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Polymer Semiconductor Homo-Junction Diode Fabricated by Wet Process

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Abstract

Evaporative Spray Deposition using Ultra-dilute Solution (ESDUS) method has enabled both high efficient pn doping and layer by layer deposition of polymer semiconductor. We prepared homo-junction diodes composed of an n-doped polymer semiconductor with varied doping concentration. They showed typical rectification. The behavior at the reverse bias and the temperature dependence of the ideality factor of the diodes indicate that they obey the diffusion theory.

1. Introduction

Organic semiconductor devices such as an organic light emitting diode (OLED) and an organic thin-film solar cells (OPV), are mostly used in the non-doped state, which is most unique feature of organic devices. Since the conductivity is very low due to the low carrier density in the organic semiconductors, organic semiconductors are used as a ultrathin film with submicron thickness.

The carrier doping can be realized by mainly co-evaporation of organic semiconductors together with a donor molecule or an acceptor molecule [1-3]. The conductivity can be improved drastically and the pn control can lead to more sophisticated device design.

The p-doping in polymer semiconductors has been investigated for long. However, efficient n-doping and fabrication of layer-by-layer structure to construct a pn junction are still remaining issue.

We have reported n-type doping for poly(2-methoxy-5-(2 ' -methyl-hexyloxy)-p- phenylene-vinylene) (MEH-PPV: LUMO: 3.1 eV, HOMO: 5.2 eV, Fig (a)) with Evaporative Spray Deposition using Ultra-dilute Solution (ESDUS, Fig. 1) method. The doping efficiency for n-type can be 15% [4, 5]. In this work, we deposited the n-doped film on the non-doped MEH-PPV to produce a polymer semiconductor homo junction diode with varying the doping concentration. The non-doped MEH-PPV is known to show p-type behavior due to the unintentional doping by oxygen or other impurities. Therefore, the homo-junction with highly n-doped polymer can be regarded as the one-sided abrupt junction. We report to evaluate the current-voltage (J-V) characteristics and the temperature dependence of the device.

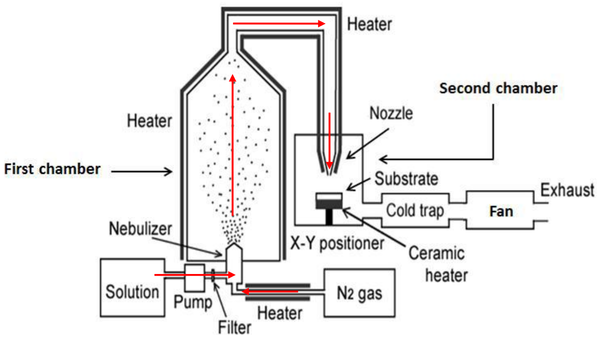

Fig. 1 Schematic illustration of ESDUS apparatus.

2. Experimental methods

After the ITO substrate UV ozone cleaning, PEDOT:PSS (Baytron P VP AI 4083: H. C. Starck) film was formed by spin-coating method (2000rpm, 30s). Then, non-doped layer (100 nm) of MEH-PPV and the n-doped (100 nm, Cs_2CO_3 Fig. 2 (b), 0-2 wt%) layer were fabricated by ESDUS methods. Ca (40 nm) and Al (100 nm) electrode were formed of on the organic layer by vacuum deposition (Fig. 3 (c)).

J-V characteristics and temperature dependence were measured, and calculated diode ideality factor.

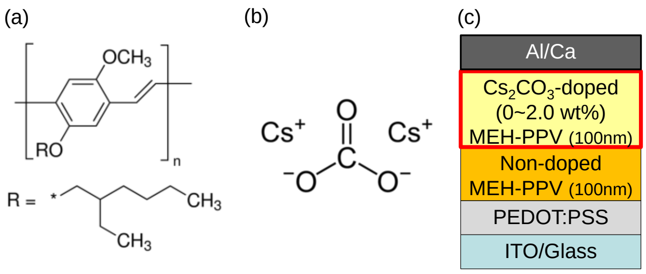

Fig. 2 (a) Molecular Structure of MEH-PPV, (b) Molecular Structure of Cs_2CO_3, (c) Device structure.

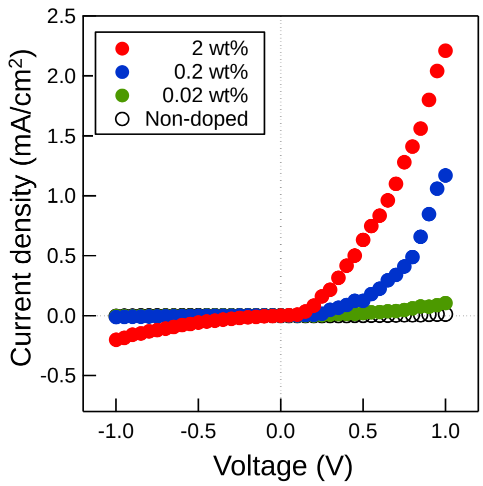

Fig. 3 J-V characteristics of homo-junction diode doped with Cs2CO3, at dopant concentration of 0, 0.02, 0.2, 2 wt %.

