



Impact of solution casting temperature on power conversion efficiencies of bulk heterojunction organic solar cells



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ABSTRACT

The power conversion efficiency (PCE) of P3HT:PCBM bulk heterojunction solar cells highly depend on the processing conditions of the blend film. Among many factors investigated, the effect of blend solution temperature for spin casting on PCE of solar cells is currently missing in the literature. In this work, we have systematically analyzed the effect of solution casting temperature on solar cell performance of P3HT:PCBM bulk heterojunction layer. We have found that the ideal casting temperature is $\sim 60^\circ\text{C}$ for the blends. Further annealing of the blend does not change the surface morphology substantially at the ideal temperature as opposed to the films prepared at other temperatures.

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1. Introduction

Organic photovoltaic (OPV) devices have the advantage of low cost fabrication and easy processing. However the highest efficiencies of the best OPVs are currently in the teens, well short of the theoretical limit of 23% [1]. Power conversion efficiencies (PCEs) of OPV devices can be improved in various ways such as utilizing novel materials for high performing active layer, changing device architecture for optimum photovoltaic activity, and optimizing deposition parameters and conditions of each layer in device structure [2–7].

There have been a number of different studies done in which the fabrication methodology of the solar cells has been varied in hopes of finding a way to improve solar cells without having to change the components of the bulk heterojunction layer. For instance, the change in the rate of aluminum cathode deposition has been found to increase the PCE of a poly(3-hexylthiophene):[6,6]-phenyl C61 butyric acid methyl ester (P3HT:PCBM) device from 1.35% to 3.6% [8]. The choice of solvent used for spin coating has been studied by a number of groups. The solubility of the donor and acceptor components and the boiling temperature of solvents for spin casting are both important factors for determining an ideal solvent. Shaheen et al. found that using chlorobenzene rather than toluene resulted in a 2.5% efficiency increase for films of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene]

(MDMO-PPV):PCBM blends [9]. This research was expanded upon by Park et al. who varied the solvent of a poly[N-9'-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) and PCBM blend using chloroform, chlorobenzene, and 1,2-dichlorobenzene (ODCB) solvents [10]. They found that use of ODCB resulted in a higher efficiency device than the other solvents.

The ratio of acceptor and donor in the blend has also been investigated. It is essential to have a high enough acceptor concentration to ensure efficient transport of charge carriers towards electrodes. However, there cannot be too high of a concentration of PCBM, because it has been found to disrupt the crystallization of P3HT during the film formation [11,12]. The ideal ratio has been found to vary not only based on solvent, but even from laboratory to laboratory. For instance, two different groups have reported the ideal ratio for P3HT:PCBM blend as 7:3 [13] and 1:0.7 [14].

Thermal annealing has been found to induce more extensive crystallization and induce the formation of interconnected fibrils of P3HT [15]. Camaioni et al. found a 3–4 fold increase in power conversion efficiency after a mild thermal treatment ($50^\circ\text{--}60^\circ\text{C}$) with a P3HT:fulleropyrrolidine-based solar cell [16]. Padinger et al. investigated annealing after the deposition of the aluminum cathode of P3HT:PCBM devices and were able to obtain an efficiency of 3.5% [17]. Slow annealed 50 nm thick P3HT:PCBM blend incorporated device has shown fill factors approaching 73% with a PCE of 3.80% [18]. Lin et al. found that low temperature drying (-5°C) and subsequent annealing of P3HT:PCBM active layer not only leads high power conversion efficiency in devices

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but also improved lifetime due to enhanced nucleation of P3HT crystallites [19]. In a similar study, Sanyal et al. reported that drying the active layer at low temperature leads to better nanomorphology with a finer interpenetrating network in doctor bladed solar cells [20]. Thus, the device fabrication procedure and relevant parameters play a huge role in obtaining optimal photovoltaic performance of organic solar cells.

There are numerous studies in the literature that deal with the optimization of device fabrication procedures as exemplified by several reports above. Yet to our knowledge none of those studies focus on the effect of solvent temperature during deposition of the active layer. Here, we investigate this phenomenon by systematically investigating cells incorporating P3HT:PCBM blends dissolved in ODCB in order to determine the impact of solvent temperature during spin coating of the active layer. Temperature of the blend solution has been varied and both annealed and non-annealed devices have been prepared for comparison of photovoltaic parameters. This study is not intended to fabricate the highest efficiency solar cell, but to determine the effect of solvent casting temperature on PCEs of P3HT:PCBM incorporated organic solar cells.

