On the light intensity dependence of short-circuit current of bilayer organic photovoltaic cells

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ARTICLE INFO

ABSTRACT

The work presents a model of light intensity dependence of short-circuit current for a bilayer organic system. The model is based on the assumption of a uniform electric field in both organic layers and it concerns a bimolecular and monomolecular recombination of charge carriers at a heterojunction interface. The comparison between theoretical calculations and experimental results carried out on the system formed from copper phthalocyanine or bormophosphorus phthaocyanine and perylene dye is presented in the work. A good correlation between theoretical and experimental results has been achieved.

1. Introduction

An analysis of short-circuit current density dependence on light intensity ($j_{sc}(I_0)$) is often used to study the influence of transport processes and recombination of charge carriers on the performance of organic photovoltaic systems [1,2]. Within a typical range of light intensity the relation is linear or sublinear. The linear dependence of $j_{sc}(I_0)$ is observed when recombination of charge carriers is negligible or monomolecular recombination dominates, e.g. [3–9]. The existence of sublinear dependence of $j_{sc}(I_0)$ indicates the presence of bimolecular recombination or it can result from the influence of space charge on charge transport through a system [10–15]. These conclusions concern both the systems with bulk heterojunctions [5,12–15] and the systems with planar heterojunctions (e.g. bilayer devices) [3,4,7–11] and they have been derived from different theoretical models of the photovoltaic effect. The models are performed mainly as numerical solutions of a set of equations including equations describing distributions of light and excitons, the continuum equation, the transport equation and the Poisson equation [12,16–22]. In particular, the dependence of $j_{sc}(I_0)$ addressed to samples with bulk heterojunction is discussed in the works [12,16,19,21].

This work presents a simple analytical description of a short-circuit current as a function of light intensity for bilayer photovoltaic cells ($E_1/O_1/O_2/E_2$) (Fig. 1). The system taken into consideration consists of two organic layers, O_1 and O_2, forming a planar heterojunction O_1/O_2 and electrodes, E_1 and E_2. At short circuit, the electrode Fermi levels are aligned, corresponding to an internal field that will sweep charge carriers at the heterojunction towards the electrodes [1,2,17]. A photogeneration of charge carriers in such a system is a result of an exciton dissociation at the O_1/O_2 interface. Electrons and holes are separated. Consequently there is only electron current in one organic layer (e-layer) and only hole current in the other layer (h-layer). It means that generation and recombination of charge carriers may occur only in a very thin region near the O_1/O_2 interface. Taking into account a constant-field approximation for the system of two organic layers, a simple expression describing the $j_{sc}(I_0)$ relationship has been derived. This theoretical result is compared with the results obtained experimentally on the system formed from copper phthalocyanine (CuPc) or bromophosphorus phthalocyanine (PBrPc) and perylene dye (MePTCDI).

2. Model

Fig. 1 shows an energy-level diagram of the analyzed system at a short-circuit mode. Dissociation of an exciton (eks) excited, for instance, in the h-layer is also sketched. Bands transporting electrons (ETB) and holes (HTB) are shown as straight lines, accordingly to the assumption that in each organic layer the electric field is uniform. This assumption is true at a, respectively, low current density and low concentration of charge carrier traps. Moreover, it is assumed that the effect of a non-uniform electric field occurring in the thin near-electrode regions is negligible. Our model is based on a constant-field approximation suggested for a mono-layer system in the work [23] as well as on some proposals for an analysis of bilayer devices presented in the works [7,17,18,24].

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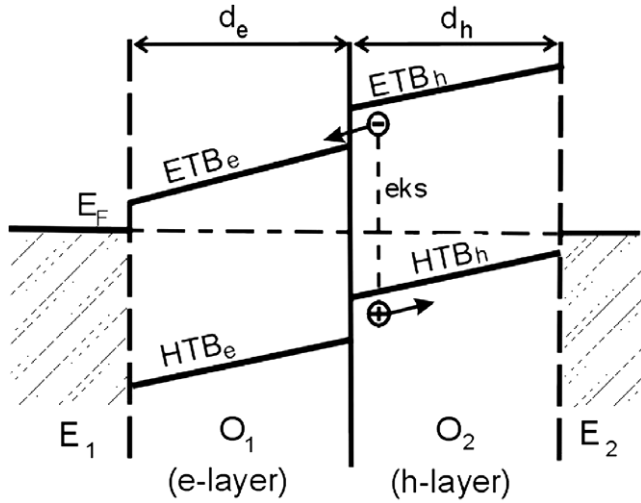

