Fabrication and characterization of poly[diphenylsilane]-based solar cells

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Abstract. Poly[diphenylsilane] (PDPS)-based photovoltaic cells were fabricated by using mixture solution of PDPS, phosphorus and boron. An influence of phosphorus and boron doping into PDPS on the performance of the photovoltaic device was investigated. The solar cell using fluorine doped tin oxide glass plates provided short-circuit current density of 0.12 mA/cm\textsuperscript{2} and open-circuit voltage of 0.28 V under simulated sunlight. Energy levels, formation mechanism and microstructure of the solar cells were discussed.

1. Introduction

Most used energy on the earth is fossil fuels in the present time, and burning fossil fuels affects on the natural environment by production of greenhouse gases. Problems of energy supply and use are related not only to global warming but also to such environmental concerns as air pollution and forest destruction. In addition, fossil fuel is limited, and other energy resources should be developed.

A mainstream of solar cell is silicon solar cells which have a high energy conversion efficiency and long lifetime. However, they are expensive and heavy-weight. On the other hand, researches on organic thin film solar cells are advanced since they have easy fabrication process, low cost, light-weight and flexible substrates. However, they provide low energy conversion efficiency and short lifetime.

Polysilanes have high hole mobility as organic semiconductors because of its $\sigma$-conjugated polymers, and it is possible to use the materials for organic thin film solar cells [1-3]. Although the polysilanes could be applied to p-type semiconductors on organic thin film solar cells, few studies on polysilane solar cells have been reported [4-6]. The purpose of the present study is to fabricate photovoltaic cells by using mixture solution of poly[diphenylsilane] (PDPS), phosphorus and boron. PDPS have high hole mobility as organic semiconductors because of its $\sigma$-conjugated polymers, and it is possible to use the materials for organic thin film solar cells

2. Experimental procedures

A thin layer of polyethylenedioxythiophen doped with polystyrene-sulfonic acid (PEDOT:PSS) (Sigma Aldrich) was spin-coated on pre-cleaned indium tin oxide (ITO) glass plates (Geomatec Co., Ltd, $\sim$10$\Omega \cdot \square$) or fluorine doped tin oxide (FTO) glass plates (Luminescence Technology Co. $\sim$14$\Omega \cdot \square$). ITO substrates have the characteristic that the resistance increase when annealed at a high temperature of 300 °C. Therefore, the FTO substrate with stability at 300 °C was used for Cell 2. Then, semiconductor layers were prepared on the PEDOT:PSS layer by spin coating using the mixture
solution of PDPS (Osaka Gas Chemical Co., Ltd) and diethylmethoxyborane (Sigma Aldrich) in 1 ml o-dichlorobenzene. After annealing at 250 °C for 10 min or 300 °C for 10 min in N$_2$ atmosphere, a next layer was prepared by spin-coating using the mixture solution of PDPS and phosphoric acid (Sigma Aldrich) in 1 ml o-dichlorobenzene. After annealing at 250 °C for 10 min or 300 °C for 10 min in N$_2$ atmosphere, aluminum (Al) metal contacts were evaporated as the top electrode. A schematic diagram of the present solar cells is shown in Figure 1.

The current density-voltage (J-V) characteristics (Hokuto Denko, HSV-100) of the solar cells were measured 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 or FTO substrates, and the illuminated area was 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 PDPS thin films were investigated by X-ray diffractometry (XRD, Philips X’Pert-MPD System) with CuKa radiation at 40 kV operating voltage and 40mA operating current.

![Cross-sectional structure of heterojunction solar cells and atomic structure of PDPS.](image)

**Figure 1.** Cross-sectional structure of heterojunction solar cells and atomic structure of PDPS.

### 3. Results and discussion

Measured current density-voltage (J-V) characteristic of solar cells under illumination is shown in Figure 2. Photocurrents were observed under the illumination, and each structure showed characteristic curves with short-circuit current and open-circuit voltage.

Measured parameters of the solar cells are summarized in Table 1. Cell 2 provided the higher power conversion efficiency ($\eta$) of 0.010 %, fill factor (FF) of 0.31, short-circuit current density ($J_{sc}$) of 0.12 mA/cm$^2$ and open-circuit voltage ($V_{oc}$) of 0.28 V.

Figure 3 shows UV-visible-IR absorption spectra of solar cells. The PDPS:phosphorus/PDPS:boron structure shows broad absorption in range of 300 and 1800 nm.

X-ray diffraction pattern of the annealed PDPS thin film is shown in Figure 4. A broad peak at 20 of ~28.5° would be a reflection of Si 111, which would indicate an amorphous Si structure. Other several broad peaks are due to PDPS or decomposed PDPS, and this thin film would be a nanocomposite film with amorphous Si and PDPS.

**Table 1.** Measured parameters of solar cells

| Cell | Glass substrate | Annealing temperature (°C) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF | $\eta$ (%) |
|------|-----------------|---------------------------|-------------|---------------------|----|------------|
| Cell 1 | ITO (10 $\Omega/\Box$) | 250 | 0.23 | 0.019 | 0.25 | 1.1×10$^{-3}$ |
| Cell 2 | FTO (14 $\Omega/\Box$) | 300 | 0.28 | 0.12 | 0.31 | 0.010 |
Energy level diagram of the solar cells is summarized as shown in Figure 5(a). Previously reported values were used for the energy levels [4, 5]. The incident of light is from ITO or FTO side. Energy barrier would exist near the semiconductor/metal interface. Electronic charge separation was caused by light irradiation from the ITO or FTO substrate side. Separated holes could be transferred from the valence band of Si doped with B to the ITO or FTO, and separated electrons could be transferred from the conduction band of Si doped with P to the Al electrode. To improve the efficiency, control of microstructure by annealing would be important. In addition, there would be energy barrier at the semiconductor/metal interfaces as indicated by band bending in Fig. 5(a), and the heavy doping of B or P would reduce the contact resistance.

**Figure 2.** Measured J-V characteristic of solar cells under illumination.

**Figure 3.** UV-visible-IR absorption of PDPS thin films with phosphorus and boron.
Figure 4. XRD pattern of PDPS thin film after annealing at 300 °C for 10 min.

Figure 5. (a) Energy level diagram and (b) doping process of the present solar cells.
Doping process is summarized as shown in Figure 5(b). Polysilanes decompose to form amorphous silicon when heated to high temperature. Amorphous silicon doped with boron would function as p-type semiconductor. On the other hand, amorphous silicon doped with phosphorus would function as n-type semiconductor. Energy levels would be different between PDPS with B and PDPS with P. Several broad peaks were observed in the X-ray diffraction pattern of the annealed PDPS films, and the present solar cells would have a nanocomposite structure of amorphous Si and PDPS. Further annealing would be effective for the decomposition of PDPS and crystallization of amorphous Si. To improve the efficiency, control of microstructure by annealing would be important. Optimization of annealing temperatures and electrical conductivity due to doping or microstructural change would increase the efficiencies of solar cells.

4. Conclusions
Polysilane-based solar cells were fabricated by using mixture solution of PDPS, phosphorus, and boron, and characterized by electrical measurements. A device using FTO substrate provided $\eta$ of 0.010%, FF of 0.31, $J_{sc}$ of 0.12 mA/cm$^2$ and $V_{oc}$ of 0.28 V. The solar cell showed broad absorption in range of 300 and 1800 nm. Microstructure analysis showed formation of a nanocomposite structure amorphous Si and PDPS. Energy levels of the molecules and carrier transport mechanism were discussed.

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