Fabrication and characterization of polysilane/C_{60} thin film solar cells

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Abstract. Polysilane/fullerene bulk heterojunction solar cells were fabricated on indium tin oxide electrode by a spin-coating method, and performance and microstructures of the solar cell were investigated. Poly-methyl-phenylsilane, poly-phenylsilane, deca-phenyl-cyclopentasilane and [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM), poly[3-hexylthiophene] (P3HT) were used for the present cells. A device based on the P3HT and PCBM provided better efficiency, fill factor, and short-circuit current compared to those of a device based on P3HT and fullerene.

1. Introduction
Solar cell technology using organic semiconductors has been developed as next generation systems. Organic thin film solar cells have advantages of low cost, flexible and light weight product, and photovoltaic and optical properties of the organic solar cells have been studied [1-4]. Polysilane has high hole mobility as p-type semiconductor, and has been applied as electrical conductive materials and photovoltaic systems [5-7].

The purpose of the present work is to fabricate and characterize bulk heterojunction solar cells with polysilane and fullerene (C_{60}). C_{60} is a good electronic acceptor. Light induced carrier separation with charge transfer was investigated by experimental measurements. Electronic structures and energy levels of the molecules were calculated by molecular orbital calculation. Optical absorption of the solar cells was measured by UV-vis spectroscopy. Microstructure analysis was investigated by transmission electron microscopy and atomic force microscopy. Photovoltaic mechanism was discussed on the basis of the experimental results. The purpose of the present work is to fabricate and characterize polysilane/C_{60}-based solar cells.

2. Experimental
Three-types polysilanes were used in the present work as follows: poly-methyl-phenyl-silane (PMPS), poly-phenyl-silyne (PPSi), poly-diphenyl-silane (PDPS) [8]. Figure 1 shows molecular structures of PMPS, PPSi and PDPS to fabricate solar cells and structure of bulk-heterojunction solar cells. Indium tin oxide (ITO) grass plates (Geomattec, ~10Ω/□) were cleaned by an ultrasonic bath with acetone and methanol, and were dried by nitrogen gas. A thin layer of polyethylenedioxythiophene doped with polystyrene-sulfonic acid (PEDOT:PSS, Sigma Aldrich) was spin-coated on the ITO substrates. Then,
semiconductor layers were prepared on a PEDOT:PSS layer by spin coating using a mixed solution of 
(1) C$_{60}$ (Material Technologies Research, 99.98%), (2) C$_{60}$ and P3HT (Sigma Aldrich) [9], (3) PCBM 
(Frontier Carbon) and P3HT [1, 10-13], PMPS (Osaka Gas Chemical Co, Ltd), PPSi (Osaka Gas 
Chemical Co, Ltd) or PDPS (Osaka Gas Chemical Co, Ltd) in 1 mL o-dichlorobenzene. Total weight 
of C$_{60}$:PMPS, C$_{60}$:PPSi or C$_{60}$:PDPS were 10 mg, and weight ratio of C$_{60}$:PMPS, C$_{60}$:PPSi or 
C$_{60}$:PDPS was 8:2. Aluminium (Al) metal contacts were evaporated as a top electrode. Finally, the 
devices were annealed at 140°C for 30 min in N$_2$ atmosphere.

Current density-voltage (J-V) characteristics (Hokuto Denko Corp., 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) in N$_2$ atmosphere. 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 (JASCO, V-670ST).

![Figure 1](image)

**Figure 1.** Polysilanes to fabricate solar cells and structure of bulk-heterojunction solar cells.

### 3. Results and Discussion

Measured parameters of PMPS:C$_{60}$, PPSi:C$_{60}$ and PDPS:C$_{60}$, PMPS:P3HT:C$_{60}$, PPSi:P3HT:C$_{60}$ and 
PDPS:P3HT:C$_{60}$ bulk heterojunction solar cells are summarized in Table 1. A solar cell with PMPS-
B:P3HT:C$_{60}$ structure provided the highest power conversion efficiency ($\eta$) of 2.7 x 10$^{-3}$ %, fill factor 
(FF) of 0.20, short-circuit current density ($J_{SC}$) of 0.06 mA/cm$^2$ and open-circuit voltage ($V_{OC}$) of 0.22 
V, which is better than those of other devices. It is considered that the efficient charge separation 
would be increased by interface area of PMPS-B:P3HT:C$_{60}$ sample. The molecular weights of PMPS-
A and PMPS-B are 22100 and 1800, respectively.

| Sample          | $V_{OC}$ (V) | $J_{SC}$ (mA/cm$^2$) | FF  | $\eta$ (%) |
|-----------------|--------------|----------------------|-----|------------|
| PMPS-A:C$_{60}$ | 0.060        | 2.0x10$^{-4}$         | 0.26| 3.1x10$^{-6}$|
| PMPS-B:C$_{60}$| 0.10         | 9.0x10$^{-3}$         | 0.29| 2.6x10$^{-4}$|
| PMPS-C$_{60}$  | 0.10         | 4.5x10$^{-2}$         | 0.25| 1.2x10$^{-4}$|
| PMPS-B:P3HT:C$_{60}$ | 0.22 | 6.0x10$^{-2}$         | 0.20| 2.7x10$^{-3}$|
| PPSi:C$_{60}$  | 2.5x10$^{-3}$| 7.0x10$^{-5}$         | 0.26| 4.6x10$^{-8}$|
| PPSi:P3HT      | 0.17         | 1.2x10$^{-2}$         | 0.20| 4.1x10$^{-4}$|
| PDPS:C$_{60}$  | 0.050        | 5.0x10$^{-3}$         | 0.24| 6.0x10$^{-5}$|
| PDPS:P3HT      | 0.13         | 1.5x10$^{-3}$         | 0.20| 3.5x10$^{-5}$|
Figure 2. UV-vis absorption spectra of (a,b) PMPS:C$_{60}$, (c) PPSi:C$_{60}$ and (d) PDPS:C$_{60}$ bulk heterojunction solar cells.

