Solar Energy Materials & Solar Cells 94 (2010) 465–470

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

# Thickness dependence and solution-degradation effect in poly (3-hexylthiophene):phenyl-C61-butyric acid methyl ester based solar cells

Hui Jin*, Juuso Olkkonen, Markus Tuomikoski, Pälvi Kopola, Arto Maaninen, Jukka Hast

*VTT Technical Research Centre of Finland, P. O. Box 1100, FI-90571 Oulu, Finland*

ARTICLE INFO

*Article history:*
Received 26 August 2009
Received in revised form
4 November 2009
Accepted 5 November 2009
Available online 1 December 2009

*Keywords:*
Photovoltaic
Polymer
Fullerene
Film thickness
Degradation

ABSTRACT

The performance of bulk-heterojunction solar cells made with poly(3-hexylthiophene) (P3HT) as the donor and phenyl-C61-butyric acid methyl ester (PCBM) as the acceptor depends strongly on various factors in fabrication processes. This work studies the effect of the thickness of the P3HT:PCBM layer produced in the spin coating process on photovoltaic performances. Thickness dependent optical absorption in P3HT:PCBM layer is numerically modelled and the results are compared with experimental data. In addition, it is analyzed how degradation of air-exposed P3HT:PCBM blends depends on the storage time in nitrogen atmosphere.



## 1. Introduction

As a potential alternative for low-cost renewable energy sources, polymer-based solar cells have been widely studied and rapidly developed in recent years. Poly (3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) have become promising materials exhibiting power conversion efficiency about 4% [1,2]. On the road to improve the efficiency of polymer-based solar cells, various attempts have been taken in the fabrication processes, such as thermal annealing, solvent annealing, post-treatment and so on. In fact, processing in the fabrication plays an extremely important role for improving the performance of plastic solar cells.[3,4]

The thickness of P3HT:PCBM film is related to the absorption efficiency and the charge transport of solar cells, and the optimal thickness of P3HT:PCBM film has been reported to be around 210–230 nm [5]. However, research groups have used various thicknesses between 80 and 220 nm to obtain the similar efficiencies [6–8]. In this work, the thickness dependent optical absorption in P3HT:PCBM layer was modelled. It was found that the modelled data agreed well with the experimental results.

The degradation of P3HT:PCBM samples have been investigated by several research groups [9–13]. However, the degradation mechanism of the photoactive solutions and its effect on the resulting solar cells is still ambiguous and worth further study, since it would be closely involved with the development of printing ink, the fabrication of organic photovoltaic modules and even the roll-to-roll manufacture of flexible polymer solar cells [14–17]. In this work, the effect of air exposure of blends on the fabricated solar cells was analyzed via current–voltage characteristics, optical absorption spectra and Raman spectroscopy.

## 2. Experimental details

The indium tin oxide (ITO)-coated glass substrates were cleaned by ultrasonic treatment in deionized water, acetone and isopropyl alcohol sequentially, followed by N2-gas blowing to dry. After the UV–ozone treatment for 3 min, the square resistance of ITO-coated glass can be 16–17 Ω/κ. The solution of poly(3,4-ethylenedioxythiophene): poly(styrenesulphonate) (PEDOT:PSS) (Clevios P VP Al 4083) was filtered by 0.45 μm PVDF filter and then spin-coated on the UV–ozone treated ITO glass. The resulting PEDOT:PSS film was heated on a hot plate at 150 °C for 20 min and the thickness was about 35–40 nm, measured by Veeco Dektak 150. P3HT and PCBM were directly used to be blended as purchased from Rieke Metals and Nano-C. The P3HT:PCBM weight ratio was about 1:1 (if no special explanation). The solutions were prepared by dissolving solid materials into dried 1,2-dichlorobenzene (DCB) in a glove box. Immediately after the solution passed through 0.45 μm Acrodisc filter, the photoactive layers were spin-coated on PEDOT:PSS film in the air. When the colour of photoactive layers turned to dark purple, the samples were transferred to the glove box for performing a thermal annealing process and then put in the

* Corresponding author. Tel.: +358 40 4865373, fax: +358 20 722 2320.
*E-mail address:* hui.jin@vtt.fi (H. Jin).

