Fabrication and characterization of silicon naphthalocyanine/fullerene-based photovoltaic devices with inverted structures

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Fullerene-based photovoltaic devices with an inverted structure containing silicon 2,3–naphthalocyanine bis(trihexylsilyloxide) (SiNc) were fabricated and characterized. SiNc worked as a donor material, and showed optical absorption at ~800 nm. C_{60} and [6,6]–phenyl–C_{61}–butyric acid methyl ester (PCBM) were used as acceptor materials, and C_{60} or PCBM/SiNc system solar cells showed incident photon to current conversion efficiency in the range of 700~800 nm. The PCBM/SiNc solar cell provided high open circuit voltage of 0.74 V. From the energy level diagram, the higher lowest unoccupied molecular orbital level of PCBM contributed to the high open circuit voltage. The surface roughness at the C_{60}/SiNc interface is larger compared to that at the PCBM/SiNc interface, which resulted in the high short circuit current density of the C_{60}/SiNc solar cell.

1. Introduction

Organic photovoltaic devices have been attracted much attention for next generation solar cells. They show great promise in flexible, lightweight, large-area, energy–generation applications, and much works on designing new materials, device structures and processing techniques have been carried out to improve the power conversion efficiency of the devices [1–4]. The solar cells with an inverted structure have a gold (Au) back electrode, and Au is hardly-oxidized and have good stability in air. There are some reports of the inverted structure, and an improvement of stability has been reported [5–8]. Metal phthalocyanines (MPc) show Q–band absorption in the near–IR range, and they have stability under the light and chemical stability [9]. Especially, absorption range of naphthalocyanines (Nc) are longer than that of phthalocyanines [10,11]. Heterojunction solar cells using copper phthalocyanine and fullerene have been fabricated by evaporation method, and its conversion efficiency was achieved to ~3 % [12]. The phthalocyanines were also combined with polymer and fullerene to fabricate solar cells [13–17]. Electron conductivity and absorption range can be changed by changing a central metal.

The purpose of the present work is to fabricate and characterize fullerene/phthalocyanine heterojunction photovoltaic devices with an inverted structure. Silicon 2,3–naphthalocyanine bis(trihexylsilyloxide) (SiNc) was selected as a p–type semiconductor material in the present work. The SiNc absorb light in the near-infrared region [18,19], and fullerene/SiNc systems are expected to provide photoelectric conversion in the near-infrared region, which will be applied for tandem solar cells with high efficiency. C_{60} fullerene and [6,6]–phenyl–C_{61}–butyric acid methyl ester (PCBM) were also used as n–type semiconductor materials in the present work. Photovoltaic mechanism, light induced charge separation and charge transfer of the photovoltaic devices with the inverted structures were discussed on the basis of light induced current density–voltage (J–V) curves, incident photon to current conversion efficiency (IPCE) and optical absorption. Effects of
surface structures of the thin films on the photovoltaic properties were investigated by atomic force microscopy (AFM). The energy level diagram of the present photovoltaic devices was discussed.