Fig. 1. Energy-level diagram of a bilayer system at short circuit and interfacial exciton dissociation. E_F – Fermi energy of electrodes, E_1, E_2 – electrodes, O_1 – electron transporting layer (e-layer) of d_e thickness, O_2 – hole transporting layer (h-layer) of d_h thickness, ETB_e, ETB_h and HTB_e, HTB_h – electron and hole transporting bands in e-layer and h-layer.

Let us start our consideration with the e-layer. The electron current flowing through this layer is described by the following equation:

$$j = -e\mu_e n(x)\frac{d\varphi_e(x)}{dx} + \mu_e kT\frac{dn(x)}{dx} = j_{sc}, \qquad (1)$$

where μ_e – electron mobility, $n(x)$ – concentration of electrons at x, $\varphi_e(x)$ – electric potential at x, e – elementary charge, k – Boltzmann constant, T – temperature.

Solving this equation with respect to $n(x)$ with two pairs of boundary conditions: $n(x = 0) = n_0$, $n(x = d_n) = n_{jth}$ for $j = 0$ and $n(x = 0) = n_0$, $n(x = d_n) = n_j$ for $j = j_{sc}$ and remembering that $\frac{d\varphi_e(x)}{dx} = const$, it is easily to obtain:

$$n_j = n_{jth} + j_{sc}a_e, \qquad (2)$$

where n_{jth}, n_j – concentrations of electrons in the O_1/O_2 heterojunction either in thermal equilibrium (n_{jth}) or in the presence of current j_{sc} (n_j), and

$$a_e = \frac{d_e\left(1 - \exp\left(-\frac{e\,U_{be}}{kT}\right)\right)}{e\mu_e U_{be}}, \qquad (3)$$

in which

$$U_{be} = \frac{kT}{e}\ln\frac{n_0}{n_{jth}}, \qquad (4)$$

is the built-in potential for the e-layer and n_0 is concentration of electrons at the electrode (E_1).

The same attitude to the h-layer leads to the following relations:

$$p_j = p_{jth} + j_{sc}a_h, \qquad (5)$$

$$a_h = \frac{d_h\left[1 - \exp\left[-\frac{eU_{bh}}{kT}\right]\right]}{e\mu_h U_{bh}}, \qquad (6)$$

$$U_{bh} = \frac{kT}{e}\ln\frac{p_d}{p_{jth}}, \qquad (7)$$

with p_{jth}, p_j – concentrations of holes in the junction O_1/O_2 in thermal equilibrium (p_{jth}) or in the presence of current j_{sc} (p_j), μ_h – hole mobility, p_d – concentration of holes at the electrode (E_2), U_{bh} – built-in potential for h-layer.
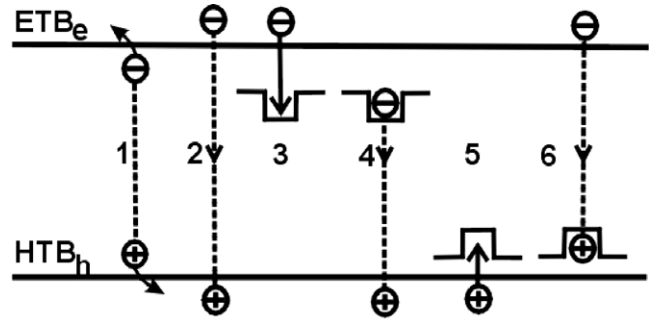

Fig. 2. The electron processes at O_1/O_2 heterojunction: ETB_e – electron transporting band of the e-layer (O_1), HTB_h – hole transporting band of the h-layer (O_2): (1) dissociation of bound electron-hole pair generated thermally or by excitons, (2) recombination of free carriers, (3) electron trapping, (4) recombination of a trapped electron and a free hole, (5) hole trapping, and (6) recombination of a trapped hole and a free electron.

