Effects of phosphorous doping to poly (methylphenyl silane) and fabrication of thin film solar cells

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Abstract. Effects of phosphorus bromine (PBr₃) doping to polysilane were investigated for spin-coating thin films. Phosphorus doped poly (methylphenyl silane) (PMPS) provided n-type semiconductor behavior, which was confirmed by Hall effect measurements. Desorption of phenyl and methyl groups in doped PMPS thin films was observed after annealing at 300 °C from Raman scattering measurements and theoretical calculations. The band gap energy of PMPS was measured to be 3.2 eV. Decrease of photoluminescence intensity of PMPS was observed by phosphorus doping. Microstructures of the doped PMPS thin films were investigated by using X-ray diffraction, which indicated doped PMPS had an amorphous structure after annealing. A solar cell with PMPS(PBr₃):poly[3-hexylthiophene] bulk-heterojunction structure was fabricated, and provided a photovoltaic behavior. Formation mechanism and carrier transport mechanism of the doped PMPS thin films were proposed.

1. Introduction

Thin film solar cells using organic semiconductors have 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]. However, the power conversion efficiency of the organic cells is lower than inorganic cells. A primary cause of this is low mobility of charge carriers. Polysilanes a p-type semiconductor, and has been applied as electrical conductive materials and photovoltaic systems [5-7]. Polysilanes are known as σ-conjugate polymers, and hole mobility is $10^{-4}\text{cm}^2\text{V}^{-1}\text{s}^{-1}$[5]. Although the polysilanes could be applied to p-type semiconductors on organic thin film solar cells for these characteristics, few studies on polysilane solar cells have been reported [6, 8-11]. Doped polysilanes as n-type semiconductor have been applied for organic solar cells [12].

The purpose of the present work is to fabricate photovoltaic solar cell by using mixture solution of polysilane doped with phosphorus, and to investigate the effect of annealing temperatures and doping of phosphorous (P) on their electronic properties and microstructures. It is expected that amorphous silicon doped with phosphorus would function as n-type semiconductor. Spin-coating is a low-cost method, and is essential for mass production of any solar cells. Light induced carrier separation with charge transfer was investigated by experimental measurements. Doping effect of phosphorus into polysilane was investigated by Hall effect measurement and Raman scattering spectra, and microstructure analysis was also investigated by X-ray diffraction (XRD).
2. Experimental
Poly (methyl phenyl silane) (PMPS) was used in the present work. Figure 1 shows solar cell structures and molecular structures of PMPS, phosphorus bromine (PBr$_3$) and poly[3-hexylthiophene] (P3HT) (Sigma Aldrich). Indium tin oxide (ITO) grass plate (Geomatec, $\sim$10Ω/□) was cleaned by an ultrasonic bath with acetone and methanol, and was dried by nitrogen gas. Then the sol-gel procedure for producing TiO$_x$ is as follows: titanium tetra-isopropoxide (TTIP) was prepared as a precursor and mixed with 2-methoxyethanol and acetylacetone. Then the TiO$_x$ precursor solution was spin-cast in air on the ITO substrate. The substrate was heated at 140 °C for 60 min in air. PBr$_3$ (0.02 mL, Wako) and PMPS (24 mg, Osaka Gas Chemicals Co., Ltd) were mixed in 1 mL o-dichlorobenzene, and then P3HT was mixed. The mixed solution was spin-cast (1000 rpm) on the resultant substrate, and then was heated at 300 °C for 10 min in an inert-atmosphere (N$_2$) glovebox. Highly conducting poly (3,4-ethylenedioxylenetthiophene): polystyrene sulfonic acid (PEDOT:PSS) was spin-cast (2000 rpm) and was heated at 140 °C for 60 min in a glove box. Gold contacts were evaporated as a top electrode. Finally, the devices were annealed at 140 °C for 30 min in N$_2$ atmosphere.

![Figure 1. Structures of PMPS, PBr$_3$ and P3HT to fabricate solar cells PMPS (PBr$_3$):P3HT bulk-heterojunction solar cells.](image)

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 mWcm$^{-2}$ 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).

