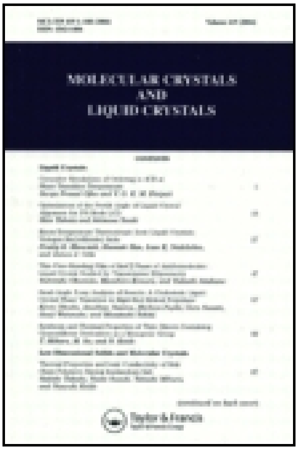

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Performance of P3HT/C_{70}-PCBM Polymer Photovoltaic Devices According to Manufacturing Conditions

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In order to improve the P3HT/PCBM polymer photovoltaic devices, C_{70}-PCBM ([6,6]-phenyl C_{71}-butyric acid methyl ester) was employed instead of C_{60}-PCBM ([6,6]-phenyl C_{61}-butyric acid methyl ester). C_{70}-PCBM showed significant increase of visible region light absorption to enhance the photocurrent. To optimize the device performance, we changed the device fabrication conditions such as atmosphere, solvents, post-annealing time, active layer materials composition, and thickness. The best power conversion efficiency of 4.7% was achieved under AM 1.5 G, 75 mA/cm^2 condition.

Keywords: C_{70}-PCBM; organic solar cell; polymer photovoltaic device

INTRODUCTION

Recently, the polymer photovoltaic (PV) cells using the composites of conjugated polymer and soluble fullerene derivative have attracted much attention due to their possibilities of low production cost and easy manufacturing by solution processes [1]. Theoretically, a single composite layer of polymer/fullerene solar cells efficiency can reach maximum of 11% by optimizing active layer material energy levels, bandgaps, and charge mobilities. And even P3HT/PCBM solar cells can be expected to reach 8.4% by minimizing the energy loss in the

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electron transfer [2]. However, the power conversion efficiency (PCE) of the polymer PV cells is still far away from that theoretical limit. To improve the PCE in polymer PV cells, more efforts should be paid to an efficient light harvest of photoactive layer, an enhanced interface contact between the metal electrode and photoactive layer, and an improvement of charge carrier mobility [3].

One of the strategies for more efficient light harvest is to extend the solar light absorption of active layer to a longer range, thereby increasing the PCE of photovoltaic cells. The C_{60}, which constitutes the active material as an electron acceptor, has rather a poor absorption strength in a low energy realm because of the optical forbidden transition due to the symmetrical structure [4]. Therefore, a less symmetrical structure like C_{70} can allow to harvest the forbidden low-energy transition, leading to the enhanced light harvest in a low energy range [5]. A few photovoltaic devices which used the C_{70}-PCBM as an electron acceptor [6,7], especially with low band gap polymer [8,9], was available in literature, but the systematic approach to find the optimum condition was not yet studied.

In this work, we fabricated the photovoltaic cells using the composite of the semiconducting polymer P3HT and the soluble C_{70}-PCBM ([6,6]-phenyl C_{71}-butyric acid methyl ester). In order to optimize the device fabrication conditions, atmosphere, solvent, post-annealing time, active materials composition and the thickness of active layer were controlled.

EXPERIMENTAL

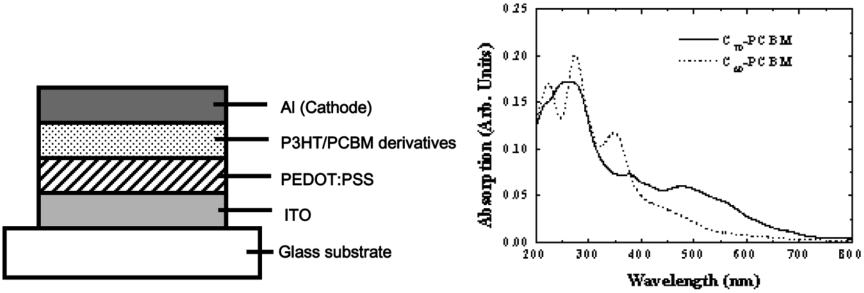
Materials

All solvents used in this study were of HPLC grade. Poly(3-hexylthiophene) (P3HT) was purchased from Reike Metal Ltd. [6,6]-Phenyl C_{71}-butyric acid methyl ester (C_{70}-PCBM) and [6,6]-phenyl C_{61}-butyric acid methyl ester (C_{60}-PCBM) were purchased from Nano-C.

