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Investigation of optimum conditions for high-efficiency organic thin-film solar cells based on polymer blends

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Abstract

Organic thin-film solar cells based on poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-buteric acid methyl ester (PCBM) blend system attracts most attention. We studied the effects of P3HT:PCBM blend composition and thermal annealing treatment on the device performance. P3HT:PCBM weight ratio mainly influenced short circuit current (J_{SC}) and power conversion efficiency (PCE). For the cells with P3HT:PCBM ratio of 1:0.66 showed the maximum PCE of 1.4%. Thermal annealing improved the photovoltaic characteristics and we achieved PCE of 2.0% with the annealed device. Furthermore, we observed transient photocurrent responses of devices to solar simulated light (air mass 1.5 G, 100 mW/cm^2) irradiation. Annealing treatment resulted in suppression of the decay of photocurrent, suggesting that carrier transport network was improved by thermal annealing.

Keywords: Organic thin-film solar cells; Polythiophene; Fullerene; Bulk heterojunction; Photocurrent response

1. Introduction

Photovoltaic (PV) cells will hopefully lead to clean and renewable energy source. Organic thin-film solar cells have potential advantages in their mechanical flexibility, portability and the low manufacturing cost [1]. Recently, organic PV cells based on conjugated polymer and fullerene have been improved in their efficiencies. Especially, poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-buteric acid methyl ester (PCBM) blend system attracts most attention (Fig. 1) [2–4]. To obtain high efficiency P3HT:PCBM-blend solar cells, we tried to find the optimum conditions for preparation. In this study, we optimized the P3HT:PCBM weight-ratio of the cells and studied effects of thermal annealing treatment on the device performance. Additionally, we observed slow transient photocurrent responses of the cells under continuous illumination. These slow transient phenomena, generally ascribed to charge trapping and recombination, have been reported and raised the possibility that observations of slow photocurrent responses would be a useful tool for testing stability of organic solar cells [5].

2. Experimental

2.1. Sample preparation

To prepare P3HT:PCBM solutions, regioregular P3HT and PCBM were dissolved in 1,2-dichlorobenzene. Glass substrates with an indium–tin oxide (ITO) electrode were used for sample preparation. The substrates were cleaned up by exposing to ozone for 30 min. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was deposited by spin coating at 3000 rpm and then dried at 135 °C for 10 min to smooth the substrate surface. Subsequently, the P3HT:PCBM solutions were spin coated at 1500 rpm onto the substrates. The resulting samples were quickly transferred to a vacuum chamber (the samples were exposed to air ambient at this time). Al electrodes of approximately 50 nm thickness were deposited by vacuum evaporation. The active layer of the cell, defined by shadow mask, was 0.04–0.07 cm^2. Once the electrodes were deposited, the devices were stocked in a N_2-filled glove box. As for the thermal annealing, the cells were held on a hot plate of 110 °C for 10 min under N_2 atmosphere.

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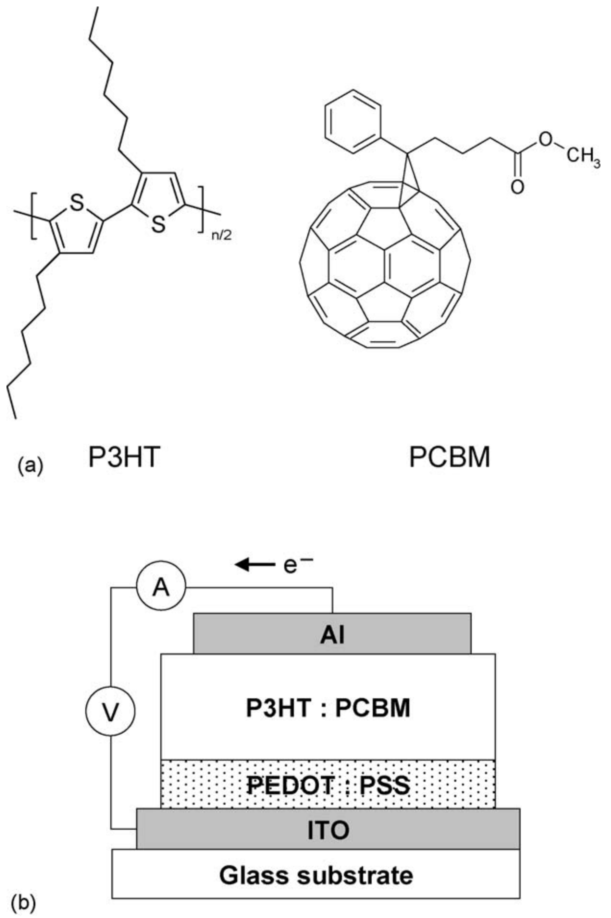

