Organic Electronics 40 (2017) 8–12

Contents lists available at ScienceDirect

Organic Electronics

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

Validation of opposed two-diode equivalent-circuit model for S-shaped characteristic in polymer photocell by low-light characterization

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A R T I C L E I N F O

Article history:
Received 9 September 2016
Received in revised form
17 October 2016
Accepted 20 October 2016

Keywords:
Photocell
Equivalent-circuit model
S-shaped curve
Bulk heterojunction composites
Indoor light harvesting
Polymer

A B S T R A C T

The opposed two-diode equivalent-circuit model consisting of a traditional one-diode photocell model and a parasitic diode with a parallel resistance is known to somehow reproduce the S-shaped current-voltage curve of poor organic photocells. Here, the light-intensity dependencies of the parameters in the model are experimentally studied. On the assumption that the parasitic part is light-insensitive, the parameters of the main part, which are extracted by fitting the current-voltage curves under various illumination intensities with the model, are found to change as those of healthy photocells do. The reasonable separation of light-sensitive main and light-insensitive parasitic parts validates the model.

1. Introduction

Photocells based on printable organic materials are attracting much attention, because it is believed that they can be large-area low-cost renewable electric power source in the near future [1–4]. The S-shaped current-voltage characteristics are occasionally observed in the studies of such photocells using organic bulk heterojunction composite or bilayer. The S-shape is typically referred as a sign of poorly performing photocell, since it effectively reduces the fill-factor (FF) and thus the power conversion efficiency (PCE) of the photocell. Although the physical origin of the S-shaped characteristics is not fully understood, it has been pointed out that some deficiency between the layers, which potentially produces strong dipole or creates traps, and/or the unbalanced hole/electron mobility can cause the anomaly [5–10].

The opposed two-diode equivalent-circuit model shown in Fig. 1, which consists of a normal one-diode model for photocell and a parasitic opposed diode connected with a parallel resistance, has been known to somehow reproduce the S-shaped current-voltage characteristics [11,12]. Although the addition of the parasitic part is apparently intended to model the permanent deficiency that causes the S-shape, the physical origins of the parameters in the model have never been experimentally validated so far.

The transcendental nature of current-voltage equations for the model, which requires iterative calculation to solve, can be a serious barrier for the experimental researchers who are unfamiliar with code writing. However, the current-voltage relation of the model can be described by an exact expression by using the Lambert W-function $W_0(x)$ which is defined as the real solution of a simple transcendental equation $W(x)\cdot\exp[W(x)] = x$ for $x \in [-\exp(-1), +\infty]$ [13].

$$
\begin{aligned}
V = {} & I\cdot R_s - n_1\cdot V_t\cdot W_0\left\{\frac{I_{s1}\cdot R_{p1}}{n_1\cdot V_t}\cdot\exp\left(\frac{\left(I+I_{s1}+I_{ph}\right)\cdot R_{p1}}{n_1\cdot V_t}\right)\right\} \\
& + \left(I+I_{s1}+I_{ph}\right)\cdot R_{p1} \\
& + n_2\cdot V_t\cdot W_0\left\{\frac{I_{s2}\cdot R_{p2}}{n_2\cdot V_t}\cdot\exp\left(\frac{-(I-I_{s2})\cdot R_{p2}}{n_2\cdot V_t}\right)\right\} \\
& + (I-I_{s2})\cdot R_{p2},
\end{aligned}
\tag{1}
$$

where I_{ph} is the ideal photocurrent, R_s and R_{p1} are the series and upper parallel (shunt) resistance respectively, and I_{s1} and n_1 are the

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http://dx.doi.org/10.1016/j.orgel.2016.10.031
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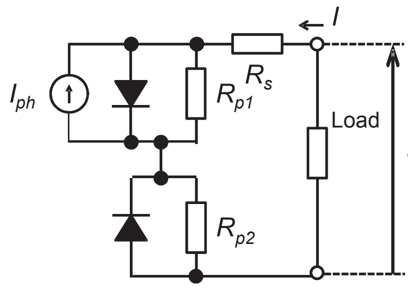

Fig. 1. Opposed two-diode equivalent-circuit model.

reverse saturation current and the ideality factor of the upper main diode respectively, in Fig. 1. The thermal voltage V_t at room temperature is 26 mV. The parameters with subscript 2 correspond to the lower parasitic part. Eq. (1) has been implemented in a Microsoft Excel spreadsheet which is provided as supporting information of the previous study [14], enabling one to estimate the circuit parameters by using Solver function of the program.

In this study, the low-light characteristics of a solution-processed polymer bulk heterojunction photocell, which shows S-shaped characteristics under AM1.5G 1 sun (100 mW/cm^2) illumination, are analyzed in order to investigate the light-intensity dependences of the parameters in the opposed two-diode equivalent-circuit model. The low-light characterization of photocell is becoming important issue in terms of the indoor light harvesting, where light power is typically lower than outdoor by 2–3 orders of magnitude [15–17]. Thus, the development of a suitable circuit model is not only helpful for understanding the device behavior, but also critically important for practical electronic circuit design.

