Organic Electronics 15 (2014) 2141–2147

Contents lists available at ScienceDirect

Organic Electronics

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

Temperature and light dependent diode current in high-efficiency solution-processed small-molecule solar cells

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ARTICLE INFO

Article history:
Received 27 February 2014
Received in revised form 18 May 2014
Accepted 5 June 2014
Available online 21 June 2014

Keywords:
Bulk heterojunction
Solar cell
Current transport
Surface states

ABSTRACT

This paper reports on the detail analysis of the DC electrical and photoelectrical properties of the high-efficient (η = 8.01% under standard 100 mW/cm^2 AM1.5 illumination) small molecule bulk heterojunction (SM BHJ) solar cells p-DTS(FBTTh$_2$)$_2$/PC$_{70}$BM. In this SM BHJ solar cell, the dark diode current is determined by the multistep tunnel-recombination via interface states at low forward bias ($V < 0.65$ V) and the interface state assisted thermionic emission at high forward bias ($V > 0.65$ V). The effect of illumination on the diode current was also quantitatively investigated. It was observed a reduced Shockley–Read–Hall recombination via interface states at large forward bias (from the maximum power point to the open-circuit conditions). The expression of the load *I–V* characteristic of the illuminated high-efficient SM BHJ solar cells was derived in the presence of the light dependent series and shunt resistance.

1. Introduction

The bulk-heterojunction (BHJ) solar cells, based on the concept of intermixing acceptor and donor materials in nano-scale phase separation, have been attracting in solar cell research since more than a decade ago [1–3]. A unique feature of BHJ solar cells is that they offer low-cost and large-scale production by techniques like printing or roll-to-roll coating from solution like ink [4]. Conjugated polymers become a good candidate for BHJ solar cells due to their spontaneous phase-separation with acceptor and desirable film forming properties. On the other hand, molecular solid is also possible for solution-processing, like polymer counterparts. Despite poor performance of solution-processed small molecule (SM) donor at initial works [5–7], evolution of molecular design (from initial work of oligothiophenes and (polycyclic) acenes to push–pull type chromophores) [5–10] result in improved device performance comparable to that of polymer based devices. Solution-processed small molecule bulk-heterojunction (SM BHJ) solar cells with high efficiency over 8% have been reported, recently [11,12]. This is the reason for the rapidly increasing interest in the research of this type of organic solar cells in order to determine the recombination mechanisms and, thus to understand the main efficiency limiting factors [11,13,14].

Recently, we have shown that the first-order monomolecular recombination of photo-induced charge carriers dominates in the SM BHJ solar cells based on the blend of 7,7′-(4,4-bis(2-ethylhexyl)-4H-silolo[3,2-b:4,5-b′]dithiophene-2,6-diyl)bis(6-fluoro-4-(5′-hexyl-[2,2′-bithiophen]-5-yl)benzo[*c*][1,2,5]thiadiazole) (p-DTS(FBTTh$_2$)$_2$) and [6-6]-phenyl C$_{70}$ butyric acid methyl ester (PC$_{70}$BM) with the optimized Ca layer thickness of 20 nm from the short-circuit condition to the maximum power point and evolve to bimolecular recombination in the range of forward bias from the maximum power point to the open-circuit condition [11]. It should be noted that the monomolecular recombination mechanism at low forward bias is rather

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http://dx.doi.org/10.1016/j.orgel.2014.06.010
1566-1199/

the Shockley–Read–Hall (SRH) recombination via interface states [15] then geminate recombination before mobile carriers are created [16,17]. However, further detailed quantitative analysis of the electrical and photoelectrical properties of the SM BHJ solar cells, in particular diode current, should be carried out. The dominating current transport and recombination mechanisms, which determine the diode current through a solar cell, strongly affect on the photoelectric efficiency [18]. These mechanisms depend on illumination conditions in the case of heterojunction solar cells due to the presence of interface states, which can interact with incident photons [19,20]. Therefore, the diode *I–V* characteristics, measured at different temperatures and illumination conditions, should be analyzed in order to determine the light sensitive dominating current transport and recombination mechanisms. This information is very important for the further development and improvement of high-efficient SM BHJ solar cells.

The aim of this paper is to carry out the detail quantitative analysis of the temperature and light dependences of the electrical and photoelectrical properties of the high-efficient SM BHJ solar cells in order to get insight into the dominating current transport mechanisms as well as to derive the equation of the load *I–V* characteristic of the solar cells under illumination.