Figure 2 shows UV-visible absorption spectra of the present solar cells. Polysilane:C$_{60}$ structures provided higher photo-absorption in the range of 300-400 nm and 400-500 nm. The absorption peaks at ~350 nm and at ~450 nm for the polysilane:C$_{60}$ structures is due to C$_{60}$. Moreover, polysilane:P3HT:C$_{60}$ structures provided higher photo-absorption than that of polysilane:C$_{60}$ structures. The increased absorption peaks is due to P3HT.

Figure 3. J-V-characteristics of PMPS:PCBM:P3HT, PPSi:PCBM:P3HT and PDPS:PCBM:P3HT bulk heterojunction solar cells under illumination.
Table 2. Experimental parameters of polysilane:PCBM solar cells.

| Sample                | $V_{OC}$ (V) | $J_{SC}$ (mA/cm²) | FF  | $\eta$ (%) |
|-----------------------|--------------|-------------------|-----|------------|
| PMPS-A:PCBM:P3HT      | 0.54         | 1.1               | 0.14| 0.080      |
| PMPS-B:PCBM:P3HT      | 0.53         | 1.8               | 0.33| 0.31       |
| PPSi:PCBM:P3HT        | 0.50         | 1.5               | 0.32| 0.24       |
| PDPS:PCBM:P3HT        | 0.27         | 0.9               | 0.27| 0.070      |

The J-V characteristics of the PMPS:P3HT:PCBM, PPSi:P3HT:PCBM and PDPS:P3HT:PCBM structure under illumination is shown in Figure 3. Measured parameters of these bulk heterojunction solar cells are summarized in Table 2. A solar cell with PMPS-B:PCBM:C$_{60}$ structure provided the highest $\eta$ of 0.31 %, FF of 0.33, $J_{SC}$ of 1.8 mA/cm² and $V_{OC}$ of 0.53 V, which is better than those of other devices. It is considered that the efficient charge separation would be increased by interface area of PMPS-B:P3HT:PCBM sample. In the present study, the PMPS:C$_{60}$ bulk heterojunction solar cell provided $\eta$ of 0.32 %, FF of 0.31, $J_{SC}$ of 17 mA/cm² and $V_{OC}$ of 0.37 V. PMPS has a characteristic of cross-linked and mixed with organic layer with polymer chain [5], which results in the increase of carrier transport. PPSi has a characteristic of compatibility, and uniform spin-coating would be possible. Although PDPS has a high refractive index, spin-coating was not so uniform, which results in the low carrier transport.

An energy level diagram of polysilane:C$_{60}$ and polysilane:PCBM:P3HT solar cells is summarized as shown in Figure 4. Previously reported values were used for the energy levels [14]. For the polysilane:PCBM:P3HT solar cells, the combination of P3HT and polysilane would increase the carrier separation, which would results in the increase of efficiency. The incident direction of light is from ITO side. Energy barrier would exist near the semiconductor/metal interface. Electronic charge is transferred by light irradiation from the ITO substrate side. Holes are transported to an ITO substrate and electrons are transported to an Al electrode. A relation between $V_{OC}$ and polymer oxidation potential was reported as $V_{OC}=(1/e)(|E_{\text{Poly}^\text{HOMO}}|-|E_{C_60^\text{LUMO}}|)-0.3$ (V), where $e$ is the elementary charge. The value of 0.3 V is an empirical factor, and this is enough for efficient charge separation.

Figure 4. Energy level diagrams of (a) polysilane:C$_{60}$ and (b) polysilane:PCBM:P3HT bulk heterojunction solar cells.
Since PMPS has the excellent cross-linked feature, cross-links are formed with other molecules in a solvent. This promotes the charge transfer within a solar cell, which would result in the improvement of conversion efficiency as listed in Table 1 and Table 2. In addition, PMPS-B with a lower molecular weight provided higher conversion efficiency compared to the PMPS-A, which would be due to the easy cross-linked reaction.

PPSi has a network type polysilane that has a silanol group (Si-OH) at the end, and it has excellent compatibility and cross-links. When heated, this polysilane is cured, making cross-links with other reactive compounds, and it is possible to suppress changes in the film thickness. Although combination of compatibility and cross-links would be effective for film formation, the carrier transport would be disturbed by oxygen atoms at the cross-links, and the conversion efficiency was low compared with the PMPS-B.

Since PDPS has a cyclic structure, its refractivity is so high to confine light compared to the other polysilanes in the present work. When it is used, higher conversion efficiency would be expected. However, in the present work, since the charge transfer was not so smooth compared to the other polysilanes, which would result in the low efficiency.

4. Conclusion
Polysilane:C$_{60}$, polysilane:P3HT:C$_{60}$ and polysilane:P3HT:PCBM solar cells were fabricated and characterized. Four types of polysilane were used in the present work. A device based on PMPS:P3HT:C$_{60}$ structure provided the highest $\eta$ of 0.31 %, FF of 0.33, $J_{SC}$ of 1.8 mA/cm$^2$ and $V_{OC}$ of 0.53V, which was better than those of other devices in the present work. Energy levels of the molecules were investigated and discussed.

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