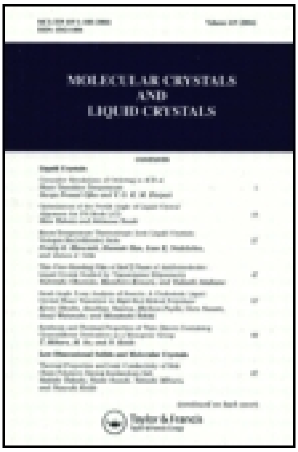

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Thermal Annealing Effect of Subphthalocyanine (SubPc) Donor Material in Organic Solar Cells

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We report that the S-shaped kink of current density-voltage (J-V) characteristics, which reduce fill factor of organic photovoltaic cells, can be removed by substrate heating during donor layer deposition process. Subphthalocyanine (SubPc) donor film in combination with buckminsterfullerene (C_{60}) acceptor film has been studied in a planar bilayer donor/acceptor heterojunction by J-V characterization under AM 1.5 simulated illuminations with various thicknesses of SubPc donor film. The substrate heating process enhances hole mobility of SubPc film, resulting 8.7% of efficiency enhancement with markedly improvement of S-shaped kink in J-V curves.

Keywords Organic photovoltaic cells; bilayer heterojunction; subphthalocyanine; substrate heating; S-shaped kink

Introduction

As the growing market demand for renewable energy sources, organic photovoltaic cells (OPVCs) are considered promising candidates due to its easy fabrication and potential for low-cost production. Since the first report on the planar bilayer donor/acceptor (D/A) heterojuction based OPVCs, [1] the main research has been focused on increasing the power conversion efficiency (PCE) through the use of new materials and device structures. However, when using new materials, unwanted S-shaped kink in the current density-voltage (J-V) characteristics, which can lead to a lowered FF, is frequently reported [2–5]. There are several explanations for the reason of these strange J-V characteristics. Recently, some paper said that S-shaped kink in the J-V curves are attributed to strong imbalanced charge carrier mobilities (hole mobility of donor and electron mobility of acceptor) larger than 10^2 in the comparable layer thickness [6].

In the case of SubPc/C_{60} based planar heterojunction solar cells, SubPc is a very useful material for the donor layer due to its deep HOMO level giving rise to high V_{OC} and PCE. However, the hole mobility of SubPc is considerably low as the order of 10^{-5} cm^2/(Vs)

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because its non planar chemical structure hinders good molecular packing. On the other hand, the electron mobility of C_{60} is relatively higher as the order of 10^{-2} $cm^2/(Vs)$ [7,8]. Because of this strong imbalance in charge carrier mobilities, S-shaped kink in J-V curve of SubPc/C_{60} based solar cells is occurred seriously. In the previous paper, there was a report that SubPC molecular packing can be improved by thermal annealing after thermal deposition of SubPc film [9]. In this paper we investigate the effects of substrate heating process to SubPc/C_{60} based planar heterojunction solar cells. We report that substrate heating process enhances hole mobility of SubPc film, resulting 8.7% of efficiency enhancement with markedly improvement of S-shaped kink in J-V curves.

Experimental

To fabricate organic solar devices, a clean glass substrate coated with a 150 nm thickness of ITO layer which having a sheet resistance 15 Ω/square was used. The active patterns of 2 × 2 mm^2 were formed by the photolithography and wet etching processes. The ultrasonic cleaned glass substrate in an isopropyl alcohol, acetone, and methanol was rinsed in deionized water, and finally was treated in ultraviolet (UV)-ozone for 3 min. The ozone gas was generated by using UV light to excite the oxygen in the air inside the chamber. The photovoltaic devices were fabricated by the vacuum evaporation of SubPc, C_{60}, and bathocuproine (BCP). All organic materials were deposited under a pressure of $\sim 10^{-7}$ Torr with a deposition rate of ~0.5 Å/s. Subsequently, 100 nm thickness of aluminum (Al) with a deposition rate of ~2.0 Å/s was deposited in vacuum chamber without breaking the vacuum and used as a cathode. A surface profiler was used to measure the thickness of organic thin films. A xenon light source was used to give simulated irradiance of 100 mW/cm^2 (equivalent to an AM1.5 irradiation) at the surface of the device. The measurements of J-V characteristics were carried out in a dark chamber with a window slit of 5 mm^2 area for illumination. For investigation of film surface morphology, atomic force microscopy (AFM) of Park systems XE-100 was used.