2. Experimental procedures

Molecular structures of active layer materials and a device structure of the photovoltaic device are shown in Fig. 1. Photovoltaic devices were fabricated by a following process. ITO glass plates (Geomatec, ∼10 Ω/□) were cleaned by an ultrasonic bath with acetone and methanol, and were dried by nitrogen gas. The TiO₂ (Solaronix, HT–LSC) nanoparticle–dispersed solution was spin-coated at 3000 rpm for 60 s and annealed at 120 °C for 5 min. TiO₂ thin films were used as electron transfer layer. After annealing, a C₆₀ or PCBM layer was prepared on the surface of the TiO₂ layer. The C₆₀ layer was evaporated by vacuum deposition, and PCBM layer was spin–coated at 1000 rpm for 60 s. After preparation of the C₆₀ or PCBM layer, the samples were annealed at 140 °C for 5 min. A SiNc layer was evaporated on the C₆₀ or PCBM layer by vacuum deposition. Poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS) was spin–coated at 2000 rpm for 60 s on the active layer, and annealed at 140 °C for 5 min. PEDOT:PSS thin films were used as hole transfer layer. Gold metal contact were prepared by vacuum deposition as a top electrode and annealed at 140 °C for 5 min. The photovoltaic device with C₆₀ was denoted as C₆₀/SiNc, and the photovoltaic device with PCBM was denoted as PCBM/SiNc. J–V characteristics of the photovoltaic devices 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) and (Hokuto Denko Co. Ltd., HSV–110). The photovoltaic devices were illuminated through the side of the ITO substrates, and the illuminated areas were 0.16 cm². Optical absorption of the photovoltaic devices was investigated by means of optical spectroscopy (Jasco, V–670ST). Photocurrent spectra were converted to IPCE spectra using a photocurrent spectrum with a calibrated Si-photodiode upon the same irradiation (Pecell Technologies, PEC–S20). The surface morphology of the thin films was investigated by AFM (SII Nano Technology, SPA400–AFM).

![Fig. 1. (a) Molecular structures of SiNc and PCBM. (b) Structure of photovoltaic devices.](image-url)
3. Results and discussion

*J*-*V* characteristics of photovoltaic devices under illumination at 100 mW cm$^{-2}$ by using an AM 1.5 solar simulator are shown in Fig. 2. Measured parameters of the present photovoltaic devices are summarized as Table I. The PCBM/SiNc photovoltaic device provided power conversion efficiency ($\eta$) of 4.1×10$^{-2}$%, fill factor (FF) of 0.19, and short-circuit current density ($J_{SC}$) of 0.29 mA cm$^{-2}$ and open-circuit voltage ($V_{OC}$) of 0.74 V. On the other hand, the C$_{60}$/SiNc photovoltaic device provided $V_{OC}$ of 0.23 V. The PCBM/SiNc photovoltaic device provided the treble $V_{OC}$ compared with C$_{60}$/SiNc, and $J_{SC}$ of PCBM/SiNc photovoltaic device was half of C$_{60}$/SiNc. The PCBM/SiNc cell also shows a *J*-*V* curve with a pronounced S-shape (kink), which indicates a high interfacial resistance.

Figure 3 shows optical absorption spectrum of SiNc thin film. The measurement region was in the range of 300 to 900 nm. Some peaks on absorption region from 300 to 450 nm correspond to Soret band of SiNc. Several peaks on absorption in the range of 700 to 800 nm correspond to Q band of SiNc, and the absorption peak at ~800 nm was particularly conspicuous. IPCE spectra of photovoltaic devices are shown in Fig. 4. IPCE peaks were observed at ~360, 720 and 800 nm. The IPCE peak at 360 nm corresponds to the Soret band of SiNc, and the IPCE peaks at 720 and 800 nm correspond to the Q band of SiNc. The IPCE peak of 800 nm was smaller compared to the absorption peak in Fig. 3, which indicates exciton generation in this region would be inefficient. Comparing the IPCE of C$_{60}$/SiNc photovoltaic device, the IPCE of PCBM/SiNc photovoltaic device was smaller in the range of 320 to 900 nm. The PCBM/SiNc photovoltaic device had lower photocurrent, and its photo-excitation is more inefficient.

