

Efficiency limiting factors of organic bulk heterojunction solar cells identified by electrical impedance spectroscopy

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Available online 12 December 2006

Abstract

The current–voltage characteristic and the performance of organic bulk-heterojunction solar cells are very sensitive to small variations in the production steps or environmental influences. In our experiments, we found a large variation of the short-circuit current, which does not correspond to the device thickness as one might expect. The fill factor of some devices is below 25% under illumination, while the best devices have a fill factor of about 70%. Electrical impedance spectroscopy can provide information about the conductivity of different regions within the device. In earlier measurements, it was observed that devices with a thick absorber layer might consist of a conductive bulk region and a very poorly conductive depletion region at the metal contact. Using a standard semiconductor device model, it is shown in this paper that this reduces the charge collection efficiency under short-circuit conditions, as there is no electrical field in the bulk region, supporting the charge separation. For devices with the low fill factor, a thin-current limiting layer under forward bias can be identified by electrical impedance spectroscopy and is suggestive of a corroded metal contact.

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Keywords: Organic photovoltaics; Impedance spectroscopy; Doping; Kink; Model

1. Introduction

The absorber of organic bulk-heterojunction solar cells is made of a blend of two different materials [1]. Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) are among the most promising materials for such devices [2]. Due to the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the two materials, P3HT upon optical excitation acts as an electron donor, while PCBM as an acceptor. After the photo-induced charge transfer, P3HT provides an electrically conductive network to transport the hole to the anode of the solar cell. The electron is transported by the PCBM network to the cathode. For sake of simplicity, the absorber can be regarded as one effective semiconductor,

where the LUMO corresponds to the conduction band edge and the HOMO to the valence band edge of an inorganic semiconductor.

We observed that the photovoltaic performance of bulk-heterojunction solar cells can vary a lot from batch to batch or even within one batch. Obviously, the device performance depends critically on the exact production steps, some of which are difficult to perform completely reproducible in a pre-industrial manual device fabrication, such as time and temperature control during the annealing of the devices [3] or the vacuum deposition of the electrodes.

In this article, we show how impurity doping of the absorber and possibly corrosion of the top contact can be identified by electrical impedance spectroscopy (EIS). We think that both doping and corrosion of the contact are influenced by variation in the mentioned production steps. Based on classical transport equations for semiconductors, the influence of the two effects on the current–voltage characteristic (*iv*-curve) is modeled and compared with the experimental findings.

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2. Experimental

The standard solar cells were fabricated on indium tin oxide (ITO) covered glass substrates. First an approximately 40 nm thick layer of poly(3,4 ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) was spin-coated from aqueous dispersion (Baytron P AI 4083, H.C. Starck). On top, the absorber blend (80–200 nm) was spin-coated from 0-dichlorobenzene solution (15 mg/ml P3HT) with a ratio of 3:2 wt, P3HT:PCBM (P3HT 4002 by Rieke Metals, PCBM by Nano-C). The top electrode is made of a 100 nm thick layer of aluminium (Al), which is thermally evaporated under vacuum. Usually, the evaporation rate is about 0.2 nm/s while the pressure is less than 5×10^{-4} Pa. For the low fill factor device discussed later, the rate was approximately 2.0 nm/s while the pressure went up to 1.0×10^{-3} Pa during the evaporation.

The impedance spectra of the devices were recorded from 1 Hz to 1 MHz with a Zahner IM6 electrochemical workstation. The current–voltage characteristic of the solar cell was measured in dark or under illumination with a Steuernagel sun simulator.

