SELECTED ASPECTS OF ORGANIC SOLAR CELL PREPARATION

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1. Introduction

Recent progress in organic solar cell (OSC) power conversion efficiency (PCE) has been stimulated by advances in knowledge of both physical mechanism of charge generation and transport in organic semiconductors [1], and development of new organic materials [2]. Besides their markedly reduced production cost in comparison with conventional types, their flexibility, low weight and transparency belong to significant advantages as well. The active layer of a typical organic solar cell is blended of two components: an electron donor and an electron acceptor, which generate free charges from incident photons via exciton separation at the interface [3]. It was found that −besides tailoring electronic properties−the bulk film morphology of the blend is crucial for the photovoltaic performance.

This paper focuses on the preparation of polymer solar cells based on the blend of P3HT (Poly(3-hexylthiophene-2,5-diyl)) semiconductor and PCBM (Phenyl-C61-butyric acid methyl ester) in the role of donor and acceptor semiconductors, respectively. An optimization of selected technological steps of spin-coated P3HT:PCBM blend, particularly P3HT:PCBM weight ratio and post deposition annealing treatments are reported. The parameter optimization yields solar cells prepared routinely with PCE of 2.9 %.

2. Sample preparation and characterization

Prepared OSCs consist of glass substrate covered with indium tin oxide (ITO) layer, active layer of the organic blend (typically of 140 nm), and back cathode electrode. Solar cell preparation includes substrate cleaning (ultrasonically in acetone and isopropanol and UV irradiated), solvent preparation, spin-coating of active layer, post deposition annealing (solvent and/or thermal), and back electrode typically consisted of 15 nm of Ca followed with 150 nm of Ag.

2.1 Spin coating

In order to prevent material oxidation, spin-coated active layers were prepared in nitrogen atmosphere in glove box. Cleanness of substrates and glove−box ambient, and filtration of solvent are necessary requirements to prevent active layer inhomogenities deteriorating the layer quality. Important parameters of the spin-coating are the solution concentration, the rotational speed determining the thickness of active layer, and duration of spin coating determining the wetness of the deposited layer. The blend solutions with different P3HT:PCBM ratio (1:2, 1:1, 1.5:1, 2:1, 4:1) were prepared in 1,2-dichlorobenzene with 2 weight % concentration.

2.2 Annealing

Post-deposition annealing treatments of the active layer belong to crucial technological steps which determine the final operating efficiency of OSC. The annealing can increase the crystallinity of P3HT and also determines the separation of the P3HT and fullerenes and improves the bulk film morphology. There were used two annealing procedures. The first procedure is solvent annealing, which refers to slowed drying of still wet film when the spin coating is stopped before entire drying of the film. Specifically, the time of the spin-coating was shortened followed by slowed-down drying of the layer in enclosed Petri dish at room temperature for 30 min. The thermal annealing refers to the annealing at 110°C for 5 min in inert atmosphere. The separation of P3HT and PCBM phases by means of the annealing eliminates isolated domains, which act as charge traps [4]. On the other hand, the excessive annealing induces the decrease of the area of donor-acceptor interface, resulting in the decrease in the power conversion efficiency.

2.2 Sample characterization

Optical absorbance of active layer with different P3HT:PCBM weight ratios and annealing treatments was measured using Shimadzu UV-Vis-NIR spectrophotometer in the double beam operation with ITO substrate as a reference sample in one light path. To determine the structural modification and to correlate it with optical properties grazing-incidence X-ray diffraction (GIXRD) measurement were performed on the same samples as for UV-Vis absorption. Namely, correlation of these two diagnostic techniques represents a useful tool for optimization of active layer microstructure, which vitally determines electro-optical properties of the solar cell. Desired microstructure is indicated in absorption spectra as an increase of the absorbance due to better resolved vibronic sidebands at 560 nm and 610 nm of P3HT and in GIXRD patterns with an increase of the diffraction (100), (200), and (300) peaks owing to the improved crystallinity of P3HT chains [5].

Solar cells incorporating the active layer characterized beforehand by optical absorbance and X-ray diffraction were evaluated by I-V measurement under standard solar spectrum illumination (AM 1.5) G with 100 mWcm^{-2} at ambient temperature of 25°C. Basic parameters, such as the open circuit voltage, V_{oc}, the short circuit current, J_{sc}, the fill factor, FF, and the PCE, η, were determined. Each sample consisted of several OSCs with an area of 5-7 mm^2.

