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Microstructures and Photovoltaic Properties of Polysilane/C_{60}-Based Solar Cells

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ABSTRACT

Polysilane/C_{60}-based solar cells were fabricated and investigated. Two-types of devices with bulk heterojunction and heterojunction structures were examined and characterized. Addition of silicon-based polymer to the organic solar cells improved the conversion efficiency by wide optical absorption and high carrier mobility. Microstructures of the solar cells were investigated by using X-ray diffraction and transmission electron microscopy. Energy levels in the present solar cells were discussed.

Keywords: Bulk Heterojunction; Polysilane; Fullerene; Microstructure

1. Introduction

Solar cells are one of the important candidates for renewable energy sources. Silicon (Si) solar cells which are the mainstream of renewable energy sources have high-conversion efficiency with long lifetime. However, production processes are complicated, and the cost is high. Although organic thin film solar cells which are expected as an alternative to the Si-based solar cells have been investigated, the efficiencies have not been high enough for commercial application [1].

Recently, C_{60}-based solar cells have been investigated and reported [2,3]. These organic solar cells have a potential for use in lightweight, flexible, inexpensive and large-scale solar cells [4-6]. By combining p- and n-type organic semiconductors, the organic solar cells show wide wavelength absorption. However, significant improvements of photovoltaic efficiencies are mandatory for use in the future solar power plants. One of the improvements is to increase p-n heterojunction interface of the photoelectric conversion region in the devices by using blends of donor-like and acceptor-like molecules or polymers, which are called bulk heterojunction solar cells [7-9].

The bulk heterojunction solar cells based on copper tetrakis (4-cumylphenoxy) phthalocyanine (CuPc) with C_{60} have been studied in the previous work [10]. CuPc showed a wild optical absorption around 700 nm, which would suggest higher potential for photon harvesting. C_{60} has a property to attract an electron, which is suitable for solar cells. However, its conversion efficiency was not enough for commercial use, and it is necessary to improve the efficiencies of the solar cells further.

The purpose of the present work is to fabricate and characterize the CuPc/C_{60} solar cells with the Si-based polymers. The present work aimed at efficiency improvement for expansion of the absorption wavelength by silicon addition to CuPc/C_{60} solar cells. Two types of the Si-based polymers of poly [dimethylsiloxane-co-methyl (stearoyloxyalkyl) siloxane] (PDSi) and dimethylpolysilane (DMPS) were used. PDSi has been used as a non-toxicity and high resolvability. Polysilanes are σ-conjugated polymers exhibiting attractive characteristics such as photoconductivity, high hole mobility and effective light emission [11,12]. By blending C_{60} to polysilanes, it would suppress the recombination of photo-separated charge carriers by assisting the electron transfer from polysilanes [13]. The bulk heterojunction solar cells based on C_{60} with polysilane derivatives have also been studied [14]. To examine the additive effect of polysilane, DMPS/C_{60} solar cells were also produced. Device structures were produced, and the efficiencies, optical absorption and microstructure were investigated to improve efficiency of the organic solar cells with the polysilane.

2. Experimental Procedures

A thin layer of poly3,4-ethylenedioxythiophene doped with poly(-styrenesulfonate (PEDOT:PSS) (Sigma Aldrich) was spin-coated on pre-cleaned indium tin oxide (ITO) glass plates (Geomatec Co., Ltd., ~10 Ω/ϒ). Then, semiconductor layers were prepared on a PEDOT:PSS