![Fig. 2. J-V characteristic of C$_{60}$/SiNc and PCBM/SiNc photovoltaic devices.](image)

Table I. Measured parameters of photovoltaic devices.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$/SiNc</td>
<td>0.51</td>
<td>0.23</td>
<td>0.28</td>
<td>3.3×10$^{-2}$</td>
</tr>
<tr>
<td>PCBM/SiNc</td>
<td>0.29</td>
<td>0.74</td>
<td>0.19</td>
<td>4.1×10$^{-2}$</td>
</tr>
</tbody>
</table>
The surface morphology of the thin films was investigated by AFM. Figure 5 show AFM images of ITO, ITO/TiO₂, ITO/TiO₂/C₆₀, ITO/TiO₂/SiNc, ITO/TiO₂/PCBM and ITO/TiO₂/PCBM/SiNc. The root-mean-square (RMS) surface roughness of C₆₀/SiNc and PCBM/SiNc were 3.78 nm and 2.13 nm, respectively. SiNc layer on C₆₀ indicate cluster structure with a size of ~25 nm, and PCBM/SiNc layer indicates more flat surface. The C₆₀ clusters with 20–30 nm in diameter are observed on the surface of ITO/TiO₂/C₆₀ in Fig. 5(c), and the RMS surface roughness was 22 nm. The surface morphology of ITO/TiO₂/PCBM is a fine structure as observed in Fig. 5(e), and RMS surface roughness was 1.2 nm. Rough surface of ITO/TiO₂/C₆₀ was conceivable to contribute to form the donor–acceptor interface with larger area, which resulted in the increase of photo-separation of excitons. Compared to the $J_{SC}$ of C₆₀/SiNc photovoltaic device, the $J_{SC}$ of PCBM/SiNc photovoltaic device was lower, which depended on the interfacial morphology.
Fig. 5. AFM images of (a) ITO, (b) ITO/TiO$_2$, (c) ITO/TiO$_2$/C$_{60}$, (d) ITO/TiO$_2$/C$_{60}$/SiNc, (e) ITO/TiO$_2$/PCBM, and (f) ITO/TiO$_2$/PCBM/SiNc.
An energy level diagram of the present photovoltaic devices is shown in Fig. 6. Previously reported values were used for the energy levels in the figure by adjusting to the present work.[16–18] Electrons are transported to an ITO substrate, and holes are transported to an Au electrode. The $V_{oc}$ of organic photovoltaic devices is related with the energy gap between the highest occupied molecular orbital (HOMO) of SiNc and lowest unoccupied molecular orbital (LUMO) of $C_{60}$ or PCBM. When $C_{60}$ is used for n-type semiconductor, the energy barrier would exist at the TiO$_2$/C$_{60}$ interface. To reduce the energy barrier, PCBM with the higher LUMO levels was suitable for n-type semiconductor in the present work. HOMO of SiNc is -5.0 eV. LUMO of $C_{60}$ and PCBM are -4.2 and -3.7 eV respectively, and the difference is 0.5 eV. The measured $V_{oc}$ of $C_{60}$/SiNc and PCBM/SiNc were 0.23 and 0.74 V, respectively, which can be explained by the difference of LUMO level of $C_{60}$ and PCBM. Controlling of the energy levels is important to improve the photovoltaic performance.

Fig. 6. Energy level diagram of the present photovoltaic devices.

### 4. Conclusion

SiNc and fullerene-based photovoltaic devices were fabricated and characterized. Optical properties of SiNc showed absorption at ~800 nm. The PCBM/SiNc device exhibited $\eta$ of 4.1x10$^{-2}$ %, FF of 0.19, $V_{oc}$ of 0.74 V and $J_{sc}$ of 0.29 mA cm$^{-2}$, and the $V_{oc}$ increased by introducing PCBM. From the energy level diagram, the LUMO level of PCBM and $C_{60}$ are -3.7 eV and -4.2 eV respectively, and the PCBM was suitable to adjust the LUMO level of TiO$_2$. Energy gap between LUMO of PCBM and HOMO of SiNc was wider than that of $C_{60}$ and SiNc, which resulted in the increase of $V_{oc}$ of the PCBM/SiNc photovoltaic device. The surface roughness at the $C_{60}$/SiNc interface is larger compared to the PCBM/SiNc interface from the AFM analysis, which resulted in the increase of $J_{sc}$ of the $C_{60}$/SiNc photovoltaic device.
References