Annealing treatment effects on the performances of solar cells based on different composition systems

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The solar cells based on different composition ratio blends of poly(3-hexylthiophene) (P3HT) as donors and [6 , 6]-phenyl C61 –butyric acid methyl ester (PCBM) as acceptors are fabricated. Annealing treatment effects on the performances of solar cells based on different composition ratio blend systems are analyzed by ultraviolet-visible absorption spectroscopy (UV-vis), photoluminescence spectroscopy (PL) and the dark *J –V* characteristics. The results show that as PCBM weight increases (P3HT/PCBM=2:1,1:1,1:2), 400-650 nm vibronic absorption peaks intensity attributed to the P3HT $\pi-\pi^*$ transition increase, but photoluminescence spectra intensity lower, and the open circuit voltage of solar cells also increases. The voltage at which the transition from the exponential region to space charge limited behavior in the dark *J –V* characteristics also increases with the increase in the PCBM concentration. 130 ^{o}C heat treatment produces different results on the performance of solar cells based on different proportions of P3HT:PCBM system. We discuss the causes of these phenomena by UV-vis absorption, PL spectroscopy and dark current-voltage curve.

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1. Introduction

Polymer-fullerene bulk heterojunction solar cells (PSCs) have attracted much attention due to their potential application in flexible, lightweight, and large-area devices through low-cost solution processing [1-5]. Before the commercialization of PSCs, significant efforts including new narrow bandgap materials, new devices structures and controlling morphology of active layers and so on have been dedicated to make sure the high efficiency and long term life stability [6-10]. Among the many organic materials, P3HT and PCBM are currently the most investigated. Because of their high charge mobility, stability and good environment, as a material of solar cells, people have paid attention to them, and achieved good performance [11-15].

While, annealing treatment was found to be a useful method to enhance the device efficiency. In the past few years, the way of thermal annealing had been applied in many literature and different effects were reported [16-20]. They owned the effect of annealing treatment mainly to change the morphology at the interface between polymer and electrode, change the transport properties and so on. In this article, we pay attention to the effect of annealing treatment on bulk heterojunction solar cells made from blends of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) with different composition ratio, analyze the physical mechanisms of their properties changes. We also study and want to discover the reason of improved device performance after annealing treatment on different blend composition ratio.

2. Experimental

Photovoltaic devices were fabricated in a typical sandwich structure. The ITO-coated glass substrates were cleaned by ultrasonic treatment in deionized water, acetone, detergent, and isopropyl alcohol sequentially, followed by spin coating a 40 nm thin layer of poly(3,4-ethylenedioxythiopene) (PEDOT):poly(styrenesulfonate) (PSS) (Bayer Baytron P 4083). After baking at 80^{o}C for 10 h, the substrates were transferred into a nitrogen-filled glove box. P3HT(Poly(3-hexylthiophene)) (purchased from Aldrich, used as received) was dissolved in 1,2-dichlorobenzene (OCB) to make a 20 mg/ml solution, followed by blending with PCBM (purchased from Nano-C, used as received) in three P3HT:PCBM composition ratios (2:1,1:1, and 1:2). The blend was stirred for 10 h in the glove box, and spin-coated onto the surface of the PEDOT:PSS. The typical film thickness was about 100 nm. Lastly, the cathode, consisting of 1-nm-thick LiF and 100-nm-thick Al layers, was then thermally evaporated on top of the blend film under vacuum of 3×10^{-4} Pa. The active area of the device was 0.15 cm^2. Bulk heterojunction cells with the sandwich structure ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al were fabricated. For UV-vis and PL spectra studies the composite was deposited on a glass plate. The thickness of all the films is similar (100 nm), and the annealing time for all films is 5 min, the heat treatment temperature is 130 ^{o}C.

The absorption spectra were measured by a HP 8453 UV－vis spectrophotometer. The photoluminescence spectra were recorded on a fluorometer (JY FL-3). Power conversion efficiencies were measured under AM 1.5 solar simulator (Model Oriel 91192, 1000 W) with light intensity of 100 mW/cm^2. The current-voltage (*J-V*) characteristics were measured with a Keithley 2400 source meter. The thickness of the films was measured using a Tencor Alpha-Step 500 surface profilometer.