The microstructures of the PMPS thin films were investigated by XRD (Philips X’Pert-MPD System) with CuKa radiation at 40 kV operating voltage and 40 mA operating current. Surface resistivity, carrier concentration and mobility of doped thin film were measured by Hall effect measurement system (TOYO Corporation, Japan, Resti Test 8320). Raman scattering spectra were recorded with a laser Raman spectrometer (JASCO Co., Ltd., NRS-5100). Raman mode and optical image of the thin film after annealing was observed using excitation laser wavelength at 532 nm. The molecular structures of phosphorus bromine and polysilane monomers and phosphorus complex were optimized by CS Chem3D (Cambridge Soft). Molecular orbital calculations were carried out by MOPAC (Fujitsu Ltd.). The isolated molecular structures were optimized by ab-initio quantum calculation using density functional theory using B3LYP/6-31G (d) as basis function (Gaussian 03). Active modes in Raman scattering spectra were calculated by DFT/B3LYP/6-31G (d) using frequency mode.
3. Results and Discussion
Doping effects of phosphorus on the PMPS were investigated. Surface resistivity, carrier concentration and mobility of doped thin film with phosphorus are summarized in Table 1. Although non-doped PMPS films showed high electrical resistivity (~10^8 Ω cm), doped PMPS thin film showed n-type behaviour, low resistivity and high hole mobility. The experimental results at room temperature on doped film with phosphorus complex showed improvement of surface resistivity, carrier concentration and mobility of 0.15, 2.1×10^19 cm^-3 and 2.0 cm^2V^-1s^-1, respectively. After annealing at 300 °C, the electronic properties of the doped thin film were changed to be 0.26, 1.0×10^19 cm^-3 and 2.4 cm^2V^-1s^-1. However, after annealing at 500 °C, the electronic properties of the doped thin film were deteriorated. The doping of phosphorus at 300 °C provided a good performance for transport phenomena.

| Temperature | Resistivity (Ω cm) | Carrier concentration (cm^-3) | Mobility (cm^2V^-1s^-1) |
|-------------|--------------------|------------------------------|------------------------|
| R. T.       | 0.15               | 2.1×10^19                   | 2.0                    |
| 300 °C      | 0.26               | 1.0×10^19                   | 2.4                    |
| 500 °C      | 48                 | 1.9×10^17                   | 0.69                   |

Figure 2 shows Raman scattering spectra of PMPS and the doped PMPS thin film. As comparison, the calculated Raman scattering spectra was also shown in Figure 2 for identifying each active mode of PMPS monomer. As shown doped PMPS, Raman active mode of the film was obtained as follows: 693, 854, 1645, 2394, 3178, 3185, 3192, 3199 and 3206 cm^-1. The middle peaks at 693, 854, 1645 and 2394 cm^-1 were identified as phenyl group vibration modes in PMPS. Strong peaks at 3178, 3185, 3192, 3199 and 3206 cm^-1 were identified as methyl group vibration modes in PMPS [13-15]. Raman peaks observed in PMPS was conformed as vibration mode of carbon bond of phenyl and methyl group in PMPS monomer. After doping of PBr_3 with annealing at 300 °C, the peaks at 2394, 3178, 3185, 3192, 3199 and 3206 cm^-1 disappeared. Peak around 1500 cm^-1 appeared as a new mode of modified PMPS with phosphorus complex. In addition, the Si crystal peaks around 520 cm^-1 was not observed in PMPS and doped PMPS thin film. Doping effect of phosphorus bromide on the PMPS was characterized.

![Raman spectra](image)

Figure 2. Raman scattering spectra of calculation PMPS, PMPS thin film and doped PMPS thin film.

Figure 3 shows XRD patterns of PMPS, doped PMPS thin films after annealing, and Glass substrate, respectively. There is no sharp diffraction peak in Figure 3. Peak observed in PMPS, as shown was
polysilane specific crystalline peak. After doping of PBr$_3$ with annealing at 300 °C, the peak was disappeared. From this result, the structure of doped PMPS thin film which indicates formation of an amorphous structure from the crystalline structure. In addition, doping of phosphorus bromine into PMPS would enhance the decomposition of the PMPS to the amorphous structure.

Figure 3. XRD patterns of PMPS, doped PMPS thin films after annealing at 300 °C and glass substrate.

