Fabrication and characterization of silicon naphthalocyanine,
gallium phthalocyanine and fullerene-based organic solar cells
with inverted structures

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Abstract. Fullerene/phthalocyanine solar cells with inverted structures were fabricated, and the photovoltaic properties, optical absorption and microstructures were investigated. Silicon naphthalocyanine, gallium phthalocyanine, and poly(3-hexylthiophene) were used for donor materials, and 6,6-phenyl C₆₁-butyric acid methyl ester was also used as an acceptor material. The solar cells with the inverted structure provided higher conversion efficiencies by addition of silicon naphthalocyanine, and had more stability compared to that with normal structure in the air. Nanostructures of the solar cells were investigated by transmission electron microscopy, which indicated the dispersion of nanocrystals in the active layers. Energy levels of the molecules were calculated, and a carrier transport mechanism was proposed.

1. Introduction

Organic thin film solar cells have an advantage for renewable energy resources because of their low cost, flexible, light weight and fabricate at low temperatures by spin-coating and printed method [1-3]. Recently, polymer/fullerene solar cells have been investigated, and the conversion efficiency of ~10% was obtained [4]. Metal phthalocyanines (MPc) are a group of small molecules with Q-band absorption in the red to near-IR range. Since MPcs have chemical stability and photovoltaic properties, they are used for donor materials for organic thin film solar cells. The heterojunction solar cells using copper phthalocyanine and fullerene have been fabricated by evaporation method, and its conversion efficiency was ~3% [5]. The characteristics such as electron conductivity and optical absorption are strongly dependent on the central metal atoms [6-9].

Organic thin film solar cells with normal structures have no stability in air. Aluminium (Al) metal has often been used as the back electrode of the organic solar cells with normal structures, due to its low work function. However, the Al is oxidized to insulating Al₂O₃ at the Al/organic interface, and the diffused Al into the active layer acts as a recombination site. An acidic poly(3,4-ethylenedioxylenethiophene): poly(4-styrene sulfonic acid) (PEDOT:PSS) would damage the device performance due to the corrosion to indium-tin-oxide (ITO). Both of which make lifetime of the cell
very short, and one of the approaches to solve the problems of stability is to use cells with an inverted structure. The cells with the inverted structure have a TiO$_2$ layer, which works as an electron transport layer. There are some reports of inverted structure, and an improvement of stability has been reported [10-12].

The purpose of the present work is to fabricate and characterize MPc/fullerene solar cells with an inverted structure. Gallium phthalocyanine (GaPc), tetrakis (trimethylsilyl) [bis(trihexylsiloxy) silicon 2,3-naphthalocyanine] (SiNc) and poly(3-hexylthiophene) (P3HT) were used for donor materials, and 6,6-phenyl C$_{61}$-butyric acid methyl ester (PCBM) was also used as an acceptor material. Gold (Au) was used for the back electrodes instead of aluminium. TiO$_2$ thin films were fabricated by sol-gel method, and used as electron transfer layer. Photovoltaic mechanism, the light induced charge separation and charge transfer of the solar cells with the inverted structures were discussed on the basis of light-induced current density voltage (J-V) curves, and optical absorption. Nanostructures of the solar cells were investigated by transmission electron microscopy (TEM) and X-ray diffraction (XRD), and the energy levels of the molecules were calculated and discussed.

2. Experimental procedures

Solar of cells with an inverted structure were fabricated by using TiO$_2$ layer on transparent conducting oxide, as shown in Fig. 1. A heterojunction structure of PCBM/GaPc and a bulk heterojunction structure of PCBM:P3HT:SiNc were fabricated in the present work. The TiO$_2$ precursor solutions were prepared from titanium isopropoxide (TTIP), 2-methoxyethanol and acetylacetone. TTIP (0.46 ml) was added to 2-methoxyethanol (2.5 ml). After stirred for 1h, acetylacetone (0.61 ml) as the stabilizer was slowly added, and stirred for 12 h [12]. The TiO$_2$ precursor solution was spin-coated on fluorine doped tin oxide (FTO) substrate (Luminescence Technology, ~14 Ω/□).

![Figure 1. Structures of (a) PCBM/GaPc heterojunction and (b) PCBM:P3HT:SiNc solar cells. Molecular structures of (c) GaPc and (d) SiNc.](image-url)
After annealing at 100 °C for 10 min in N₂ atmosphere, solution of PCBM in 1 ml chlorobenzene on a TiO₂ layer by spin-coat method. Then, gallium phthalocyanine layer were prepared on a PCBM layer by evaporation. Bulk heterojunction structures of PCBM:P3HT:SiNc were also prepared by spin-coating of solution of PCBM:P3HT:SiNc (8 mg, 10 mg, x mg) in 1 ml o-dichlorobenzene on a TiO₂ layer. Quantities of SiNc (x mg) were 2, 5, and 10 mg. A PEDOT:PSS (Sigma Aldrich) was spin-coated onto the active layers. Au metal contacts were evaporated as a top electrode and annealed at 140 °C for 10 min in N₂ atmosphere.

Current density-voltage (J-V) characteristics (Hokuto Denko Corp., HSV-110) 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 was 0.16 cm². Optical absorption of the solar cells was investigated by means of UV-visible spectroscopy (JASCO, V-670ST). The microstructures were investigated by X-ray diffractometer (XRD, PHILIPS X’Pert-MPD System) with CuKα radiation operating at 40 kV and 40 mA, and TEM observation was carried out by a 200 kV TEM (Hitachi H-8100) [13,14]. The molecular structures were optimized by CS Chem3D (Cambridge Soft) and molecular orbital calculations using Gaussian 09.

