

Electron Injection on Metal/n-doped Polymer Semiconductor

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Abstract

Evaporative Spray Deposition using Ultra-dilute Solution (ESDUS) method enables highly efficient n-type doping of polymer semiconductors. In this study, sandwich cells with symmetric electrodes (Al/polymer/Al) and asymmetric electrodes (Al/polymer/Ca) were prepared and electron injection properties on metal/n-doped polymer. The asymmetric cells showed rectification when doping ratio was low. However, it disappeared at the high doping ratio (10 wt%) due to quantum tunneling.

1. Introduction

The polymer semiconductors are promising materials for organic light emitting diodes and organic solar cells fabricated by a wet process. Although the conductivity can be improved by carrier doping, efficient n-type doping was not established since the dopants dose not dissolve in same organic solutions of polymer semiconductors [1-3]. Evaporative Spray Deposition using Ultra-dilute Solution (ESDUS, Fig. 1) method enabled it recently. We have already reported efficient n-type doping of poly(2-methoxy-5-(2'-methyl-hexyloxy)-p-phenylene-vinylene) (MEH-PPV: LUMO: 3.1 eV, HOMO: 5.2 eV). The high doping efficiency as much as 15% was realized [4, 5]. In organic devices composed of non-doped organic semiconductors, electron injection barrier is basically equal to the gap between LUMO of the organic semiconductor and work function of the electrode. It is still open question how the barrier is formed in the n-doped polymer/electrode. The metal/semiconductor junction of n-doped polymer has not been studied yet.

In this research, we have fabricated electron only devices (EOD) of an n-doped polymer semiconductor using electrodes of Al and Ca. The electron injection from Al or Ca was examined.

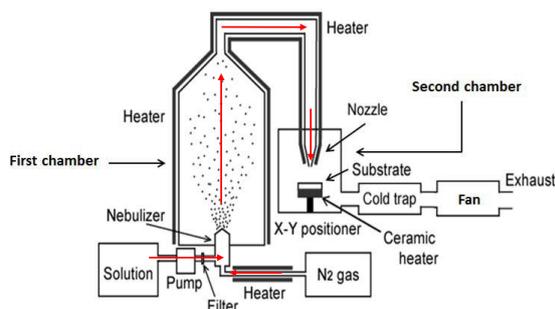


Fig. 1 Schematic illustration of ESDUS apparatus

2. Experimental methods

MEH-PPV ($M_w = 40,000$ - $70,000$ Aldrich, Fig. 2(a)) and Cesium carbonate (Cs_2CO_3 , Japan Pure Chemical, purity of 99.999% Fig. 2(b)) were used as a host polymer and an n-type dopant, respectively. MEH-PPV showed a bipolar transporting material, and the conductivity and doping efficiency of n-doped MEH-PPV has been reported elsewhere [4]. The asymmetric EOD using Al for both bottom and top electrodes and the symmetric EOD using a bottom Al electrode having a relatively deep work function (4.3 eV) and a top Ca electrode having a lower work function (3.0 eV) were fabricated (Fig. 2(c)). The current-voltage (J-V) characteristics and capacitance-frequency (C-F) measurement were measured in vacuum without breaking vacuum after the top electrode deposition.

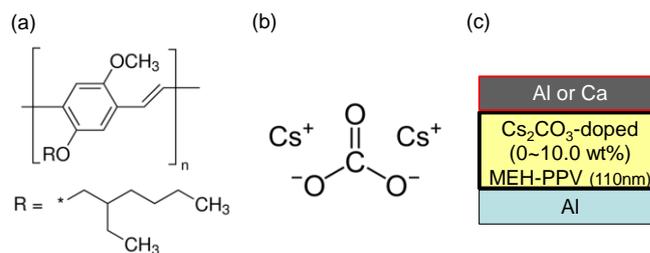


Fig. 2 (a) Molecular Structure of MEH-PPV, (b) Molecular Structure of Cs_2CO_3 , (c) Device structure.

3. Results and Discussion

J-V characteristics of the symmetric EOD, Al(50nm)/MEH-PPV: Cs_2CO_3 (110nm)/Al(50nm), and the asymmetric EOD, Al(50nm)/MEH-PPV: Cs_2CO_3 (110nm)/Ca(50nm) are shown in Fig.3. In both EODs, the current density was drastically increased as the doping concentration increased. In the symmetric EODs, J-V curves were overlapped in the bias direction at every doping concentration. This is because the device structure is symmetrical and the same height of the carrier injection barrier is formed at Al/MEH-PPV junction. On the other hand, in the asymmetric EODs, current density in the forward bias was about 1 order of magnitude larger than that in reverse bias at low doping concentration at 0, 0.2, 2.0 wt%. This is because the larger carrier injection barrier is formed at Al/MEH-PPV than Ca/MEH-PPV junction due to the difference in work function between Al and Ca. This result shows that electron injection from the Ca is more efficient than from the Al electrode. However, almost the current density was almost overlapped in forward and reverse bias at the doping con-

centration of 10wt%. The disappearance of the rectification property suggests that the quantum tunneling takes place due to the very thin depletion layer at Al/MEH-PPV junction at the high doping concentration.

