Synthesis and Annealing Study of Silicon- and Fluorine-containing Low Bandgap Conjugated Polymers for Solar Cell Applications

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Abstract

Two donor-acceptor alternating conjugated copolymers were synthesized as the donor materials of the active layer in polymer solar cells via Stille coupling reaction. Both copolymers consisted of dithienosilole as the donor unit and nonfluorinated 2,1,3-benzooxadiazole or fluorinated 2,1,3-benzooxadiazole as the acceptor unit. The nonfluorinated polymer and fluorinated polymer were designated as P1 and P2, respectively. The structures of copolymers were confirmed by FT-IR, ^{1}H NMR, and ^{13}C NMR. Optoelectronic properties of the polymer were investigated and observed by UV-vis spectrum, photoluminescence spectrum, and cyclic voltammetry. Both polymers exhibited a panchromatic absorption ranging from 300 nm to 1100 nm and displayed low band gaps of 1.46 eV and 1.42 eV, respectively. Both of the synthesized materials were used as the donor material in the bulk heterojunction (BHJ) solar cells and then power conversion efficiency (PCE) measurements were conducted in different weight ratios of the polymer:$PC_{61}BM$ blends.

Compared to the nonfluorinated one, the fluorinated polymer exhibited a higher PCE of 2.67% at room temperature under the illumination of AM 1.5 (100 mW/cm^2). Study of the effect of annealing on the performance of the P1/$PC_{61}BM$ devices using a 1:2 blend ratio of P1:$PC_{61}BM$ exhibited the highest short-circuit current density of 5.88 mA/cm^2 and a power conversion efficiency of 2.76% at annealing temperature of 125^{o}C. The bulk heterojunction polymer solar cell employing P2 and $PC_{61}BM$ at a blend ratio of 1:2 exhibited the highest short-circuit current density of 6.44 mA/cm^2 and a power conversion efficiency of 3.54% at annealing temperature of 150 ^{o}C.

Keywords: donor-acceptor, solar cell, dithienosilole, 2, 1, 3-benzooxadiazole, low band gap, power conversion efficiency

1. Introduction

Except the "weak donor–strong acceptor" concept for the design of D-A alternating copolymers with low band gaps and high V_{oc}s for solar cell applications [1], adding electron-withdrawing groups to the polymer backbone is also considered as an efficient approach. Recently, fluorine has attracted much attention as an electron-withdrawing group in the synthesis of conjugated polymers for high-efficiency solar cells [2-3]. According to a theoretical study by Brédas et al., the introduction of fluorine atom as a substituent of the conjugated polymer would lower both of the HOMO and LUMO energy levels of the synthesized polymer [4].

On the other hand, silole-containing aromatic moieties have attracted much attention as new building units of conjugated polymers because of their unique optoelectronic properties. As regards their carbon analogues, silole-containing polymers have quite low-lying LUMO levels, which are attributed to the fact that the σ-orbital of the Si-C bond can effectively interacts with the π-orbital of the butadiene fragment [5]. By transforming PCPDTBT to the silole-containing polymer, poly{[4,4'-bis(2-ethylhexyl)dithieno(3,2-b;2',3'-d)silole]-2,6-diyl-alt-(2,1,3-benzothidiazole)-4,7-diyl} has been recently realized and a PCE of as high as 5.6% has been achieved [6]. Therefore, the dithieno[3,2-b:2',3'-d]-silole (DTS) unit has frequently used as the si-

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lole-containing donor unit in the development of high-efficiency PSCs.

Herein, we have investigated the effect of silole-containing and fluorination on the photovoltaic performances of the D-A conjugated copolymers. Two D-A copolymers comprising DTS unit and nonfluorinated and fluorinated 2,1,3-benzooxadiazole (BO) unit has been synthesized to study the effect of silicon and fluorine substitution. The effect of annealing on the device performance of the polymer solar cells fabricated from the nonfluorinated and fluorinated polymers has been investigated in detail.

2. Method

2.1. Synthesis of Polymers

In this study, two D-A type copolymers were synthesized via Stille coupling reaction. For convenience, they are designated as P1 and P2. The synthetic routes are shown in Fig. 1.