2. Experimental part

2.1. Fabrication of SM-BHJ solar cells (p-DTS(FBTTh$_2$)$_2$/PC$_{70}$BM)

ITO substrates purchased from Thin Film Devices, Inc. were cleaned by detergent, DI water, acetone and isopropanol with ultrasonication for 30 min, sequentially. The hole transport layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) (Clevious PH) was spin-cast at 5000 rpm for 40 s to obtain a thickness of ~35 nm. The blended BHJ solution was prepared by p-DTS(FBTTh$_2$)$_2$:PC$_{70}$BM = 3:2 weight ratio with an overall concentration of 35 mg/ml in chlorobenzene with 0.4 v/v% of 1 8-diiodooctane (DIO) processing additive. The BHJ solution was stirred at 300 rpm on the 60 °C hotplate overnight, and the prepared solution was annealed at 90 °C for 15 min before film casting. The spin-casting of BHJ solution at 2000 rpm for 45 s yielded the thickness of the active layer ~100 nm. After spin casting, the films were heated to 80 °C for 10 min to dry residual solvents. The surface morphology (the height and phase distributions) of the BHJ thin film is shown in Fig. 1. Then, Ca layer was evaporated with a thickness of a 20 nm after which Al cathode was thermally deposited with thickness of ~80 nm at the vacuum condition of 4×10^{-6} torr. The fabricated solar cells were encapsulated with epoxy and cover glass.

2.2. Measurements and characterization

For the device measurement, the light source was calibrated using by silicon reference cells with an intensity of 100 mW/cm^2 (AM 1.5 Global) at the solar simulator. The *J–V* curves of the solar cells were measured by a Keithley 2400 Sourcemeter at different temperatures and illumination conditions. The temperature control was carried out by a thermal inducing vacuum platform ThermoChuck TP0315B. In order to test the solar cells under various light intensities, the intensity of the light was modulated with a series of two neutral density filters wheels of six filters apiece, allowing for up to 35 steps in intensity from 100 to 0.4 mW/cm^2. The intensity of light transmitted through the filter was independently measured via a power meter. The cell area was determined by the 4.50 mm^2 aperture during the measurement for accurate PCE values.

The surfaces of the films were imaged by AFM (AFM Asylum MFP3D) to characterize the surface morphology of the p-DTS(FBTTh$_2$)$_2$/PC$_{70}$BM BHJ film.

3. Results and discussions

3.1. Dark diode I–V characteristics

The SM BHJ solar cells under investigation possess good rectifying properties within the measured temperature range (273–313 K) that provides evidence on the formation of high quality electric junction (see Fig. 2). The rectification ratio (RR), determined as the ratio of the absolute current through the SM BHJ solar cells at ±1 V, increases with the increase of temperature (the inset in Fig. 2), as opposite to other heterojunctions where the RR decreases with the increase of temperature [21,22]. The mechanism of rectification is governed by the dominating current transport mechanisms, which depend on the polarity and value of applied bias.

Let us consider the electrical properties of the SM BHJ solar cells at forward bias (positive potential "+" is applied to the front ITO contact) under dark conditions. One can see three sharply defined regions of the forward branches of the *I–V* characteristics with different slopes (Fig. 2). It is naturally to assume that these regions result from the domination of different charge transport processes. Therefore, more detailed analysis should be carried out.

Fig. 3 shows the forward branches of the *I–V* characteristics of the solar cells under investigation. It is seen that the current increases with the rise of temperature as well as the *I–V* characteristics approach the linear dependencies at large forward bias. The built-in voltage across the cell V_{bi} can be estimated by the extrapolation of the linear parts of the *I–V* characteristics toward the interception with the voltage axis [23,24]. The temperature dependence of the built-in voltage is well governed by the following linear equation:

$$V_{bi}(T) = V_{bi}(0) - \beta_{V_{bi}} T, \tag{1}$$

where $\beta_{Vbi} = 1.92 \times 10^{-3}$ V K^{-1} is the temperature coefficient of the built-in voltage, $V_{bi}(0) = 1.43$ V is the value of the built-in voltage at $T = 0$ K.

The values of the series resistance R_s of the heterojunctions under investigation can be determined from the voltage dependence of their differential resistance R_{diff} at different temperatures [23,24]. The forward bias decreases the internal electric field and finally the electric current is determined only by the series resistance R_s of a heterojunc-