



Evaluation of the Performance of an Organic Thin Film Solar Cell Prepared Using the Active Layer of Poly[[9-(1-octylonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-Diyl-2,5-thiophenediyl]/[6,6]-Phenyl C₇₁ Butyric Acid Methyl Ester Composite Thin Film

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Organic solar cell devices were fabricated using poly[9-(1-octylonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] PCDTBT/ [6,6]-phenyl C₇₁ butyric acid methyl ester (PC71BM) active layer deposited by spin coating. Moreover, the relationship between solar cell performance and buffer layer thickness was investigated by spin coating speed and AFM imaging of the buffer layer surface. The performance of the organic solar cell with spin-coated active layer was then evaluated, and the power conversion efficiency of the solar cell was determined to be > 5%.

Keywords: Solar cell, Organic materials, Fabrication, PCDTBT/PC₇₁BM, Atomic force microscopy

1. INTRODUCTION

A tidal wave and great earthquake caused the catastrophic disaster in the shore of East Japan on March 11, 2011. In particular, the First nuclear power plant in Fukushima Prefecture suffered destructive damage by the tidal wave. Nuclear reactor 1-3 experi-

enced meltdown resulting in evacuation of residents within a 20 km radius of the power plant. Although the promotion of nuclear power generation was dominant to that point in time, the exploitation of renewable energy has gained popularity due to global warming and the decrease of the fossil fuel since the great earthquake disaster in Eastern Japan. In particular, solar cell research has attracted much attention worldwide, specially for green energy production.

The use of silicon-based solar energy converters has become dominant in solar cell technology over the past few decades. Many photovoltaic modules are made of silicon materials, such as crystalline silicon (single-crystalline or multicrystalline) and

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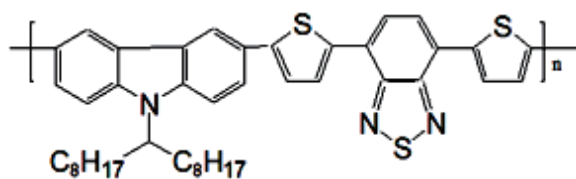
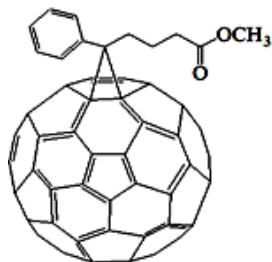


Fig. 1. Molecular structure of PCDTBT.

Fig. 2. Molecular structure of PC₇₁BM.

amorphous silicon. However, high production costs and sophisticated fabrication processes have motivated researchers to venture for environmentally-friendly, cost-effective, and simpler fabrication processes using polymeric materials [1,2]. Polymer solar cells have attracted much attention due to their potential for low-cost solar energy harvesting and their applications to flexible, light-weight and large-area devices [3-5]. Since the solution technique is possible, the solar cell price will be low [6]. Until now, the power conversion efficiency exceeding 4.7-7% is attained using materials with a low band gap and a broadband absorption wavelength [7-9]. In this paper we report on an organic thin film solar cell with improved surface smoothness of an active layer and a TiO_x buffer layer prepared using a solution technique that attained a power conversion efficiency of 5.07%.

1.1 Acceptor and donor molecules

1.1.1 Donor molecule

The electron-rich thiophene unit is the most important key element, and it is ubiquitously incorporated into D-A conjugated polymers to adjust the optical and electronic properties to optimal levels. Recently, poly (2,7-carbazole) derivatives have gained momentum as a class of promising alternative materials to poly (3-hexylthiophene) (P3HT) in organic solar cell applications. Among them, poly[[9-(1-octylnonyl)-9H-carbazole-2,7-diyl]-2,5-thiophenediyl-2,1,3-benzothiadiazole-4,7-diyl-2,5-thiophenediyl] (PCDTBT) has a relatively deeper highest occupied molecular orbital (HOMO) of 5.45 eV compared to the HOMO of 5.1 eV of the P3HT. PCDTBT is the new material and narrow band gap polymer. Moreover, since the electron and hole generation rate is high and the mobility of the electron and hole is also high, a short-circuit current increase is expected.

