Electronic Organic Thin Film Devices for Solar Energy Harvesting

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Abstract: We have established fabrication process of a multi-layered P3HT/PCBM based bulk-heterojunction photovoltaic cells with the P3HT layer as the hole transport layer and the PCBM layer as the electron transport layer between the electrodes and a blended P3HT/PCBM layer in order to widen the photon harvesting layer. Current density has increased about 1 mA/cm2 by the insertion of P3HT layer and the resulting conversion efficiency has been improved about 20% compared with the single layer device. The device with a cm-scale active area with an efficiency of ~1% has been fabricated by the developed method. We have fabricated the P3HT/PCBM p-i-n BHJ cells for the first time. The device structure was ITO/MoO3/P3HT(p)/P3HT:PCBM(i)/PCBM(n)/Ag. In the as-fabricated cells, the open circuit voltage of p-i-n BHJ cells with PCBM concentration 10 mg/ml, 15 mg/ml and 20 mg/ml were 0.56V, 0.71V and 0.74V respectively, and increased compared with 0.50V in the ordinary BHJ (i-type) cell. After post annealing, the short-circuit current density of p-i-n BHJ cell with PCBM concentration 10 mg/ml has been improved by 20% compared with the ordinary i-type cell and the power conversion efficiency has been also improved by 10% up to over 2%. We have discussed the molecular distribution within the organic layers. We have demonstrated that the organic p-i-n BHJ structure is useful to enhance and optimize power conversion efficiency of the organic thin film BHJ cells.

Key Words: Organic Semiconductor, Thin Film Device Fabrication, Nano Technology, Characterization and Properties, Solar Cells, Efficiency, Cell Design, pin multilayer, dye-doping intermediate level

1. Introduction

Bulk-Heterojunction (BHJ) organic thin film photovoltaic (PV) cells are promising as future energy sources for electricity and as novel smart energy sources compatible with the advanced organic electronic systems such as organic computers. The organic thin film solar cell is thus promising as a solar cell of the next generation because of its light weight, cheapness and ease of fabrication. BHJ generates charge carries at the hetero-interfaces between the electron donor (D, p-type organic semiconductor) and acceptor (A, n-type organic semiconductor) molecules such as Poly(3-hexylthiophene) (P3HT) and [6,6]–phenyl-C61-butyric acid methyl ester (PCBM), respectively. BHJ forms three-dimensionally stacked molecular junctions, i.e. D/A interfaces which have been expected to act as photoelectric conversion region throughout the BHJ layer independent of layer thickness [1]. Thick BHJ layer has a potential for fabrication of high efficiency solar cell .

Development of oxide interfacial layer using such as MoO_3 and V_2O_5 as an anode interface and the effect of P3HT:PCBM composition on the carrier mobility has been discussed [2]. Furthermore, BHJ has been improved by optimization of morphology and appropriate thermal annealing to result in the enhancement of conversion efficiency [3] and henceforth improved efficiencies up to 6% by single cell [4] and 6.5% by tandem cells, although investigation on enlargement of thickness and area of the photon harvesting BHJ layer including organic junction structures have been still limited up to now.

In addition, active area dependence of characteristics is also important to realize organic thin film PV cells, nevertheless many efforts have demonstrated on the small size device [1].

Molecular distribution within BHJ layer plays an important role to improve the photovoltaic characteristics. Phase separation has been characterized by utilizing structures of organic layers, composition ratio, thermal annealing. It has been shown that vertical molecular distribution within BHJ thin films is not uniform and is reversed [4]. Reversal of molecular distribution has been studied by segregation and stacking layers in BHJ cells [5]. A so-called p-i BHJ cells have been successfully reported [3]. However, to our best knowledge, investigation of structurally designed control of p-i-n molecular distribution and interface structure are not enough and the optimal structure has not been clarified yet.

Evaporated small molecular organic p-i-n structure have been expected to lead to optimization of molecular distribution including organic/electrodes interface by the sole presence of p-layer and n-layer as anode and cathode electrode interfacial layers, respectively, as an analogy of inorganic cells [2]. In our previous study, we have fabricated p-i/n BHJ cell in which open circuit voltage (V_{OC}) increased about 65% while short circuit current density (J_{SC}) decreased about 70% compared with the ordinary i-type cell by stacking the n-layer onto the p-i-layer [1]. Effective n-layer depositions onto i-layer by solution process have not been reported up to now.

