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Effect of the active layer thickness on the device performance of polymer solar cells having [60]PCBM and [70]PCBM as electron acceptor

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Abstract

Recently it has been shown that the use of [70]PCBM as electron acceptor in polymer solar cells can improve the current output of such devices because C₇₀ derivatives have a stronger and broader absorption compared to C₆₀ ones. In this work we studied the influence of the fullerene on the optical behaviour of the photoactive blend film of a polymer solar cell. We simulated the optical absorption of the active layer inside the device structure and we calculated the maximum achievable short circuit current density with the aim to correlate the variation of the optical constants to the output current of the device. Afterward, we realized several polymer solar cells and we proved the theoretical findings.

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Keywords: Polymer solar cells; optical modelling; fullerene; Short circuit current

1. Introduction

In the last years, polymer solar cells have attracted a lot of interest due to their advantages of low-cost manufacturing, light-weight and good flexibility [1-3]. Actually the most promising device architecture is based on the bulk heterojunction (BHJ) concept where a semiconducting polymer is intimately mixed with a fullerene derivative giving a nanometer phase separation [4]. The active layer is sandwiched between two electrodes with different work functions. The most studied material combination is based on

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a blend of the the regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester ([60]PCBM) (electron acceptor). Using these materials, polymer solar cells with a power conversion efficiency (PCE) above 5% have been realized [5].

The short circuit current (J_{sc}) of these cells is strictly related to the absorption of the blend film. Recently it has been shown that the use of [70]PCBM as electron acceptor can improve the current output of such device because C_{70} derivatives have a stronger and broader absorption compared to C_{60} ones [6, 7]. The aim of this work is to study the influence of the fullerene ([60]PCBM or [70]PCBM) on the optical behaviour of the photoactive blend film of a polymer solar cell. We have determined the optical constants of polymer blend film based on P3HT and [60]PCBM or [70]PCBM. We simulated the optical absorption of the active layer inside the device structure and we calculated the maximum achievable J_{sc} with the aim to correlate the variation of the optical constants to the output current of the device. Afterward, we realized several polymer solar cells (glass/ITO/PEDOT:PSS/P3HT:[60 or 70]PCBM/Al) varying the thickness of the blend film in order to prove the theoretical findings.

2. Experimental

2.1. Device realization

The photovoltaic BHJ devices, having the structure glass/ITO/PEDOT:PSS/P3HT:[60 or 70]PCBM/Al, were prepared according to the following procedure.

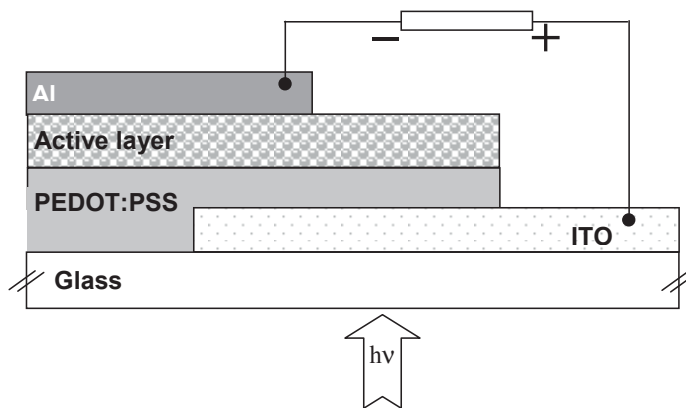


Fig. 1. Schematic device structure of the investigated bulk heterojunction solar cell. The active layer, a blend film of P3HT and [60]PCBM or [70]PCBM, is sandwiched between two contacts: an indium-tin-oxide electrode coated with a hole transport layer PEDOT:PSS and an aluminium top electrode.

