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Self-organization effect in poly(3-hexylthiophene): methanofullerenes solar cells*

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This paper studies the self-organization of the polymer in solar cells based on poly(3-hexylthiophene): [6, 6]-phenyl C_{61}-butyric acid methyl ester by controlling the growth rate of active layer. These blend films are characterized by UV-vis absorption spectroscopy, charge-transport dark $J-V$ curve, x-ray diffraction pattern curve, and atomic force microscopy. The results indicate that slowing down the drying process of the wet films leads to an enhanced self-organization, which causes an increased hole transport. Increased incident light absorption, higher carrier mobility, and balanced carrier transport in the active layer explain the enhancement in the device performance, the power conversion efficiency of 3.43% and fill factor up to 64.6% are achieved under Air Mass 1.5, 100 mW/cm^2.

Keywords: solar cell, polymer, slow drying, performance
PACC: 8630J, 7360F, 7855K

1. Introduction

Plastic solar cells have received considerable attention recently as low cost, light weight and mechanically flexible photovoltaic devices after the introduction of new concepts of bulk heterojunction (BHJ) and bi-continuous interpenetrating network of acceptor and donor materials.[1−10] Here, acceptor-type fullerene molecules are dispersed in a polymer matrix, giving a photoactive film with a large geometrical interface between donor and acceptor. The thin absorber film is sandwiched between two electrodes with asymmetric work functions, with each electrode forming an ohmic contact with the respective p- or n-type semiconductor. Upon irradiation, the conjugated polymer absorbs the photons and produce excitons. The excitons are separated into free charges at the interface of polymer and fullerene, the electrons from the excitons in the conjugated polymer transfer to fullerene, and the holes from the excitons in the fullerene transfer to the conjugated polymer. The separated electrons and holes move to cathode and anode respectively by their own pathways, resulting in the formation of photocurrent and photovoltage. So this structure can significantly enhance charge separation and transport processes, thereby photovoltaic performance.[1]

One of the most studied systems is regioregular-poly(3-hexylthiophene-2, 5-diyl) (P3HT) blended with [6, 6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). Over the last five years, major improvements have been achieved in the performance of polymer solar cells in different institutions.[11−13] This strong increase of the efficiency has been attributed to an increase of the hole transport due to crystallization of the polymer, a better morphology, and an improved overlap with the solar spectrum due to a red-shift of the absorption upon annealing.[12,14−16] Controlling the growth rate of active layer is another important method of increasing device performance. Slowing down the drying process of the wet films leads to an enhanced self-organization, which is expected to enhance the hole transport in the P3HT. Here we demonstrate that the performance of the polymer BHJ photovoltaic cells can be significantly increased by controlling the growth rate of active polymer layer from solution to solid state. We achieved the device fill factor (FF) of 64.6%, power conversion efficiency

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(PCE) of 3.43% under the standard AM 1.5G 1 Sun test condition.

2. Experimental section

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°C for 10 h, the substrates were transferred into a nitrogen-filled glove box. P3HT (purchased from Aldrich, used as received) was dissolved in 1, 2-dichlorobenzene, followed by blending with PCBM (purchased from Nano-C, used as received) in 50%. 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 200 nm. The growth rate of the polymer layer was controlled by varying the film solidification time. The spin-coated films of device No.1 were covered in a glass petri dish for slow growth while drying, the spin-coated films of device No.2 were baked at 45°C for fast growth. At last, the cathode, consisting of 1 nm of LiF and 100 nm 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. BHJ cells with the sandwich structure ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al were fabricated.