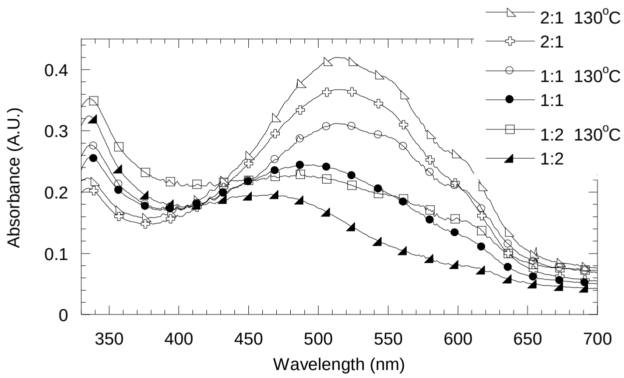

Fig. 1. Absorption spectra of different composition ratio (1:2, 1:1, 2:1) P3HT:PCBM blend film with and without 130 ^{o}C treatment.

3. Result and discussion

Firstly, we pay attention to absorption spectra of different ratio P3HT and PCBM blend with and without annealing treatment. From Fig. 1 we find that different ratios of P3HT and PCBM films proccess different absorption peak intensity and position. For the blend films of 1:1 P3HT and PCBM proportion without heat treatment, absorption peak position is 337 nm and the range of 400-650 nm, the absorption peak around 337 nm peak stems from PCBM absorbance, the behind 400-650 nm vibronic absorption peaks are attributed to the P3HT $\pi-\pi^*$ transition [21,22]. As can be observed, the peak absorption for P3HT increases with increased P3HT percentage loading. Furthermore upon annealing at 130 ^{o}C, all the blend absorption intensity has significantly improved, and 400-650 nm vibronic absorption peaks also show a red shift, and the shoulders 550 nm and 602 nm become more distinguishable. Because P3HT is the main material to absorb the visible light in the blend system, the blend films with high P3HT concentration correspond to the high absorb efficiency. Annealing treatment process makes strong interchain -interlayer interactions among the P3HT chains as well as good polymer ordering in the blend films. The increasing interchain interaction among the P3HT chains because of annealing treatment results in more delocalized conjugated π electrons, the lowering of the band gap between π and π^*, and the increase of the optical $\pi-\pi^*$ transition, which results in the observed red shift in the peak absorption wavelength [23,24].

Photoluminescence spectra (PL) not only provide direct evidence for exciton dissociation, but also provide further evidence for the formation of polymer crystallites [22]. And thus efficient PL quenching is necessary to obtain efficient polymer solar cells. But this does not necessarily mean that the stronger the PL quenching, the better performance of the solar cells. From Fig. 2 we can find the blend films have lower photoluminescence spectra intensity by increasing the ratio of PCBM. While, after annealing treatment at 130 ^{o}C, the photoluminescence spectra intensity of all different ratio blend films elevate. In our point of view, high ratio PCBM ratio means high opportunity of the donor and acceptor interface formation in the condition without annealing treatment, so it is benefit to exciton dissociation, which corresponds to low photoluminescence spectra intensity. Heat treatment makes the P3HT aggregation in the blend films, improving the ordering of polymer chains in the blend films, some photogenerated excitons cannot reach the neighbouring fullerene molecule within the limited lifetime of the excitons and recombine radiatively, which gives rise to added photoluminescence signal. Heat treatment can improve the photoluminescence spectra intensity and decrease the separation of photogenerated charge, but it can improve the degree of polymer order, raise the mobility of charge carriers, which helps to improve the energy conversion efficiency of solar cell. So we should make it more balance between the blend ratio, the annealing treatment temperature and annealing treatment time. Because nanoscale control of the morphology of the donor-acceptor interpenetrating network is the critical factors to realize high efficiency solar cells.

