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MODELING OF PHOTOVOLTAIC PROPERTIES OF BILAYER ORGANIC SYSTEMS

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The work presents a theoretical description of current-voltage dependence and photovoltaic effect of a system formed from two organic layers and electrodes. The model is based on the assumption that in one of organic layers only an electron current can flow, while in the other only a hole current. Taking into account a constant-field approximation simple expressions describing the current-voltage relationship and short-circuit current have been obtained. The influence of space charge in organic layers related to trapped charge carriers is analysed on the basis of numerical calculations. The obtained results enable to estimate the role of electrodes, charge carrier traps and generation-recombination processes in photovoltaic properties of an organic bilayer system.

Key words: organic photovoltaic cells, organic heterojunctions.

Photovoltaic properties of organic heterojunctions have been widely studied due to the prospect of obtaining stable, efficient and low cost solar cells. The power-conversion efficiency in dye-sensitized solar cells has already overcome 10% and in the polymer bulk heterojunction and small molecular weight multilayer solar cells 5% [1–3]. The further progress in organic photovoltaic technology will be determined among others by the progress in the theoretical description of photovoltaic phenomenon. However, due to a wide variety of organic systems [1, 2, 4, 5] it is not possible to elaborate the universal model of this phenomenon.

There are many works, in which authors focused their attention on different processes determining photovoltaic parameters. As an example, in the works [6–8] a short-circuit current generated as a result of exciton dissociation at the interface of two organic layers is calculated, while in the works [9–11] numerical calculations of current-voltage relationships of either bilayer [9, 10] or bulk photovoltaic [11] devices are presented. Moreover, electric equivalent circuit of organic solar cells is discussed in the works [12–14] and factors limiting the power conversion efficiency of molecular photovoltaic devices are analysed in [15, 16].

This work deals with modeling of current-voltage characteristics of bilayer organic systems. In particular, a concentration of charge carriers at electrodes, generation-

recombination processes in junction and trapping of charge carrier in bulk of layers have been taken into account.

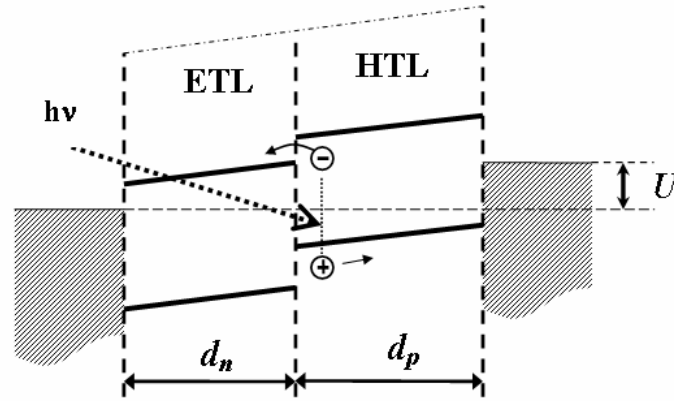


Fig. 1. An energy-level diagram of bilayer organic system

Fig. 1 shows an energy-level diagram of the analysed system. The system consists of two organic layers and electrodes. One of organic layers is an electron-transporting layer (ETL) of d_n -thickness, while the other is a hole-transporting layer (HTL) of d_p -thickness. Bands transporting electrons and holes are schemed as straight lines. The band-bending or potential jumps resulting from dipole layers, which can appear at electrodes or organic-organic interface, are not respected. Free charge carriers are generated only at the ETL-HTL interface either by thermal generation or by exciton dissociation. Thickness of the region, where the charge carrier generation occurs, is small, compared to the thickness of organic layers.

The main assumption of this model supposes that in ETL only an electron current flows, while in HTL only a hole current flows [9, 10].

Let us assume that in each organic layer the electric field is uniform. This assumption is true at low current intensity, low concentration of trapping states and strong built-in electric field. The effect of non-uniform of electric field occurring in thin near-electrode regions is assumed to be negligible.

Now the ETL will be considered as an example. Current density flowing through this layer is described by the expression:

$$j = -e\mu_n n(x) \frac{d\varphi_n(x)}{dx} + \mu_n k T \frac{dn(x)}{dx}, \quad (1)$$

where μ_n – electron mobility, $n(x)$ – concentration of electrons at x , $\varphi_n(x)$ – electric potential at x .