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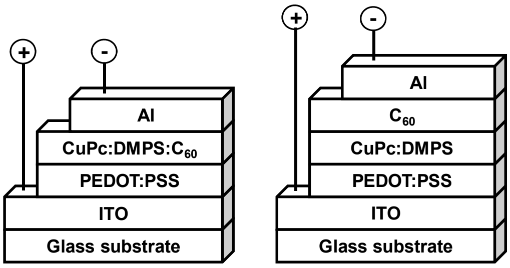
layer by spin coating using a mixed solution of CuPc (Sigma Aldrich, 97%), C_{60} (Material Technologies Research, 99.98%) and PDSi (Sigma Aldrich) or DMPS (Strem Chemicals) in 1 ml o-dichlorobenzene. Weight ratios of CuPc:C_{60} were 1:8 (2 mg:16 mg), and PDSi (1 mg) or DMPS (3 mg) was added into the o-dichlorobenzene solution. The thickness of the blended device was approximately 150 nm. A schematic diagram of the bulk heterojunction solar cells of CuPc:(PDSi or DMPS): C_{60} is shown in **Figure 1(a)**. Heterojunction solar cells were also fabricated by spin coating of CuPc:DMPS solution and spin coating of C_{60} solution, as shown in **Figure 1(b)**. The bulk heterojunction indicates a one layered composite structures with p- and n-type semiconductors, which is denoted as DMPS:C_{60}. The common heterojunction solar cell with two separated layers was also investigated for comparison, which is denoted as DMPS/C_{60}. After annealing at 100˚C for 30 min in N_2 atmosphere, aluminum (Al) metal contacts with a thickness of ~100 nm were evaporated as top electrodes, and annealed at 140˚C for 25 min in N_2 atmosphere. To compare the performance, the solar cells without CuPc were also fabricated (DMPS:C_{60}, DMPS/C_{60}).

Current density-voltage (J-V) characteristics (Hokuto Denko Co., HSV-100) of the solar cells were measured both in the dark and under illumination at 100 mW/cm^2 by using an AM 1.5 solar simulator (San-ei Electric, XES-301S). The solar cells were illuminated through the side of the ITO substrates, and the illuminated area is 0.16 cm^2. Optical absorption of the solar cells was investigated by means of UV-visible spectroscopy (Hitachi, Ltd., U-4100). The microstructures of the thin films were investigated by X-ray diffractometer (XRD, PHILIPS X'Pert-MPD System) with Cu Kα radiation operating at 40 kV and 40 mA and a transmission electron microscope (TEM, Hitachi, Ltd., H-8100).

3. Results and Discussion

J-V characteristics of CuPc:C_{60}, CuPc:DMPS:C_{60} and DMPS:C_{60} bulk heterojunction structures under illumination are shown in **Figure 2**. The J-V curves of the solar cells showed a typical rectification behavior with open circuit voltage and short circuit current. Measured parameters of these solar cells are summarized in **Table 1**. Open-circuit voltage, short-circuit current density, fill factor and power conversion efficiency are denoted as V_{OC}, J_{SC}, FF and η, respectively. A solar cell with DMPS/C_{60} heterojunction structure provided η of 0.022%, FF of 0.33, J_{SC} of 0.20 mA/cm^2 and V_{OC} of 0.34 V, which was better than those of other devices.



(a) (b)

Figure 1. Structures of (a) CuPc:DMPS:C_{60} bulk heterojunction and (b) CuPc:DMPS/C_{60} heterojunction solar cells.

Figure 3 shows optical absorption of CuPc:C_{60}, CuPc:DMPS:C_{60} and DMPS:C_{60} bulk heterojunction solar cells. The CuPc:DMPS:C_{60} and DMPS:C_{60} bulk heterojunction structures provided a increase of optical absorption in a wide range of 500 to 1200 nm (which correspond to 2.5 and 1.0 eV, respectively), compared to the CuPc:C_{60} structure. As a result, the conversion efficiencies were improved as listed in **Table 1**.

X-ray diffraction patterns of CuPc:DMPS:C_{60} and DMPS:C_{60} thin films were shown in **Figures 4(a)** and **(b)**, respectively. The diffraction patterns showed several diffraction peaks, which were corresponded to DMPS and C_{60} [15]. Lattice spacings and crystallite sizes of DMPS and C_{60} in thin films of CuPc:DMPS:C_{60} and DMPS:C_{60} are listed in **Tables 2(a)** and **(b)**, respectively. The crystallite sizes were estimated using Scherrer's formula of $D = 0.9\lambda/\beta\cos\theta$. Where λ, β and θ represent

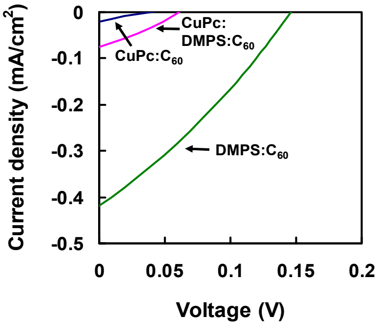


Figure 2. J-V characteristics of CuPc:C_{60}, CuPc:DMPS:C_{60} and DMPS:C_{60} bulk heterojunction solar cells.