3. Results and discussion

J-V characteristics of PCBM:P3HT:SiNc solar cells under illumination at 100 mW cm⁻² by using an AM 1.5 solar simulator are shown in Figure 2. The photocurrent was observed under illumination, and the PCBM:P3HT:SiNc structure showed characteristic curves with short-circuits current and open-circuit voltage. Measured parameters of the present solar cells are summarized as Table 1. A solar cell with a PCBM:P3HT:SiNc structure showed the highest power conversion efficiency (η) as the quantity of SiPc increased up to 10 mg. The PCBM:P3HT:SiNc(10 mg) solar cell provided η of 0.22 %, fill factor (FF) of 0.37, and short-circuit current density (J_sc) of 1.6 mA cm⁻² and open-circuit voltage (V_oc) of 0.36 V.

![Figure 2. Measured J-V characteristic of PCBM:P3HT:SiNc solar cells under AM 1.5 illumination.](image-url)
Table 1. Measured parameters of the present solar cells.

| Sample                        | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | FF  | $\eta$ (%) |
|-------------------------------|--------------|--------------------------|-----|------------|
| PCBM:P3HT:SiNc (2 mg)        | 0.085        | 1.4                      | 0.27| 0.032      |
| PCBM:P3HT:SiNc (5 mg)        | 0.22         | 1.6                      | 0.26| 0.092      |
| PCBM:P3HT:SiNc (10 mg)       | 0.36         | 1.6                      | 0.37| 0.22       |
| PCBM/GaPc                     | 0.56         | 0.44                     | 0.24| 0.059      |
| PCBM/GaPc (After 2 month)     | 0.64         | 0.25                     | 0.21| 0.033      |

Figure 3. Absorption spectra of glass/TiO$_2$/SiNc:P3HT:PCBM thin films.

Although solar cells with a normal structure provided a conversion efficiency of 0 % after 24 h, a PCBM/GaPc solar cell with an inverted structure have more stability in air than that with a normal structure. Since PEDOT:PSS would prevented oxygen diffusion into active layers, active layers did not oxidized.

Figure 3 shows UV-visible absorption spectra of TiO$_2$/SiNc:P3HT:PCBM thin films. As the amount of SiPc increased, optical absorption increased in the range of 650 to 850 nm. Optical absorption at 330 nm corresponds to that of TiO$_2$ and PCBM. Absorption in the range of 400-600 nm corresponds to that of P3HT. Since the absorption was observed in the wide region, the sunlight would be efficiently absorbed.

An X-ray diffraction pattern of PCBM:P3HT:SiNc bulk heterojunction thin film is shown in Fig. 4. Diffraction peaks corresponding to SiNc and P3HT are observed as indicated by arrows, and slight shift of peaks were observed by mixing PCBM, P3HT and SiNc. No peak corresponding to PCBM was observed, which indicates the PCBM had an amorphous structure.

A TEM image and an electron diffraction pattern of PCBM:P3HT:SiNc thin film are shown in Fig. 5(a) and 5(b), respectively. The TEM image shows dispersion of P3HT and SiNc nanocrystals in the PCBM matrix, which would contribute the increase of the efficiencies. The electron diffraction pattern also indicates Debye-Scherer rings, which are due to the dispersion of nanocrystals.
A TEM image, an electron diffraction pattern and a high-resolution image of TiO$_2$ thin films are shown in Figure 6(a), (b) and (c), respectively. The particle size of TiO$_2$ is in the range of 20-50 nm from the TEM image, and the electron diffraction pattern and high resolution image show formation of the TiO$_2$ anatase structure by annealing at 450 °C.

Energy level diagrams of the present PCBM/GaPc heterojunction and PCBM:P3HT:SiNc bulk heterojunction solar cells with the inverted structures were summarized as shown in Fig. 7. Previously reported values were used for the energy levels of the figures by adjusting to the present work [15-17]. Energy barrier would exist near the semiconductor/metal interface. In the cells with an inverted structure, electrons are transported to an FTO substrate, and holes are transported to an Al. When C$_{60}$
is used for the inverted structure, the energy barrier would be at the TiO$_2$/C$_60$ interface. To reduce the energy barrier, PCBM with higher LUMO levels is suitable as used in the present work. Voc of organic solar cells is related with energy gap between HOMO of MPc and LUMO of PCBM, and control of the energy levels is important to improve the photovoltaic performance [15].

Figure 6. (a) TEM image, (b) electron diffraction pattern and (c) high-resolution image of TiO$_2$ thin film.

Figure 7. Energy level diagrams of (a) PCBM/GaPc and (b) PCBM/P3HT:SiNc solar cells.

4. Conclusion

Photovoltaic properties, optical absorption and microstructres of PCBM/GaPc and PCBM:P3HT:SiNc solar cells with inverted structures were investigated. The PCBM:P3HT:SiNc solar cells with the inverted structure provided higher conversion efficiencies by addition of SiNc. TEM images, electron diffraction, and high-resolution images confirmed that the active layer had nanocrystalline structures, and the TiO$_2$ electron transport layer had an anatase structure. A device with inverted cell using GaPc/PCBM showed more stability in the air than that of a normal structure. Energy levels of the molecules were calculated, and a carrier transport mechanism was discussed.
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