Solving this equation with respect to $n(x)$ and integrating the obtained expression over $\langle 0, d_n \rangle$ as well as applying the constant-field approximation (e.g.[17]), the following current-voltage relationship can be derived:

$$j = \frac{e\mu_n}{d_n} \left(\frac{kT}{e} \ln \frac{n_o}{n_j^{th}} + U_n \right) \frac{n_j \exp\left(\frac{eU_n}{kT}\right) - n_j^{th}}{\exp\left(\frac{eU_n}{kT}\right) - \frac{n_j^{th}}{n_o}}, \quad (2)$$

where U_n – voltage across ETL, n_o – concentration of electrons at the electrode, n_j^{th} , n_j – concentrations of electrons in heterojunction either in thermal equilibrium (n_j^{th}) or in the presence of current or illumination (n_j).

Furthermore, it will be assumed that the concentration n_o is independent of voltage and illumination (ohmic contact), and the concentration of electrons in heterojunction is determined by the monomolecular-kinetic equations:

$$G_{thn} - R_n n_j^{th} = 0 \quad \text{– for unilluminated system,} \quad (3)$$

$$G_{ex} + G_{thn} - R_n n_j = \frac{j}{ea} \quad \text{– for illuminated system.} \quad (4)$$

In the above equations G_{thn} is a rate of thermal generation, G_{ex} is a rate of photogeneration, R_n is a rate constant of recombination and a is a thickness of generation-recombination region. It is usually assumed that this region is limited to two monomolecular layers located on both sides of a heterojunction interface.

The rate of thermal generation is determined by an energy gap between a valence band of HTL and a conduction band of ETL. The rate constant of photogeneration of charge carriers, G_{ex} , is determined by a flux of exciton reaching the heterojunction interface and by quantum efficiency of exciton dissociation. Usually, G_{ex} is proportional to a light intensity I_o , i.e. $G_{ex} \sim I_o$ [7, 8]. The monomolecular recombination assumed in Eqs. (3) and (4), and characterized by the rate constant R_n , is noticeable in the presence of adequately high concentration of trapping-recombination centers in the junction.

If now Eqs. (3) and (4) are taking into account then the current-voltage relationship given by Eq. (2) takes the form:

$$j = \frac{\mu_n e}{d_n} \frac{G_{thn}}{R_n} \frac{\frac{G_{ex}}{G_{thn}} + 1 - \exp\left(-\frac{eU_n}{kT}\right)}{1 - \exp\left(-\frac{e(U_n + U_{bin})}{kT}\right)} + \frac{\mu_n}{a d_n R_n}, \quad (5)$$

$$\text{where } U_{bin} = \frac{kT}{e} \ln \frac{n_o}{n_j^{th}} = \frac{kT}{e} \ln \frac{n_o R_n}{G_{thn}} \quad (6)$$

is the built-in potential for ETL.

In particular, Eq. (5) leads to the following formula of:

- open-circuit current (when $j=0$):

$$U_{ocn} = \frac{kT}{e} \ln \left(\frac{G_{ex}}{G_{thn}} + 1 \right), \quad (7)$$

- short-circuit current (when $U_n=0$):

$$j_{sc} = \frac{e \mu_n}{d_n} \frac{G_{ex}}{R_n} \left(\frac{1 - \exp\left(-\frac{eU_{bin}}{kT}\right)}{U_{bin}} + \frac{\mu_n}{a d_n R_n} \right)^{-1} \quad (8)$$

Since $G_{ex} \sim I_o$ it can be concluded that both current densities, namely j (Eq. (5)) and j_{sc} (Eq. (8)) are proportional to light intensity I_o , while the voltage U_{ocn} (Eq.(7)) exhibits logarithmic dependence on I_o . Such relationships are often noticed in organic heterojunctions [1,4,10,18]. Analysis of Eq. (5) indicates that for high positive values of U_n the current yields:

$$j = e a (G_{thn} + G_{ex}) \quad (9)$$

and it is the sum of saturation-current density of the junction:

$$j_{sat} = e a G_{thn} \quad (10)$$

and the maximal value of short-circuit-current density:

$$j_{scmax} = e a G_{ex} \quad (11)$$

From Eq. (8) it can be noticed that short-circuit current reaches the maximal value when the built-in potential is enough high:

$$U_{bin} \gg \frac{kT}{e} \quad \text{and} \quad \frac{1}{U_{bin}} \ll \frac{\mu_n}{a d_n R_n} \quad (12)$$