In this study, we have studied detailed dependence of the P3HT/PCBM BHJ PV cells on the composition ratio and thickness of the BHJ layer in order to investigate the effect of inserting P3HT layer as the hole transport layer and PCBM layer as the electron transport layer between electrode and blended P3HT/PCBM layer as a structure for p-i and p-i-n junctions to widen the photon harvesting layer. We have also tried to enlarge the size of active area up to cm scale. In this study, we have fabricated the organic p-i-n BHJ cells by optimizing PCBM concentrations for n-layer deposition and have studied their current-voltage characteristics. We have elucidated the n-layer thickness dependence of the photovoltaic characteristics in organic p-i-n BHJ cells. We have discussed the molecular distribution within BHJ layer based on cell characteristics and film thickness of organic layers.

2. Experimental

2.1 Widening of BHJ layer and dissolution owing to successive coating

The device structures were ITO/MoO_3/P3HT:PCBM/Ag, ITO/MoO_3/P3HT/P3HT:PCBM /Ag and ITO/MoO_3/P3HT/P3HT:PCBM/PCBM /Ag. The buffer layer of 10 nm MoO_3 was evaporated onto the 150 nm thick ITO substrate under a vacuum of ~10^{-3}Pa. The blended P3HT:PCBM in which composition ratio has been varied between 0.6 and 1.6 to optimize the cell characteristics using the ratio of the weight of PCBM divided by that of P3HT ($R=W_{PCBM}/W_{P3HT}$) was dissolved in chloroform under air ambient. The blended P3HT/PCBM layer with the thickness between 50 nm and 160 nm has been deposited on top of the P3HT layer whose thickness was 15 nm after depositing top BHJ layer taking dissolution into consideration and also the 20 nm thick PCBM layer has been deposited on the top BHJ layer furthermore by successive spin coating under air ambient. Finally the 100 nm thick Ag was evaporated on the active layer. The active area of the devices was 0.04 cm^2. The wide area device with area from 0.04 to 1 cm^2 was prepared by changing the Ag electrode area. All cells were not annealed.

2.2 Modified i-layer thickness dependence and annealing effect

Figure1 shows the molecular structure of the P3HT and PCBM used in this study.

Figure2 shows a schematic diagram of the device structure for p-i-n BHJ cell.

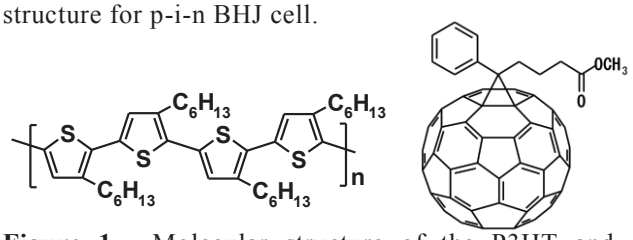


Figure 1. Molecular structure of the P3HT and PCBM

The device structures were indium tin oxide (ITO)/MoO_3/P3HT(p)/ P3HT:PCBM(i)/PCBM(n)/Ag

(p-i-n type) and ITO/MoO_3/P3HT:PCBM/Ag (i type) as reference. MoO_3 was evaporated onto the ITO coated glass substrates. Organic layers were deposited by the spin coating using chloroform solutions. The composition ratio of P3HT:PCBM blends for active layer was 1:0.8 by weight. The typical p-i layer thickness was 85 nm. PCBM concentrations were 10 mg/ml, 15 mg/ml and 20 mg/ml. The corresponding n-layer thickness were 10 nm, 20 nm and 70 nm, respectively. Ag was evaporated as cathode. The active area of the device was 0.04 cm^2. The cells were thermally annealed at 100 °C for 3 min. The film thickness was measured by the ultraviolet-visible differential interference optical spectromicroscopy (Otsuka Elec. co., FE-3000). The current-voltage characteristics under AM1.5 was measured by using the calibrated solar simulator (Yamashita Denso co., YSS-50A) under simulated AM 1.5G illumination of 100 mW/cm^2.

