

Establishing pn junction of doped organic semiconductors by wet process

Naoki Mizutani¹, Toshinori Hayashida², Katsuhiko Fujita^{1,2}

¹ Institute Materials Chemistry Engineering, Kyushu University

² Interdisciplinary Graduate School of Engineering Science, Kyushu University

6-1 Kasuga Kouen, Kasuga, Fukuoka 816-8580, JAPAN

Phone&Fax: +81-92-583-7532 E-mail: katsuf@sem.kyushu-u.ac.jp

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 without damaging bottom layers. We used this method to prepare n-type doping in polymer semiconductors and establish pn junction. The device characteristics indicated drastic improvement of conductivity and depression layer with finite width.

1. Introduction

Organic devices such as organic light emitting devices (OLEDs), photovoltaic cells (PVs) and transistors are prepared with non-doped organic semiconductors and driven by injected carriers from electrodes. It requires very thin film at some hundred nanometers for active layers due to the low conductivity of organic semiconductors. It is not easy to form such very thin films at large scale without any defects or pin holes. It was a largest obstacle to printed electronics. Since p-doped polymer semiconductors, such as PEDOT:PSS, have been used in various organic devices, problems are lying in the n-doping. The known n-dopants are almost insoluble in organic solvent which can dissolve the semiconductor materials. This is main reason that the research of n-doping in solution processes

We have reported that a polymer thin film preparation technique, ESDUS has enabled preparing an organic thin film from highly diluted solutions at a concentration of 1 ppm, and fabricating PLEDs [1], organic photovoltaics [2] and organic field-effect transistors [3]. In addition, this method has been exhibited that a successive polymer layer can be deposited without damaging the proceeding polymer layer using a same organic solvent for each layer deposition [4,5].

Some alkaline metal salts are slightly soluble in relatively polar organic solvent. Tetrahydrofuran (THF) is good solvent for most of polymer semiconductors and contains no halogen or aromatic moieties, and can dissolve Cs_2CO_3 at several ppm concentration. We attempted n-doping by mixing the dopant and polymer semiconductor at appropriate ratio and pn junction by stacking p-doped polymer and n-doped polymer with ESDUS technique.

2. Experimental

2.1 Fabrication of electron only device (EOD) and pn devices

Tiny amount of Cs_2CO_3 was dissolved in THF. The concentration was determined with inductively coupled plasma (ICP) method using standard Cs ion solution as a reference. The Cs_2CO_3 solution was added to 10 ppm THF solution of Poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT) at desired ratio.

For an EOD, a glass substrate with Al (100nm) was used.. The F8BT: Cs_2CO_3 solution was supplied to the ESDUS apparatus and sprayed onto the substrate to obtain 50 nm thick film. The upper Al electrode was formed in the vacuum evaporator.

For a pn device, ITO coated glass substrate were used. Onto the pre-cleaned substrate Poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate)(PEDOT:PSS) was spun, followed by annealing at 150°C for 10min. The solution of Poly(3-hexylthiophene)(P3HT) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), 1:5x10⁻⁵ w/w in chloroform was spun on the PEDOT:PSS to obtain 100 nm p-doped P3HT film. The n-doped F8BT was deposited by ESDUS method and upper Al electrode was formed by vacuum deposition as described above.

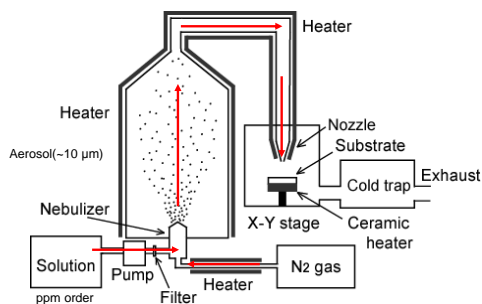


Fig.1 Schematic illustration of ESDUS apparatus

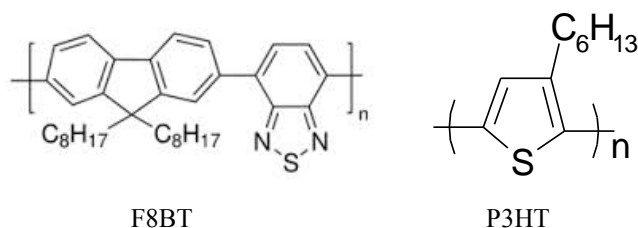


Fig.2 The molecular structure of the polymers used.