The absorption spectra were measured by a HP 8453 UV-vis spectrophotometer. The x-ray diffraction (XRD) pattern was measured with X' PertPRo diffractometer (PANalytical), for the step = 0.02, time/step = 5 s, with the same slits for two samples. The target is Cu Kα, with the power 30 kV×30 mA. Solar power conversion efficiencies were measured under an illumination of 100 mWcm^{-2} with an AM1.5 solar simulator (Oriel model 91192). The current-voltage ($J-V$) characteristics were measured with a Keithley 236 source-measure unit. The spectral response of the devices was measured with a photomodulation spectroscopic setup (model Merlin, Oriel). Tapping-mode atomic force microscopy (AFM) images were obtained using a NanoScope NS3A system (Digital Instrument) to observe the areas of the device where no top electrode was deposited.

3. Results and discussion

Figure 1 shows the results of UV-vis absorption spectra measurements for two types of films, slow grown (No.1) and fast grown (No.2). For the slow grown film the absorption spectra show four peaks at 335 nm, 511 nm, 552 nm and 600 nm. 335 nm absorption peak stems from the PCBM absorbance, the behind vibronic three absorption peaks are attributed to the P3HT $\pi-\pi^*$ transition.[17] The absorption spectra below 450 nm are very similar for all the films, indicating that all the films have a similar thickness (i.e., similar amounts of P3HT and PCBM). The PCBM absorption is clearly unaffected by drying time, which indicates that the driving force for better device properties is the self-organization of the polymer through a solvent drying process. For comparison with the fast grown film (No.2), the absorption in the red region of the slow grown film (No.1) is much stronger. The three vibronic absorption shoulders (peaks) are much more pronounced in film No.1, indicating strong interchain–interlayer interactions among the P3HT chains as well as good polymer ordering in the blend films.[18−21] The characteristic vibronic peak absorption wavelength for the slow grown film shows a red-shift compared to the fast grown film, indicating a higher degree of ordering. Significant red-shift appears in the more ordered films as high crystalline order involves an enhanced conjugation length and hence a shift of the absorption spectrum to lower energies. So the chains of the slow grown film become mobile and self-organization can occur to form ordering.[22]

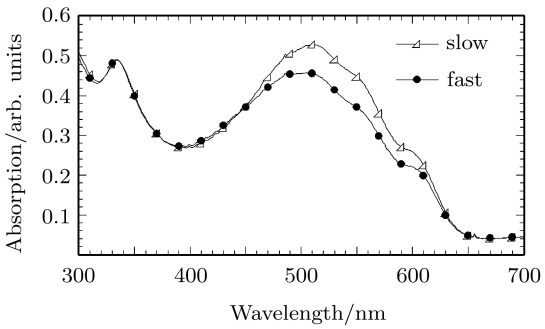


Fig.1. Absorption spectra of 1:1(w/w) P3HT:PCBM films fabricated by spin-coating for different drying rates.

Self-organization has been shown to improve field-effect carrier mobility in P3HT by more than a factor of 100 to 0.1 $cm^2V^{-1}s^{-1}$.[23,24] The slow grown will assist the formation of self-organized ordered struc-

ture in the P3HT:PCBM blend system. The degree of self-organization can be varied by controlling the film growth rate or, in other words, by controlling the time it takes for the wet films to solidity. Figure 2 shows XRD pattern for P3HT:PCBM films, slow grown (No.1) and fast grown (No.2). The peaks at $2\theta \cong 5.3°$ correspond to interchain spacing ($d \cong 1.62\,\mathrm{nm}$) in P3HT crystalline grains associated with the interdigitated alkyl chains.[25] Obviously, the relative diffraction intensity of the film (No.1) is much higher than the film (No.2). This further means that the slow grown film has the higher crystallinity and self-organization phenomenon.

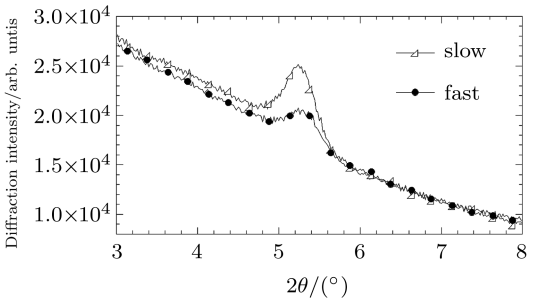


Fig.2. X-ray diffraction spectra for 1:1 (w/w) P3HT:PCBM films fabricated by spin-coating for different drying rates.