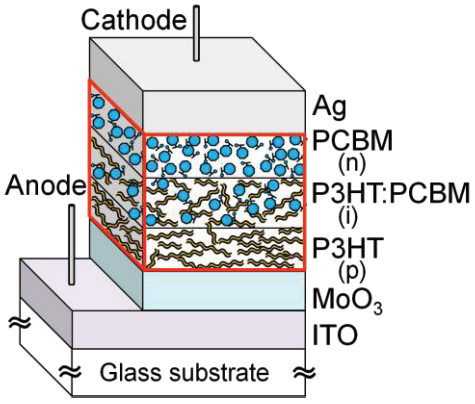


Figure 2. Device structure for p-i-n BHJ cell

3. Results and Discussion

3.1 Widening of BHJ layer and dissolution owing to successive coating

Figure3 (a)(b) shows weight ratio (R) dependence of photoelectrical conversion characteristics of the BHJ PV cells. Short circuit current density (J_{SC}), fill factor (*FF*) and efficiency (*Eff*) showed significant R dependence with optimal ratio of 0.7~0.8, while the open circuit voltage (V_{OC}) indicated linear dependence against R. This V_{OC} dependence is different from those reported since V_{OC} is affected by the difference between the LUMO level of PCBM mixed with P3HT and the Fermi level of Ag [3]. The appropriate composition ratio is *R*=0.7~0.8. The maximum efficiency was obtained at R=0.8 with

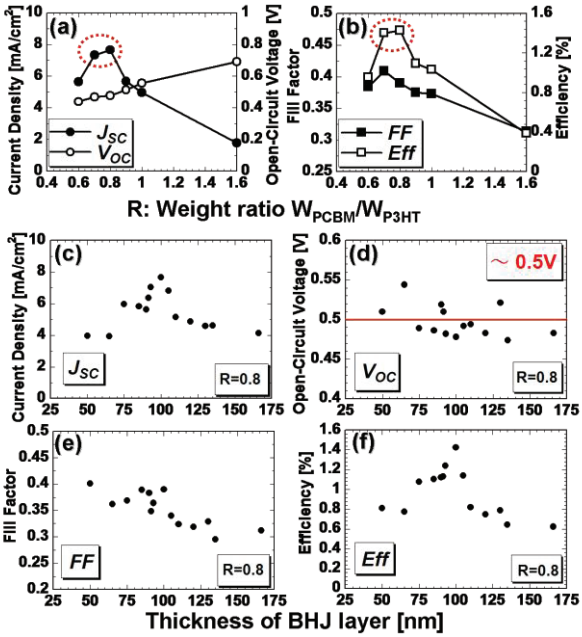


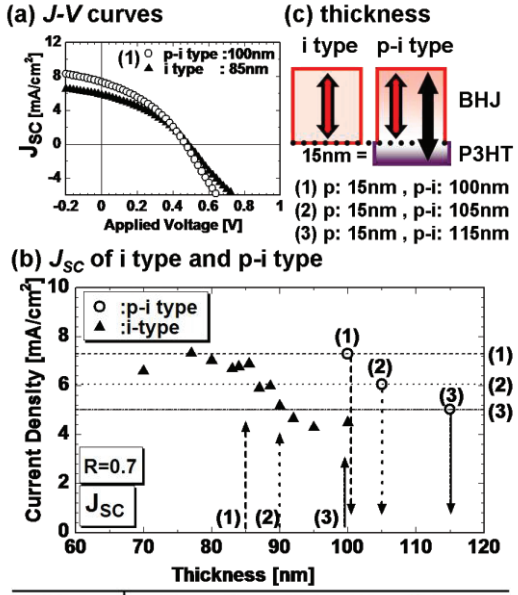
Figure 3. Dependences of (a) short circuit current density (J_{SC}) and open circuit voltage (V_{OC}), (b) fill factor (*FF*) and efficiency (*Eff*) on the composition ratio (R=W_{PCBM}/W_{P3HT}) and (c) J_{SC}, (d) V_{OC},(e) *FF*,(f) *Eff* on thickness of the BHJ layer for ITO/MoO_3/P3HT:PCBM/Ag cells

cell performance of J_{SC}=7.66 mA/cm^2, V_{OC}=0.478 V, *FF*=0.389, and *Eff*=1.43%, thus the composition ratio of R=0.7~0.8 has been selected as reasonable in the examination of thickness dependence of cell characteristics.