Fig. 1. (a) Chemical structures of regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-buteric acid methyl ester (PCBM). (b) Cross-section of the device structure of PV cells fabricated in this study.

2.2. Measurements

The power conversion efficiency (PCE) was calculated from the current density–voltage (*J–V*) characteristics under air mass 1.5 G solar simulated light irradiation of 100 mW/cm^2. The irradiation intensity was calibrated using a standard cell for a-Si solar cells (the detection area = 0.066 cm^2). Here, it is important that the active layer of the cell was similar in size to that of the standard cell. *J–V* characteristics were measured by the semiconductor characterization system (KEITHLEY 4200, Keithley Co. Ltd.) at room temperature in N_2 atmosphere.

Measurement of incident photon to converted electron efficiency (IPCE) spectra were carried out at room temperature in N_2 atmosphere. The cells were illuminated with monochromatic light of 0.1–1 mW/cm^2. The wavelength of the incident light was changed by computer-controlled monochromator. The short-circuit photocurrent density (J_{SC}) caused by light irradiation was monitored using an electrometer as a function of wavelength.

To observe transient photocurrent responses of the devices, J_{SC} was recorded as a function of time under continuous illumination with solar simulated light (air mass 1.5 G, 100 mW/cm^2) at room temperature in N_2 atmosphere.

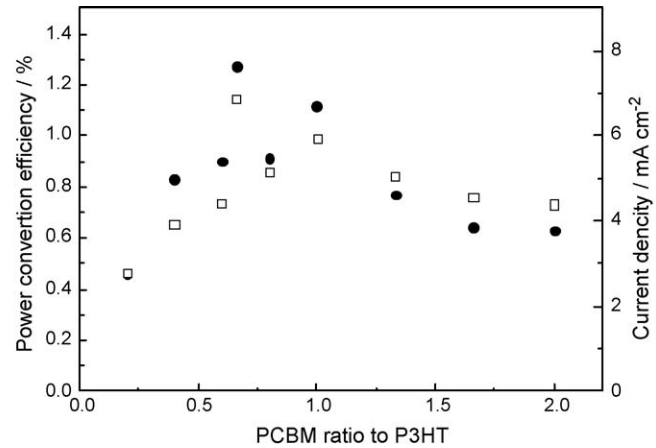

Fig. 2. Power conversion efficiency (PCE) (solid circle) and short circuit current density (J_{SC}) (open square) of cells as a function of PCBM weight ratio to P3HT.

3. Results and discussion

3.1. P3HT:PCBM blend composition

Fig. 2 shows the influence of PCBM ratio to P3HT on PCE and J_{SC}. PCE and J_{SC} varied significantly on changing the PCBM ratio, whereas the open-circuit voltage (V_{OC}) was not affected notably (data not shown). So, it is likely that the PCBM ratio influenced mainly J_{SC} rather than V_{OC}, and J_{SC} contributed predominantly to improvement of PCE. P3HT:PCBM ratio of 1:0.66 showed the maximum PCE of 1.4%.