We assume also that concentrations of charge carriers at electrodes, n_0 and p_d, do not depend on light intensity (ohmic contacts).

In further analysis let us consider processes of charge carrier generation and recombination operating at the O_1/O_2 interface, within the region of a small width in comparison to the thickness of organic layers. We consider only processes indicated in Fig. 2. Process 1 means the dissociation of a bound electron-hole pair generated either by exciton (the photogeneration) or by thermal excitation (the thermal generation). Process 2 refers to a recombination of free charge carriers. The processes denoted as 3, 4, 5, 6 occur when electron- or hole-trapping states participate. Here, it is assumed that the concentration of these states is much higher than the concentration of trapped charge carriers. Equations describing these processes (in the steady state) are as follows:

$$\alpha_p p_j n_{tj} - k_{te}n_j = 0, \qquad (8)$$

$$\alpha_n n_j p_{tj} - k_{th}p_j = 0, \qquad (9)$$

$$G_{ex} \pm G_{th} - \alpha_n n_j p_{tj} - \alpha_p p_j n_{tj} = \frac{j_{sc}}{eb}, \qquad (10)$$

in which n_{tj} and p_{tj} are concentrations of trapped electrons and trapped holes, G_{th} denotes the rate of thermal generation, G_{ex} is the rate of photogeneration, α_p, α_n, α are the rate constants of recombination (free hole-trapped electron, free electron-trapped hole and free electron-free hole, respectively), k_{te}, k_{th} are the rate constants of electron trapping and of hole trapping, b is the heterojunction region thickness.

The substitution of (8) and (9) into (10) leads to the expression

$$G_{ex} + G_{th} - k_{th}p_j - k_{te}n_j - \alpha p_j n_j = \frac{j_{sc}}{eb}, \qquad (11)$$

Solving the set of Eqs. (2), (5), (11) we obtain the following relation:

$$j_{sc}(rj_{sc} + t) = j_G, \qquad (12)$$

in which

$$j_G = ebG_{ex}, \qquad (13)$$

is the of photogeneration current density, and

$$r = eb\alpha a_e a_h, \qquad (14)$$

$$t = 1 + eb\lfloor a_e(\alpha p_{jth} + k_{te}) + a_h(\alpha n_{jth} + k_{th})\rfloor. \qquad (15)$$

The rate of charge-carrier photogeneration, G_{ex}, depends on the flux of excitons at the interface. Therefore, without going into details of processes of exciton dissociation and separation of charge carriers [17,20], it can be generally assumed that it is proportional to light intensity, $G_{ex} \sim I_0$ [25]. It enables us to write down the expression (13) in the following form:

$$j_G = qI_0, \tag{16}$$

where coefficient q means average charge generated by one incident photon.

The relations presented above explicitly indicate that we can obtain high values of j_{sc} for small values of the r and t parameters, i.e. for small values of rate constants of recombination (α) and trapping (k_{te}, k_{th}), for small thermal concentration of p_{jth}, n_{jth} in heterojunction, and small values of a_e and a_h, so consequently for high values of built-in potential U_{be} and U_{bh} (i.e. high charge carrier concentrations at electrodes n_0, p_d – ohmic contacts), and for high values of charge carrier mobilities μ_e, μ_h. Obviously the layer thickness of d_e and d_h should be submitted to optimization since they affect not only a_e and a_h, but also the q parameter [22,25].