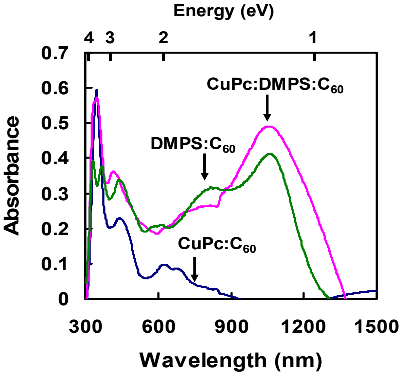


Figure 3. Optical absorption of bulk heterojunction solar cells.

Table 1. Measured parameters of the solar cells.

Sample	V_{OC} (V)	J_{SC} (mA·cm^{-2})	FF	η (%)
CuPc:C_{60}	0.037	0.020	0.24	1.8×10^{-4}
CuPc:PDSi:C_{60}	0.27	0.012	0.17	5.5×10^{-4}
CuPc:DMPS:C_{60}	0.060	0.076	0.29	1.3×10^{-3}
CuPc:DMPS/C_{60}	0.24	0.17	0.27	0.011
DMPS:C_{60}	0.15	0.42	0.31	0.020
DMPS/C_{60}	0.34	0.20	0.33	0.022

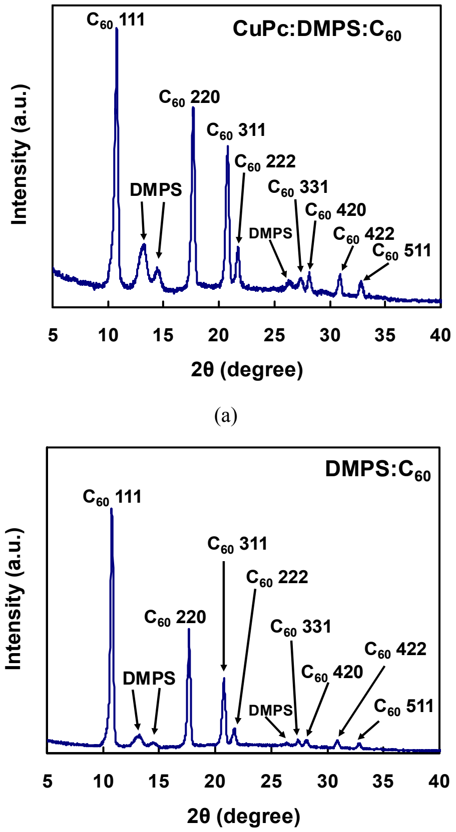
Table 2. Lattice spacings and crystallite sizes of DMPS and C_{60} in (a) CuPc:DMPS:C_{60} and (b) DMPS:C_{60} thin films. Measured parameters of the solar cells.

(a)

DMPS	C_{60}	
d (nm)	Indices	d (nm)
0.6715	1 1 1	0.8200
0.6126	2 2 0	0.5015
0.3382	3 1 1	0.4275
	Crystallite size (nm)	
12	22	

(b)

DMPS	C_{60}	
d (nm)	Indices	d (nm)
0.6726	1 1 1	0.8208
0.6102	2 2 0	0.5020
0.3381	3 1 1	0.4277
	Crystallite size (nm)	
7.4	35	



(a)

(b)

