Organic Electronics 14 (2013) 1643–1648

Contents lists available at SciVerse ScienceDirect

Organic Electronics

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

Analysis of the dynamic short-circuit resistance in organic bulk-heterojunction solar cells: relation to the charge carrier collection efficiency

C. Voz [a], J. Puigdollers [a,*], J.M. Asensi [b], S. Galindo [a], S. Cheylan [c], R. Pacios [d], P. Ortega [a], R. Alcubilla [a]

[a] Grup de Recerca en Micro i Nanotecnologia, Departament d'Enginyeria Electrònica, Universitat Politècnica de Catalunya, c/Jordi Girona 1-3, 08034 Barcelona, Spain
[b] Grup d'Energia Solar, Departament de Física Aplicada i Òptica, Universitat de Barcelona, Avda. Diagonal 647, 08028 Barcelona, Spain
[c] Institut de Ciències Fotòniques, Mediterranean Technology Park, Av. Canal Olimpic s/n, 08860 Castelldefels, Spain
[d] Department of Microsystems, IK4-IKERLAN S. Coop., Polo de Innovación Garaia, Goiru 9, 20500 Arrasate-Mondragon, Spain

ARTICLE INFO

Article history:
Received 18 September 2012
Received in revised form 19 February 2013
Accepted 23 February 2013
Available online 21 March 2013

Keywords:
Bulk-heterojunction
Organic
Solar cell
Collection
Recombination

ABSTRACT

This work studies the charge carrier collection efficiency in organic bulk-heterojunction solar cells based on polymer:fullerene blends. An equivalent circuit with a specific recombination term is proposed to describe the behavior of this type of devices. It is experimentally shown that this recombination term determines the slope of the current–voltage characteristic at the short-circuit condition. The variation of this dynamic resistance with the light intensity can be interpreted considering a dominant first-order recombination process. Finally, an analytical model under a constant electric field approximation is presented that can be used to calculate the charge carrier collection efficiency of the device. This model can be also used to estimate an effective mobility–lifetime product, which is characteristic of the quality of the active layer.

1. Introduction

Organic semiconductors are being intensely investigated for a cost-effective fabrication of novel electronic devices [1]. Among them, organic light-emitting diodes (OLEDs) [2], thin-film transistors (OTFTs) [3] and solar cells (OSCs) [4] are rapidly progressing towards commercial applications. Although it is possible to obtain crystals of organic semiconductors [5], practical applications use thin films of organic compounds with amorphous or polycrystalline microstructure [1]. In this work we focus on the photovoltaic applications of organic semiconductors. Solar cells can be made of thermally evaporated small-molecules [6,7], or polymers, which are processed in solution by different coating techniques [8]. Most OSC structures use the bulk-heterojunction concept (BHJ) [9], where electron acceptor and donor materials are intimately blended to increase exciton dissociation [10]. Concerning polymer-based solar cells, one of the most studied electron donors is the regioregular poly(3-hexylthiophene) (P3HT) polymer [11]. Among electron acceptors, a soluble fullerene derivative [6,6]-phenyl C_{61}-butyric acid methyl esther (PCBM) is undoubtedly the most usual choice. This combination has led to efficiencies exceeding 5% for this kind of devices [12]. The particular architecture of BHJ devices has motivated much effort to investigate the morphology of the blend and their respective phases by relatively complex structural characterization techniques [10,13–15]. Both the exciton dissociation efficiency and electronic transport of separated charge carriers are strongly influenced by the structure of the active layer. However, structural analyses do not provide much information on the recombination mechanisms that reduce the efficiency of the device. These

* Corresponding author. Tel.: +34 934011002; fax: +34 934016756.
E-mail address: joaquim.puigdollers@upc.edu (J. Puigdollers).

1566-1199/$ - see front matter
http://dx.doi.org/10.1016/j.orgel.2013.02.039

studies can also lack of generality, since processing conditions and subsequent treatments also affect the morphology of the blend [16,17].