Photovoltaic Device Fabrication

Composite solutions with P3HT and C_{70}-PCBM were prepared using a selected solvent among chloroform (CF), chlorobenzene (CB), and 1,2-dichlorobenzene (DCB). The concentration was controlled adequately in a range of $1.0 \sim 2.0\,wt\%$. For measurement of optical absorption spectra of PCBM, the solutions were spun on to the pre-cleaned UV-grade silica substrates.

The polymer photovoltaic devices were fabricated with a typical sandwich structure of ITO/PEDOT:PSS/active layer/Al. The ITO coated glass substrates were cleaned through a routine cleaning procedure, including sonication in detergent followed by distilled water, acetone, and 2-propanol. A 45 nm thick layer of PEDOT:PSS (Baytron P) was spin coated on a cleaned ITO substrate after exposing the ITO surface to ozone for 10 min. The PEDOT:PSS layer is baked on a hot plate at 120°C for 10 min. Active layer was spin coated from the pre-dissolved composite solution after filtering through 0.45 μm PP syringe filters. The device structure was completed by depositing 150 nm Al cathode as top electrode onto the polymer active layer under 3×10^{-6} torr vacuum in thermal evaporator and the completed device structure is shown in Figure 1(a). Current density-voltage (J-V) characteristics of all polymer photovoltaic cells were measured under the illumination of simulated solar light with 75 mW/cm^2 (AM 1.5 G) by Oriel 1000 W solar simulator. Electric data were recorded using a Keithley 236 source-measure unit and all characterizations were carried out in an ambient environment. The illumination intensity used was calibrated by a standard Si photodiode detector from Bunkoukeiki Co., Ltd. The incident photon-to-current conversion efficiency (IPCE) was measured as a function of wavelength from 360 to 800 nm (PV measurement Inc.) equipped with a halogen lamp as a light source, and calibration was performed using a silicon reference photodiode. Thickness of the thin film was measured using KLA Tencor Alpha-step 500 surface profilometer with an accuracy of ±1 nm.



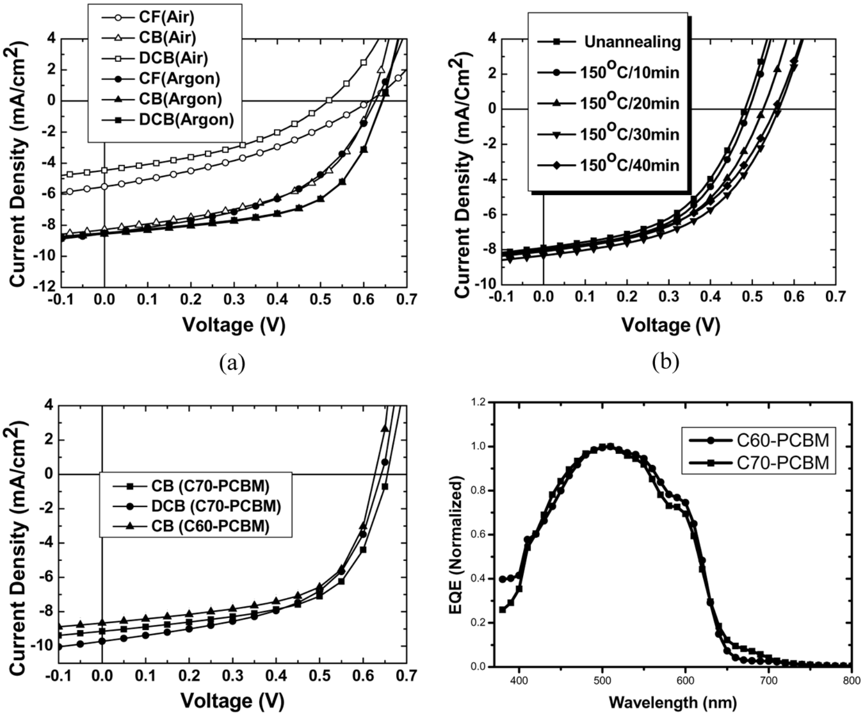
(a) (b)

FIGURE 1 Device configuration and UV-visible absorption spectra of C_{70}-PCBM and C_{60}-PCBM.