Results and Discussion

In this study, three OPVC devices were fabricated with ITO/SubPc (× nm)/C_{60} (31.5 nm)/BCP (8 nm)/Al (100 nm). The device structure of fabricated devices is shown Fig. 1. A reference device (Device 1) with 14.5 nm thickness of SubPc was fabricated without substrate heating during deposition process. Device B and C were fabricated with substrate heating at 150 degree Celsius during SubPc film deposition process. The difference between Device B and C is the layer thickness of SubPc film. Device B has 14.5 nm and Device C has 15.5 nm. J-V characteristics of three fabricated photovoltaic devices are shown in Fig. 2. Serious S-shaped kink behavior in J-V curve was observed in Device A since strong imbalance of charge carrier mobilities between SubPc and C_{60}. This S-shaped kink in Device B was disappeared with substrate heating process during deposition. With increasing the thickness of SubPc to 15.5 nm with substrate heating, S-shaped kink again appeared somewhat in Device C. The Device A shows short-circuit current (J_{SC}) of 5.17 mA/cm^2, open-circuit voltage (V_{OC}) of 0.78 V, Fill Factor (FF) of 57.0%, and PCE of 2.3% with serious S-shaped kink in J-V curves. On the other hand, the substrate heated Device B and C show J_{SC} of 4.90 and 4.68 mA/cm^2, V_{OC} of 0.80 and 0.83 V, FF of 64.5 and 56.2%, and PCE of 2.5 and 2.2%, respectively. Table 1 lists the J-V characteristics of all devices. Comparison with reference device (Device A), FF of Device B is remarkably increased from 57.0% to 64.5% due to ideal J-V curves and also PCE is increased from 2.3% to 2.5%.

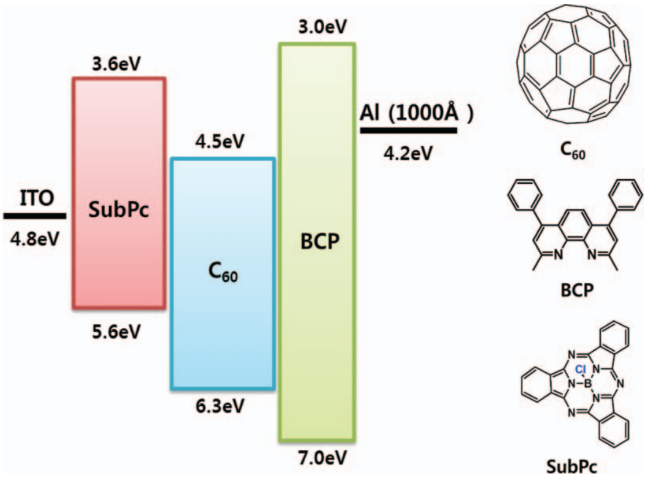

Figure 1. Device structure of fabricated solar cell devices.

These results indicate that mobility of SubPc film increases with substrate heating process during deposition. This enhanced carrier mobility of SubPc improves imbalance of charge carrier in SubPc/C_{60} organic photovoltaic cells. Device C compared with Device B shows decreased FF, PCE, and a slight S-shaped kink in J-V curve. This slight S-shaped kink is due to imbalance of charge accumulation by increased donor thickness, which means mobility increase of SubPc is not so significant.