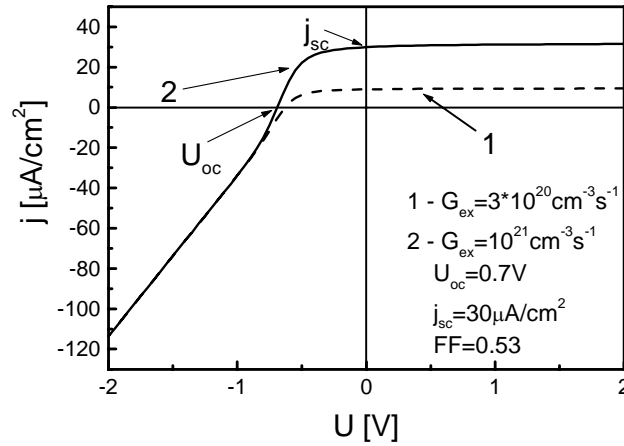


Fig. 2. Photocurrent-voltage relationships for the constant-field approximation

The analysis presented above deals with the current j flowing through ETL. Obviously, analogous relations can be ascribed to HTL. If the flow of the same current j through HTL requires U_p , then the voltage U between electrodes yields:

$$U = U_n + U_p \quad (13)$$

and $j(U)$ is the current-voltage relationship of the organic bilayer system. As an example, two current-voltage curves calculated according to Eqs. (5) and (13) for different values

of the photogeneration rate constant are presented in Fig. 2. For simplification it was assumed that $U_n=U_p=U/2$. In calculation the following values were taken: $T=290\text{K}$, $\mu_n=\mu_p=10^{-2}\text{cm}^2(\text{Vs})^{-1}$, $d_n=d_p=10^{-5}\text{cm}$, $a=2\cdot 10^{-7}\text{cm}$, $G_{thn}=G_{thp}=10^{15}\text{cm}^{-3}\text{s}^{-1}$, $R_n=R_p=10^8\text{s}^{-1}$, $n_o=p_o=10^{12}\text{cm}^{-3}$. It is seen that for positive voltage the current density is constant and is governed by Eq.(9). Within the photovoltaic range (the second quarter) the fill factor:

$$FF = \frac{(jU)_{\max}}{j_{sc} U_{oc}} \quad (14)$$

can be estimated. It yields 0.53. In the case of organic heterojunctions it is quite high value. In the third quarter the linear dependence of current density versus voltage is observed. The analysis of Eq. (5) indicates that the slop of the curves $j(U_n=U/2)$ within this range of voltage yields $\frac{e\mu_n n_o}{d_n}$ and it is determined by mobility of charge carriers, thickness of organic layers and concentration of charge carriers at electrodes.

Let us analyse now the effect of space charge on the shape of current-voltage curves of the organic bilayer system. If the space-charge concentration is enough high then assumption of uniform field is not true any more. Similarly, as in the previous chapter the attention will be focused on ETL. The space dependence of electric field $E_n(x)$ in this layer is governed by the Poisson equation:

$$\frac{dE_n(x)}{dx} = -\frac{d^2\phi_n(x)}{dx^2} = -\frac{e(n(x) + n_t(x))}{\epsilon_o\epsilon_{rn}}, \quad (15)$$

in which ϵ_o denotes vacuum permittivity, ϵ_{rn} is dielectric constant and $n_t(x)$ is the concentration of trapped charge carriers.

Let us assume that charge carriers are trapped by a discrete energy level of N - concentration and E_t - depth. The equation describing processes of trapping and thermal releasing of charge carriers takes the form:

$$\gamma_n n(x)(N - n_t(x)) - v \exp\left(-\frac{E_t}{kT}\right) n_t(x) = 0, \quad (16)$$

where γ_n is a rate constant of trapping and v is a thermal collision factor. The set of Eqs. (1), (15), (16), together with the boundary conditions of the following forms: $n(x=0)=n_o$, (3) and (4), are solved numerically with respect to $n(x)$ [19,20]. Afterwards the voltage across ETL is calculated:

$$U_n = \frac{j}{e\mu} \int_0^{d_n} \frac{dx}{n} + \frac{kT}{e} \ln \frac{n_j}{n_j^{th}}. \quad (17)$$

The same procedure is applied for HTL and as a result of this the voltage U_p is obtained. The potential difference between electrodes of the system is equal to the sum of U_p and U_n , Eq. (13).

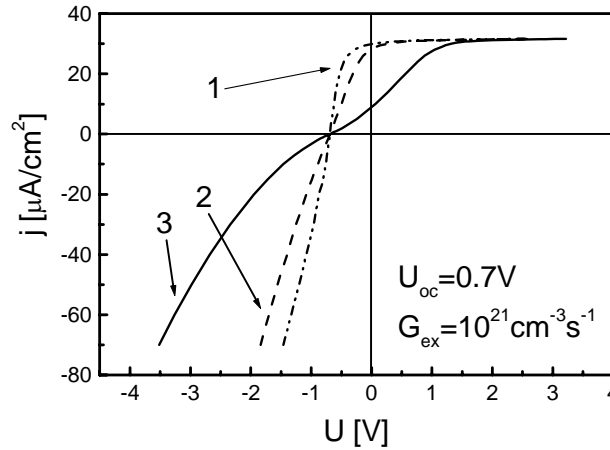


Fig. 3. Photocurrent-voltage relationships calculated numerically at various densities of charge carrier traps: 1 – $N=10^{15}\text{cm}^{-3}$, 2 – $N=10^{17}\text{cm}^{-3}$, 3 – $N=10^{18}\text{cm}^{-3}$