In order to evaluate depletion layer width on Al/MEH-PPV junction, C-F measurement was carried out. The value of the resonance frequency is determined from the result of each C-F measurement. The depletion layer width is calculated by substituting the value of the capacitance at the resonance frequency into the following equation (1).

$$W = \frac{\epsilon_0 \epsilon_r}{C} \quad (1)$$

Where ϵ_0 and ϵ_r are the vacuum permittivity and the relative permittivity, C is a capacitance at the resonant frequency. As a result of the calculation, the depletion layer width of the 0.2 wt% doped device was 16.3 nm, the 2.0 wt% doped device was 9.3 nm, and the 10.0 wt% doped device was 3.3 nm. These results suggest that the depletion layer narrows as the doping concentration increases as shown in the Fig. 4 and the rectification property disappears in the 10 wt% doped device by quantum tunneling. The depletion layer width when quantum tunneling was observed in the p-type organic device, Au/ZnPc:0.3%F4-TCNQ/Au, was 5.2nm [6]. Compared with this depletion layer width of 5.2 nm at metal / p-type organic semiconductor junction, it can be said that the value of 3.3 nm calculated this time is sufficiently narrow to observe quantum tunneling.

4. Conclusions

We measured the J-V and C-F characteristics of EODs, Al/MEH-PPV(110nm)/Al and Al/MEH-PPV (110nm)/Ca, with varying Cs_2CO_3 concentration to understand the electron injection at metal/n-doped polymer junction. In Ca upper electrode, current density about 1 order of magnitude larger than under reverse bias was observed under forward bias at the doping concentration of 0, 0.2, 2.0wt% due to the difference of the work function between Al and Ca. However, the current density of almost the same magnitude was observed under both forward and reverse bias at the doping concentration of 10 wt% and the rectification property was disappeared. Then, the depletion layer narrows as the doping concentration increases and the rectification property disappears in the 10 wt% doped device by quantum tunneling as the conventional semiconductor theory can explain.

References

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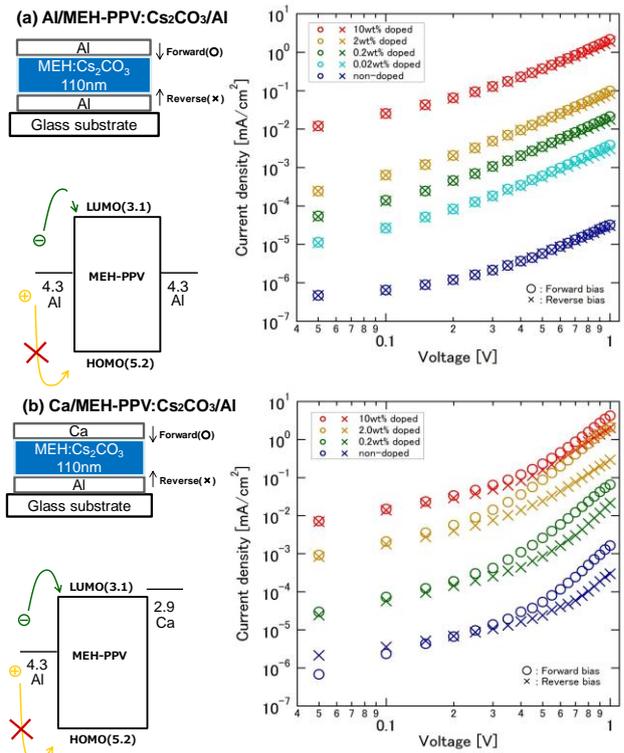


Fig. 3 J-V characteristics of (a) Al/MEH-PPV/Al and (b) Al/MEH-PPV/Ca doped with Cs_2CO_3 , at dopant concentration of 0, 0.2, 2.0, 10 wt %

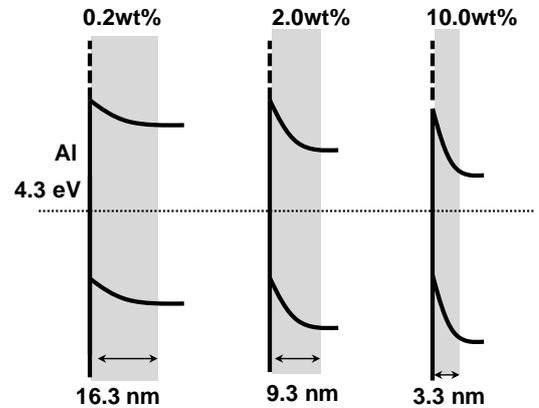


Fig. 4 Schematic diagram of the decrease of the depletion layer width by n-type doping.

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