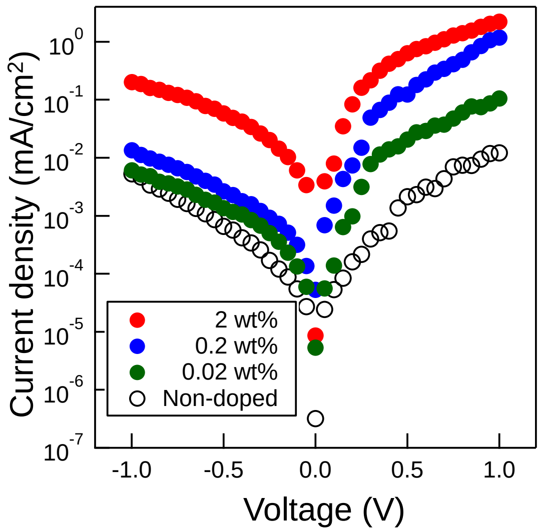

Fig. 4 The semilogarithmic plot of J-V characteristics of homo-junction diode doped with Cs_2CO_3, at dopant concentration of 0, 0.02, 0.2, 2 wt %.

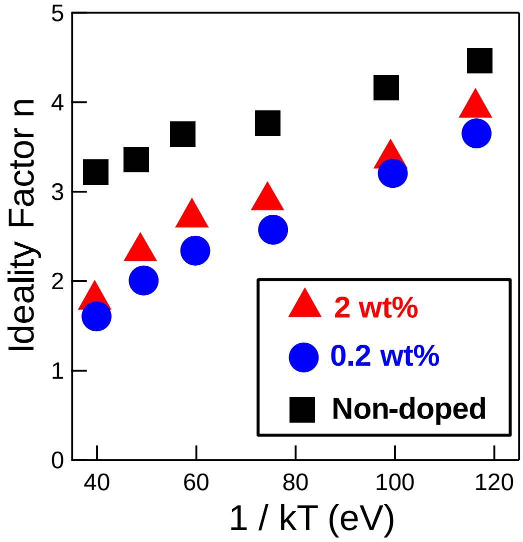

Fig. 5 The temperature dependence of the ideality factor with Cs_2CO_3, at dopant concentration of 0, 0.02, 0.2 wt %.

3. Results and Discussion

Fig. 3 shows the J-V characteristics of the polymer semiconductor homo-junction diode. The reverse current is suppressed sufficiently, showing obvious rectification. The forward current increases with the increase of the doping concentration of Cs_2CO_3. The breakdown was not observed in the reverse bias at least until the voltage where the device distructed. The hall density of non-doped layer is estimated to be 10^{21} /m^3 due to the unintentional doping. The electron density of n-doped layer is 10^{23} /m^3 at 0.2 wt%. The devices with higher doping concentration over 0.2 wt% can be regarded as a one-sided abrupt junction. Probably due to the low carrier mobility of the organic polymer semiconductor, electrons cannot be acceralated enough for the breakdown.

In order to evaluate the behavior of the diode in detail, fig. 4 shows the semilogarithmic plot of the J-V curve. In all doping concentration, it found that reverse current does not saturate. It is considered that polymer semiconductor homo-junction obeys the diffusion theory, rather than conventional diodes theory as the ZnPc diode reported [3].

Furthermore, in order to investigate the temperature dependence of the diode characteristics, the ideal factor and saturation current are calculated from the linier region of the semilogarithmic J-V curve, difution current region (Fig. 5). Using the standard Shockley equation for pn junctions

$$J=J_0[exp(qV/nkT)-1], \qquad (1)$$

where J_0 is the dark saturation current, q the unit charge, n the diode ideality factor, k the Boltzmann constant, and T is the temperature. Ideality factor of non-doped single layer device, where the rectification should be derived by the work function difference between the electrodes, shows 3.2 at room temperature. On the other hand, doped device showed an ideality factor of 1.6-1.9 at room temperature.

Ideality factor n increases with the decrease of temperature (Fig. 5), attributed to suppression of the carrier movement in density of states tail at low temperature [6]. Therefore, trap-limited recombination is easily occurred at low temperature. Especially, trap-filled MEH-PPV by doping leads to high slope of ideality factor compared with non-doped device. In the low molecular organic semiconductor ZnPc, the same device structure (i-n diode), ideality factor showed the same behavior, which suggests obeying the diffusion theory in disorder materials [3].

4. Conclusions

We have successfully prepared homo junction diodes by the ESDUS method. The forward current increased with increasing the doping concentration of Cs_2CO_3. However, breakdown at the reverse bias voltage was not observed. The reverse current did not saturate and the ideality factor of the diodes showed negative dependence on the temperature. It is, therefore, suggested that polymer semiconductor homo-junction obeys the diffusion theory, rather than conventional diodes theory.

References

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