The ITO coated Corning®1737 glass substrates, purchased from Delta Technologies, LTD, with a sheet resistance lower than $15 \Omega/\square$ were first cleaned with detergent, ultrasonicated in acetone and isopropanol, and subsequently dried in an oven. After a selective etching of a part of the ITO to define the front electrode, films of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS), purchased from HC Starck (Baytron P) were spin coated at 5000 rpm, after passing through a $0.45 \mu\text{m}$ filter. The thickness of the PEDOT:PSS layer was 50 nm. The samples were dried for 10' min at 140°C in air. The active layers containing a blend 1:0.8 of P3HT and [60 or 70]PCBM were spin coated at 600 rpm from a chlorobenzene solution, which had been stirring on a hotplate at 50°C for 48 h. By varying the concentration of the donor polymer ($10 \div 20 \text{ mg/mL}$), we obtained blend films with a thickness between

70–250 nm. The Al top electrodes were deposited by thermal evaporation in ultra-high vacuum (10^{-7} mbar) using a shadow mask to define the active area of the device (80 mm^2).

All the polymer solar cells were characterized by means of external quantum efficiency (EQE) and current voltage (IV) measurements performed in the dark and under simulated AM 1.5G illumination. Both IV dark and light characteristics were measured with a Keithley 236 source measure unit (Keithley Instruments Inc., Cleveland, USA). The voltage ramp rate, controlled by a PC program, was of 10mV/s from positive to negative potential. Simulated AM 1.5G white light illumination was provided by a class A Spectrosun® Solar Simulator, Model X25, MARK II (Spectrolab, USA) equipped with a AM1.5G filter, based on a Xenon lamp (Osram 3 kW, 3000W/H OSR), and its intensity was calibrated using a mono-Si reference cell SC080 (certified by Fraunhofer ISE) for 1 sunlight intensity of 100 mW/cm^2 . All the photovoltaic properties were recorded in ambient air at room temperature ($\sim 25 \text{ }^\circ\text{C}$). UV–VIS spectroscopic measurements were performed using a Perkin-Elmer Lambda 900 spectrophotometer.

2.2. Maximum J_{sc} determination

The values of the refractive index (n) and extinction coefficient (k) were determined by mathematical inversion applied to spectrophotometric measurements of reflectance (R) and transmittance (T) [8, 9]. This method enables the extraction of the dielectric function in the whole measured spectral range of R and T . These spectra were measured by a double beam Perkin-Elmer mod. Lambda 900 instrument equipped with a 150 mm integrating sphere. The spectral range of this instrument is 200–2500 nm.

The optical model used for the mathematical inversion is formed by an air/thin film/substrate/air structure. This structure was realized by depositing a thin film of the material to be optically characterized on a transparent substrate such as in our case the Corning®1737F.

The optical constants of all the materials of the considered device structure (glass substrate, ITO, PEDOT:PSS, P3HT:[60]PCBM, P3HT:[70]PCBM and Al) have been determined and reported in previous works [8, 9].

The optical modeling of the polymer solar cell was carried out using a home-made simulation program based on the transfer matrix formalism [10]. The reflection and transmission of the device and the absorption of the layers were computed by using this optical model, where each layer is described by a transfer matrix constructed using the thickness and the complex refractive index of the layer. The interference mechanism implemented by the simulation program is either coherent or incoherent as a function of the layer thickness.

Afterward, the total number of absorbed photons inside the photoactive layer is calculated multiplying this distribution with the AM1.5G spectrum and integrating over the wavelengths (from 300 to 800nm). The maximum current density can be obtained assuming that each absorbed photons results in a collected electron (i.e. the internal quantum efficiency, IQE, equals one); in addition, all the layers are considered homogeneous and all the interfaces flat.

3. Results and discussion

In order to evaluate the impact of the optical constants of the blend films on the performances of the solar cells, we performed the optical modelling of the device.

Starting from the optical constants of all the layers of the investigated device structure, we simulated the effective absorption in the photoactive layer for different film thicknesses (up to 300 nm). The ITO, PEDOT:PSS and Al layer thicknesses were set to 130, 50 and 100 nm respectively. Then, we calculated the J_{sc} of the device as described before.

