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Field Effect Mobility of the Annealed Thin Film Modified with Nanomaterial Interlayer in Organic Solar Cell

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Abstract

This work analyzed the effects of thermal annealing on the charge-carrying properties of P3HT: PCBM molecular-based organic solar cell devices (OSC). The anode of OSC device is modified with a 4-[4-(4-propan-2-yloxy-N-(4-propan-2-yloxyphenyl)anilino)phenyl] benzoic acid (PANPBA) (purchased from Aladdin). This layer is formed by self-assembled technique as hole transport interface for understanding the effects of thermal annealing on traps filled at saturation region of current-voltage. Charge injections mechanism and field effect mobility in OSC structure was studied via analysis of trap-free space charge limited transport (TSCLC) technique.

Keywords: Organic Solar Cell; PCBM: P3HT; Organic Semiconductor; Charge Mobility; TSCLC**.**

1. Introduction

Conjugated small molecules have a crucial role in organic electronic devices such as organic diodes, organic solar cell (OSC), organic sensors and organic light emitting diodes (OLEDs) [1-5]. In the organic semiconductor materials, charge transfer, especially the places-regions where electron-hole transfers are made, consists of π-conjugate bonds [6]. In π-conjugated systems, there is a strong coupling between the electronic structure and its geometry that controls the transport properties [7,8]. In the molecular structures of organic semiconductor crystals, charge transfer occurs thanks to the transfer of electrons from the highest energy molecular orbital (HOMO) to the lowest energy molecular orbital (LUMO). Organic semiconductor absorbs light to create a neutral excited state associated with a Frenkel exciton. The photo induced charge transfer reaction between a donor and an acceptor molecule produces a photocurrent in an organic solar cell.

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The exciton separation occurs at the interface of donor-acceptor materials (p-n type), called organic heterojunctions, and then charge transfer takes place across the respective layers. In general, approaches to increase the efficiency of solar cells are to modify the structural organization of the organic material through tunable the properties of the materials and the film morphology by different techniques such as annealing, interface modifying etc [9-12]. Poly (3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is well known as an organic semiconducting polymer for organic solar cell [13,14]. Organic semiconductor, namely P3HT: The main reason why PCBM solar cells have higher efficiency than other organic solar cells is that the n-type PCBM structure is homogeneously dispersed in the p-type polymer (P3HT)[15]. Thus, the p-n interface area is increased. In this way, the effective charge separation rate increases, thus increasing the efficiency of the cell. First of all, the active layer should absorb as much as possible the photons used to generate excitation. The thickness of the active layer is inversely proportional to the load carrier mobility. Therefore, the compatibility between the solar spectrum and the absorption spectrum of the active layer and maximizing the solar radiation absorption in thin films of 100–200 nm are important issues. From this point of view, bandgap organic semiconductors above 2 eV absorb only the green region in the visible region. For example, the film thickness of about 100 nm was increased to solve the problem that only a small part of the incident sunlight is absorbed by the P3HT: PCBM film. This way increased the amount of photons absorbed, but also increased the series resistance of the cell, so it is not a very attractive solution. The most effective solution method in this regard is to make the molecular structure of the active polymer more regular. Because the light absorbing capacity of materials with regular molecular structure increases. In addition, the charge transfer can be balanced by creating a hole transport layer with interface engineering in the device. P3HT: PCBM films give very effective and positive results on the active layer microstructure when solid state heat treatment is applied [16,17]. The first studies were in the direction of optimizing the heat treatment parameters. In these studies, the active layer was exposed to temperatures between 75-230 °C for 10 to 40 minutes. As a result, it was determined that the most efficient result was obtained from the heat treatments applied in the temperature range of 110-150 °C in a time interval of 10-20 minutes[18-23].

In order to obtain higher efficiency from organic solar cells, it is necessary to increase the p-n interface area in the active layer. Increasing the interface area is only possible with a controlled arrangement of the active layer microstructure. Basically, interface engineering and annealing of solid-state films are the two most common important device optimizations in the literature. In this study, microstructures obtained as a result of solid-state heat treatment and their effects on mobility performance were analyzed by TSCLC technique.