2. Experimental

A bulk heterojunction photocell with ITO/PEDOT:PSS/PTB7-Th:C_{70} = 1:1/PFN/Al structure is used in this study, where ITO, PEDOT:PSS, PTB7-Th and PFN stand for indium-tin oxide, poly(3,4-dioxythiophene):poly(styrenesulfonate), poly[[4,8-bis[5-(2-ethylhexyl)thiophene-2-yl]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] [18,19] and poly[9,9-bis(3'-(*N*,*N*-dimethyl)-propyl-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)], respectively. The schematic device structure as well as the molecular structures of the key materials is shown in Fig. 2. PTB7-Th and PFN are purchased from 1-materials and the active area of the devices is 3 mm × 3 mm square. The device preparation procedure is the same as that described in the previous study [20], except that the composite solution must be warmed on a hotplate heated at 100 °C for a few hours before spin-coating. This is simply due to lower solubility of the PTB7-Th sample used in the present study than that used in the previous study. Although the devices after the optimized thermal annealing yield the PCE close to 5% [20], the devices without thermal annealing show S-shaped current-voltage curve and are the target of the present study.

The current-voltage characteristics are measured with a Keithley 2400 source meter under the AM1.5G 1 sun illumination from an Asahi Spectra HAL-C100 solar simulator. The illumination light intensity is reduced by using a set of neutral density (ND) filters [21,22]. The reduction factors of the illumination light intensity are calculated by using the optical transmission spectra of the ND filters and the AM 1.5G 1 sun spectral data in the range of 350–750 nm [22].

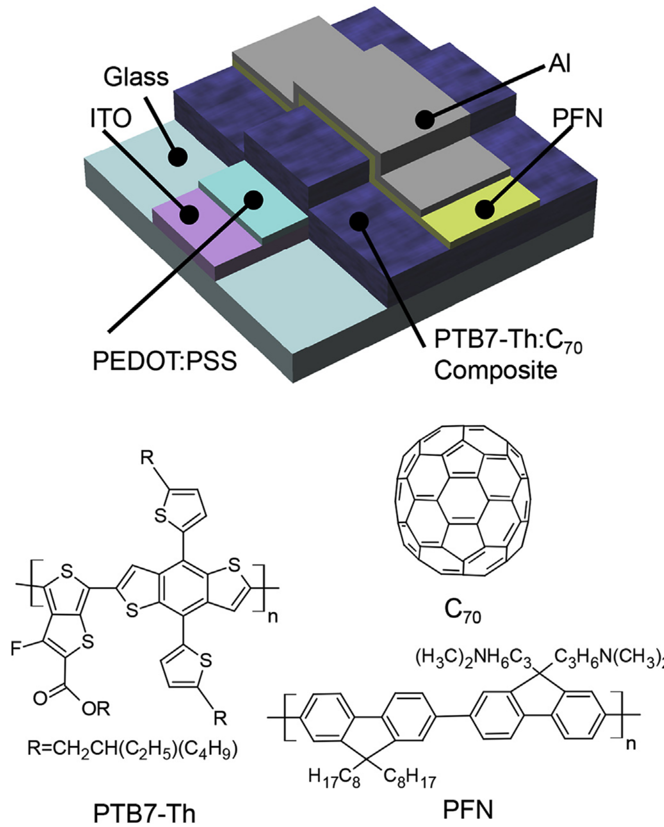

Fig. 2. Schematic structure of the photocell and molecular structures of key materials used in this study.

3. Results and discussion

The device shows typical S-shaped current-voltage characteristics under AM1.5G 1sun illumination as shown in Fig. 3. Since the device without thermal annealing in the previous study has shown normal current-voltage characteristics [20], and the S-shape disappears after the thermal annealing at 175 °C, this probably relates to some structural factor in the bulk and/or the surface of the composite film created by rapid cooling during the spin-coating. Table 1 summarizes the normalized circuit parameters obtained by fitting the data shown in Fig. 3 with the equivalent-circuit model

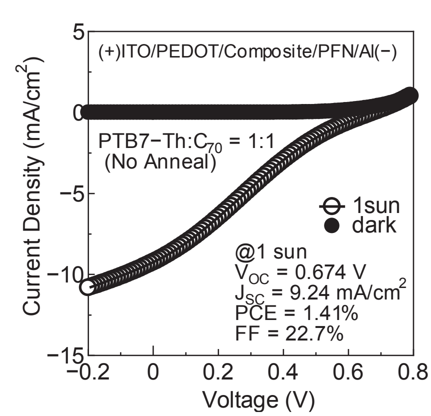

Fig. 3. Current density-voltage characteristics of the PTB7-Th:C_{70} photocell under AM1.5G 1 sun illumination and dark. The symbols and lines indicate experimental data and fitting curve, respectively.