The calculated J_{sc} as a function of the active layer thickness for the two investigated samples (P3HT:[60]PCBM and P3HT:[70]PCBM annealed at 150°C) is shown in Fig. 2. Since the electrical

losses of the device are neglected, the calculated values can be considered as an upper limit for the real achievable current.

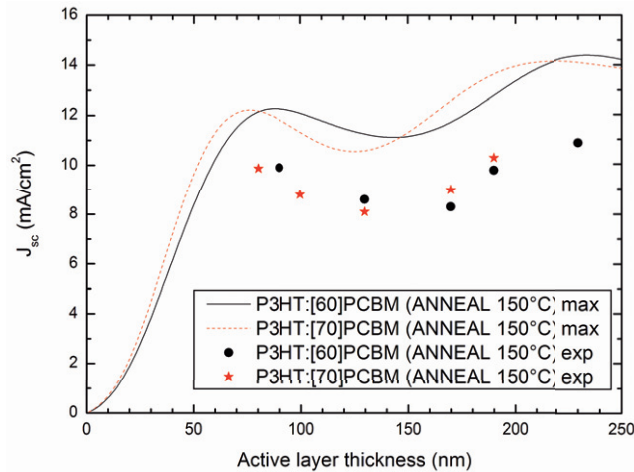


Fig. 2. Calculated J_{sc} (lines) as a function of the active layer thickness assuming an internal quantum efficiency of unity for devices based on P3HT:[60]PCBM and P3HT:[70]PCBM blend films annealed at 150 °C. The points represent the experimental J_{sc} of the devices.

The maxima of both curves are shifted (i.e. the optimum active layer thickness for each blend is different) but the J_{sc} is almost equal for the first maxima around 80nm and for the second ones around 220nm. In addition, there are thickness ranges where the J_{sc} is greater for P3HT:[60]PCBM blend (i.e. between 80 and 145nm and between 220 and 280nm) and viceversa (i.e. until 80nm and between 145 and 220nm).

In order to prove the theoretical findings, we realized several polymer solar cells (glass/ITO/PEDOT:PSS/P3HT:[60 or 70]PCBM/Al) varying the thickness of the blend film in the range 70-250nm. The realized devices were characterized by EQE and current voltage measurements performed in the dark and under simulated AM 1.5G illumination (100 mW/cm²). The best realized solar cell (with a 190 nm thick blend film of P3HT:[60]PCBM) exhibited an efficiency of 2.60%, J_{sc} of 9.87 mA/cm², V_{oc} of 0.640 V, and fill factor (FF) of 41.1% under simulated light (AM 1.5G, 100mW/cm²). The measured J_{sc} for the devices based on P3HT:[60]PCBM and P3HT:[70]PCBM are reported in Fig. 2. All the experimental points are lowered compared to the theoretical one because the electrical losses of the devices but the trend is similar to the one calculated. The FF value is lower compared to the best devices reported in literature due to non-optimal value of the series resistance. Moreover, the low FF value also indicates high recombination inside the blends, which limits the performance of thicker devices: in fact the gap between the experimental points and the theoretical ones increases with the blend thickness (i.e. there is an increase of the electrical losses). Nevertheless, for a given blend thickness, the electrical losses are almost the same between the two investigated blends. The greater current for P3HT:[70]PCBM based device reported in [7] is probably due to a non optimal blend thickness selection for the active layer.

4. Conclusions

In this paper we have investigated the effect of the optical constants of P3HT:[60]PCBM and P3HT:[70]PCBM blend films on the current output of the corresponding devices. We calculated the maximum J_{sc} achievable in a polymer solar cell as a function of the active layer thickness. We found that there are thickness ranges where the J_{sc} is greater for P3HT:[60]PCBM blend (i.e. between 80 and 145nm and between 220 and 280nm) and viceversa (i.e. until 80nm and between 145 and 220nm). Afterward, we

realized several polymer solar cells (glass/ITO/PEDOT:PSS/P3HT:[60 or 70]PCBM/Al) varying the thickness of the blend film in order to prove the theoretical findings.

Acknowledgements

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