Extended Abstracts of the 2019 International Conference on Solid State Devices and Materials, Nagoya, 2019, pp23-24

Thermal stability of the p/n doped organic diodes prepared by evaporative spray deposition using ultradilute solution

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Abstract

Evaporative Spray Deposition using Ultra-dilute Solution (ESDUS) method has been enabled n-doping in polymer semiconductors at quite high efficiency and fabricating polymer p/n junction showing high rectification ratio. The p/i/n diodes were prepared to investigate the thermal stability. The time for degradation were elongated with the i-layer thickness indicating the diffusion of the dopant should be cause the degradation.

1. Introduction

The carrier doping in polymer semiconductors can be achieved by mixing p- or n- dopants in the polymer solutions. Most of n-dopants are almost insoluble in organic solvents which are used for the polymer solution. ESDUS (Fig. 1) is the polymer film preparation method where highly diluted solution is concentrated in air by spraying it as quite small mist particles. We have already reported that both p- and n-type doping can be achieved for a poly(phenylenevinylene) derivative, MEH-PPV at high doping efficiency as much as 19% and that the p/n junction can be established with the stacked film composed of the p-doped layer and the n-doped layer.

Although the doped p/n junction showed typical capacitance – voltage characteristics indicating significant depletion and significant rectification, this diode nature was damaged after thermal annealing for a few minutes. In the present study we attempted to reveal the reason of the degradation.

We fabricated the p/i/n structure composed of the p-doping layer, region regular poly(3-hexylthiophene), P3HT, with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), the intrinsic MEH-PPV layer and the n-doping layer, MEH-PPV with Cs2CO3. The p/i/n diodes were thermally treated.

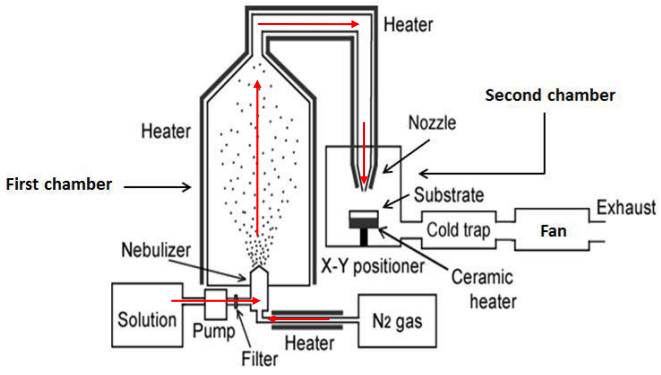

Fig. 1 Schematic illustration of ESDUS apparatus

2. Experimental methods

The p-doping layer was prepared on the indium tin oxide (ITO) electrode with spin-coating of the P3HT (Rieke metals, regioregular, MW 51k) and F4TCNQ (TCI) were dissolved in chlorobenzene at 10 mg/ml of polymer concentration and at 0.02 wt% doping concentration against polymer. The i layer was prepared at the thickness of 0. 50. 120, 150 nm with ESDUS by using MEH-PPV dissolved in THF at 10 ppm, and n-doping layer was prepared with ESDUS using MEH-PPV containing 0.02 wt % against polymer. The metal electrode and the buffwere 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.

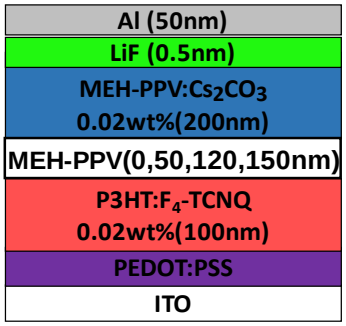

Fig. 2 (a) Device structure of p/i/n diode

3. Results and Discussion

Fig. 3 shows J-V characteristics of the p/i/n (i=0 nm) diode. The rectification ratio was 2400, typical diode characteristics.

The anealing time dependence of the forward current showed in Fig. 4. The degradation was modelate at the anealing temperature at 50 C and relatively rapid at 100 c. The glass transition temperature of MEH-PPV and P3HT were 105C and 140 C respectively. The degradation tendency seems to change at the glass transition temperature of each materials.