Figure3(c)-(f) shows the BHJ thickness dependence of the characteristics for the BHJ PV cells with R=0.8. The thickness of the BHJ layer has been varied from 50 nm to 160 nm. The J_{SC} and the *FF* changed significantly around an optimum of about 100 nm depending on thickness. On the other hand, the V_{OC} exhibits the constant value of 0.5±0.03 V. As a consequence, the optimal thickness of the BHJ layer was determined to be 100 nm in ITO/MoO_3/P3HT:PCBM(R=0.8)/Ag cell.

Therefore, we have investigated the modified ITO/MoO_3/P3HT(p)/P3HT:PCBM(i)/Ag cell (p-i type) with the three kinds of i and p-i types of PV cells with the thickness of the BHJ layer of about100 nm in the fabrication of multi-layered organic thin film PV cells under air ambient.

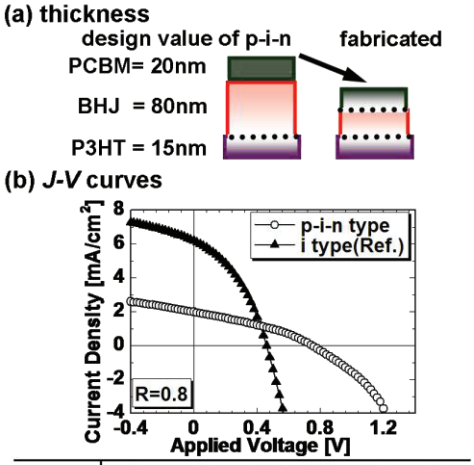
Figure 4. shows the BHJ and P3HT/BHJ thickness dependence of the characteristics for the modified BHJ PV cells with R=0.7 together with that of the ordinary BHJ (i type) cells. Three kinds of devices with different thickness have been fabricated



Thickness [nm]		J_{SC} [mA/cm²]	V_{OC} [V]	FF	Eff [%]	Rsh [Ω]	Rs [Ω]
(1)	100(p-i)	7.30	0.469	0.362	1.24	3784	799
	85 (i)	5.79	0.483	0.364	1.02	4984	1021
(2)	105(p-i)	6.06	0.399	0.335	0.81	3147	973
	90 (i)	5.18	0.440	0.319	0.73	3724	1287
(3)	115(p-i)	5.03	0.408	0.322	0.66	3584	1256
	100 (i)	4.49	0.407	0.308	0.56	3465	1539

Figure 4. (a) Short circuit current density (J_{SC}) against applied voltage curves, (b) dependence of J_{SC} on the thickness for ITO/MoO_3/P3HT:PCBM(R=0.7)/Ag cells and ITO/MoO_3/P3HT/P3HT:PCBM(R=0.7)/Ag cells, (c) Thickness of p-i type is P3HT(15nm)/BHJ(i as following;(1) p:15 nm, p-i:100 nm, (2) p:15 nm, p-i: 105 nm, (3) p:15 nm, p-i:115 nm.

The J_{SC} of both i type cell and p-i type cell varied depending on thickness of organic layer, the p-i type enhanced the current even in thicker film region than 100 nm where the current could not be carried as well in the i(BHJ) type cell. The current density has been increased about 1 mA/cm² by comparing the results of i type (85 nm) and p-i type (100 nm) cells in which the same amount of PCBM are present and act as photon harvesting molecules in the active i(BHJ) layer, thus it is considered that generated hole carriers in the BHJ layer arrive at the P3HT layer and are efficiently transported through the thin P3HT layer which works as hole transporting and electron blocking layer and also suppresses recombination between MoO_3 and the blended P3HT:PCBM layer.