2. Experimental and Materials-Method

Standard cleaning procedure was applied to ITO glasses. ITO-coated glass substrates were incubated in PANPBA solution at 24 °C for 12 hours. Thus, the active COOH portion of the PANPBA molecules is chemically bonded to the surface by ester bonds on the ITO surface rich in hydroxyl groups. ITO coated glasses with a surface resistance of 15-25 Ω/sq, P3HT and PCBM were purchased from Sigma Aldrich. The P3HT:PCBM (1:2) solution layered onto the ITO/PANPBA film by spin coating was spun at 1000 rpm for 60 seconds to form a 100 nm thick film (model SPIN150). Afterwards, the organic films were thermally annealed in the glow box at 80 ◦C, 120 ◦C and 160 ◦C for 20 minutes. 1 nm LiF was evaporated by thermal evaporation system (NANOVAK Co.). Finally, 120 nm thick aluminum was evaporated as the cathode. Electrical data of OSC were obtained using Kiethley 2401. Photovoltaic characterization of the OSC device was carried out with the Oriel 120 LCS-100 Small Field Sol1A model solar simulator under 1.5 AM.

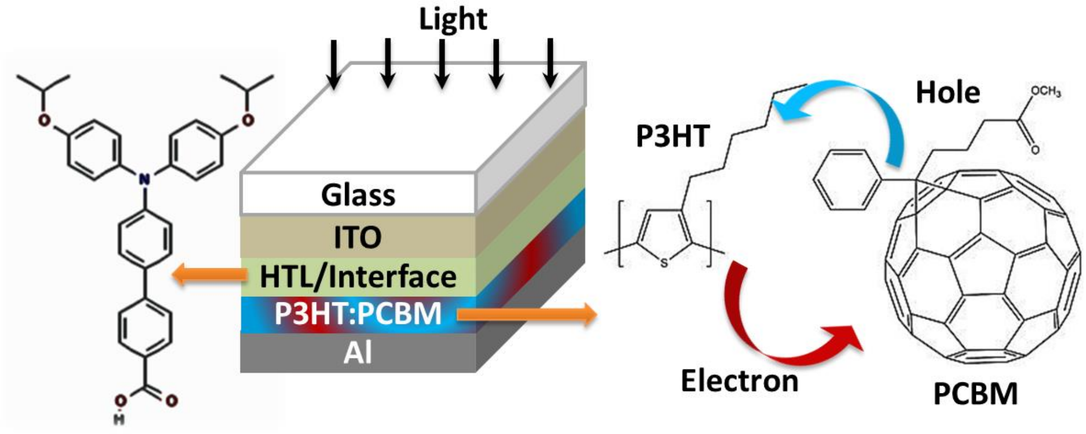


Figure 1: Schematic diagram of a donor-acceptor based organic solar cell with conventional architecture and corresponding energy band diagram in eV.

This type of organic solar cell, we used PANPBA instead of PEDOT: PSS, which is known as the hole-transport layer, the active mixture P3HT: PCBM and finally aluminum are coated on the transparent ITO coated glass surface. The photons pass through the glass, ITO, and PANPBA layers, respectively, to reach the P3HT: PCBM film, where they use their energy to form excitons, which are electron-hole pairs (Fig. 1). The electron-hole pairs are separated from each other by the electric field effect caused by the difference between the soot function levels of the ITO and aluminum electrodes. Electrons are transported to the aluminum and holes to the ITO electrode. In this way, current is formed in the circuit and the conversion of photon energy into electrical energy is completed.

3. Result and Discussion

The various techniques have been used in the literature to increase the efficiency of P3HT: PCBM-based organic solar cells. These can be listed as controlling the thermal annealing conditions, interlayer modification the anode-cathode electrodes and tunable the film thickness etc. [16,24-28]. In particular, thermal annealing is performed for the films and the devices for better light absorption and for improving the tunneling charge -hole carriers in organic solar cells. Thus, recrystallization of P3HT molecules forming the active layer is ensured. At this point, in this study, based on the idea of using Self-assembled Monolayer-SAM (PANPBA) molecules instead of PEDOT:PSS, the contribution of ITO/SAM/P3HT:PCBM films to device performance by thermal annealing was investigated [16,29]. According to our results, the ITO/SAM/P3HT: PCBM film, annealing at 120 °C for 20 min showed the best performance in terms of charge carrier transport due to its mobility 1.99×10^{-5} at 325 $E^{1/2}$. This value is the highest one comparing with mobility results of the other OSC devices. As well as the results let know how changes the surface potential energy on ITO. It is also clear that the film which is annealed at 120 C has the best performance.