In polymer BHJ solar cells an important factor in determining the device performance is the charge transport in the active layer. Efficient charge transport could be realized by electrons and holes moving in separated pathways along an interpenetrating network to the appropriate electrodes. Figure 3(a) shows the dark $J - V$ characteristics of the hole-only devices having a structure of ITO/PEDOT:PSS/P3HT:PCBM/Au with different treatments. The applied voltage was corrected for the built-in voltage (V_{BI}). Compared to the device based on the fast grown film, the device with slow grown layer shows a largely enhanced current density at the same driving voltage. This indicates that the hole mobility is significantly enhanced due to the self-organization of P3HT. So slowing down the drying process of the wet films brings about an enhanced crystallinity, which can more enhance the hole transport in the P3HT. The dark $J - V$ characteristics for the electron-only devices with a structure of Sn/P3HT:PCBM/LiF/Al are shown in Fig.3(b). The current density of the device with slow grown active layer is slightly high, a relatively small increase in electron transport upon slow growth can be obtained. So the slow growth results primarily in an increased ordering in the polymer chains which will significantly effect the hole mobility, whereas it will have small effect on the electron mobility in PCBM. For ordinary BHJ solar cells, the electron transport is several orders of magnitude higher than the hole transport in the blend. This unbalanced charge transport leads to a fundamental space-charge limit in the photocurrent, which is detrimental for the FF and efficiency.[26] However, when the hole transport is largely improved, carrier transport is more balanced in the blend, and high device performance is possible.

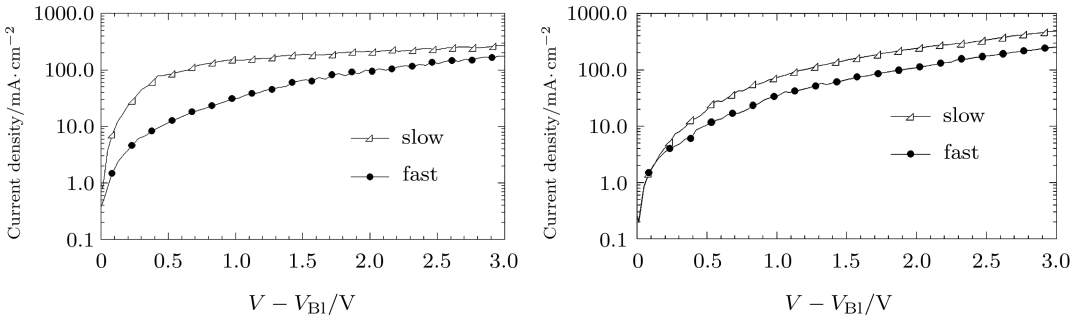


Fig.3. $J - V$ curves for hole-only (a) and electron-only (b) devices based on 1:1 (w/w) P3HT:PCBM films fabricated by spin-coating for different drying rates.

In Fig.4 we compare the $J - V$ characteristics of two types of devices with different solvent evaporation times after spin-coating. The short-circuit current density (J_{sc}) increases from 4.05 to 9.66 $\mathrm{mAcm^{-2}}$, the device series resistance (R_{S}) reduces from 4.86 to 1.85 $\Omega\mathrm{cm}^2$, and the shunt resistance (R_{P}) enhances from 7313 to 14051 $\Omega\mathrm{cm}^2$ with increasing solvent evaporation times. Series and shunt resistances were derived from the slope of the $J - V$ characteristic curve under dark conditions close to 2 and 0 V,