Structure	J_{SC} [mA/cm²]	V_{OC} [V]	FF	Eff [%]	Rsh [Ω]	Rs [Ω]
p-i-n type	1.98	0.749	0.332	0.49	14945	4858
i type	6.16	0.460	0.387	1.10	5540	810

Figure 5. (a) Thickness of design value for ITO/MoO_3/P3HT/P3HT:PCBM(R=0.8)/PCBM/Ag cell, (b) short circuit current density (J_{SC}) against applied voltage for ITO/MoO_3/P3HT/P3HT:PCBM(R=0.8)/PCBM/

Furthermore, we have investigated the modified ITO/MoO_3/P3HT(p)/P3HT:PCBM(i)/ PCBM(n)/Ag cell (p-i-n type) similarly under air ambient. Figure 5 shows the characteristics for the p-i-n BHJ PV cell together with the ordinary BHJ (i type) cell whose thickness of BHJ was 80 nm. In the p-i-n cell, V_{OC} increased about 40% and J_{SC} decreased about 70% compared with the ordinary one. The increase of V_{OC} suggests that the P3HT/P3HT:PCBM/PCBM multi-layer-structured cells can be fabricated and the deterioration of J_{SC} implied that blended P3HT:PCBM active layer had been dissolved indefinitely by the

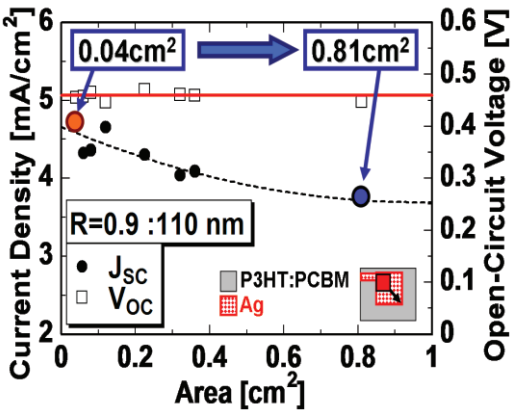


Figure 6. Short circuit current density (J_{SC}) and open circuit voltage (V_{OC}) curves against the active area for ITO/MoO_3/P3HT:PCBM(R=0.9)/Ag cells whose thickness is 110nm.

solvent.

Thus, if thickness of the BHJ layer could be maintained, the improvement of the short circuit current might well be expected [5].

Figure 6 shows the active area dependence of the characteristics for the BHJ PV cells with R=0.9. The J_{SC} were decreased depending on the active area, whereas the V_{OC} and the *FF* are not affected. It was necessary to keep uniformity of organic film to enhance organic thin film wide area PV cell characteristics.

3.2 Modified i-layer thickness dependence and annealing effect

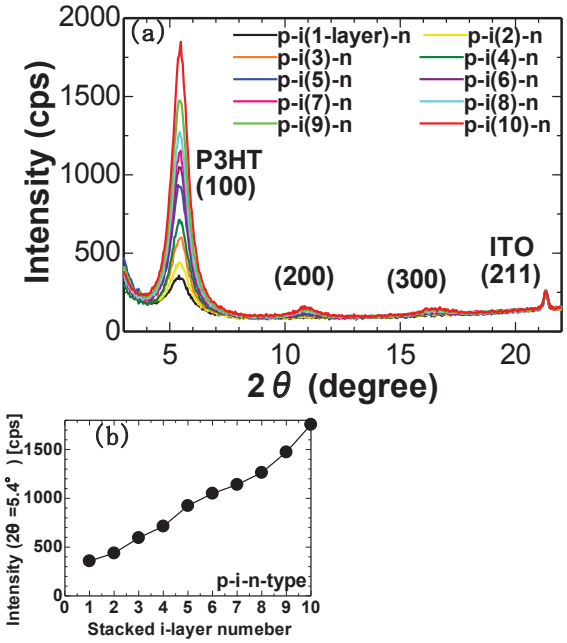


Figure 7. BHJ and P3HT/BHJ thickness dependence
(a)XRD pattern (b)2 θ =5.4° X-ray Intensity
(c) 2 θ =5.4° Ful width at half maximum

Figure 7 shows the film thickness dependence of X-ray intensities of pin-layers together with i-layers those thicknesses were changed by the coating times of each layer. The film thickness was measured at the same time by the optical method. Figure 8 shows also the film thickness dependence of absorption intensities of pin- and i-layers those thicknesses were thus determined.