We can also notice that for high values of I_0 (also high values of j_{sc}) the dependence of j_{sc} (I_0) is determined by bimolecular recombination (via the rate constant α in the expression (14)), while indirect recombination (i.e. via trapping states) can limit the value of j_{sc} also at the range of small light intensity (when the rate constants k_{te}, k_{th} are high as it is in the case of high concentration of states trapping charge carriers). Fig. 3 presents examples of j_{sc} (I_0) illustrating these remarks. Calculations have been performed for a symmetric system, i.e. with the same values of parameters for e-layer and h-layer at room temperature. We have taken the following values: $d_e = d_h = 100$ nm, $\mu_e = \mu_h = 10^{-5}$ cm^2/(Vs), $n_0 = p_d = 10^{16}$ cm^{-3}, $n_{jth} = p_{jth} = 10^{10}$ cm^{-3}, $U_{be} = U_{bh} = 0.35$ V, $b = 2$ nm (i.e. two molecular layers located on both sides of the interface of heterojunction) $q = 9.6 \times 10^{-21}$ C (i.e. 0.06 e). The abovementioned values of the charge carriers concentrations at electrodes (n_0, p_d) and at heterojunction (n_{jth}, p_{jth}) can occur for electrode barriers about 0.2–0.3 eV and for energy gap between ETB_e and HTB_h levels about 1 eV. This is for example the case of the ITO/phthalocyanine/perylene dye/Ag system.

It is worth noticing that the range of values of parameters, which can be accepted in calculations, is quite broad. For instance, typical values of charge carrier mobilities in organic material layers lie in the range of 10^{-7}–10^{-2} cm^2/(Vs) [26–30]. On the other hand, there are no experimental data about the rate constant of charge carrier recombination at heterojunction interface in a bilayer system. Therefore, in our work, this parameter is treated as free [21]. The particular values of rate constants of bimolecular recombination (α) and trapping (k_{te}, k_{th}) are presented in the caption of Fig. 3. It is worth adding also that if the charge carrier mobility

in organic layers is of the magnitude of 10^{-3} cm^2/(Vs) or higher, then (at unchanged values of other parameters) in the whole considered range of light intensity the relation j_{sc} (I_0) will be not determined by the charge carrier recombination and trapping (i.e. $j_{sc} \approx j_G$).

3. Comparison with experimental data

In order to make a comparison between the model and experimental results we have performed investigations on two systems: ITO/copper phthalocyanine (CuPc)/MePTCDI/Ag and ITO/bromophosphorus phthalocyanine (PBrPc)/MePTCDI/Ag, where MePTCDI denotes N,N'-dimethylperylene-3,4,9,10-biscarboximide. The system including the CuPc/MePTCDI heterojunction has been investigated also by other researchers (e.g. [11]), while the system with the heterojunction of PBrPc/MePTCDI has not been investigated yet. Preparation conditions of samples and measurement equipment have been the same as in the work [7]. The thickness of layers in the systems have been as follows: 35 nm of ITO, 50 nm of phthalocyanine, 80 nm of perylene dye, 40 nm of Ag. The samples have been illuminated through the ITO with monochromatic light (weak absorbed by phthalocyanine and strong absorbed by MePTCDI) of $\lambda = 460$ nm for the system with CuPc and $\lambda = 570$ nm for the system with PBrPc.

The measurements of spectral characteristics of short-circuit current exhibit that, like in other bilayer systems, charge carriers are generated near the interface of organic materials.

In our systems, phthalocyanines constitute an h-layer, while MePTCDI – an e-layer.

Fig. 4 compares the experimental and calculated dependence of $j_{sc}(I_0)$. The points have been obtained experimentally, while solid lines constitute the solution of Eq. (12) written in the form

$$j_{sc}(j_{sc} + u) = \varphi I_0, \tag{17}$$

with parameters u and φ defined by the relation (18)