3.2. Thermal annealing

Fig. 3 shows the *J–V* characteristics of the PV cells before and after annealing. Annealing brought about improvement of the photovoltaic characteristics. Especially, J_{SC} was significantly increased by annealing; suggesting that carrier transport network

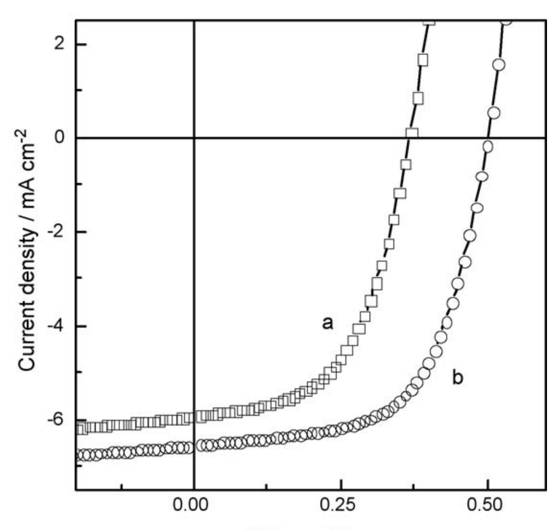

Fig. 3. *J–V* characteristics of cells: (a) an as-deposited cell and (b) a cell annealed at 110 °C for 10 min in N_2 atmosphere.

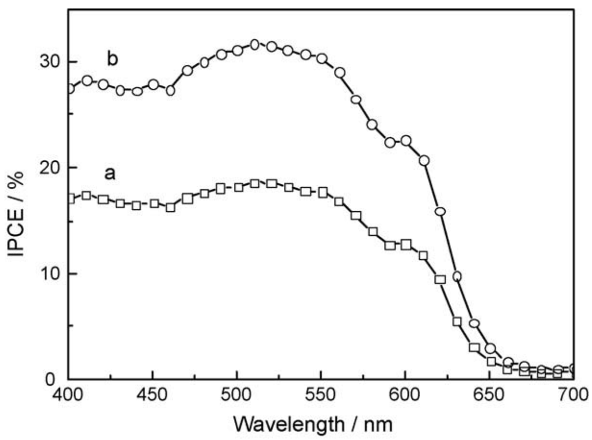

Fig. 4. Incident photon to converted electron efficiency (IPCE) spectra of cells: (a) an as-deposited cell and (b) a cell annealed at 110 °C for 10 min in N_2 atmosphere.

in the cells was promoted. It should be noted that the degree of improvement in J_{SC} by pre-electrode-deposition annealing was comparable to that by post-electrode-deposition annealing at this annealing condition (data not shown). We achieved maximum PCE of 2.0% with the annealed device.

Thermal annealing also improved IPCE as shown in Fig. 4. The efficiencies were increased at each wavelength upon annealing. Notably, the spectrum of the annealed PV cell was similar in spectral shape to that of the as-deposited one. The result suggests that improvement of J_{SC} is predominantly due to the improved charge carrier transport rather than to enhanced charge carrier generation. Worthy of mention is that there has been conflict about the annealing effect for IPCE spectra. Padinger et al. [6] observed changes in spectral shape upon annealing treatment, while Kim et al. [7] reported no effect in spectral shape. In addition, thermal annealing influenced absorption spectra of the cells prepared using chloroform and 1,2-dichlorobenzene, but not affected from chlorobenzene as solutions [4,8]. These discrepancies may be caused by the differences in the experimental conditions (solvent, purity, degree of polymerizaiton, annealing temperature, etc.). It is necessary to investigate annealing conditions more systematically for a better understanding.

3.3. Transient photocurrent response

We also examined J_{SC} responses of devices to solar-simulated light irradiation as shown in Fig. 5. J_{SC} of the aged P3HT:PCBM polymer-blend PV cell (Fig. 5(c)) gradually decreased after light-on, while the fresh PV cell (Fig. 5(b)) was as stable as a Si photodiode (Fig. 5(a)). It is possibly that hole and electron transport network have been deteriorated in the aged PV cell. It should be noted that the initial intensity of J_{SC} recovered when both the fresh and aged PV cells were maintained in the dark for several minutes before successive light irradiation. The measurement of photocurrent responses would be a useful tool for examination of damages in the cells.