Figure 9 shows current-voltage characteristics of organic p-i-n BHJ cells fabricated with different PCBM concentrations for n-layer together with the reference i-type cell. In the as-fabricated cells, V_{OC} of p-i-n BHJ cells with PCBM concentration 10 mg/ml, 15 mg/ml and 20 mg/ml were 0.56V, 0.71V and 0.74V respectively, and increased compared with i-type cell of 0.50V. V_{OC} increases in the p-i-n BHJ structure is considered to be due to contribution from lowest unoccupied molecular orbital (LUMO) of PCBM for forming junction at the cathode interface and acting effective carrier extraction layer, and V_{OC} seemed to approach to the theoretical value which depends on the energy level difference between the highest occupied molecular orbital (HOMO) of the electron donor and the LUMO of the acceptor.

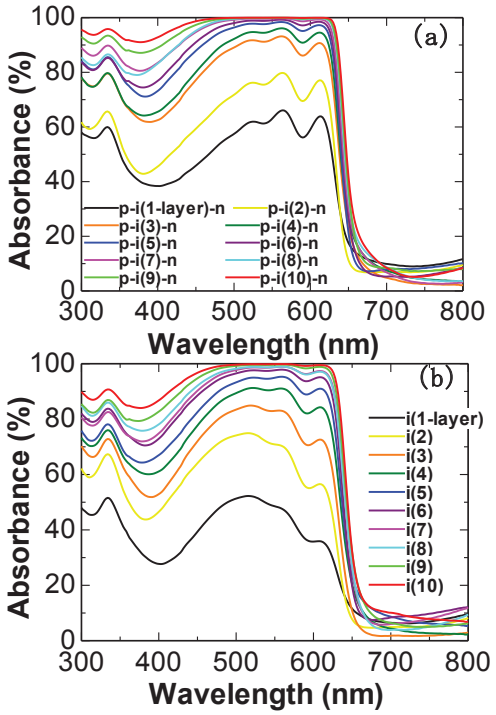


Figure 8. BHJ and P3HT/BHJ thickness dependence of absorbance
(a) p-i-n BHJ (b) i BHJ

Figure 10 shows current-voltage characteristics

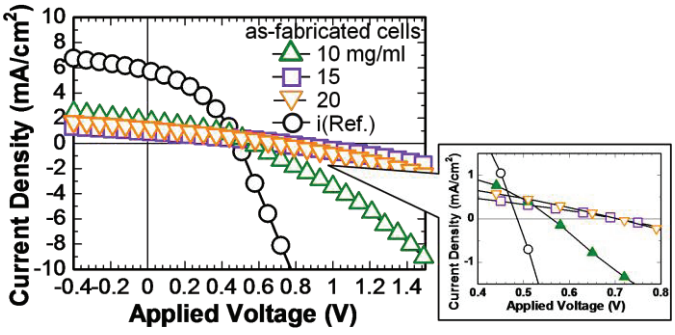


Figure 9. Current-voltage characteristics of p-i-n BHJ cells with different PCBM concentrations for n-layer

of organic p-i-n BHJ cells after post annealing at 100 °C for 3 min. The characteristics before and after post annealing are summarized in Table 2.

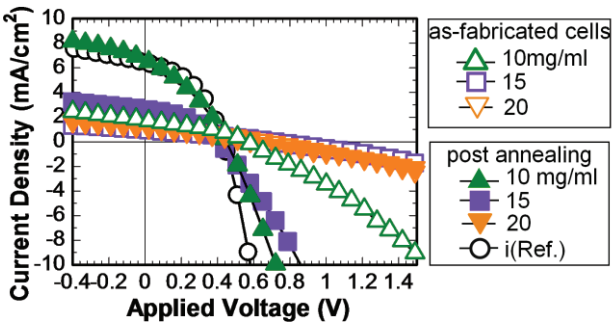


Figure 10. Current-voltage characteristics of p-i-n BHJ cells after post annealed

Table 1: Photovoltaic characteristics of the cells

Preparation Conditions	PCBM Concentration	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	Eff (%)	R_{sh} (Ω)	R_s (Ω)
as-fabricated cells	10mg/ml	**1.75**	**0.56**	34.5	0.36	13333	3200
	15mg/ml	0.92	**0.71**	28.2	0.19	24945	13745
	20mg/ml	1.25	**0.74**	28.2	0.26	18990	9961
	——	5.50	**0.50**	35.4	**0.98**	5036	1191
post annealing	**10mg/ml**	**6.63**	**0.45**	**34.5**	**1.03**	**3707**	**913**
	15mg/ml	2.61	0.43	40.8	0.45	13728	1527
	20mg/ml	1.14	0.65	27.5	0.21	18338	9991
	——	**6.97**	**0.41**	42.1	**1.21**	5617	565

