Effects of Triphenylborane Addition to Decaphenylcyclopentasilane Thin Films

Takeo Oku*, Naoki Hibi¹, Atsushi Suzuki¹, Tsuyoshi Akiyama¹, Masahiro Yamada², Sakiko Fukunishi³ and Kazufumi Kohno³

¹Department of Materials Science, The University of Shiga Prefecture, Shiga 522-8533, Japan
²Osaka Gas Co., Ltd., Osaka 554-0051, Japan
³Osaka Gas Chemicals Co., Ltd., Osaka 554-0051, Japan

E-mail: oku@mat.usp.ac.jp

(Received July 18, 2014)

Organic thin film solar cells are potential ‘next generation’ solar cells. Many p-type semiconductors have been used in organic solar cells, but there have been far fewer reports involving n-type organic semiconductors. Developing new n-type organic semiconductors is therefore desirable. Decaphenylpentasilane (DPPS) thin films were spin-coated from solutions containing boron (B), and the effects of B addition on film microstructures and electronic properties were investigated. Microstructures of DPPS thin films were investigated by X-ray diffraction, and DPPS thin films doped with B (DPPS(B)) showed the reduction of crystallinity upon annealing at 300 °C, while DPPS thin films exhibited crystalline structures. DPPS(B) thin films exhibited decreased electrical resistances upon the B doping and annealing. The desorption of phenyl and methyl groups from the DPPS(B) thin films was observed by Raman scattering measurements.

1. Introduction

Polysilanes are a p-type semiconductor, and have been applied as electronic conductive materials and photovoltaic systems [1-11]. Polysilanes are organic polymers containing main chain Si-Si bonds and side chain organic substituents, which are known as σ-conjugate polymers, and their hole mobility is \(~10^{-4}\) \text{cm}^2\text{V}^{-1}\text{s}^{-1} [1]. Although the polysilanes could be applied as a p-type semiconductor on organic thin film solar cells for these characteristics, few studies on polysilane solar cells have been reported. Doped polysilanes as an n-type semiconductor have been developed and applied for organic solar cells [11,12].

The purpose of the present work is to prepare decaphenylcyclopentasilane thin films using spin-coating mixture solutions of decaphenylpentasilane (DPPS) with triphenyl borane, and to evaluate the effect of boron (B) and annealing temperatures on their electronic properties and microstructures. It is expected that amorphous silicon doped with boron would function as a p-type semiconductor. Spin-coating is a low-cost method, and is essential for mass production of solar cells [13]. Optical property and desorption of phenyl group were investigated from ultraviolet-visible (UV-vis) absorption and Raman scattering spectra. Microstructure analysis was carried out by X-ray diffraction (XRD) analysis. The mechanism of microstructural change is discussed on the basis of the experimental results.

2. Experimental

Figure 1 shows molecular structures of DPPS and triphenyl borane, which was used for boron doping to DPPS. Indium tin oxide glass plates were cleaned by an ultrasonic bath with acetone and...
methanol, and then were dried with nitrogen gas. The triphenylborane and DPPS were mixed in 1 mL tetrahydrofuran. The mixed solution was spin-coated at 1000 rpm, and then annealed at 100–300 °C. Gold contacts were evaporated as a top electrode by vacuum deposition to measure the electrical resistance of the film. The current density–voltage characteristics (Hokuto Denko HSV-110) of the devices were measured to investigate the electrical resistances of the films. The microstructures of the DPPS thin films were investigated by XRD analysis (Philips X’Pert-MPD System) with CuKα radiation at 40 kV operating voltage and 40 mA operating current. Raman scattering spectra were recorded with a laser Raman spectrometer (Jasco NRS-5100). The Raman scattering spectra and optical images of the thin films after annealing were observed using an excitation laser with a wavelength at 532 nm. Optical properties were investigated by UV-vis absorption spectroscopy (Jasco, V-670). The molecular structures of the DPPS monomers were optimized by \textit{ab-initio} calculation based on the density functional theory using Gaussian 09. The active modes in Raman scattering spectra were calculated by DFT/B3LYP/6-31G in the frequency mode.

![Fig. 1. Structures of (a) DPPS and (b) triphenylborane.](image)

3. Results and Discussion

UV-vis absorption spectra of DPPS thin films before and after annealing are shown in Fig. 2. All three exhibited obvious absorptions at 300–350 nm, which corresponds to excited states of $\pi \rightarrow \pi^*$ transition. The wavelength of the absorption edge increased upon B doping and annealing at 300 °C, which suggests that shifted photoabsorption arose from the desorption of phenyl groups, from side chains in DPPS, and/or an increase of the length of Si-Si chains.

