl_3$ and CsF are poorly soluble in organic solvents which can dissolve polymer semiconductors, and aggregate easily in the polymer matrix by spin coat method even if they are dispersed in a polymer solution. Therefore, doping efficiency in polymer semiconductor has been very low, at highest 3%.

We have developed a polymer thin film preparation method, Evaporative Spray Deposition using Ultra-dilute Solution (ESDUS), which enables preparing polymer semiconductor films using highly diluted solution at several ppm. In the present study, we attempted p- and n-doping in a polymer semiconductor, poly(2-methoxy-5-(2'-methyl-hexyloxy)-p-phenyl enevinylene) (MEH-PPV LUMO: 3.1 eV, HOMO: 5.2 eV). It is one of most widely used conductive polymer and known as a bipolar carrier transporting semiconductor. $FeCl_3$ (work function: 5.52 eV) as a p-dopant and Cs_2CO_3 (work function: 2.96 eV) as an n-type dopant were chosen for p- and n-doping in MEH-PPV, respectively.

2. Materials and Methods

A schematic illustration of ESDUS apparatus is shown in Fig. 1. MEH-PPV was dissolved in THF at 10 ppm. After the optimization of deposition condition such as the temperature, carrier gas flow rate, and solution feed flow rate, homogeneous and continuous film with 20 nm-thickness was obtained.

Each dopant molecule was dissolved in dehydrate ethanol at the concentration of 3 mg/ml and the solution was kept in a glove box with stirring overnight at 50°C. The dopant solution was diluted by THF and added to THF solution of MEH-PPV. The concentration of polymer was kept constant at 10 ppm and the dopant concentration was varied at 0.02, 0.2, 2 wt% against polymer. The MEH-PPV solution containing each dopant was supplied to ESDUS and made into thin films. Electro-only-device (EOD): Al/MEH-PPV (100 nm)/Ca and hole-only-device (HOD): ITO/MEH-PPV (100 nm)/Au were fabricated by vacuum deposition of top electrode after ESDUS preparation of MEH-PPV layer with desired doping concentration. Current-voltage (I-V)

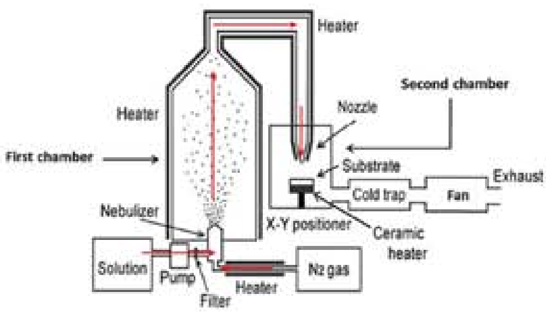

Figure 1. Schematic illustration of ESDUS apparatus.

characteristics were measured by Keithley 238 source meter without breaking vacuum after top electrode deposition. Hole and electron density of the non-doped MEH-PPV was calculated from the I-V curves. The Fermi levels of the MEH-PPV films were estimated by using surface potential meter (Keivin prove, FAC-1, Riken Keiki) in nitrogen without exposing the samples to the ambient atmosphere after ESDUS film deposition. The non-doped and doped MEH-PPV films were fabricated at 100 nm on the Al and the Fermi level was estimated with respect to the Au standard (5.03 eV).

3. Result and Discussion

The I-V characteristics of HODs with varying $FeCl_3$ concentration (Fig. 2a) and EODs with varying Cs_2CO_3 concentration (Fig. 2b) clearly indicate that the current density increases significantly as the doping concentration gets higher. The conductivity calculated from the Ohmic regions of I-V curves increases almost linearly against the doping concentration (Fig. 3). The conductivity can be affected by not only carrier density but also carrier mobility. We estimated the carrier density of the films. Since the non-doped films shows Ohmic behavior at lower than VT and space charge limited current behavior at higher, the carrier density (N) can be determined by I-V curves.

The electon density (NDi) and hole density (NAi) are estimated to be 5.9×10^{21} m^{-3} and 1.2×10^{22} m^{-3} respectively. The Fermi levels were measured by using Kelvin prove. Cs_2CO_3 doping shifts Fermi level to negative side and $FeCl_3$ doping shifts to positive side, indicating that control of n-doping and p-doping in MEH-PPV films can be achieved by changing the dopant. The electron density and hole density and doping efficiency of the doped MEH-PPV films were estimated. The carrier density increases with dopant concentration linearly and the doping efficiency is as high as 15% at low dopant concentration. It decreases gradually with the dopant concentration. In MEH-PPV films containing $FeCl_3$ at higher than 0.5 wt%,

significant aggregation was seen at surface microscopic observation. Therefore, the decrease in the doping efficiency should be caused by the dopant aggregation in the film. The high dispersion of the dopants in ultra-dilute solution lead to good doping efficiency and high charge separation with the host polymer. [3]

4. Conclusion

We demonstrated the preparation of controllable p- to n-type doping of MEH-PPV films by ESDUS method. Cs_2CO_3 and $FeCl_3$ doping using ESDUS method dramatically improve conductivity of MEH-PPV. Furthermore, the doping efficiency at as high as 15% has been achieved in both p-doping and n-doping. We can expect next stage of the printed electronics with the high doping efficiency in polymer semiconductor materials.

References

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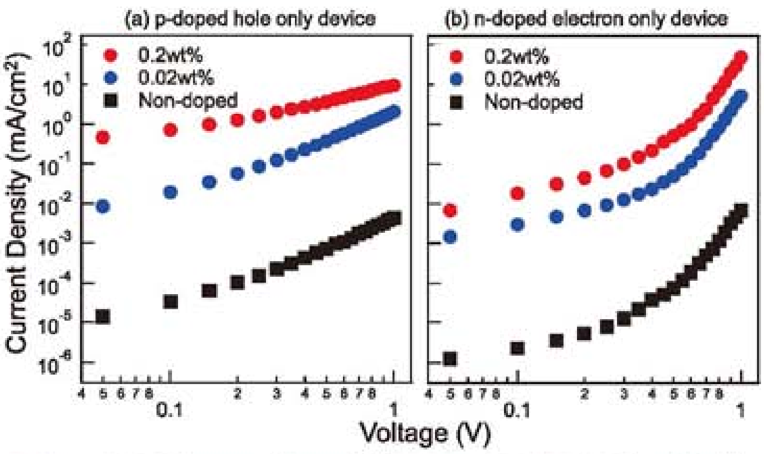

Figure 2. I-V characteristics of (a) HODs of MEH-PPV doped with $FeCl_3$ (b) EODs of MEH-PPV doped with Cs_2CO_3, at dopant concentration of 0, 0.02, 0.2 wt %

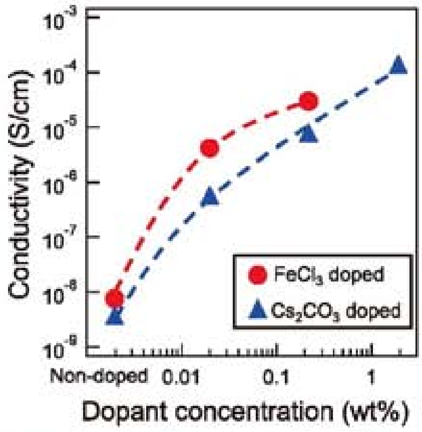

Figure 3. Conductivity of EODs and HODs with Cs_2CO_3 and $FeCl_3$ at dopant concentration of 0, 0.02, 0.2, 2 wt %.