1.1.2 Acceptor molecule

Fullerenes are highly symmetrical cage-shaped molecules constituted only by carbon atoms, which have been thoroughly studied during the last two decades [10]. Blending conjugated polymers with electron acceptors such as fullerenes, is a very efficient way to break apart photoexcited excitons into free charge carriers. Since the discovery of heterojunction PVCs, fullerene (mainly C₆₀) and its derivative, [6,6]-phenyl-C₆₁-butyric acid

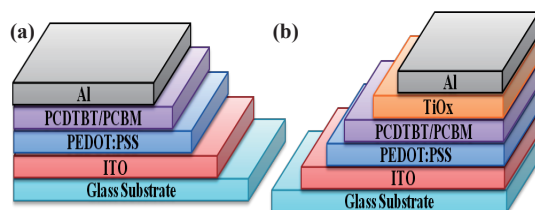


Fig. 3. The cross-sectional structure of a solar cell.

methyl ester (PC₆₁BM), or [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) are widely utilized acceptors providing PCE in the range of 2-5% when combined with selected donor materials. The fullerene PCBM core readily accepts electrons from a wide range of organic donor materials and exhibits high electron mobilities even in composite form. Despite their success, it is a non-ideal material for photovoltaic applications due to its weak absorption in the visible spectrum and excessively deep-lying LUMO level, which results in needless energy loss during electron transfer and so limits the efficiencies of the final devices their open-circuit voltages in particular. In this study, we used the soluble PC₇₁BM, the chemical structure of which is shown in Fig. 2.

2. EXPERIMENTS

In the present work, the spin-coating method was used to prepare the thin film, and the vacuum evaporation method was used to prepare the top (Al) electrode. The ITO substrate was patterned by a mask to create the electrode area. After that, the surface of the ITO substrate was washed with the supersonic for 10 minutes with the surfactant, purified water, acetone and then ethanol. After that point, the PEDOT: PSS thin film was fabricated using a spin-coating method on the ITO substrate as the buffer layer of the p-type donor under a 4,000 rpm rotational speed for 30 sec. The buffer layer was then annealed at 110 °C for 10 minutes under a nitrogen atmosphere. The PCDTBT/PC₇₁BM (4.5 mg/18 mg) mixture solution was dissolved in chlorobenzene (1 mL). After that, the active layers of the PCDTBT/PC₇₁BM bulk hetero junction thin films were prepared on the PEDOT-PSS thin films using the single spin-coating method under a 1,000 rpm rotational speed for 90 sec. On the surface of the active layer, the TiO_x thin film of the buffer layer was made using the spin-coating method as an acceptor. The cathode electrode thin film was then deposited with aluminum by a physical vapor deposition (PVD) method.

The performances of the organic thin film solar cells fabricated with an active PCDTBT/PCBM layer under various preparatory conditions were evaluated using a solar simulator (AM 1.5: 100 mw/cm²). Figure 3 shows the cross sectional structure of two kinds of organic thin film solar cells. Figure 3(a) shows the element structure without a TiO_x insertion layer and Fig. 3(b) shows the element structure with a TiO_x insertion layer.

The ultraviolet-visible (UV-vis) spectra of PCDTBT/PCBM thin films were recorded in the range 300-900 nm using a spectrophotometer. The surface of the PCDTBT: PCBM active layer of an ITO/PEDOT-PSS/PCDTBT-PCBM thin layer and the surface of the TiO_x thin layer of a ITO/PEDOT-PSS/PCDTBT-PCBM/TiO_x thin layer were observed using atomic force microscopy (AFM).

3. RESULTS AND DISCUSSION

Figure 4 shows the UV-vis spectra of the PCDTBT thin film and

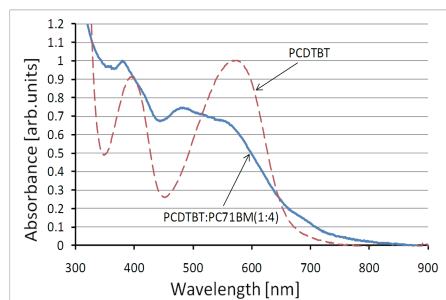


Fig. 4. UV-vis spectra of PCDTBT and PCDTBT:PC₇₁BM composite thin films.