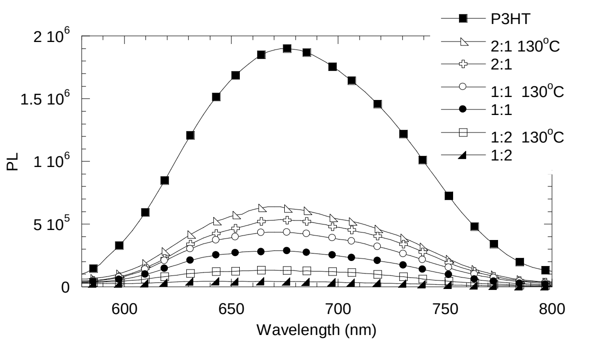

Fig. 2. PL spectra of different composition ratio (1:2, 1:1, 2:1) P3HT:PCBM blend film with and without 130 °C treatment.

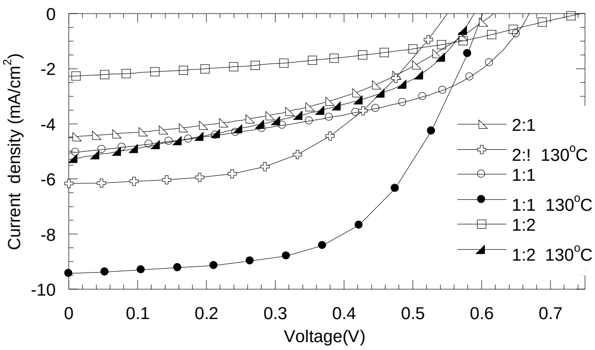

Fig. 3. Current-voltage characteristics of different blend ratio polymer solar cells with and without annealing treatment under AM 1.5 illumination at an irradiation intensity of 100 mW/cm^2.

Table 1. Photovoltaic properties of different blend ratio polymer solar cells under AM 1.5 irradiation (100 mw/cm^2).

Blend ratio	Treatment	*Voc (V)*	*Jsc (mA/cm^2)*	*FF*	*η (%)*
2:1	130^{o}C	0.57	6.17	0.49	1.72
2:1	unannealed	0.62	4.48	0.43	1.19
1:1	130^{o}C	0.58	9.34	0.60	3.25
1:1	unannealed	0.67	5.06	0.46	1.56
1:2	130^{o}C	0.59	5.29	0.42	1.31
1:2	unannealed	0.74	2.28	0.38	0.64

Fig. 3 is *J-V* characteristics of different blend ratios polymer solar cells with and without annealing treatment under AM 1.5 illumination at an irradiation intensity of 100 mW/cm^2. We can see they have excellent *J-V* curves from Fig. 3. The photovoltaic properties of different blend ratio polymer solar cells under AM 1.5 irradiation are summarized in Table 1. Performance of solar cells in Fig. 3 is consistent with the data of the performance of solar cells in Table 1.

From Table 1 we find the solar cells made with different proportions of P3HT/PCBM have various device performance. As PCBM weight increases (P3HT/PCBM=2:1,1:1,1:2), the open circuit voltage of solar cells increases, the data is 0.62V, 0.67V, 0.74V, respectively. In organic solar cells, the open circuit voltage (V_{oc}) of the device is affected by many factors, such as temperature [25,26], light intensity[27,28], work function of the electrode and the energy level structure of donor and acceptor material [29,30], etc. A reasonable explanation of the open circuit voltage change is difficult in organic solar cells. According to the experience of our experiment, the open circuit voltage of solar cell decreased with PCBM weight increase in the MEH-PPV:PCBM system. However, in the P3HT:PCBM system, the result is exactly the opposite. We will further study the specific reasons of this phenomenon. When the ratio of P3HT:PCBM is 1:1, the best performance of solar cells is achieved, V_{oc}=0.67V, J_{sc}=5.06 *mA/cm^2*, *FF*=0.46, η =1.56. Reasonable P3HT:PCBM network microstructure and charge transfer balance in solar cells is the reason for the high performance. To the 2:1 P3HT/PCBM blend ratio device, there is much more P3HT in the active layer, although they can absorb more sunlight, and yield more excitions in the blend film, the lack of enough Donor- Acceptor (D-A) interface leads to deficient excition dissociation. To the 1:2 P3HT/PCBM blend ratio device, there is much more PCBM in the active layer, their absorption efficient is the lowest, so they can not produce enough excitions in the blend film. And the extra PCBM maybe form large aggregates that deteriorated to device performance, which we can found clue from J_{sc} of the device. Charge transfer balance in solar cells is very importance, a too-low hole mobility in more PCBM blend films will lead to a build up of space-charge in the solar cell, which is detrimental to the fill factor and efficiency of the solar cells.