$$u = \frac{t}{r} \quad \text{and} \quad \varphi = \frac{q}{r}. \tag{18}$$

The values of these parameters yield: $u = 5.9 \times 10^{-5}$ A/cm^2, and $\varphi = 4.85 \times 10^{-25}$ A^2 s/cm^2 for the system with CuPc, and $u = 7.6 \times 10^{-6}$ A/cm^2 and $\varphi = 4.85 \times 10^{-25}$ A^2 s/cm^2 for the system with PBrPc. Smaller values of u and φ in the case of the system with bromophosphorus phthalocyanine result probably from a higher value of r (and consequently from a higher value of the bimolecular rate constant of recombination α) and a smaller value of q for this system in compar-
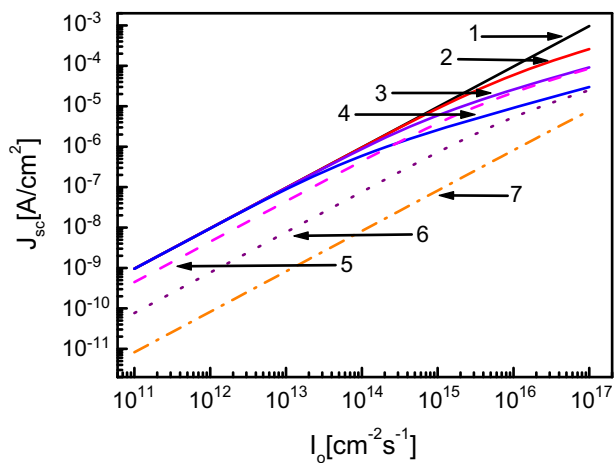

Fig. 3. Light intensity dependences of short-circuit current calculated for different values of rate constant of recombination (α) and trapping (k_{te}, k_{th}): (1) $j_G = qI_0$, $\alpha = 0$, $k_{te} = k_{th} = 0$, 2, 3, 4 – $k_{te} = k_{th} = 0$, (2) $\alpha = 10^{-9}$ cm^3 s^{-1}, (3) $\alpha = 10^{-8}$ cm^3 s^{-1}, (4) $\alpha = 10^{-7}$ cm^3 s^{-1}, (5) $\alpha = 10^{-8}$ cm^3 s^{-1}, $k_{te} = k_{th} = 10^6$ s^{-1}, (6) $\alpha = 10^{-7}$ cm^3 s^{-1}, $k_{te} = k_{th} = 10^7$ s^{-1}, and (7) $\alpha = 10^{-7}$ cm^3 s^{-1}, $k_{te} = k_{th} = 10^8$ s^{-1}.
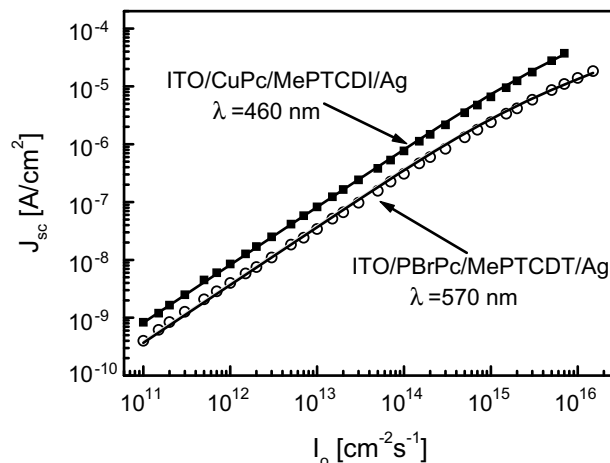

Fig. 4. Experimental (points) and calculated (solid lines) light intensity dependences of short-circuit current for ITO/CuPc/MePTCDI/Ag and ITO/PBrPc/MePTCDI/Ag systems.

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ison to the system with copper phthalocyanine. It can be noticed that for the set of curves in Fig. 3 the u parameter takes a value from the range 9.6×10^{-7} A/cm^2–1.1×10^{-4} A/cm^2, while the φ parameter from the range 9.2×10^{-27}A^2 s/cm^2–9.2×10^{-25} A^2 s/cm^2. As cab be seen, the values of u and φ parameters characterizing the experimental results are located within these ranges.

4. Conclusion

The model of a bilayer organic photovoltaic system at the short-circuit mode presented in the work permits obtaining a simple analytical relation between short-circuit current density and light intensity as well as it rationalizes the influence of such parameters as charge carrier concentration at electrodes and at heterojunction, mobilities of charge carriers and rate constant of charge carrier recombination on this relation. The obtained good correlations between experimental curves of j_{sc} (I_0) for the systems with CuPc/MePTCDI and PBrPc/MePTCDI heterojunctions and calculation results indicate the possibility to apply this model to an analysis of the photovoltaic effect in bilayer systems. The model can be easily modified if we want to consider other generation–recombination processes in heterojunction.