Post annealing on p-i-n BHJ cells improved BHJ/PCBM interface of as-deposited inferior electrical contact and thus enhanced cell performance. In particular, the drastic increase in J_{SC} of p-i-n BHJ cell with PCBM concentration 10 mg/ml was observed in comparison with the reference i-type cell. The improvement in J_{SC} is ascribed to n-layer which acts as an electron transport layer. At higher PCBM concentrations of 15 mg/ml and 20 mg/ml, increase in J_{SC} was small. The resulting difference with the 10 mg/ml case is due to the increases of PCBM aggregates by thermal that annealing caused degraded performance [18].

The shunt resistance (R_{sh}) in the p-i-n BHJ cell with 15 mg/ml and 20 mg/ml were 2.5 and 3.2 times of R_{sh} of ordinary i-layer. This is consistent with the report of the result employed high PCBM composition within BHJ layer in single layer P3HT/PCBM cell [14]. Therefore, we must accept the idea that the increase of PCBM concentration promotes the growth of aggregate of PCBM within n-layer while changes molecular distribution within BHJ layer with the increase of PCBM concentrations owing to n-layer deposition. The series resistance (R_S) was also affected by the PCBM concentrations. These results suggest that the concentration profile of PCBM has varied by decreasing stacked n-layer thickness. The R_S of p-i-n BHJ cell with PCBM concentration of 20 mg/ml did not decrease even after post annealing, and remained to be 10 times larger than that for 10 mg/ml. Thus, we have realized that interface forms an inappropriate structure for the current extraction owing to the enlarged and enriched PCBM aggregates accompanying with n-layer thickness increase and the PCBM composition change within BHJ layer. V_{OC} in both p-i-n and i type after post annealing have decreased. However, in each p-i-n cells with high PCBM concentration, V_{OC} kept high compared with that of the ordinary i-type reflecting a thick PCBM rich interface layer. On the contrary, in the optimum 10 mg/ml condition, J_{SC} increased while V_{OC} decreased only a little. Thus, the optimized p-i-n structure was found to give rise the potential to increase the short-circuit current density while maintaining high open-circuit voltage.

Figure 11 shows current-voltage characteristics of the optimized p-i-n BHJ cell with PCBM concentration of 10 mg/ml together with the reference i-type cell. The optimized characteristics are summarized in Table 3.

J_{SC} has improved by 20% compared with the ordinary i-type cell after post annealing. Power conversion efficiency has also improved by 10%. The i-layer

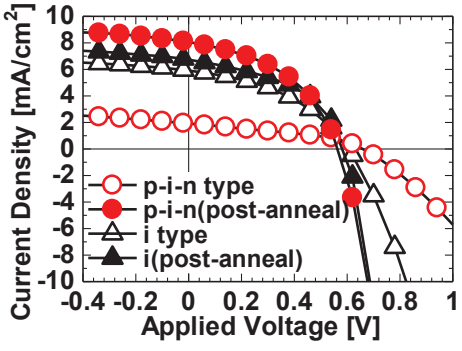


Figure 11. Current-voltage characteristics of optimized p-i-n type (PCBM solution :10 mg/ml)

thickness of the p-i-n BHJ cell decreased 13 nm compared with the ordinary i-type cell resulting from

dissolution of i-layer by PCBM solution span for n-layer deposition.

We have estimated molecular distribution in the organic layer from a comparison of photovoltaic characteristics in p-i-n BHJ cell before and after post annealing, organic layer thickness and the molecular diffusion by thermal annealing [10,19,20]. Figure 10 shows a schematic diagram of organic layers for model structure and an estimated structure.