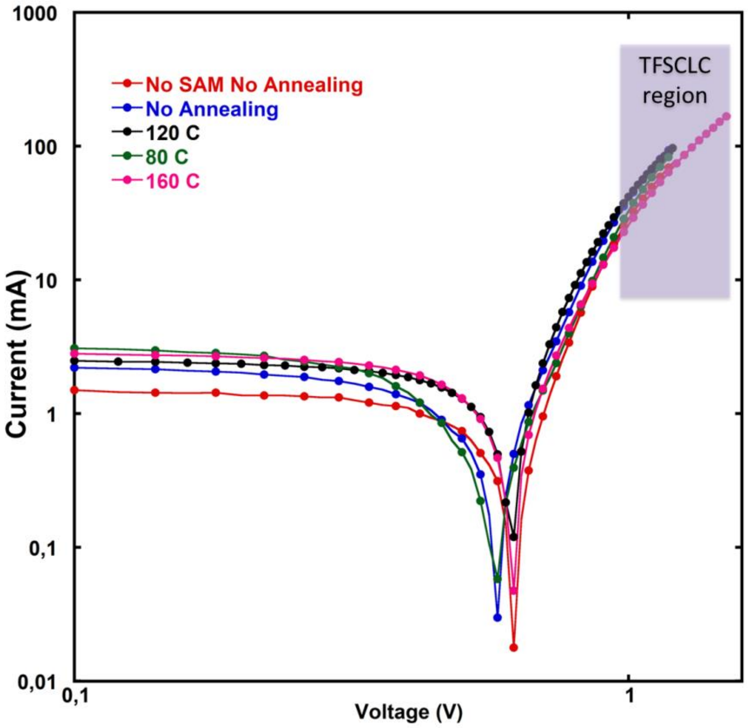


Figure 2: The I-V characteristic of P3HT:PCBM based organic solar cell modified with PANPBA self-assembled interlayer.

In the saturation region (the highest part of I-V), the charge tunneling is associate with trap dominated SCLC approaches (Fig. 2) that traps located at near to conduction energy band up to the expression [30,31],

$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\theta\mu\frac{V^2}{L^3} \tag{1}$$

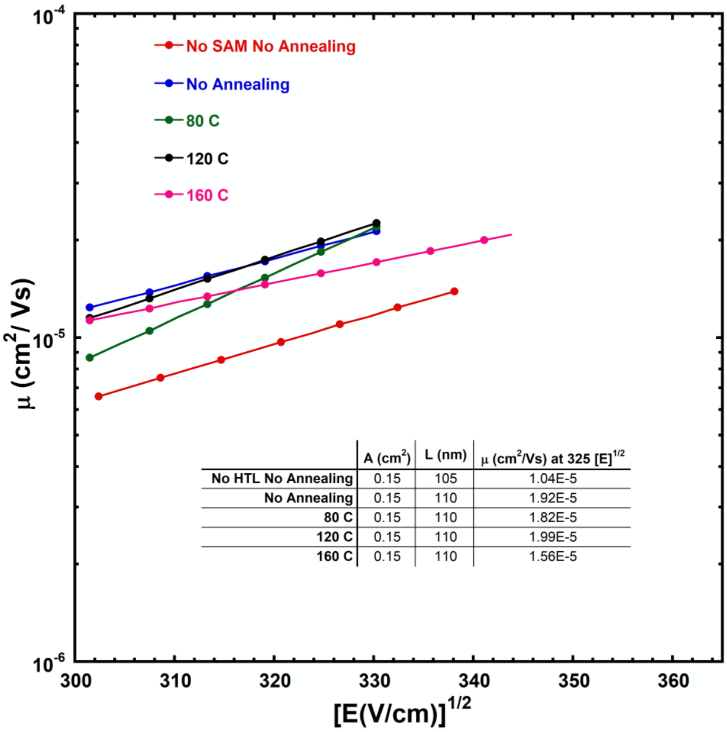
Here $\boldsymbol{\varepsilon_0 = 8.85x10^{-12}}$ is the permittivity of free space, $\boldsymbol{\varepsilon_r = 3}$ is the relative permittivity of the active blend [30], θ is the trap limiting factor [32]. The current density-voltage part of the TFSCLC at saturation region is defined by Child's law [30,31]