Current-voltage curves calculated according to the above procedure for the sample under illumination at three different concentrations of traps are presented in Fig.3. Similarly as in the chapter 2.1 it was assumed that $U_n=U_p=U/2$. Values of parameters are the same as those taken for Fig.2 and additionally $\epsilon_r=3,5$, $n_o=p_o=10^{12}\text{cm}^{-3}$, $\nu=10^{12}\text{s}^{-1}$, $E_t=0.5\text{eV}$, $\gamma_n=10^{-9}\text{cm}^3\text{s}^{-1}$.

It is easy to notice that the curve 1 is the same as the curve 2 in Fig.2. It means that charge carrier traps with the concentration not higher than 10^{15}cm^{-3} (and the depth 0.5eV) do not limit the current flowing through the system. For higher values of the trap concentration the short-circuit current (j_{sc}) and the fill factor (FF) are lower than in the approximation of constant field. The curve 3 departs quite significantly from the curves 1 and 2. Such a shape of current-voltage curves both within and in the vicinity of the photovoltaic range is often recognized as the result of an effect of electric field on the efficiency of charge carrier photogeneration [10,11]. However, in this work such an effect was not respected.

Analysis of current-voltage relationships as well as photovoltaic properties of bilayer organic system presented in this work was based on two main assumptions, namely that exciton dissociation occurs in very thin region near the organic-organic interface and that electrons are transported only by one of organic layers and holes by the other. Simple analytical expressions can be obtained when approximations of constant electric field within organic layers and of monomolecular recombination at organic-organic interface are applied. On the basis of them the role of such parameters as the rates of thermal- and photo-generation of charge carriers, the rate constant of recombination, charge carrier concentrations at electrodes and thickness of organic layers in electric properties of the system can be estimated. In particular, the obtained relations predict the linear dependence of photocurrent and short-circuit current versus light intensity. However, if bimolecular recombination at organic-organic interface is assumed [11, 18]:

$$G_{th} + G_{ex} - \alpha n_j p_j = \frac{j}{e a} \quad (18)$$

with α denoting the rate constant of bimolecular recombination and n_j , p_j denoting concentrations of electrons and holes in heterojunction, then applying the same procedure as in the chapter 2,1 it can be easily proved that the dependence of short-circuit current versus light intensity ($j_{sc}(I_0)$) is a square root function but within the range of low values of light intensity this dependence can be approximated by a linear function.

If the approximation of constant-electric field is not fulfilled then the numerical calculations have to be performed. Results presented in the chapter 2,2 show the effect of charge carrier traps on the shape of current-voltage curves within the photovoltaic range. The trap concentration enough high results in the same effect as field dependence of photogeneration of charge carriers, namely leads to the decrease of values of short-circuit current j_{sc} and fill factor FF . In the analysis of the influence of charge carrier traps it was assumed only a discrete trapping level of the depth E_b , however the same procedure can be applied also for a different trap distribution, e.g. the Gaussian one [20]. Spectral dependences of photocurrent and other quantities characterizing the photovoltaic effect were not considered in this work. These relationships are additionally determined by the relation between the rate of charge carrier photogeneration and the wavelength, i.e. $G_{ex}(\lambda)$, hence they depend on absorption coefficient, length of exciton diffusion, quantum efficiency of exciton dissociation and thickness of layers.

The theoretical description of photovoltaic effect presented in this work was based first of all on parameters, which values can be modified experimentally when designing a photovoltaic system.

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**МОДЕЛЮВАННЯ ФОТОГАЛЬВАНІЧНИХ ВЛАСТИВОСТЕЙ
ДВОХШАРОВИХ ОРГАНІЧНИХ СИСТЕМ****Р. Сігнерські**

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У статті наведено теоретичний опис вольт-амперної характеристики та фотогальванічного ефекту систем, сформованих з двох органічних шарів та електродів. Модель ґрунтується на припущенні, що один органічний шар має лише електронну, а другий – лише діркову провідності. Припускаючи, що електричне поле є постійним, отримано прості співвідношення, що описують вольт-амперну залежність та струм короткого замикання. Вплив просторового заряду органічних шарів на можливість захоплення носіїв заряду було покладено в основу числових розрахунків. Отримані результати дали змогу оцінити вплив електродів, пасток носіїв заряду та генераційно-рекомбінаційних процесів на фотогальванічні властивості органічних двошарових систем.

Ключові слова: органічна фотогальванічна комірка, органічний гетеро-перехід.

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