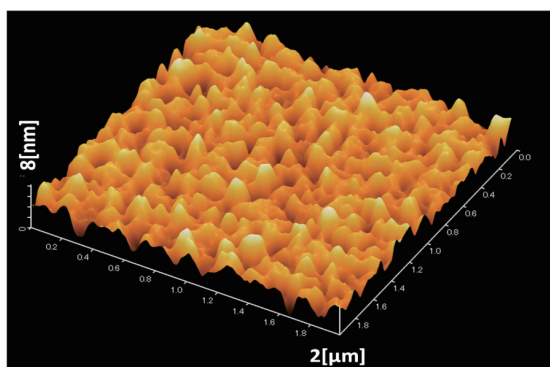


Fig. 5. AFM image of the surfaces of PCDTBT:PC₇₁BM (1:4) composite thin films.

Table 1. The RMS roughness values of PCDTBT/PC₇₁BM composite thin films.

PCDTBT/PC ₇₁ BM ratio	RMS roughness (nm)	Distance between minimum valley and maximum top (nm)
1:1	0.4350	4.563
1:2	0.6292	5.487
1:3	0.9631	7.463
1:4	1.184	8.224
1:5	1.333	9.127

the PCDTBT: PC₇₁BM composite thin film (1:4). The peak at 580 nm of the PCDTBT thin film decreases in the spectrum of the PCDTBT-PC₇₁BM composite thin film and a new peak appears around 500 nm. These results show the mixed state of a PCDTBT and a PC₇₁BM molecule in the PCDTBT-PC₇₁BM composite thin film.

Table 1 shows the RMS roughness obtained from the AFM imaging (Figs. 5,6), and the value acquired from the differences between mountains and valleys. From the AFM images, the RMS roughness, and the difference between minimum bottom and maximum top were observed. The increase of the ratio of PC₇₁BM forms larger aggregation than the low ratio of PC₇₁BM. This finding suggests that the network of PC₇₁BM is good and has high electron mobility. The power conversion efficiency of the organic thin film solar cell can be expected to improve by increasing the PC₇₁BM ratio. However, if the PC₇₁BM ratio of a PCDTBT:PC₇₁BM composite thin film increases and the PC₇₁BM aggregation increases the interpenetrating network of donor molecules and acceptor molecules is disturbed.

The current-voltage (I-V) characteristics of the devices were measured inside the glove box using an Advantest-R-6441

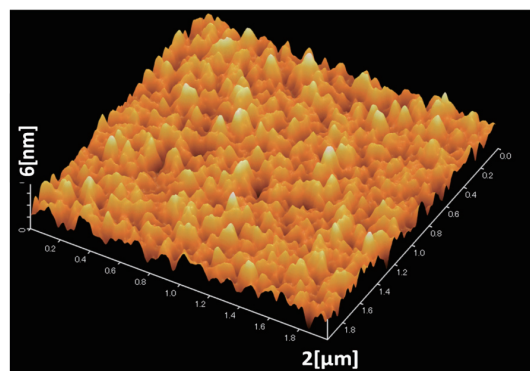


Fig. 6. AFM image of the surface of a PCDTBT: PC₇₁BM (1:5) composite thin films.

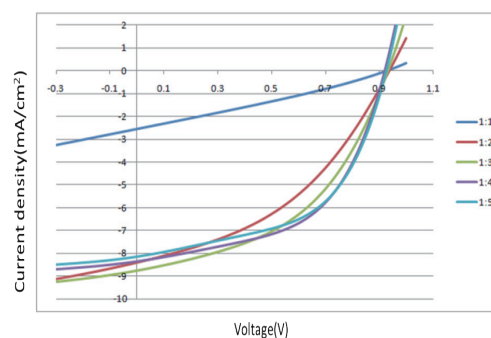


Fig. 7. J-V characteristics of PCDTBT-PC₇₁BM thin films.

Table 2. Organic thin film solar cell performance parameters against the PCDTBT/PC₇₁BM ratio.