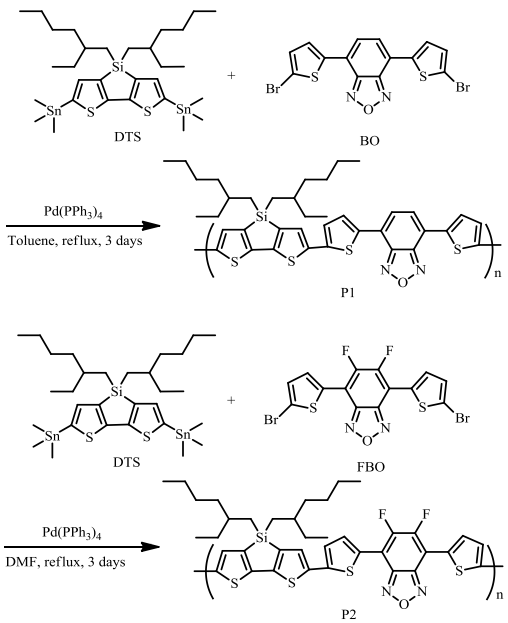

Fig. 1 Polymer synthesis

2.2. Annealing Study

The device structure of PSCs for current density-voltage (J-V) measurements is ITO/PEDOT: PSS/Polymer: PC61BM/LiF/Al. The films of active layers were annealed directly on top of a hot plate in the glove box, and the temperature was monitored by using a thermocouple touching the top of the substrates. After removal from the hotplate, the substrates were immediately put onto a metal plate at the room temperature. Ultraviolet-visible (UV-Vis) spectroscopic analysis was conducted on a Perkin–Elmer Lambda 35 UV-Vis spectrophotometer. The J-V curves were measured using a Keithley 2400 source meter, under illumination from a solar simulator. The intensity of solar simulator was set with a primary reference cell and a spectral correction factor to give the performance under the AM 1.5 (100 mW/cm2) global reference spectrum (IEC 60904-9).

3. Results and Discussion

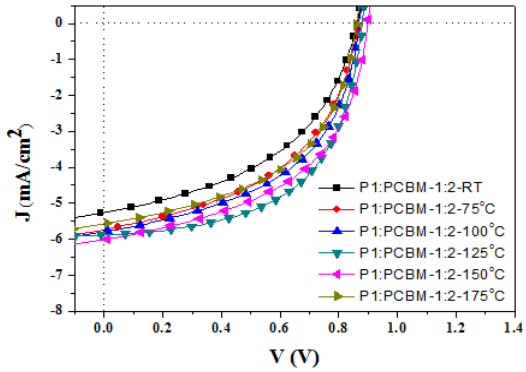

Fig. 2 J-V characteristics of devices for P1 after annealing at different temperatures for 30 min

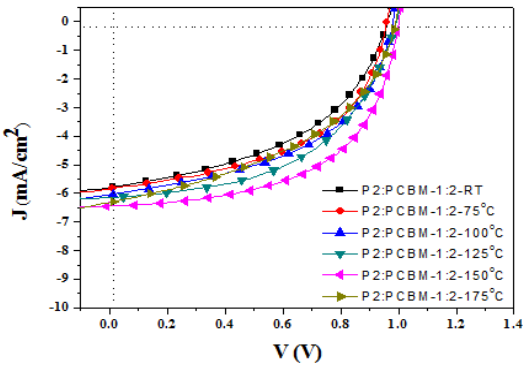

Fig. 3 J-V characteristics of devices for P2 after annealing at different temperatures for 30 min

Figs. 2 - 3 show the J-V characteristics under white light illumination (100 mW/cm^2) for photovoltaic devices subjected to thermal annealing. For the P1 polymer, the device annealed at 125 °C shows the best efficiency of 2.76%, while the P2 polymer shows the optimum efficiency of 3.54% at 150 °C. Thus, it is clear that

annealing treatment affects the device performance significantly and that there exists optimum range of the annealing temperature. It is noteworthy that the V_{oc} values of P2 are higher than those of the P1 polymer because the introduction of F into the conjugated backbone has lowered the HOMO and LUMO energy levels of the copolymer. Due to the values of V_{oc} are remarkable for the P2 polymer, the power conversion efficiencies of the solar cell for P2 are much improved.

4. Conclusions

Two D–A type copolymers based on DTS as the donor unit and nonfluorinated and fluorinated BO as the acceptor unit have been synthesized and employed as the donor materials in the active layer of BHJ-type polymer solar cells. As a result of annealing treatment at an optimum condition (125 °C/30 min), the PV cell performance of P1 was dramatically enhanced and the power conversion efficiency of device reached to 2.76%. Through the modification by fluorination on the BO units, the photovoltaic performance of P2 at 150 °C was much improved due to the increased J_{sc} and enhanced V_{oc} and the power conversion efficiency of the device reached 3.54% under white light illumination (100 mW/cm^2).

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