After 130^{o}C annealing treatment, short circuit current, fill factor and energy conversion efficiency of the solar cells in various proportions of P3HT:PCBM system are greatly improved, however the open circuit voltage is decreased. Heat treatment makes the P3HT ordered arrangement in the P3HT:PCBM system, improves the hole mobility, which makes the higher and more balance charge transportin solar cells, and UV-vis absorption spectra also significantly increase, thus improving the energy conversion efficiency of the solar cells [18].

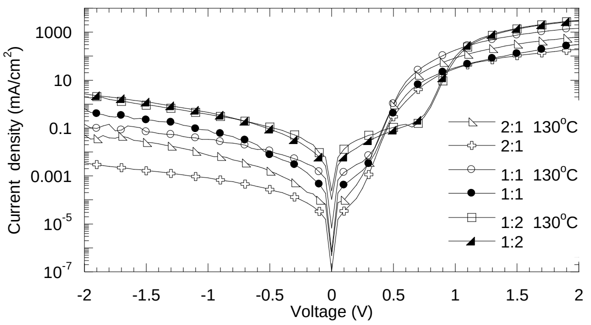

Fig. 4. Current-voltage characteristics in dark of different blend ratio polymer solar cells with and without annealing treatment.

The dark J –V characteristics of different blend ratio polymer solar cells with and without annealing treatment are shown in Fig. 4. It can be observed from Fig. 4 that the dark J –V characteristic of the device has three distinct regimes: When the cell is under negative or slightly positive bias, the current is limited by the shunt resistance of solar cells, which is dominated by local leakage currents due to weak spots in the films, giving rise to ohmic behavior. The second regime, at higher voltages, shows exponential behavior where the current density is controlled by the diode characteristics. In this regime the current is diffusion dominated, since the built-in electric field opposes the direction of the current. The third regime occurs at still higher positive bias, where the current is limited by the series resistance of solar cells. The current becomes space charge limited (SCL), and the drifting current is dominated. Consequently, the built-in voltage can be read at the cross point between the exponential and SCL regime. This value can be taken as an upper limit for V_{oc}. V_{oc} is directly related to the built-in potential of a solar cell, the larger the built-in electric field the better to exciton dissociation, and the higher the V_{oc}, and enlarging the built-in potential can obviously enhance V_{oc} [30]. From Fig. 4 we can find that the voltage at which the transition from the exponential section to SCL region also increases as PCBM weight increase, this might be the reason that the open circuit voltage of solar cell increases with PCBM weight increase.

At negative or slightly positive bias the dark current increases with the increase in the PCBM concentration. The increase is very large for the 1:2 P3HT/PCBM blend ratio device. This is because that electron mobility in PCBM is considerably larger than the hole mobility in P3HT. The dark J-V curve shows a small leakage current (10^{-6} mA/cm^2) and a rectification ratio of 10^4 at ± 2 V for the 1:1 P3HT/PCBM blend ratio device with 130 °C treatment.

4. Conclusions

The effect of blend composition and device 130 °C annealing is studied for organic solar cells with blend films of regioregular P3HT and PCBM. The weight ratio composition affects the performance of the solar cells, heat treatment can dramatically improve the efficiency of solar cells by balanced carrier mobilities and high transport properties in the blend films. The solar cells for the 1:1 composition after 130 °C thermal annealing possess fine performance, and achieve an open circuit voltage (V_{oc}) of 0. 58 V, short circuit current density (J_{sc}) of 9.34 mA/cm^2, fill factor (FF) of 60. 0 % and power conversion efficiency (η) of 3.25 % under 100 mW/ cm^2 air-mass 1.5 solar simulator illumination .

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