3. Results and discussion

As a first step, spin-coating parameters (spin-coating rotational speed and critical spin-coating time) of the active layer were optimized. The critical spin-coating time represents time when layer becomes dry during spin-coating. Importantly, time of spin-coating has to be short enough, so that spin-coated layer is sufficiently wet, otherwise the solvent annealing is ineffective. On the other hand spin-coating should be long enough to ensure the homogenous layer. Layer drying was determined according to color changes. These dependences are useful for deposition of the active layer with targeted thickness. The first optimization step led to setting the thickness of the active layer to 130 nm at the spin-coating rotational speed of 25 revolutions per second (rps) and spin-coating time of 45s.

3.1 P3HT:PCBM weight ratio dependence

The morphology (the donor-acceptor phase separation) determining exciton dissociation and proper charge transport channels for collecting the electrons and holes is dependent on the P3HT:PCBM weight ratio. Besides well-developed vibronic sidebands at 560 nm and 610 nm of P3HT, proportion with the peak at 340 nm of PCBM has to be kept for optimal morphology (Fig. 1a). The corresponding GIXRD patterns (Fig. 1b) show that the

most developed crystallinity of P3HT phase still preserving the PCBM phase was achieved for the ratio of 1.5:1. Note that these layers were solvent and thermal annealed (section 3.2).
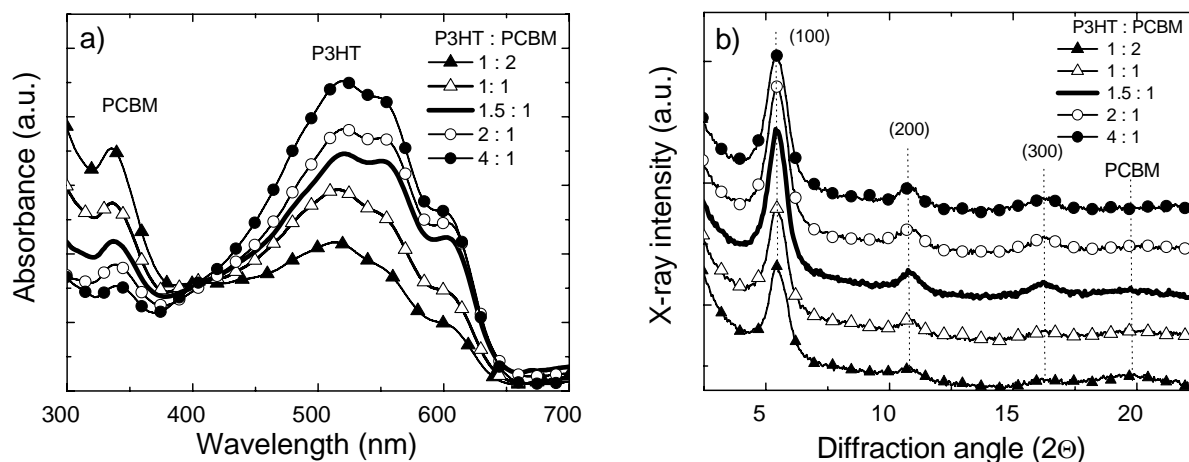

Fig. 1: *a) UV-Vis absorption spectra of blend layers with different P3HT:PCBM weight ratio.); b) Grazing-incidence X-ray diffraction patterns measured on the same blend layers as in Fig.1a). The (100), (200), and (300) diffraction peaks correspond to P3HT.*

3.2 The effect of the solvent and thermal annealings

The effect of the solvent and thermal annealings has been studied on the active layer with P3HT:PCBM weight ratio of 1.5:1 and thickness of 135 nm. Annealings induce an enhanced molecular mobility within the blend, enabling spatial rearrangement of the polymer chains and fullerene molecules. Thus, P3HT chains form higher crystallinity, which is reflected in both absorption (Fig. 2a) through the more pronounced shoulder centered at 610 nm, which has been assigned to a highly interchain-delocalized excitation [6], and more pronounced peaks in GIXRD patterns (Fig. 2b). The intensity of the vibronic shoulder has previously been correlated with the degree of P3HT crystallinity [7].