respectively.[27] The FF consistently increases from 57.1 to 64.6%, the PCE also increases from 1.50 to 3.43%. The summary of device performance for various photovoltaic (PV) devices fabricated in this work is provided in Table 1. Under the dark conditions, the rectification ratios are close to 10^7 at a bias of ± 2 V for the slow drying devices from Fig.4(b). The measurements carried out in the dark reveal excellent diode behaviour. The optimum overall performance of a polymer solar cell can be achieved via balancing the various requirements on light absorption, transport, and extraction of charge carriers. We believe that this enhancement on device performance originates from two important contributions, an increase in the charge-carrier mobility and increased absorption in the slow grown active layer. Slow drying leads to significant enhancement of the hole mobility, this mobility increase makes the more balanced transport of holes and electrons, and reduces the accumulation of space charges in films with the necessary thickness to absorb most of the incoming photons. The enhancement of the device R_{P}, reduction of the device R_{S} and the balanced charge transfer in the slow drying films make the device FF increase. The resulting enhancement in short-circuit current together with the enhanced FF increases the PCE of these cells to a value of 3.43%.

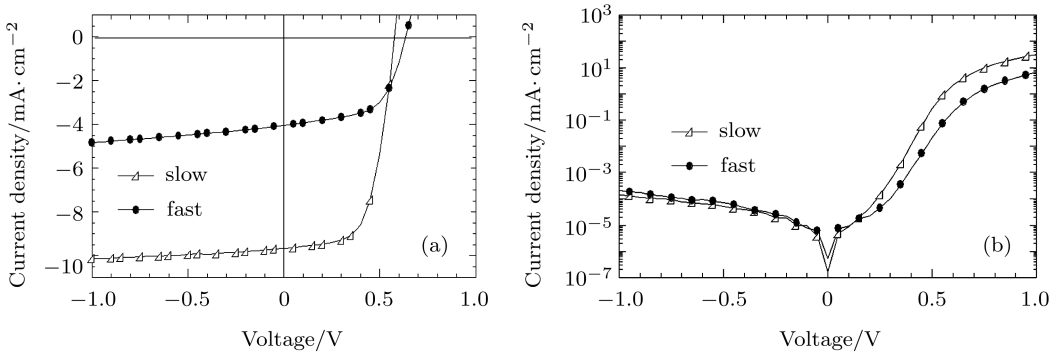


Fig.4. Illuminated (a) and dark (b) J–V characteristics of 1:1 (w/w) P3HT:PCBM films fabricated by spin-coating for different drying rates.

Table 1. Summary of device performance for different drying rates.

	100/mWcm^{-2}				Dark	
Device no	V_{oc}/V	I_{sc}/(mA cm^{-2})	FF	η/%	$R_{\mathrm{S}}/\Omega\mathrm{cm}^2$	$R_{\mathrm{P}}/\Omega\mathrm{cm}^2$
1 (Slow)	0.55	9.66	64.6	3.43	1.85	14051
2 (Fast)	0.65	4.05	57.1	1.50	4.86	7313

Metal–insulator–metal[28] picture is not sufficient to explain the V_{oc} variety in polymer solar cells, the most widely propagated belief is that V_{oc} varies linearly with the energy difference between the donor the highest occupied molecular orbital (HOMO) and the acceptor lowest unoccupied molecular orbital (LUMO) for systems with ohmic contact at both electrodes.[29−32] However, here, it is interesting to see a variation of ca. 0.1 V in two types device V_{oc} from Table 1. A likely explanation for this is in slow grown films, P3HT has a enhanced conjugation length on average than in fast grown,[33] as indicated by the much stronger absorption intensity in the longer wavelength region, as discussed above. Therefore, the reduction in V_{oc} is reasonable which gives that the difference between the effective HOMO of the polymer and the LUMO of the acceptor decreases.