2. Experimental

Organic solar cells were fabricated on patterned indium tin oxide (ITO) glasses with a sheet resistance of $20 \Omega/\text{sq}$. The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropanol, and then treated in a bench-top plasma cleaner (PE-50 bench top cleaner, the Plasma Etch, Inc., USA) for 2 min. Poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) (Clevios P VP Al 4083 H. C. Stark, Germany) solution was filtered through a $0.45 \mu\text{m}$ filter and then spin coated at 4000 rpm for 60 s on the ITO coated glass substrate. Subsequently, the PEDOT:PSS layer was baked at 100°C for 40 min in the air. The PEDOT:PSS coated substrates were transferred to a N_2 filled glovebox. A blend solution of P3HT (Rieke Metals, Inc., MW = 17kDa) and PCBM (Nano-C) at a concentration of 25 mg/mL (1:1, w/w) in 0.25 mL of ODCB was prepared. The solution was heated and agitated at different temperatures for three hours before spin coating on top of PEDOT:PSS layer with a spinning speed of 475 rpm for 45 s. In order to ensure homogeneous heating of blend, an aluminum block with holes that can accommodate the vial with blend solution on a hot plate was used.

After an hour of solvent aging, half of the P3HT:PCBM blend films were thermally annealed at 105°C for 5 min. The solar cell was capped with a cathode consisting of LiF ($\sim 1 \text{ nm}$) and Al ($\sim 100 \text{ nm}$), which were thermally evaporated on the active layer under a shadow mask in a base pressure of 1×10^{-6} mbar. The device active area was $\sim 7.9 \text{ mm}^2$. The J - V measurement of the devices was conducted on a computer controlled Keithley 2400 source meter. The J - V measurement system uses a solar simulator with a Class-A match to the AM1.5 Global Reference Spectrum. It was calibrated with KG5-filtered silicon reference cell with calibration traceable to NREL and NIST. Film absorption spectra of the blend films were compared with a Varian Cary 50 Bio UV/vis spectrophotometer. Atomic force microscopy (AFM) images of the samples were recorded on a Veeco DI-3100 atomic force microscope.

3. Results and discussion

The optical absorbance profiles of the annealed and non-annealed films are given in Fig. 1. Non-annealed blend films show a featureless broad absorption band located at 460 nm. Optical density of the non-annealed films decreases as the casting temperature is increased from 35°C to 105°C . This is not

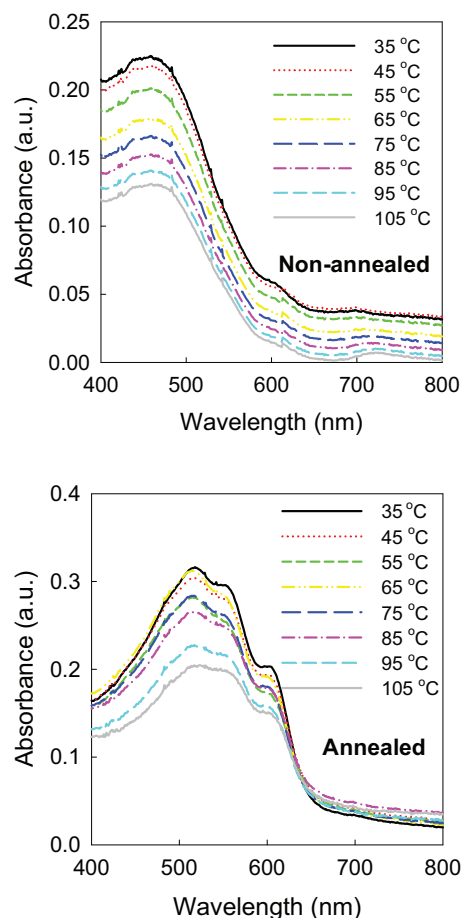


Fig. 1. UV optical absorbance spectra of films cast from blend solutions at various temperatures. (For interpretation of the references to color in the text, the reader is referred to the web version of this article.)

unexpected since the viscosity of the solution decreases with increasing temperature. Thus, the blend solution with low viscosity at high temperature probably causes the formation of thinner films during spin coating process. The optical density of the non-annealed film at 35°C casting temperature is almost twice as much that of film prepared at 105°C casting temperature. However, that does not necessarily mean that the thickness is also halved for 105°C non-annealed film. The optical absorbance of P3HT:PCBM blend is mostly dominated by absorption coming from P3HT fraction since the molecular absorption coefficient of PCBM is quite low compared to that of P3HT. Thus, one may speculate that the film thickness is somewhat smaller for the films prepared at high casting temperatures.

The optical profiles of annealed films are also given in Fig. 1. Upon annealing of the samples at 105°C , the absorption spectra shift to the red with maxima around 515 nm while gaining vibronic structure. The sharpness of vibronic bands indicates the extent of P3HT ordering in the blend film. It can be said that for the films up to 85°C casting temperature, the vibronic structure is similar among the films. With films prepared at 95 and 105°C casting temperatures, the vibronic structure becomes less distinct, hinting possible decrease in the crystallization of P3HT chains within the presence of PCBM. The optical density of the films at absorption maxima increases by 30–40% upon annealing. It is noteworthy to mention that the annealed film absorption spectral intensity decreases with an increase in temperature, except for 65°C annealed sample. The blend absorption spectrum measured at 65°C resembles very much like that of 35°C annealed film. The film

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