PCDTBT/PC ₇₁ BM	V _{oc} ^a [V]	J _{sc} ^b [mA/cm ²]	FF ^c	η ^d [%]
1:1	0.92	2.55	0.29	0.67
1:2	0.93	8.15	0.44	3.32
1:3	0.93	8.56	0.48	3.81
1:4	0.91	8.36	0.55	4.16
1:5	0.92	7.62	0.54	3.77

^aOpen circuit voltage. ^bShort circuit current density. ^cFill factor.

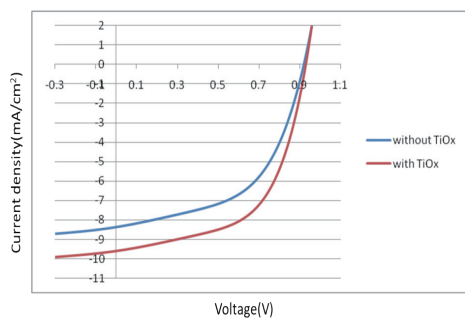
^dPower conversion efficiency measured under AM 1.5 G conditions

source/measure unit under AM 1.5 G illuminations at 100 mWcm⁻². Suitable electrical contacts were developed for the I-V measurements. ITO was taken as the positive contact, while the vacuum-deposited aluminum served as the negative contact. Figure 7 shows the dependence of the composite ratio of PCDTBT-PC₇₁BM thin film of the J-V characteristics. Table 2 shows the organic thin film solar cell performance parameters against the ratio of PCDTBT/PC₇₁BM.

The PCDTBT/PC₇₁BM composite showed an increase in the photocurrent with the increasing PC₇₁ contact (up to a certain limit). The addition of PC₇₁ allows ultra-fast photo induced electron transfer from the PCDTBT to the PC₇₁ and enhances the charge carrier generation in the PCDTBT by preventing recombination. The fill factor also increases with an increasing concentration of PC₇₁. The I-V measurements confirmed that the current rate increase with increasing concentration of PC₇₁ up to 1:4. Therefore 1:4 PCDTBT/PC₇₁BM composite ratios were found to be the optimum choice. This finding also indicates that the optimal interpenetrating networks of donor molecules and acceptor mol-

Table 3. Organic thin film solar cell performance parameters against the spin speed of the PCDTBT/PC₇₁BM active layer.

Spin speed	V _{oc} [V]	J _{sc} [mA/cm ²]	FF	η [%]
500 rpm	0.91	8.01	0.51	3.69
1,000 rpm	0.91	8.36	0.55	4.16
1,500 rpm	0.92	7.63	0.56	3.90

**Fig. 8.** J-V characteristics of organic solar cell without or with a TiOx thin film.

ecules in the active layer exist according to the PCDTBT/PC₇₁BM ratio.

Table 3 shows the organic thin film solar cell performance parameters against the spin speed of the PCDTBT/PC₇₁BM active layer. The maximum power conversion efficiency is obtained at a spin speed of 1,000 rpm indicating that the optimal thickness of the active layer exists at 1,000 rpm.

We reported here that new devices fabricated with a TiOx layer between the PCDTBT/PC₇₁BM and the Al layer show improved performance in terms of J_{sc} and the power conversion efficiency. Figure 8 shows the J-V characteristics of the organic solar cell without a TiOx thin film or with a TiOx thin film. Table 4, shows an organic thin film solar cell with a TiOx thin film percentage of efficiency of > 5% therefore, the TiOx thin film works with a buffer layer and an optical spacer.

4. CONCLUSIONS

Our finding indicate that the PCDTBT and PC₇₁BM interface is enhanced by increasing the PC₇₁BM ratio. The organic solar cell prepared using the 1:4 (PCDTBT:PC₇₁BM) ratio and a 1000-rpm spin speed is the PCE of 4.16%. The J_{sc} of organic thin film solar

Table 4. Organic thin film solar cell performance parameters without or with a TiOx thin film.

1,000 rpm	V _{oc} [V]	J _{sc} [mA/cm ²]	FF	η [%]
Without TiOx	0.91	8.36	0.55	4.16
With TiOx	0.93	9.59	0.57	5.06

cell increases by insertion of the TiOx thin film, the performance parameters are improved, and the PCE yields a conversion efficiency of 5.06%.

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