RESULTS AND DISCUSSION

As shown in Figure 1(b), the absorbance of the visible region is much higher in C_{70}-PCBM than C_{60}-PCBM. This indicates that C_{70}-PCBM is better candidate than C_{60}-PCBM at the standpoint of the solar light harvest.

J-V characteristics of the devices fabricated with three different solvents and two different atmospheres with the active materials composition of P3HT:C_{70}-PCBM = 1:1 wt ratio are presented at Figure 2(a). The open symbols represent the devices whose active layers were spin coated and 10 minutes post-annealed under air circumstance. The device which made from CB solvent showed the best performance



(a) (b)

(c) (d)

FIGURE 2 J-V characteristics of P3HT:C_{70}-PCBM devices: (a) depend on solvents and atmospheres; (b) depend on post annealing time; (c) comparison with C_{60}-PCBM device, and (d) the comparison of incident photon to current conversion efficiency (IPCE) spectra of P3HT:C_{70}-PCBM and P3HT:C_{60}-PCBM devices.

among the open symbol devices, and the performances of all devices dropped rapidly with increasing the annealing time more than 10 minutes. The filled symbols in Figure 2(a) represent the devices whose active layers were spin coated and 30 minutes post-annealed under inert atmosphere inside the glove box filled with argon. The optimum post-annealing time under argon atmosphere was chosen from the annealing time experiment results shown in Figure 2(b), where both open circuit voltage (Voc) and short-circuit current density (Jsc) were gradually increased until 30 minutes post-annealing but turned to decrease after that. This result is in accordance with the results of Heeger group's P3HT:C_{60}-PCBM post annealing case [10], and the increased of performance should be attributed to the increased crystallinity of the P3HT polymer, the improved nanoscale morphology and the improved contact to the Al top-electrode. But when the device was post-annealed under air circumstance, the above positive factors compete with the negative factors such as decomposition of active layer materials and/or electrodes from the reaction with oxygen and moisture. The negative factors overwhelm the positive factors post-annealed beyond 10 minutes, but even before reaching that critical time the negative factors already exist. So it is important to fabricate the polymer photovoltaic devices under inert condition. Even under inert atmosphere the solvent dependency was observed. The devices fabricated using CB and DCB solvents showed better photovoltaic performance than CF solvent. This solvent dependence of P3HT:C_{70}-PCBM device might be attributed to the difference in the solubility of P3HT and C_{70}-PCBM in given solvent. The different solubility of active layer materials affect the domain size of solutes precipitated out of the solvent during the coating process and thus the final photovoltaic performance of polymer solar cells [11]. Devices fabricated using CB and DCB solvents under argon atmosphere showed quite similar performance but better than CF. Therefore, further experiments for the dependence of active layer material compositions and thickness were performed with both CB and DCB solvents.

The dependence on active layer materials composition was shown in Table 1, and the best photovoltaic performance was observed at the composition of 1:1 weight ratio of P3HT and C_{70}-PCBM for both CB and DCB solvents (**device d** and **i** in Table 1). When increasing the C_{70}-PCBM to get the composition to 1:1.2 ratio, the Jsc dropped rapidly with the gentle drop of fill factor (FF) (**device e** and **j** in Table 1). The increased portion of C_{70}-PCBM in active layer inhibit the crystallinity of P3HT and/or block the hole transport.

TABLE 1 Performance of P3HT:C_{70}-PCBM Devices Depend on Active Material Composition Under a Simulated Photovoltaic Light with 75 mA/cm^2 Illumination (AM 1.5).

Device	Solvent	P3HT:C_{70}-PCBM wt. ratio	Jsc (mA/cm^2)	Voc (V)	FF	PCE (%)
a	CB	1:0.6	8.26	0.63	0.56	3.90
b	CB	1:0.7	8.35	0.63	0.57	4.02
c	CB	1:0.8	8.45	0.63	0.57	4.08
d	CB	1:1.0	8.57	0.64	0.58	4.22
e	CB	1:1.2	8.01	0.62	0.55	3.63
f	DCB	1:0.6	8.19	0.63	0.57	3.94
g	DCB	1:0.7	8.14	0.64	0.58	4.04
h	DCB	1:0.8	8.66	0.63	0.57	4.15
i	DCB	1:1.0	8.49	0.64	0.58	4.20
j	DCB	1:1.2	7.51	0.64	0.55	3.49