Electrical characteristics (J-V curves) of completed devices measured under illumination definitely include such recombination losses. Anyhow, extracting clear information on recombination mechanisms from electrical characteristics is not a simple task. Although this problem can be faced by numerical simulation [18,19], the multiplicity of uncertain parameters could hide the physical mechanisms governing the operation of the device. Moreover, additional factors such as optical absorption, carrier injection at the contacts and eventual parasitic resistances also shape the electrical characteristic of the device. An alternative approach consists in the use of an equivalent circuit [20], a rather common way to describe the electrical characteristics of electronic devices. In the case of solar cells, the proposed circuit consists of a photogenerated current source J_{ph} superposed to the usual diode term. Besides, series and parallel resistances are included to take into account the electrodes and also possible shunts in the device (Fig. 1). This macroscopic description can accurately describe the behavior of devices like crystalline silicon solar cells, where most recombination losses can be included in a diode term [21]. The situation in solar cells based on thin films of disordered semiconductors is rather different, since a significant recombination takes place within the active layer of the device. In order to describe this effect it is reasonable to include an additional loss term J_{rec} represented by the current sink of Fig. 1. According to this equivalent circuit, the J–V characteristic can be expressed by the following implicit equation:

$$J = -J_{ph} + J_o\left[\exp\left(\frac{V - R_sJ}{nV_T}\right) - 1\right] + \frac{V - R_sJ}{R_p} + J_{rec} \tag{1}$$

where the diode term is characterized by its saturation current density J_o and ideality factor n. The value of the thermal voltage V_T at room temperature is around 25 mV. In Eq. (1), J_{ph} represents the maximum photogenerated current that we would obtain if all the charge carriers were collected. The photogenerated current can be considered independent of the applied voltage, since there is not a significant field-dependence in the generation rate for typical BHJ solar cells based on P3HT:PCBM blends [22]. Intuitively, J_{rec} is expected to be dependent on the illumination level and the applied voltage. In this work, we will show that the slope of the J–V curve at the short-circuit condition is mainly determined by the recombination term. Then, we propose an analytical expression for J_{rec} that describes the behavior of the device for illumination levels ranging from 0.1 to 2 suns. This model allows calculating a charge carrier collection efficiency that will be related to the charge transport and recombination processes that take place in the active layer of the device.

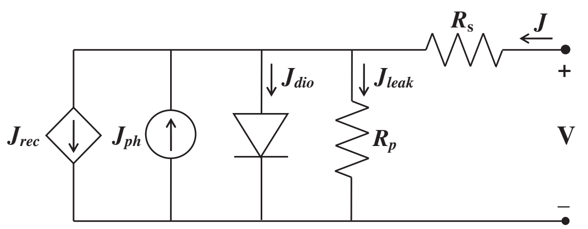

Fig. 1. Equivalent circuit proposed in this work to describe the behavior of BHJ solar cells. The standard equivalent circuit of photovoltaic devices is modified by an additional term J_{rec} to account for recombination losses in the active layer.

2. Experimental

A widely studied P3HT:PCBM combination was selected in this work to study the charge carrier collection in organic BHJ solar cells. The devices were fabricated on glass substrates coated with indium-tin-oxide (ITO) transparent electrodes (15 Ω/square). These substrates were first cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, rinsed in DI water and finally dried by an intense nitrogen flow. An ultraviolet ozone (UVO) treatment was then applied for 15 min to the ITO electrodes. Next, the substrates were introduced inside a glovebox to continue the fabrication process that involves organic materials. A standard poly(3,4-ethylenedioxythiophe);poly (styrenesylfonate) (PEDOT:PSS) hole conducting layer was spin coated from an aqueous solution and dried at 130 °C for 15 min to obtain a final thickness of 50 nm. The active layer of the device was spin coated from a 1:1 by weight ratio solution of P3HT and PCBM in chlorobenzene. The thickness of the active layer after complete evaporation of the solvent was around 80 nm. Subsequently, the device was introduced in a high-vacuum chamber (10^{-7} mbar) to evaporate a 100 nm thick aluminium cathode. A shadow mask was used to define a device area of 12.7 mm^2. The fabrication process ends with a last annealing of the complete devices at 160 °C for 10 min. Then, the solar cells were extracted from the glovebox to do the electrical characterization in ambient conditions. The J–V curves were measured with a programmable Keithley 2636A Source Meter Unit. The solar cells were illuminated with a Xenon lamp (300 W) through an AM1.5 filter (Oriel). The illumination level was varied from 10 mW cm^{-2} (0.1 suns) to 200 mW cm^{-2} (2 suns) by means of neutral grey filters to preserve the spectral distribution of the incident light. Finally, we checked that the devices had not suffered a significant degradation during the electrical characterization.

3. Results

In Fig. 2 we plot the J–V characteristic of one of the fabricated BHJ solar cells measured in dark. This curve can be used to fit the diode term and to calculate the values of the parasitic resistances, since in dark conditions both the photogenerated and recombination currents are equal to zero. The parameters J_o and n of the diode term are obtained by fitting the exponential behavior observed at moderate applied voltages. In the region of low applied voltages, the leakage current through the parallel resistance must be also taken into account to fit experimental data. The parallel resistance can be attributed to shunts and eventual pinholes through the device. Finally, at high applied voltages a significant voltage drop in the series