To understand further the effect of substrate heating during SubPc layer deposition process, hole mobility and topology of SubPc film were measured by using space charge limited current (SCLC) and atomic force microscopy (AFM), respectively. The hole only devices which having the layer sequence of ITO (150 nm)/MoO_3 (1 nm)/SubPc (100 nm)/MoO_3 (10 nm)/Al (100 nm) were fabricated to evaluate the hole mobility of SubPc film with and without substrate heating during SubPc layer deposition. The thin MoO_3 layer on metal electrode was inserted to make ohmic contact so that SCLC region can be investigated clearly in these devices [10]. The carrier mobility to electric field dependence, μ (E), in our devices was plotted using the reported method [10]. By plotting logarithm of $J/E^2 = f(\sqrt{E})$, based on the following semiempirical SCLC equation accounting for the mobility

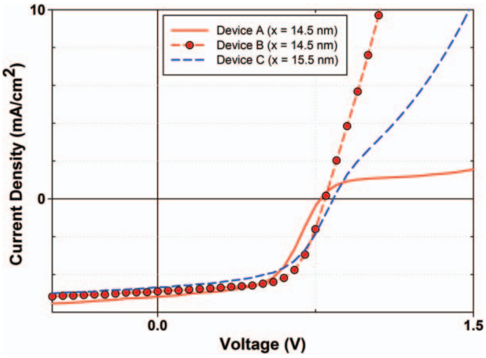

Figure 2. J-V characteristics of Device A, B, and C under 1 sun AM 1.5G simulated illumination.

Table 1. The short circuit current (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF), and power conversion efficiency (PCE) of Device A~C

Devices	SubPC Thickness	J_{SC} [mA/cm^2]	V_{OC} [V]	FF [%]	PCE [%]
Device A	x = 14.5 nm (without heating)	5.17	0.78	57.0	2.3
Device B	x = 14.5 nm (with heating)	4.90	0.80	64.5	2.5
Device C	x = 15.5 nm (with heating)	4.68	0.83	56.2	2.2

field-dependence: $J = \frac{9}{8}\varepsilon_r\varepsilon_0\frac{E^2}{L}\mu_0\exp(\beta\sqrt{E})$, where J is the density of current and E the electric field, the slope and y-intercept give the Poole-Frenkel factor β and the zero-field mobility μ_{o}, respectively. The relative dielectric constant ε_r is assumed to be 3 based on reference [10] and the permittivity of the free space ε_0 is 8.85×10^{-12} F/m. Based on Fig. 3, $\log(\mu) = f(\sqrt{E})$ and the Poole Frenkel equation, $\mu = \mu_0\exp(\beta\sqrt{E})$, the hole mobility of SubPc without substrate heating is estimated to be 9.1×10^{-5} cm^2/(Vs) at electric field of 0.3 MV/cm by this SCLC method. This value is well matched compared with reported

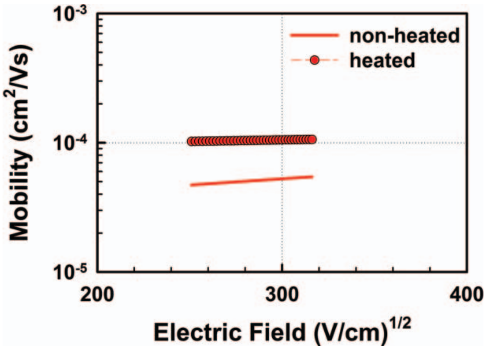

Figure 3. Carrier mobilities of SubPc films with and without substrate heating.