Acknowledgment

References

[1] C.J. Brabec, V. Dyakonov, J. Parisi, N.S. Sariciftci (Eds.), Organic Photovoltaics, Springer, 2003.

[2] S.-S. Sun, N.S. Sariciftci (Eds.), Organic Photovoltaics, Taylor & Francis, 2005.
[3] J. Rostalski, D. Meissner, Sol. Energy Mat. Sol. Cells 63 (2000) 37.
[4] P. Peumans, A. Yakimov, S.R. Forrest, J. Appl. Phys. 93 (2003) 3693.
[5] D. Gebeyehu, M. Pfeiffer, B. Maenning, J. Drechsel, A. Werner, K. Leo, Thin Solid Films 451&452 (2004) 29.
[6] I. Riedel, J. Parisi, V. Dyakonov, L. Lutsen, D. Vanderzande, J.C. Hummelen, Adv. Funct. Mater. 14 (2004) 38.
[7] R. Signerski, J. Non-Cryst. Solids 352 (2006) 4319.
[8] E. Kymakis, E. Koudoumas, I. Franghiadakis, Sol. Energy Mat. Sol. Cells 90 (2006) 1705.
[9] R. Signerski, B. Kościelska, Opt. Mater. 27 (2005) 1480.
[10] D. Wöhrle, L. Kreienhoop, G. Schnurpfeil, J. Elbe, B. Tennigkeit, S. Hiller, D. Schlettwein, J. Mater. Chem. 5 (1995) 1819.
[11] R. Signerski, G. Jarosz, J. Godlewski, Synth. Met. 94 (1998) 135.
[12] W.U. Huynh, J.J. Milliron, A.P. Alivisatos, K.W. Barnham, Phys. Rev. B67 (2003) 115326.
[13] I. Riedel, N. Martin, F. Giacalone, J.L. Segura, D. Chirvase, J. Parisi, V. Dyakonov, Thin Solid Films 451&452 (2004) 43.
[14] J. Nelson, S.A. Choulis, J.R. Durrant, Thin Solid Films 451&452 (2004) 508.
[15] L.J.A. Koster, V.D. Mihailetchi, H. Xie, P.W.M. Blom, Appl. Phys. Lett. 87 (2005) 203502.
[16] J. Nelson, Phys. Rev. B67 (2003) 155209.
[17] J.A. Barker, C.M. Ramsdale, N.C. Greenham, Phys. Rev. B67 (2003) 075205.
[18] M. Koehler, L.S. Roman, O. Inganäs, M.G.E. da Luz, J. Appl. Phys. 96 (2004) 40.
[19] N. Tessler, N. Rappaport, J. Appl. Phys. 96 (2004) 1083.
[20] L.J.A. Koster, E.C.P. Smits, V.D. Mihailetchi, P.W.M. Blom, Phys. Rev. B72 (2005) 085205.
[21] F. Kozlowski, PhD thesis, TU Dresden, 2005.
[22] D.W. Sievers, V. Shrotriya, Y. Yang, J. Appl. Phys. 100 (2006) 114509.
[23] K.J. Hall, J.S. Bonham, L.E. Lyons, Aust. J. Chem. 31 (1978) 1661.
[24] G.G. Malliaras, J.R. Salem, P.J. Brock, J.C. Scott, J. Appl. Phys. 84 (1998) 1583.
[25] T. Stübinger, W. Brütting, J. Appl. Phys. 90 (2001) 3632.
[26] J. Sworakowski, K. Janus, S. Nešpůrek, M. Vala, IEEE Trans. Dielectrics Electr. Insulation 13 (2006) 1001.
[27] R.F. Salzman, J. Xue, B.P. Rand, A. Alexander, M.E. Thompson, S.R. Forrest, Org. Electron. 6 (2005) 237.
[28] H. Graaf, W. Michaelis, G. Schnurpfeil, N. Jaeger, D. Schlettwein, Org. Electron. 5 (2004) 237.
[29] H. Méndez, I. Thurzo, D.R.T. Zahn, Phys. Rev. B75 (2007) 045321.
[30] Y. Terao, H. Sasabe, C. Adachi, Appl. Phys. Lett. 90 (2007) 103515.