The I-V characteristics of related OSCs are shown in Fig. 3 and their parameters are summarized in Tab. 1. Even though both annealing processes improve the solar cell parameters, the solvent annealing is superior to the thermal annealing.
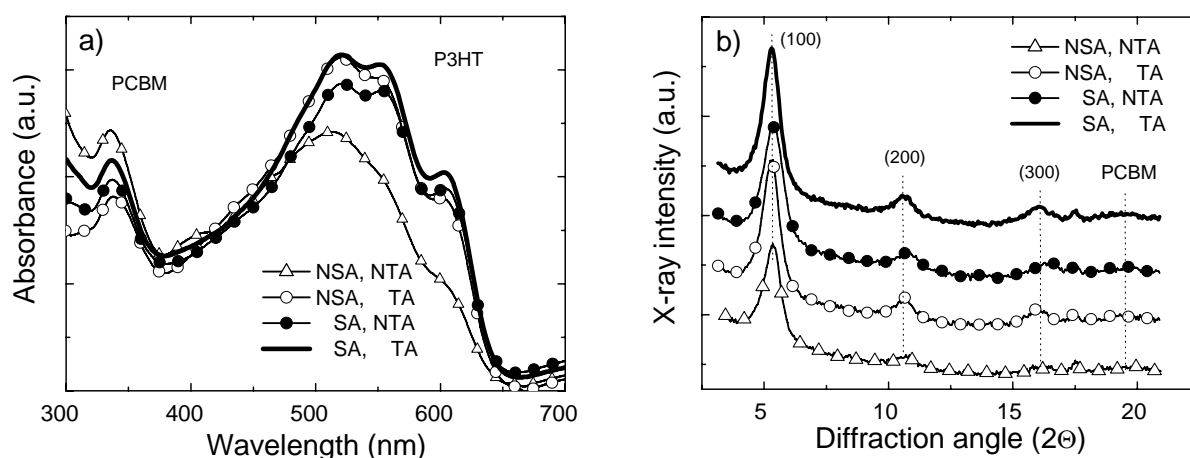

Fig. 2: *Evolution of UV-Vis absorption (a) and grazing-incidence X-ray diffraction (b) measured on P3HT:PCBM blend layer with weight ratio 1.5:1 after different combinations of annealings: Not Solvent / Not Thermal (NSA / NTA), Not Solvent / Thermal (NSA / TA), Solvent / Not Thermal (SA / NTA), Solvent / Thermal (SA / TA) Annealed.*
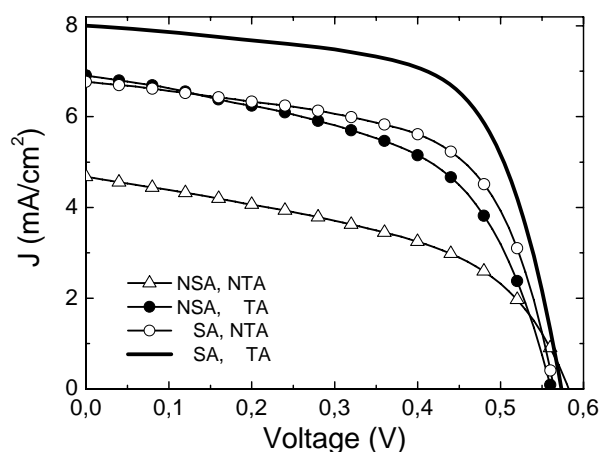
Fig. 3: *Light I-V characteristics (illumination at 100 mWcm^{-2}, AM 1.5) of OSCs prepared by different combinations of annealings: Not Solvent / Not Thermal (NSA / NTA), Not Solvent / Thermal (NSA / TA), Solvent / Not Thermal (SA / NTA), Solvent / Thermal (SA / TA) Annealed.*

Tab. 1. *Parameters of OSCs prepared by different combinations of annealings: Not Solvent / Not Thermal (NSA / NTA), Not Solvent / Thermal (NSA / TA), Solvent / Not Thermal (SA / NTA), Solvent / Thermal (SA / TA) Annealed.*

Annealing treatments		FF [%]	V_{oc} [V]	J_{sc} [mA/cm^2]	PCE [%]
NSA	NTA	48	0.58	4.7	**1.3**
	TA	54	0.56	6.9	**2.1**
SA	NTA	60	0.56	6.8	**2.3**
	TA	64	0.57	8.0	**2.9**

4. Conclusion

An optimization of chosen technological parameters of P3HT:PCBM based solar cells in terms of their basic parameters has been carried out. The thickness optimum of the active layer was found about 130 nm. The optimal spin-coating parameters for 2 wt% blend solution in dichlorobenzene processed at 25°C are as follows: the spin-coating rotational speed around 25 rps and spin-coating time around 45 s. The optimal P3HT:PCBM weight ratio was found to be about 1.5:1 (60 wt% P3HT). Both the solvent annealing and the thermal annealing had a beneficial effect on the parameters of the solar cell. The former method has proved to be superior. The optimization of these parameters yields solar cells prepared routinely with the power-conversion efficiency of 2.9 %.

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