Table 2 represents the dependence of photovoltaic performance on active layer thickness. The best power conversion efficiency of 4.74% was observed at 100 nm active layer thickness with CB solvent with Voc of 0.66 V, Jsc of 9.14 mA/cm^2, and FF of 0.59 (**device l** in Table 2) under 75 mA/cm^2 illumination (AM 1.5). The best power conversion efficiency of 4.53% for DCB solvent was also found at 100 nm active layer thickness with Voc of 0.64 V, Jsc of 9.72 mA/cm^2, , and FF of 0.55 (**device q** in Table 2). When compared the **device l** and **q**, which are the best performance devices for CB and DCB solvents, **device q** has a better Jsc of 9.72 mA/cm^2 than **device l** of 9.14 mA/cm^2, while the better FF is observed for the **device l** of

TABLE 2 Performance of P3HT:C_{70}-PCBM Devices Depend on Active Layer Thickness Under a Simulated Photovoltaic Light with 75 mA/cm^2 Illumination (AM 1.5).

Device	Solvent	Thickness (nm)	Jsc (mA/cm^2)	Voc (V)	FF	PCE (%)
k	CB	80	9.09	0.66	0.59	4.68
l	CB	100	9.14	0.66	0.59	4.74
m	CB	120	9.07	0.64	0.58	4.52
n	CB	130	9.24	0.63	0.56	4.37
o	CB	140	8.99	0.63	0.56	4.22
p	DCB	80	8.80	0.64	0.57	4.25
q	DCB	100	9.72	0.64	0.55	4.53
r	DCB	120	8.65	0.63	0.53	3.87
s	DCB	140	8.07	0.61	0.51	3.34

0.59 than **device q** of 0.55. This difference was mainly attributed to the evaporation rates of two solvents. The high boiling point of DCB (178–180°C) evaporates slowly than low boiling point of CB (132°C). So the high boiling DCB could get bigger and higher crystalline P3HT and C_{70}-PCBM domains by its long evaporation time than CB, and its increased domain size and crystallinity improve the Jsc, but its big domain size leads to poor morphology to give negative effect on FF.

Figure 2(c) shows the comparison of the present device performance with P3HT:C_{60}-PCBM device, which has the efficiency of 4.15% with Voc of 0.63 V, Jsc of 8.66 mA/cm^2, and FF of 0.60 under 75 mA/cm^2 illumination (AM 1.5). In our experiments, the use of C_{70}-PCBM as an electron acceptor showed the improved Jsc than the case of C_{60}-PCBM. The comparison of normalized incident photon to current conversion efficiency (IPCE) spectra between two devices of P3HT:C_{70}-PCBM and P3HT:C_{60}-PCBM was shown at Figure 2(d). The distinguished difference between two IPCE spectra was found between 650 nm and 700 nm, where P3HT:C_{70}-PCBM device has relatively higher incident photon to current conversion efficiency.

The meaningful absorption of this range of solar spectrum was only done by C_{70}-PCBM, so it could be an evidence that the absorbed photons by C_{70}-PCBM caused to the generation of better photo current than C_{60}-PCBM. From this, it is clear that the increased Jsc of P3HT:C_{70}-PCBM devices relative to P3HT:C_{60}-PCBM device as shown at Figure 2(c) comes from the additional absorption of incident light by C_{70}-PCBM.

CONCLUSIONS

In the fabrication of polymer photovoltaic devices with P3HT and C_{70}-PCBM, the fabrication conditions like atmosphere, the solvents, the active layer materials composition, and the active layer thickness were controlled to improve the energy conversion efficiency. Active layer spin coating and post-annealing should be performed under inert atmosphere to prevent the decomposition of active layer materials and/or electrodes from the reaction with oxygen and moisture. The best efficiency was found with the condition of CB solvent, P3HT:C_{70}-PCBM = 1:1 ratio, and 100 nm thickness of active layer when fabricated and post-annealed under argon atmosphere. The increased Jsc of P3HT:C_{70}-PCBM devices relative to P3HT:C_{60}-PCBM comes from the additional absorption of incident light by C_{70}-PCBM.

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