Fig.5 is the rectification ratio vs aneallin time at 100 C of p/i/n dipdes (i= 50, 130 and 150) The retio showed clear peaks depending on the i layer thickness. The time of the peak was

shifted right as the thickness got larger. The thickness of the i layer is almost propotional to the root of the anealing time which means the defusion controll.

4. Conclusions

We fabricated carrier doped p/i/n diodes of polymer semiconductors. The rectification ratio showed degradation after thermal treatment. The beginning time of the degradation was clearly dependent on the I layer thickness. This indicates that the degradation takes place due to the dopant diffusion. When p and n dopants meet in the organic layer, the chemical reaction of the dopants should damage the diode characteristics.

References

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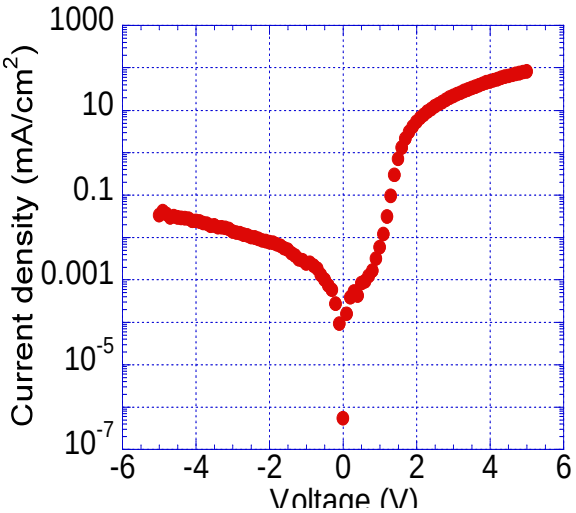

Fig. 3 J-V curve of p/i/n diode (i=0)

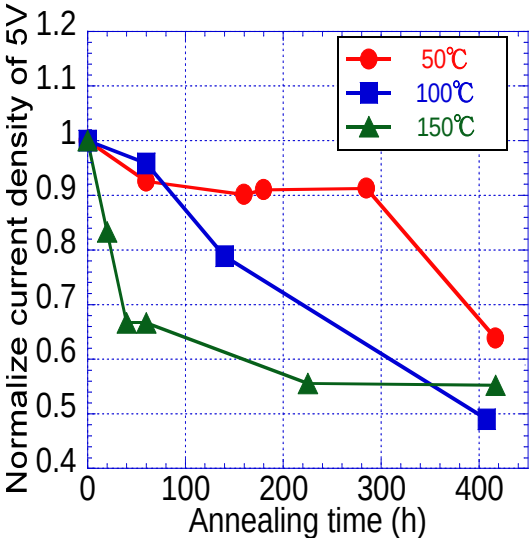

Fig.4 forward current vs annealing time of p/i/n diode

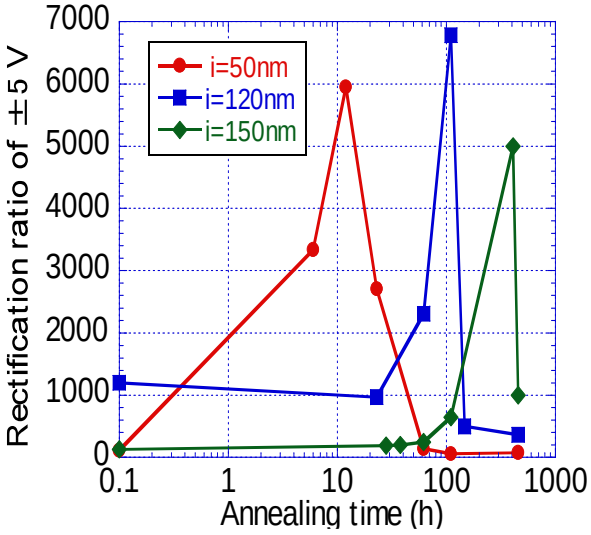

Fig.5 rectification ratio vs annealing time of p/i/n diode