Raman scattering spectra of DPPS thin films after annealing are shown in Fig. 3. Raman active modes of the DPPS film were observed at ~1000, ~1600 and ~3000 cm$^{-1}$. From calculation of Raman spectra, peaks at ~1000, ~1600 and ~3000 cm$^{-1}$ in the spectra of DPPS were attributed to vibration modes of phenyl group–Si, phenyl ring itself and C-H bonds in phenyl group, respectively. Strong vibrations of the Si crystal lattice at ca. 520 cm$^{-1}$ [14] were not observed in the spectra of the thin films. Adding triphenylborane to DPPS caused the peaks to disappear, which suggests desorption of the phenyl group and enhancement of the decomposition of the DPPS to the amorphous structure.
Fig. 2. UV-vis absorption spectra of DPPS thin films with and without B doping.

Fig. 3. Raman spectra of DPPS thin films annealed with or without B doping.
Figure 4 shows XRD patterns of DPPS thin films before and after annealing at 300 °C. Diffraction peaks of DPPS were observed in the range of 8–9° in XRD patterns. After annealing at 300 °C, the diffraction intensity was increased. On the other hands, the intensity of the diffraction peak decreased by triphenylborane addition to DPPS thin film, which indicates the decomposition of the DPPS structure, and formation of an amorphous structure from the crystalline structure by boron doping. XRD results for DPPS thin films were summarized in Table I. The d-spacings of ~1.0 nm might be distances of the DPPS plane layers.

**Table I.** Summary of XRD results for DPPS thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing temperature (°C)</th>
<th>Position (2θ)</th>
<th>FWHM (2θ)</th>
<th>d-spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPPS</td>
<td>–</td>
<td>8.389</td>
<td>0.048</td>
<td>1.053</td>
</tr>
<tr>
<td>DPPS</td>
<td>300</td>
<td>8.363</td>
<td>0.086</td>
<td>1.056</td>
</tr>
<tr>
<td>DPPS(B)</td>
<td>300</td>
<td>9.036</td>
<td>0.038</td>
<td>0.9780</td>
</tr>
</tbody>
</table>
J-V characteristics of the DPPS thin films were measured in the dark, and electrical resistances of the DPPS thin films were calculated. Film thickness was measured to be ~200 nm by an atomic force microscope. Volume resistivities of as-prepared, annealed, and annealed with B doping DPPS were measured to be $6.6 \times 10^4$, $5.6 \times 10^4$, and $5.5 \times 10^4 \Omega \text{cm}$, respectively. The DPPS(B) thin films exhibited decreased electrical resistances upon B doping and annealing.

![LUMO and HOMO](image)

**Fig. 5.** Calculated electronic structures of DPPS.

Absorption spectra of DPPS thin films in Fig. 2 indicated that the absorption edge shifted to longer waves by the B doping and annealing at 300 °C, which suggested that the increase of the length of Si-Si chain would decrease the energy gaps by increasing highest occupied molecular orbital (HOMO) energy levels keeping the lowest unoccupied molecular orbital (LUMO) energy levels [15]. A calculated result of HOMO and LUMO is shown in Fig. 5. The length of main Si-Si chain affects the non-locality of $\sigma$ electrons, which would affect the absorption spectra.

Figure 6 shows proposed mechanisms for B doping in DPPS. A Si ring opening reaction occurred in DPPS. Si-Si bonds were broken, and numerous phenyl groups desorbed from DPPS side chains during annealing at 300 °C, and B bound to DPPS side chains, and an amorphous structure formed from the Si chain structure [16]. This type of DPPS thin films would be used for a p-type semiconductor, which would be expected for the use of $pn$ junction solar cells.

![Proposed microstructure](image)

**Fig. 6.** Proposed changes in microstructure of DPPS(B) during annealing.
4. Conclusion

DPPS thin films were fabricated by spin-coating, and the effect of doping with B was investigated. DPPS(B) thin films exhibited an amorphous structure after annealing at 300 °C, while DPPS thin films were crystalline after annealing. DPPS thin films exhibited decreased electrical resistances upon annealing and B doping. The B doping and annealing at 300 °C caused the desorption of phenyl groups from DPPS(B) side chains.

References