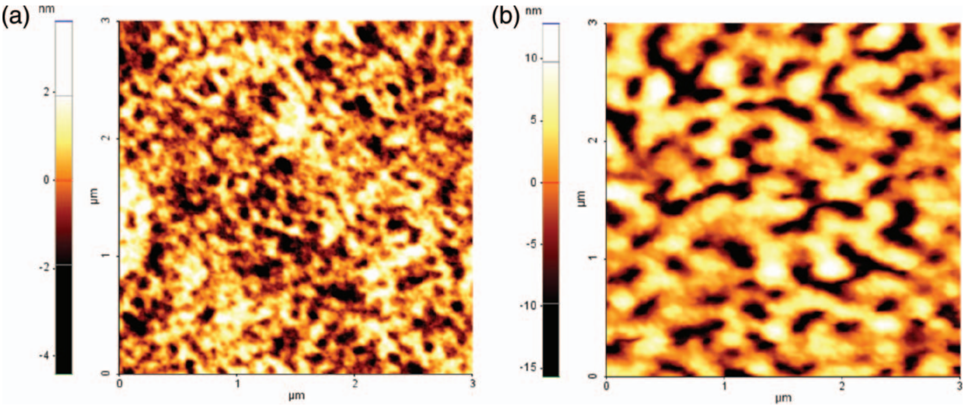

Figure 4. AFM images (3 um × 3 um area) of 14.5 nm of SubPc on ITO a) without substrate heating, and b) with substrate heating at 150°C during the SubPc layer deposition process, respectively.

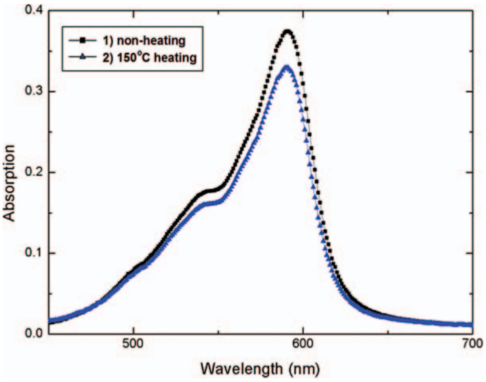

Figure 5. UV-visible absorption spectra of 14.5 nm SubPc film on ITO with and without substrate heating.

SubPc mobility value of $\sim 10^{-5}$ cm^2/(Vs) [8]. On the other hand, the hole mobility of substrate heated one shows a higher value which is estimated to be 1.2×10^{-4} cm^2/(Vs) at electric field of 0.3 MV/cm. This result implies that substrate heating during deposition process results in denser molecular packing of SubPc film. Real mobility increase by substrate heating is not quite high, which is well matched to our real S-kink results of Device B and C.

The AFM images were taken from 14.5 nm thickness of SubPc on ITO both with and without substrate heating. The AFM images of both SubPc films with and without substrate heating are shown in Fig. 4. It is clear that substrate heated SubPc film is more aggregative than that of counterpart. After substrate heating, the peak to value and root mean square roughness (rms) of SubPc film are enhanced from 8.0 nm to 27.9 nm and from 1.0 nm to 4.7 nm, respectively. This topology change is well agreement with enhancement of mobility.

Indeed, interesting S-kink improvement by substrate heating process is observed in SubPc/C60 OPVCs. However, substrate heated devices (Device B and C) show some loss in J_{SC}. This mainly relates to decreased interface of donor and acceptor or absorption decrease of SubPc. In our device, surface roughness of substrate heated SubPc film is much rougher. Photocurrent generation at the donor accepter interface is not a problem in our Device B and C. The absorption spectra of SubPc with and without substrate heating were investigated. Figure 5 shows UV-visible absorption spectra of 14.5 nm SubPc films on ITO with and without substrate heating. When SubPc film is heated during the deposition, light absorbance is decreased due to different molecular packing situation. Lower light absorption results in decrease of Jsc in substrate heated OPVCs.

Conclusions

In this study, the S-shaped kink of J-V characteristics in SubPc: C_{60} OPVCs is removed by substrate heating during donor layer deposition process. Increased hole mobility and higher molecular packing of SubPc film by substrate heating process could remove this S-shaped kink with improvement of charge unbalance in OPVCs. SubPc: C_{60} OPVC fabricated by substrate heating during SubPc deposition has about 8.7% efficiency enhancement with significantly improvement of FF. However, there is some decrease of Jsc owing to some optical loss.

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