As shown in Fig. 6, photocurrent response to the light irradiation was also improved by thermal annealing. The J_{SC} of the annealed PV cell showed little decay at 60 s after irradiation

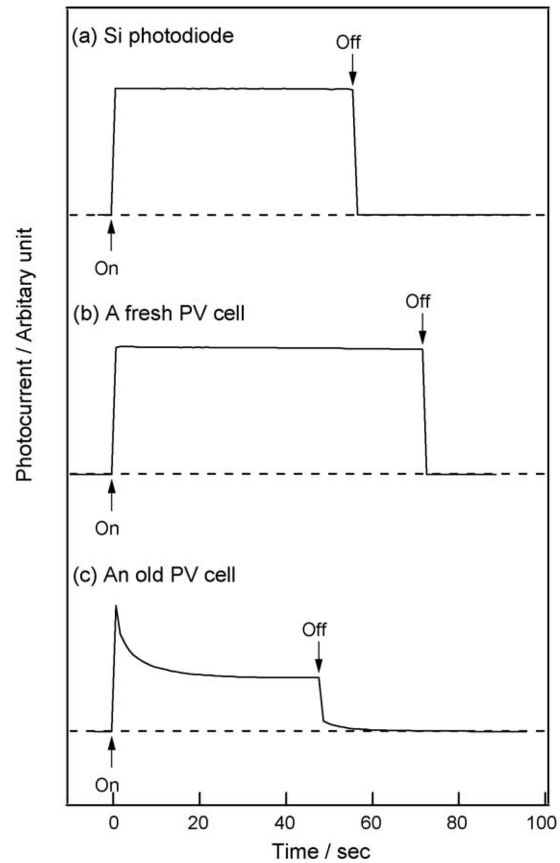

Fig. 5. J_{SC} responses of cells for solar simulated light irradiation (air mass 1.5 G, 100 mW/cm^2): (a) Si photodiode; (b) a fresh cell stored for 1 day after preparation in N_2 atmosphere under dark condition and (c) the same one subsequently stored for 30 days in air under dark condition. These current–time characteristics are normalized with respect to the intensity of initial photocurrent.

(Fig. 6(b)), while that of the as-deposited one decreased to 96% with respect to the intensity of initial photocurrent (Fig. 6(a)). The result suggests that carrier transport had become more efficiently and carrier trapping in the organic layer were suppressed.

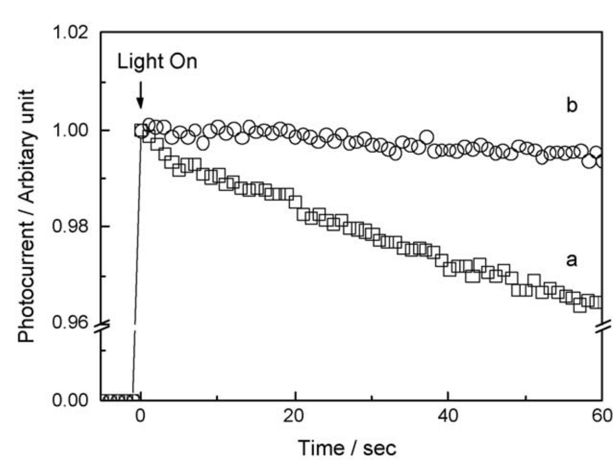

Fig. 6. J_{SC} response of cells to solar simulated light irradiation (air mass 1.5 G, 100 mW/cm^2): (a) an as-deposited PV cell and (b) a cell annealed at 110 °C for 10 min in N_2 atmosphere. These current–time characteristics are normalized with respect to the intensity of initial photocurrent.

The result also supports that improvement of J_{SC} by annealing is due to improvement of carrier transport rather than enhancement of carrier generation as mentioned in Section 3.2.

4. Concluding remarks

For the cells with P3HT:PCBM ratio of 1:0.66 showed the maximum PCE of 1.4% without thermal annealing. Thermal annealing led to the improvement of the photovoltaic characteristics and we achieved PCE of 2.0%. The spectral shape of IPCE spectrum was not influenced remarkably by thermal annealing in this study. However, there has been conflict about the annealing effect for IPCE and absorption spectra [4,6–8]. So, systematic investigation is needed to a better understanding of the effect of annealing treatment.

Transient J_{SC} response was deteriorated by exposure to air ambient. On the other hand, thermal annealing showed the improvement of stability of cells to continuous illumination. The measurement of transient J_{SC} responses would be a useful tool for examination of carrier transport in the cells.

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