$$\boldsymbol{J = \frac{9}{8}\varepsilon\varepsilon_0\,\mu_{(in\ the\ TFSCLC\ region)}\,\frac{V^2}{L^3}} \tag{2}$$

the TFSCLC comes into play, the whole charges flow conform to Child's law when the tunneling charge carriers from the electrodes numerically surpass the thermally generated carriers and all traps are filled [30,31,33]. That is why the charge carrier mobility is field dependent. Based on eq. (2) and using the identified data, it is graphed $\ln(J/E^2)$ vs $E^{1/2}$ for each annealed value of the devices. The slope of each of the $\ln(J/E^2)$ vs. $E^{1/2}$ curves was found by using synchronously with eq.(2) to determine the mobility.

Table1: The charge carrier mobility's organic solar cell based P3HT/PCBM film modified by hole injection layer and the device annealing with different temperature; 80 °C, 120 °C and 160 °C.

	No HTL No anneal.	**No anneal.**	**80 °C**	**120 °C**	**160 °C**
A (cm^2)	0.15	0.15	0.15	0.15	0.15
L (nm)	105	110	110	110	110
μ (cm^2/Vs) at 325 E$^{1/2}$	1.04x10^{-5}	1.92x10^{-5}	1.82x10^{-5}	1.99x10^{-5}	1.56x10^{-5}



	A (cm^2)	L (nm)	μ (cm^2/Vs) at 325 [E]$^{1/2}$
No HTL No Annealing	0.15	105	1.04E-5
No Annealing	0.15	110	1.92E-5
80 C	0.15	110	1.82E-5
120 C	0.15	110	1.99E-5
160 C	0.15	110	1.56E-5

Figure 3: Field effect mobility results of the PANPBA (SAM) of OSC with conventional architecture.

The most important parameter in OSC devices is the high efficiency excitons formation with photon excitation and the separation of these excitons. But separation of excitons does not always result in the formation of free charge carriers because a significant amount of the separated excitons may remain bound due to a coulombic attraction at the interface. For example, it has been shown that the dissociation efficiency of bonded electron-hole pairs at the donor acceptor interface is a dominant factor influencing photocurrent in conjugated polymer-fullerene blends. If the coulomb radius is higher than the jump distance of the charges, the positive and negative carriers is not able to escape from each other's columbic attraction, and as a result they are not able to recombine and form free-moving charge carriers. Therefore, the mobility of charge carriers and the coulomb radius are the two most important parameters that affect the dissociation efficiency of coulombically bonded charge pairs. Materials with high mobility and dielectric constant or the presence of dipoles at the transmitter-receiver interface increase the efficiency in the formation of mobile carriers. In addition, the deposition of free charge carriers on the electrodes is usually accomplished by the transparent and conductive oxide layers of indium tin oxide (ITO) on one side of the cell and the metal contact on the other. The interface modification is usually carried out as a hole transport layer or electron transport layer to overcome this obstacle. In this study, the self-assembled organic semiconductor PANPBA molecule was applied as an interface modification on the ITO side, and this modification showed that the charge mobility of the devices increased compared to the unmodified and un-annealed ones (Fig. 3).

4. Conclusion

In conclusion, considering the effect of SAM layer on mobility result, it can be said that the dominant recombination process occurs via trap-assisted recombination. Also, such a mechanism develops as a result of increased trap density at higher annealing temperatures. ITO/SAM/P3HT: PCBM film was thermally annealed and the effect of this annealing on the performance of the device was investigated. In order to examine the charge transfer performance of OSC devices based on the modified ITO film, I-V data were obtained under the Solar simulator system (1.5 AM). This study showed that charge injection of the device modified with PANPBA can be improved without PEDOT: PSS as the hole transport layer in the device. I-V measurements of organic solar cells were analyzed by TFSCLC technique, and it was concluded that while the mobility of the 120 °C annealed device was the highest on the other hand the lowest mobility was in the non-SAM annealed device. As can be seen from Table 1, an anomaly was detected only in the totally un-annealed device and annealed device at 80 °C devices. It can be said that the temperature in these devices is not enough for the P3HT molecules to become sufficiently regular in the PCBM. However, in general, it has been observed that there is an increase in the mobility values of the devices for values around 120 °C of the annealing temperature of the films, and this result is compatible with the literature.

Acknowledgments

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