0927-0248/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2009.11.007

evaporator to deposit metal top electrodes. If there is no special explanation, thermal annealing was processed at 110 °C for 5 min and the cathode consisted of Ca (25 nm) and Ag (80 nm). The shadow mask of ~10 mm$^2$ utilized during cathode deposition defined the active area of the device. All devices were encapsulated by UV-cured epoxy (DELO 681) in the glove box with dry nitrogen atmosphere.

The thickness of photoactive layer was controlled by setting the spin speed and the concentration of the solution. The P3HT master solutions are 17, 20, 22 and 25 mg/ml in DCB. PCBM was dissolved in the P3HT master solutions with the ratio of about 1:0.95 (P3HT:PCBM). Fig. 1 shows the thickness of the P3HT:PCBM films as a function of the spin speed for four concentrations. The spin speeds of 600, 800, 1000 and 1200 rmp were selected because a speed lower than 600 rmp easily caused a non-uniform film and a speed higher than 1200 rmp easily led to a bad morphology due to the fast solvent evaporation before the thermodynamic balance was achieved. By using these selected concentrations and spin speeds, two batches of samples with 15 thicknesses were prepared. For each thickness, 4–6 samples were tested for the average and the error value. The first batch was prepared by using the master solution of 17 and 20 mg/ml, and tested under the illumination of 100 mW/cm$^2$, while the second batch was prepared by using the solution of 22 and 25 mg/ml, and tested under the illumination of 85 mW/cm$^2$. The cathodes for all the samples in the two batches were Ca-20 nm/Al-100 nm.

Three batches of blend solutions (1#, 2# and 3#) were prepared for studying the degradation of the solutions after exposed to air for a few hours and stored in a glove box for a time. The solutions were prepared in the glove box by dissolving PCBM into 20 mg/ml P3HT DCB solutions. The ratios of P3HT:PCBM were about 1:1. After the blend solutions were ready, a fresh sample was prepared immediately for comparison. The remaining solutions were stored for preparing studied samples. Solutions 1#, 2# and 3# were stored in the glove box for 5, 12 and 55 days after exposed to air for a few hours, and a part of solution 2# was directly stored for 12 days and never exposed to air.

The characterization was done on the encapsulated samples in the ambient air at room temperature. Current–voltage curves were recorded with a Keithley 2400 source measurement unit. Illumination tests were carried out under AM1.5 irradiation by using a 300 W Cermax lamp-based solar simulator. The illumination setup was calibrated and proved that the irradiation of the test plane was well above the 100 mW/cm$^2$ specified in the IEC 904-3 standard. Ultraviolet–visible (UV–vis) absorption spectra were recorded on Varian Cary 5000 spectrophotometer. Raman spectra were collected with a scanning Raman microscope with a laser wavelength of 785 nm as the excitation source. A Peltier-cooled CCD detector (Andor Newton DU-971N-BV) with 1600 × 400 pixels was operated at −60 °C. The integration time was 1 ms and the spectral rate was 600 spectra/s.

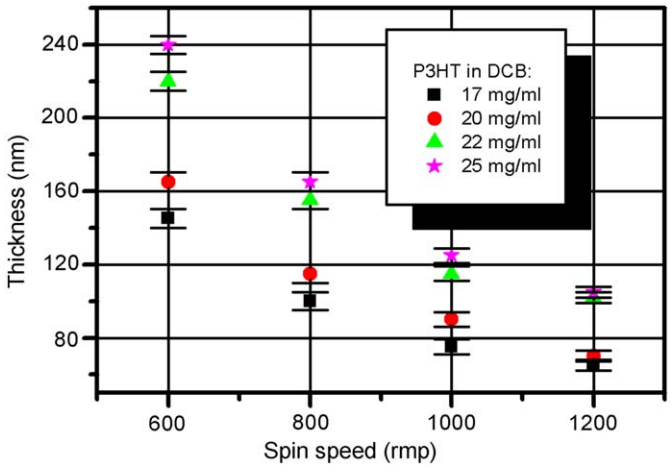


**Fig. 1.** The corresponding relation of the thickness of P3HT:PCBM films and the spin speed at various concentrations of solutions (P3HT: 17, 20, 22 and 25 mg/ml).

