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Effective p-type doping in poly-3-hexylthiophene by evaporative spray deposition using ultra-dilute solution

Shin Sakiyama[1], Naoki Mizutani[2], and Katsuhiko Fujita[1,2]

[1] Interdisciplinary Graduate School of Engineering Science, Kyushu University
[2] Institute for Materials Chemisty and Engineering, Kyushu University
6-1, Kasuga-koen, Kasuga-city Fukuoka 816-8580, Japan
Phone: +81-92-583-7532 E-mail: katsuf@asem.kyushu-u.ac.jp

Abstract

Evaporative Spray Deposition using Ultra-dilute Solution (ESDUS) method is promising method to achieve high efficient doping for polymer semiconductor. In this study, we fabricated F4TCNQ doped P3HT by ESDUS method. The conductivity of doped P3HT improves to 243 Scm^{-1}. By using the ESDUS method, aggregation of the dopant can be suppressed and the charge transfer complex is formed more efficiently than the spin-coating method.

1. Introduction

The doping efficiency, the ratio of increased carrier density to dopant concentration, of polymeric semiconductors was quite low whereas that of the inorganic semiconductors is usually 100% with ion implantation method. The carrier doping for polymer semiconductors was conducted by co-dissolve of an electron donor with the semiconductors at the film preparation. The efficiency in the polymer films fabricated by the spin-coating method was 5% at highest [1-3].

We have already reported that Evaporative Spray Deposition using Ultra-dilute Solution (ESDUS, Fig. 1) method enables both p- and n-type doping for a poly(phenylenevinylene) derivative, MEH-PPV at more than 15% of the doping efficiency [4]. This is probably due to the suppression of the dopant aggregation during the film deposition.

The carrier mobility of MEH-PPV is not so high that the doped film shows relatively low conductivity even at the high doped. We have attempted the p-type doping to the polymers with higher carrier mobility. The regioregular poly(3-hexylthiophene), P3HT, is known as a good hole transport polymer and well studied about p-type doping with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ). In the present study, the effective p-doping and quite high conductivity was achieved even at low dopant concentration.

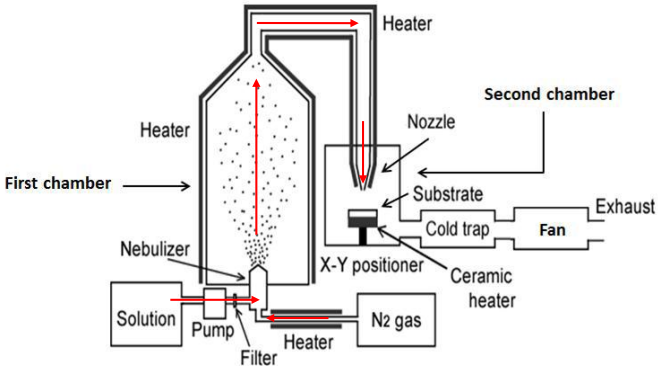

Fig. 1 Schematic illustration of ESDUS apparatus

2. Experimental methods

The hole-only devices (HOD), Al / MoO_3 / P3HT (100 nm) / ITO / Glass (Fig.2) were fabricated as follows. The ITO substrate was cleaned with detergent wash and UV ozone treatment. P3HT layer deposited by spin-coating or ESDUS method. In spin-coating the P3HT (Rieke metals, regioregular, MW 51k) and F4TCNQ (TCI) were dissolved in chlorobenzene at 10 mg/ml of polymer concentration and at 0.1 wt% doping concentration against polymer. In ESDUS, P3HT and F4TCNQ were dissolved in THF at 10 ppm, and 0.1 wt % against polymer, respectively. The metal electrode and the buffer layer were formed by a vacuum evaporation method. J-V characteristics were measured in a nitrogen atmosphere using Keithley 238 source meter. The absorption spectra of F4TCNQ doped P3HT/Glass were measured with Shimadzu UV-3150.

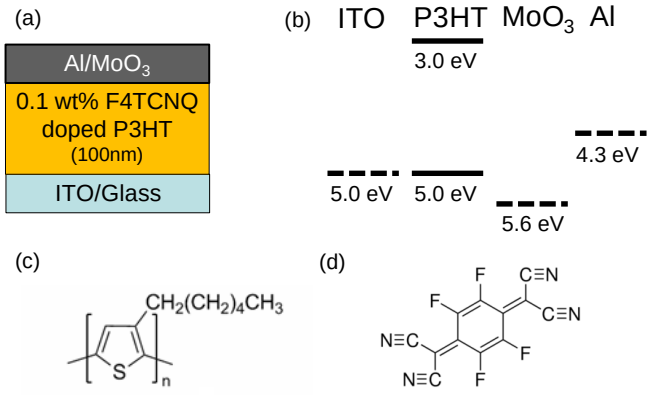

Fig. 2 (a) Device structure of hole-only device, (b) energy diagram of hole-only device, (c) molecular structure of P3HT, (d) molecular structure of F4TCNQ

3. Results and Discussion

Fig. 3 shows J-V characteristics of the HOD of nondoped P3HT and 0.1wt% F4TCNQ doped P3HT with spin-coating and ESDUS. The nondoped device fabricated by the spin coating shows inflection at 0.3V where the slope changes from 1.21 to 1.82. This is due to conduction mechanism change from ohmic to space charge limited current (SCLC).

On the other hand, the device doped with F4TCNQ show the constant slope, ohmic characteristics, at the observed voltage range due to the drastically increased hole density.