Figure 4 shows UV-vis diffuse reflection absorption spectra of PMPS and doped PMPS. PMPS structure provided higher photo-absorption in the range of 300-400 nm. After doping of PBr$_3$ with annealing at 300 °C, the peak was decreased. From this result, the decrease of photo-absorption peak was affected of organic functional group of side chain of PMPS desorption.

Figure 4. UV-vis diffuse reflection absorption spectra of PMPS and doped PMPS.

Figure 5 shows photoluminescence spectra of PMPS and doped PMPS. PMPS structure provided photoluminescence in the range of 300-450 nm. After doping of PBr$_3$ with annealing at 300 °C, the peak was decreased, significantly. Decrease of photoluminescence intensity of PMPS was observed by doping of phosphorus which was due to structural transition by doping of PBr$_3$ after annealing at 300 °C [16]. This characteristic was explained by the light-induced charge separation between PMPS
units and phosphorus. Also, the band gap energy of doped PMPS was calculated from Figure 5 and the value was 3.2 eV.

Figure 5. Photoluminescence spectra of PMPS and doped PMPS.

Figure 6 shows proposed a mechanism of PBr$_3$ doping to PMPS in the present work. Annealing from room temperature to 300 °C, several phenyl and methyl groups of side chain of PMPS desorbed and -PBr$_2$ bound of side chain of PMPS. In this case, methyl bromide and benzene bromide were generated, and an amorphous structure was formed from the main Si chain structure. Annealing at 300 °C, the structure closed in amorphous structure.

Figure 6. Microstructure change of PMPS (PBr$_3$) during annealing.

Measured parameters of the present solar cell using Doped PMPS and P3HT as photoactive layer are summarized in Table 2. Open-circuit voltage, short-circuit current density, fill factor and power conversion efficiency are denoted as $V_{OC}$, $J_{SC}$, FF and $\eta$, respectively. A solar cell with PMPS (PBr$_3$):P3HT structure was sure using doped PMPS. The present solar cells fabricated by spin cast have simple fabrication process and better cost performance. Further, the conversion efficiency improved using the present fabrication process.
Table 2. Measured parameters of the PMPS (PBr$_3$):P3HT bulk-heterojunction solar cells.

| Sample         | $V_{oc}$ (V) | $J_{sc}$ (μAcm$^{-2}$) | FF  | $\eta$ (%) |
|----------------|--------------|-------------------------|-----|-------------|
| PMPS(PBr$_3$):P3HT | 0.064        | 3.8                     | 0.36| 8.8×10$^{-5}$|

An energy level diagram of PMPS (PBr$_3$): P3HT bulk-heterojunction solar cell is summarized as shown in Figure 7. Previously reported values were used for the energy levels [17-18]. For the PMPS (PBr$_3$): P3HT bulk heterojunction solar cell, the combination of P3HT and doped PMPS would generate the carrier separation, which indicated 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 Au electrode and electrons are transported to an ITO substrate.

![Energy level diagram of PMPS (PBr$_3$):P3HT bulk heterojunction solar cells.](image)

Figure 7. Energy level diagram of PMPS (PBr$_3$):P3HT bulk heterojunction solar cells.

4. Conclusion

Thin film of doping phosphorus to PMPS was fabricated by using spin-coating method and the effect was also investigated. Doped PMPS provided n-type semiconductor behavior and indicated a good performance for transport phenomena by a Hall effect measurement. From Raman scattering measurements and theoretical calculations, desorption of phenyl and methyl groups in doped PMPS thin film was observed after annealing at 300 °C. The band gap energy of doped PMPS was 3.2 eV and decrease of photoluminescence intensity of polysilane was observed by doping of phosphorus. This characteristic was explained by the light-induced charge separation between PMPS unit and phosphorus. Microstructures of the doped PMPS thin film were investigated by using X-ray diffraction, which indicated doped PMPS had an amorphous structure after annealing. A solar cell with PMPS (PBr$_3$):P3HT bulk-heterojunction structure was fabricated, and provided a photovoltaic behavior. Energy level of the molecules was suggested that the solar cell was provided a photovoltaic behavior. Investigation of percentage of doping concentration and optimization of the structure of doped PMPS would improve the cell performance using the present fabrication process.

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