2.2 Characterization

Current-voltage (J-V) characteristic and capacity-voltage (C-V) characteristics were measured by Keithley 238 source meter and Solartron 1260 impedance analyzer, respectively. The ionization potential was measured with photo yield spectroscopy (PYS, AC-2 riken keiki)

3. Result and discussion

The I-V characteristics of EODs with Cs_2CO_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 device showed the slope of 2 indicating typical space charge limited current. The slopes for the doped devices were 1 which indicated the Ohmic behavior.

$$J = e\mu NVL^{-1} \quad (1)$$

The carrier density, N , can be estimated to be $3 \times 10^{13} \text{ cm}^{-3}$ from the eq. (1) under the assumption of the carrier mobility is identical to the non-doped state. The doping efficiency was 0.07%. This value is much higher than that of Alq_3 : Cs_2CO_3 prepared by vacuum deposition[5].

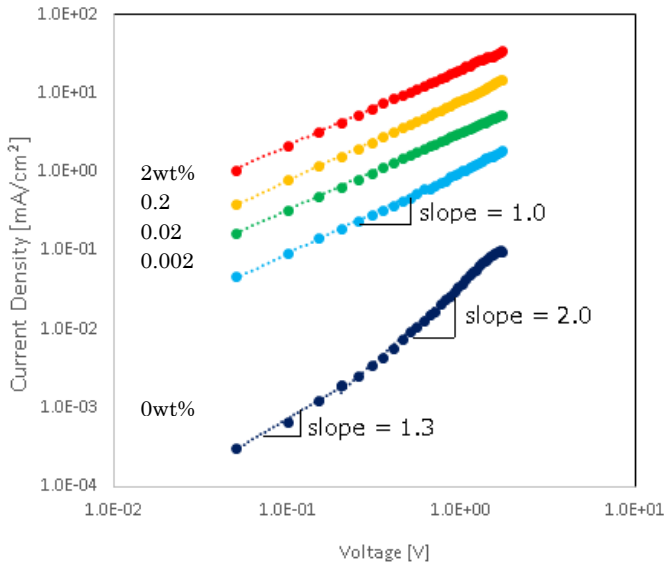


Fig. 3 I-V characteristics of EODs with Cs_2CO_3 at doping concentration at 0, 0.002, 0.02, 0.2, 2 wt%.

The stacked device of p-doped P3HT/n-doped F8BT showed rectification. The C-V characteristics with Cs_2CO_3 at various doping concentration are measured. In the non-doped device the capacitance was constant. However, doped device showed significant increase at the forward bias. One over the capacitance squared against V is plotted in Fig. 4.

$$C^{-2} = 2(V_{bi} - V) / e\epsilon_s N \quad (2)$$

The depletion capacitance follows equation (2). The capacitance behavior suggests existence of the depletion layer.

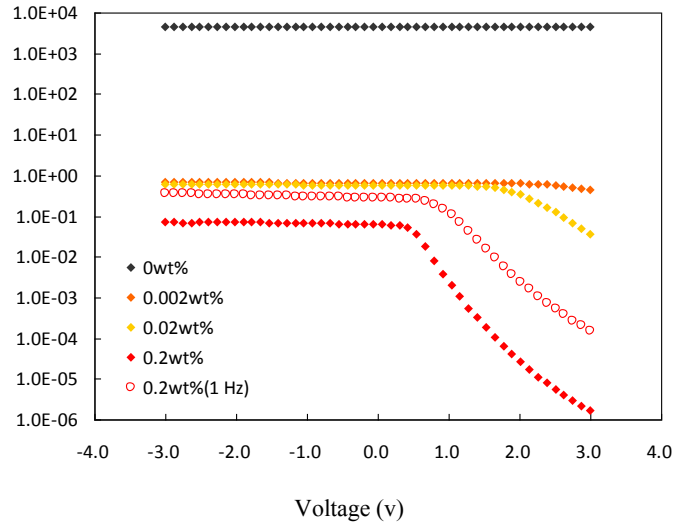


Fig. 4 $1/C^2$ vs V characteristics of the stacked devices with the n-doping concentration at 0, 0.002, 0.02, 0.2, 2 wt%.

4. Conclusions

The pn junction based on the p-doped and n-doped polymer semiconductor was fabricated by ESDUS technique. Many problems in printed devices could be solved by the doped devices. For example, the higher conductivity of the doped devices would enable much thicker active layer.

References

- [1] K. Fujita, T. Ishikawa, T. Tsutsui, *Jpn. J. Appl. Phys.* **41**, L70. (2002)
- [2] T. Ishikawa, M. Nakamura, K. Fujita, T. Tsutsui, *Appl. Phys. Lett.* **84**, 2424(2004).
- [3] K. Sagane, M. Shakutsui, T. Tsutsui, K. Fujita, *J. Photopolym. Sci. Tec.* **21**, 193 (2008)
- [4] T. Ishikawa, K. Fujita, T. Tsutsui, *Jpn. J. Appl. Phys.* **44**, 6292(2005).
- [5] P. Tyagi, *Organic Electronics* **14**, 1391–1395 (2013)