The optical absorption spectra of F4TCNQ doped P3HT can be copared with the nondoped P3HT film (Fig. 4) The doped film fabricated by the spin coating method shows slight red-shift compared with nondoped P3HT. This indicates the polaron geration by forming charge trancefer complex of $P3HT^{+}$-$F4TCNQ^{-}$. On the other hand, that by ESDUS method shows drastic change in the spectrum. The absorption peak shifted in 30 nm to long wavelength. The absorption peak appears at 630 nm attributed to F4TCNQ anion [3]. It is clearly shown that the ESDUS method can form charge transfer complex more effectively than the spin coating method.

The conductivity and doping efficiency caliculated from the carrier density estimated from the J-V characteristics. (table. 1) The conductivity improved 100000 times in the device fabricated by ESDUS method. The doping efficiency is 32% in the device by the ESDUS whereas it is nearly 5% in the device by the spin coating which is very close to already reported value [3,5]. It should be due to the suppression of dopant aggregation and efficient formation of charge transfer complex at the small solution particles during spray deposition.

Table. 1 Conductivity and doping efficiency of doped P3HT fabricated by spin-coating and ESDUS

	Conductivity (S/cm)	Doping Efficiency (%)
Nondope by Spin-coating	2.85.E-03	-
0.1wt% doping by Spin-coating	6.18.E-01	4.82
0.1wt% doping by ESDUS	2.43.E+02	32.1

4. Conclusions

We fabricated 0.1wt% F4TCNQ doped P3HT film by ESDUS method and achieved high conductivity at 243 Scm^{-1} and high doping efficiency at 32 %. The obvious absorption peak attributed to F4TCNQ anion was observed in the doped film prepared by ESDUS. These should be caused by the effective suppression of dopant aggregation by the ESDUS method.

References

[1] C. Ohashi, Y. Shinmura, M. Kubo, and M. Hiramoto, Org. Electr. 27, (2015).
[2] Pingel P. and Neher D. Phys. Rev. B 87 115209, (2013)
[3] K. Harada, A. Werner, M. Pfeiffer, C. Bloom, C. Elliott, and K. Leo, Phys. Rev. Lett. 94, 3 (2005).
[4] S. Sakiyama, N. Mizutani, and K. Fujita, Jpn. J. Appl. Phys. 55, 4S (2016).
[5] N. C. Giebink, G. P. Wiederrecht, M. R. Wasielewski, and S. R. Forrest, Phys. Rev. B 82, 15 (2010).

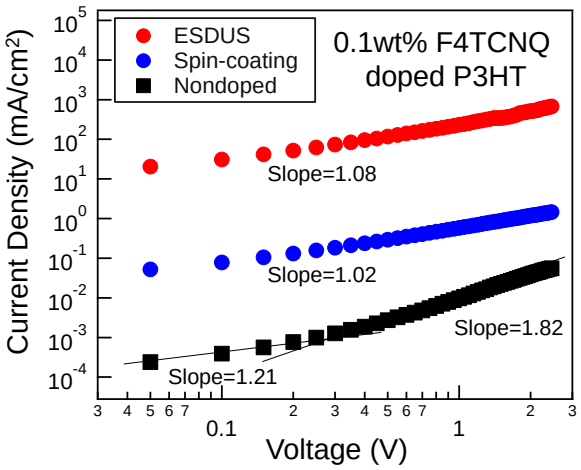

Fig. 3 J-V characteristics of 0.1 wt% doped and non-doped hole-only devices fabricated by spin-coating and ESDUS.

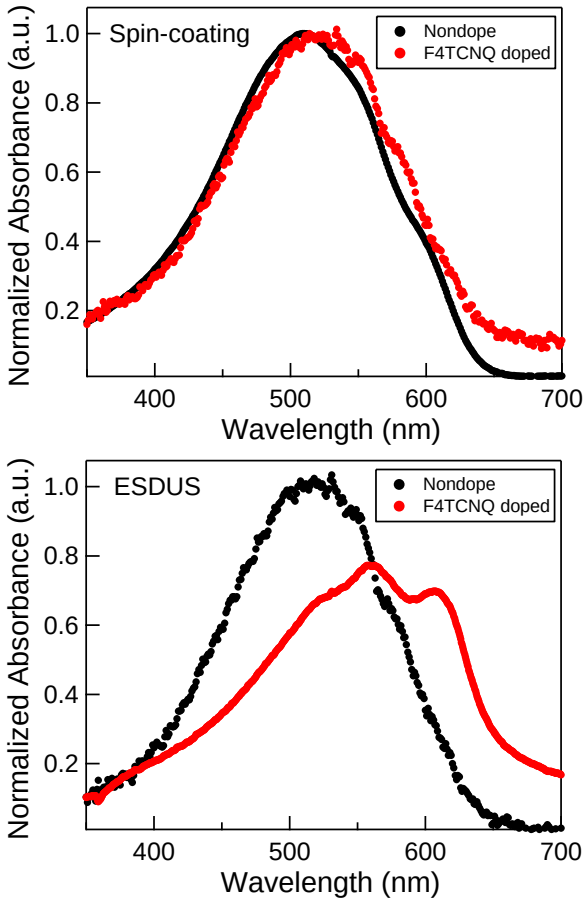

Fig. 4 Absorption spectra of 0.1 wt% doped and nondoped hole-only devices fabricated by spin-coating and ESDUS.