Table 2: Photovoltaic characteristics of optimized cells (PCBM solution :10 mg/ml)

device structure	J_{SC} [mA/cm^2]	V_{OC} [V]	FF	Eff [%]	R_{sh} [Ω]	R_s [Ω]
p-i-n	1.92	**0.73**	0.35	0.48	14174	2521
(post-anneal)	**8.07**	0.57	0.45	**2.07**	7524	455
i	**5.92**	0.61	0.42	**1.50**	10136	885
(post-anneal)	**6.73**	0.59	0.47	**1.88**	8481	483

It is considered that molecular distribution within organic layers were P3HT-rich at the anode side while PCBM-rich at the cathode side due to molecular diffusion which occurred during annealing between the P3HT-layer and BHJ layer and also between BHJ-layer and PCBM layer [19,20]. These P3HT-Rich region and PCBM-Rich region act as a hole transport layer and an electron transport layer, respectively, and redistributed the inverted molecular distribution throughout organic layers [5]. Therefore, the increase of J_{SC} in p-i-n BHJ structure is larger than that of the ordinary i-type cell in spite that the i-layer thickness is small compared with that of the i-type cell.

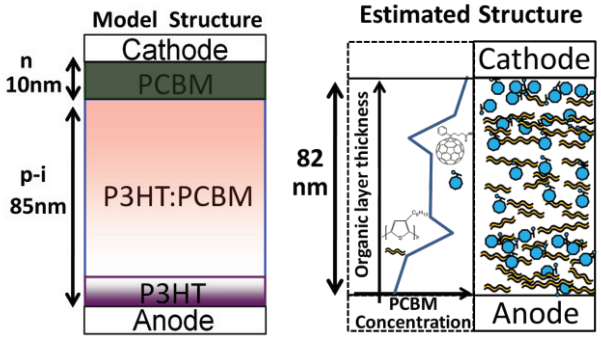


Figure 12. Schematic diagram of organic layers for a model structure and an estimated structure

4. Conclusions

We have elucidated the effect of insertion of P3HT as the hole transport layer and PCBM as the electron transport layer between electrode and P3HT/PCBM BHJ layer by spin coating based on the detailed composition ratio and thickness dependence of the BHJ layer. The p-i type BHJ PV cells enhanced the current in thicker film region than 100 nm where the current decreased in pure i-type cells and hence this structure is useful to widen the photon harvesting layer of the organic thin film BHJ PV cells. The p-i-n type BHJ cell could be fabricated, although the dissolution couldn't be avoided.

We also have made clear n-layer solution concentration dependence of the photovoltaic characteristics in P3HT/PCBM p-i-n BHJ cell by changing PCBM concentrations for n-layer deposition, and have revealed the n-layer dependence on the photovoltaic characteristics in organic p-i-n BHJ cells for the first time. The short-circuit current density of p-i-n BHJ cell with PCBM concentration 10 mg/ml has improved by 20% compared with i-type cell and power conversion efficiency has also improved by 10%. We have demonstrated that organic p-i-n BHJ structure is useful to enhance power conversion efficiency of the organic thin film BHJ cells by optimizing the molecular distribution within organic layers.

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References

[1] H. Kitami, T. Sakai, T. Hishinuma, A. Sanda, H.

Kusano, and M. Kitagawa, *SOLMAT*. **95** 357-360 (2011).
[2] K. Suemori, T. Miyata, M. Yokoyama, and M. Hiramoto, *Appl. Phys. Lett*. **86**, 063509 (2005).
[3] L. Zeng, C.W. Tang and S.H. Chen, *Appl. Phys. Lett.* **97** 053305 1-3 (2010).
[4] P.G. Karagiannidis D. Georgiou, C. Pitsalidis, A.Laskarakis, and S. Logothetidis, *Mat. Chem. and Phys*. **129** 1207 (2011).
[5] J.Y. Oh, W.S. Jang, T.I. Lee, J.M. Myoung, and H.K. Baik, *Appl. Phys. Lett.* **98** 023303 1-3 (2011).
[6] A. Kumer, G. Li, Z. Hong, and Y.Yang, *Nanotechnology* **20** 165202 1-4 (2009).
[7] T. Hishinuma, H.Kusano and M. Kitagawa PVSEC-21 4D-5P-05 139(2012)
[8] Vishal Shrotriya, Gang Li, Yan Yao, Chin-Wei Chu, and Yang Yang, *Appl. Phys. Lett.* **88** (2006) 073508

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