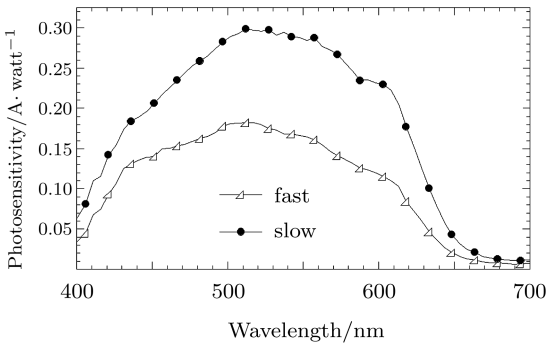


Fig.5. The photosensitivity spectrum of 1:1 (w/w) P3HT:PCBM films fabricated by spin-coating for different drying rates.

The photocurrent action spectrum of two types of device with different active layer grown rates is shown in Fig.5. Compared to the device based on fast grown film, device with slow grown active layer shows an enhanced photosensitivity (PS) at each wavelength. Notably, the spectrum of the slow grown solar cell is similar in spectral shape to that of the fast grown device. Two important factors, an increase in the charge-carrier mobility and increased absorption in the active layer, contribute to this increase in device PS.

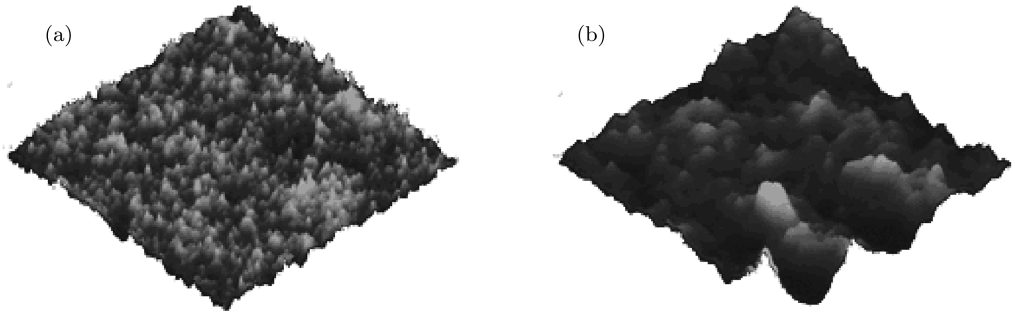


Fig.6. AFM height images of the surface of the active layer consisting of P3HT:PCBM (in 1:1 weight ratio) for a $2\,\mu\text{m} \times 2\mu\text{m}$ (a) fast-grown, (b) slow-grown.

The interface between the polymer and the electrode plays an important role in determining the electrical characteristics of the devices and the morphology of the spun-cast polymer film has to be studied in order to understand the nature of the metal-polymer interface.[34,35] In order to understand the morphological changes that occur in the polymer layer as a result of different drying rate, we studied the AFM images of the active layer surface with various solidification times. Figure 6 shows the AFM images for samples that have undergone various grown rate. For the fast grown film the surface is very smooth with a root-mean-square (rms) roughness of 0.568 nm. However, the surface of the slow grown film becomes rougher and the rms roughness becomes 3.625 nm. The obvious relation between the device performance and the surface roughness of the films, concluded from the morphology study, is that the higher roughness of the film will give higher efficiency device. The rough surface is probably a signature of polymer self-organization, which in turn enhances ordered structure formation in the thin film. This indicates improved phase segregation with characteristic dimensions comparable to the exciting diffusion length. So rough surface enhances the ordered structure formation, and increases the carrier mobility.

4. Conclusion

In conclusion, the self-organization in the slow grown polymer film was investigated by UV-vis spectroscopy, charge-transport dark J–V curve, XRD pattern curve, and AFM picture. The experimental results show that the polymer self-organization makes the active layer to possess the higher crystallinity, which leads to an enhancement of the absorption and an increase in the charge-carrier mobility. Therefore, the performance of P3HT:PCBM bulk heterojunction solar cells, made with slowly dried active layer films, is largely increased.

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