3. The model

To get a more profound understanding of the device behavior upon certain variation of parameters such as the doping level, the bimolecular-recombination rate or the charge-carrier mobilities, a one-dimensional model for the device is proposed. It is based on drift and diffusion current of electrons and holes, a bimolecular recombination of the charge carriers and metallic-boundary conditions for the electrical contacts. Hence, the following system of differential equations has to be solved:

$$J_n = e\mu_n n(x)\phi'(x) + kT\mu_n n'(x), \quad (1)$$

$$J_p = e\mu_p p(x)\phi'(x) - kT\mu_p p'(x), \quad (2)$$

$$0 = \frac{1}{e}J_n'(x) + G(x) - \beta n(x)p(x), \quad (3)$$

$$0 = \frac{1}{e}J_p'(x) + G(x) - \beta n(x)p(x), \quad (4)$$

$$0 = e(p(x) - n(x) - N_A) + \varepsilon\varepsilon_0\phi''(x). \quad (5)$$

With the boundary conditions:

$$n_0^{p/n} = N_{\text{LUMO}} \exp\left(-\frac{\phi_B^{p/n}}{kT}\right), \quad (6)$$

$$p_0^{p/n} = N_{\text{HOMO}} \exp\left(-\frac{\Delta - \phi_B^{p/n}}{kT}\right), \quad (7)$$

$$\phi^p = V_{\text{ext}} - \phi_B^p/e, \phi^n = -\phi_B^n/e, \quad (8)$$

$$J_n^{p/n} = ev_n^{p/n}(n^{p/n} - n_0^{p/n}), \quad (9)$$

$$J_p^{p/n} = ev_p^{p/n}(p^{p/n} - p_0^{p/n}), \quad (10)$$

where Eqs. (1) and (2) are the equation for electron and hole current, with the elementary charge e , the electron and hole mobility μ_n and μ_p , the Boltzmann constant k , the temperature T and the electron and hole density $n(x)$ and $p(x)$, respectively. Eqs. (3) and (4) are the continuity equations for electrons and holes, where $G(x)$ is the optical generation rate and β the bimolecular recombination rate. Eq. (5) is the Poisson equation with the electrical potential $\phi(x)$, the density of charged acceptors N_A , the vacuum dielectric constant ε_0 and the dielectric constant of the absorber blend ε . Eqs. (6) and (7) describe the Boltzmann occupation by electrons and holes directly at the electron-contact (index n) and the hole contact (index p), when the device is at equilibrium. Here N_{LUMO} is the spatial density of LUMO states of the acceptor molecule in the blend and N_{HOMO} is the spatial density of HOMO states of the donor polymer. $\phi_B^{p/n}$ is the barrier height between the LUMO-level of the acceptor and p- or n-contact, respectively. Δ is the difference between acceptor LUMO-level and donor HOMO-level (effective electrical band gap). The boundary conditions for the electrical potential are given by Eq. (8), where V_{ext} is the externally applied voltage. Finally, Eqs. (9) and (10) describe the electron/hole injection and extraction at the interfaces. $v_n^{p/n}$ is the injection rate at the respective contacts for electrons and $v_p^{p/n}$ for holes. $n^{p/n}$ is the occupation density of the p- and n-contact, respectively, by electrons at a certain voltage, $p^{p/n}$, the occupation density by holes.

These equations are solved numerically by the semiconductor device simulation software DESSIS by ISE-TECAD.

This approach is not meant to give an outright explanation for all aspects of the iv -curve, as some phenomena specific to organic semiconductors are not included; for example, the field or concentration dependence of the mobility [4,5]. A similar model was proposed

Table 1

Input parameters for device calculation used throughout if not differently stated

Absorber blend thickness	80 and 150 nm
Density of states, N_{LUMO} and N_{HOMO}	$5 \times 10^{20} \text{ cm}^{-3}$
Dielectric constant of the absorber blend, ε	3.8
Electron and hole mobility, μ_n and μ_h	$1 \times 10^{-4} \text{ cm}^2/(\text{V s})$
Optical generation rate, $G(x)$	$4 \times 10^{21} \text{ cm}^{-3}$ (spatially constant)
Contact work functions, $\phi_B^{p/n}$	4.1 eV (n-contact) and 5.0 eV (p-contact)
LUMO- and HOMO-level	4.3 (LUMO) eV and 5.2 eV (HOMO)
Injection rates, $v_n^{p/n}$, $v_p^{p/n}$	1000 cm/s
Bimolecular recombination rate, β	$6 \times 10^{13} \text{ cm}^3/\text{s}$
p-doping level, N_A	$5 \times 10^{16} \text{ cm}^{-3}$

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