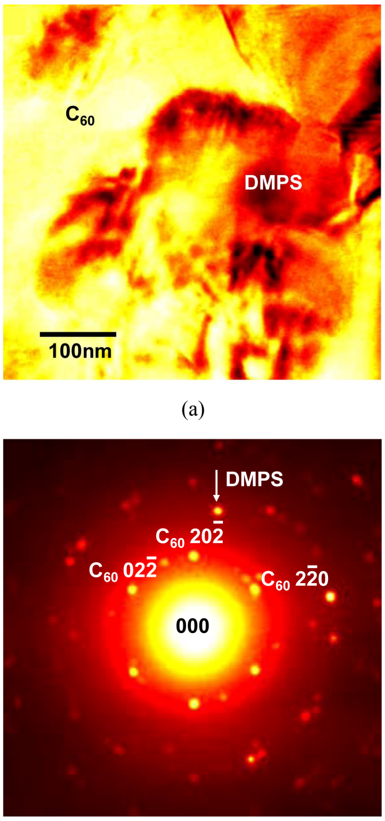
Figure 4. XRD patterns of (a) CuPc:DMPS:C_{60} and (b) DMPS:C_{60} thin films.

the wavelength of the X-ray source, the full width at half maximum and the Bragg angle, respectively [16]. Although the peak positions and lattice spacings are similar, the crystallite sizes were different from one another as shown in **Figure 4** and **Table 2**.

A TEM image and electron diffraction pattern of the DMPS:C_{60} composite film are shown in **Figures 5(a)** and **(b)**, respectively. In **Figure 5(a)**, many nanoparticles consisting of a Si element in the C_{60} matrix were observed. The electron diffraction pattern of **Figure 5(b)** showed many diffraction spots and Debye-Scherrer rings, which indicated microcrystalline structures of C_{60} and DMPS.

An energy level diagram of CuPc:DMPS:C_{60} solar cells was summarized as shown in **Figure 6**. Previously reported values [6,10,17-20] were used for the energy levels of the figures by adjusting to the present work. Electronic charge-transfer separation was caused by light irradiation from the ITO substrate side. Electrons are transported to an Al electrode, and holes are transported to an ITO substrate. It has been reported that V_{OC} is nearly proportional to the band gap of the semiconductors, and control of the energy levels is important to increase efficiency [21].

Polysilane/C_{60}-based solar cells were fabricated by a spin-coating method without vacuum evaporation in the present work. The heterojunction structures were also prepared only by spin-coating. In the **Table 1**, DMPS/C_{60} structure yielded the highest efficiency, compared to the other structures. It would be due to a mixture of p- and n-layers formed by spin-coating. The photoelectron conversion region in the DMPS/C_{60} solar cells would be larger than those of the ordinary heterojunction structures, which results in the improvement of conversion efficiency.



(a)

(b)

Figure 5. (a) TEM image and (b) electron diffraction pattern of DMPS:C_{60} structure.

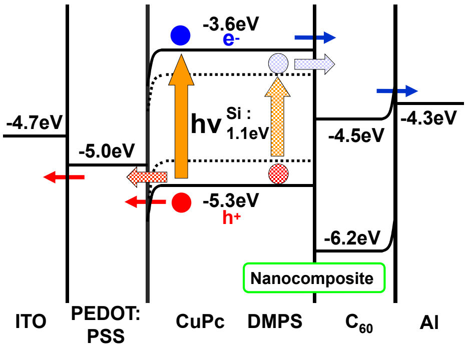


Figure 6. Energy level diagram of CuPc:DMPS:C_{60} solar cells.

As a factor of the low efficiency, carrier recombination would be a main cause. The defects produced by inadequate crystalline at the p-n interface would cause carrier recombination. Optimization of the microstructures would increase the efficiency of solar cells, which was expected by improving charge separation and the electronic charge transportation [22,23]. There might be carrier recombination of electrons and holes at the rear surface of n-type electrode (ITO). Energy conversion efficiency could be improved by addition of exciton-diffusion blocking layer such as BCP or PTCDA to inhibit carrier recombination at the contact surfaces [24,25].

4. Conclusion

Polysilane/C_{60}-based solar cells were produced and characterized. A device based on the DMPS/C_{60} structure provided η of 0.022%, FF of 0.33, J_{SC} of 0.20 mA/cm^2 and V_{OC} of 0.34 V, which was better than those of other devices in the present work. Microstructures of the solar cells were investigated by using XRD and TEM. The carrier transport mechanism was discussed by the energy level diagram using the experimental results.

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