## 3. Results and discussion

The thickness of the photoactive layer has always been considered to have an effect on photovoltaic (PV) parameters. According to the transfer matrix formalism (TMF) [18,19], light absorption in a solar cell with the structure of Glass/ITO/P3HT:PCBM (1:1)/Ag was modelled. The refractive index of Schott BK7 was used for the glass slide and the refractive indexes of ITO, PEDOT:PSS, P3HT:PCBM, Ca and Ag were taken from the Refs. [20–24], respectively. The layer thicknesses given in Fig. 2c were chosen to correspond with the fabricated cells. TMF assumes that the incident light is perfectly monochromatic, and thus if the glass slide is included in the model, additional interference effects are seen in the results that do not coincide with the experimental data. This is due to the fact that the coherence length of visible sunlight is on the order of 1 μm [25]. Therefore, we assumed in TMF calculations that light is incident in glass and calculated the light transmittance through the first air/glass interface separately.

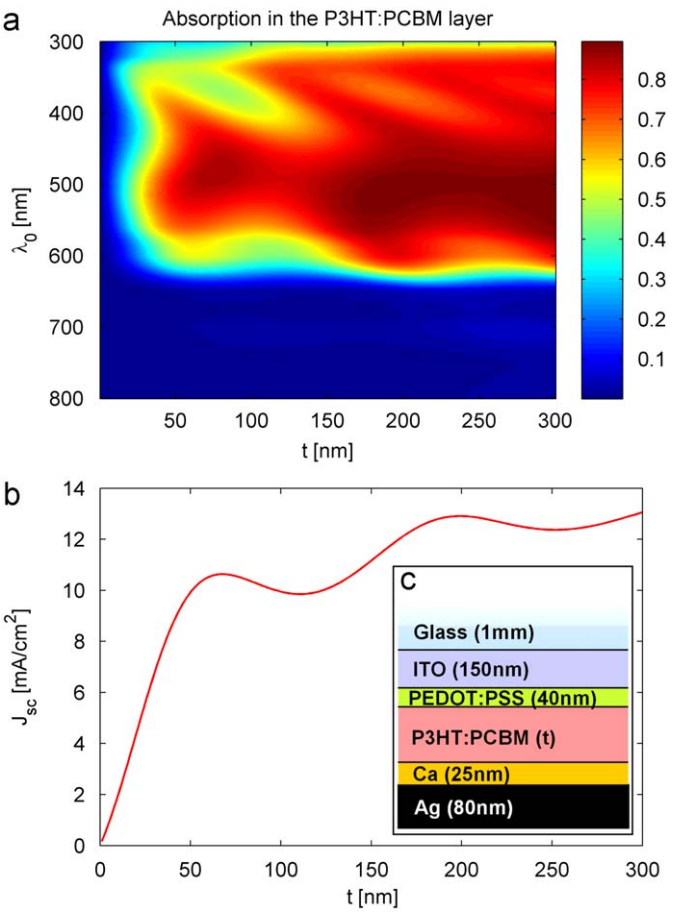


**Fig. 2.** (a) Simulated absorption in the P3HT:PCBM layer as a function of the photoactive layer thickness ($t$) and the free space wavelength of the incident light ($\lambda_0$). (b) Thickness-dependent short-circuit current of the cell (calculated from the P3HT:PCBM absorption data with the assumption of internal quantum efficiency of unity). (c) Layer thicknesses of the modelled cell.