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NEW PERSPECTIVES FOR PHOTOELECTRIC PHENOMENA*

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The functioning of the solar cells (and photoelectric phenomena in general) relies on the photo-generation of carriers in p–n junctions and their subsequent recombination in the quasi-neutral regions. A number of basic issues concerning the physics of the operation of solar cells still remain obscure. This paper reports on some unsolved basic problems, namely: a model of the recombination processes that does not contradict Maxwell's equations; boundary conditions; the role played by space charges in the transport phenomena, and the formation of quasi-neutral regions under the presence of nonequilibrium photo-generated carriers. In this work, a new formulation of the theory that explains the underlying physical phenomena involved in the generation of a photo-e.m.f. is presented.

Keywords: photoelectric phenomena, solar cells, Dember effect, transport equations, recombination, nonequilibrium carriers

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1. Introduction

Charge carrier transport underlies the electrical behaviour of any semiconductor device [1–4] and, in particular, of solar cells [5, 6]. Despite the efforts made to correctly model such transport in semiconductors over the years, many questions still remain open. These questions need to be addressed in order to correctly model future devices.

One of these open questions is how to model carrier recombination. The mathematical expression routinely used to model the recombination rate [7] is basically incorrect. It has recently been demonstrated that it contradicts Maxwell's equations, and hence a new corrected model must be developed [8]. This problem was partly addressed in previous works (see, for example, Ref. [9]). Recombination is a key feature when describing carrier transport in semiconductors because it strongly affects the electrical response of the semiconductor at all levels of external excitation. This phenomenon is not limited to pure electrical problems but is very general, since the nonequilibrium charge carriers created by several physical sources (photo-generation, for instance) will lead to similar situations that need to be described using the same model [10–14]. The last remark that must be made about the need for a correct modeling of recombination is that in devices operating under a strong excitation regime (the operation of solar cells lies in this regime) the importance of a correct formulation of the recombination terms is even more important [15, 16].

Since in general the set of Poisson and transport equations cannot be solved analytically, some simplifications must be introduced if we are to achieve a closed form solution. One approximation commonly used to solve this system of equations is

* Dedicated to the blessed memory of Juras Požela – a wonderful man and prominent physicist

the assumption of quasineutrality (QN) [17–19]. The use of the QN approximation is acceptable if the sample's and the diffusion lengths are both larger than the Debye length. Although QN has been routinely used in semiconductor device modeling for many years, the role of space charge in the formation of the current–voltage characteristic (CVC) in a semiconductor is still controversial. One of the main aims of this paper is to address the problems detailed earlier in the text.

The functioning of solar cells relies on the photo-generation of carriers in p–n junctions and their subsequent recombination in quasi-neutral regions. A number of basic issues concerning the physics of the operation of solar cells still remain obscure.

A very important question is the choice of boundary conditions used when solving the carrier-transport equations. It should be noted that the expressions commonly used are valid only for semiconductor devices operating in open-circuit conditions (see, for instance Ref. [20]). Since in normal operation a current flows at the terminals, a widespread use of boundary conditions for open-circuit conditions is incorrect. For closed-circuit conditions, a different set of boundary conditions needs to be derived. This problem has only been addressed in the last few years [21–23].

All the abovementioned issues need to be addressed when modeling any semiconductor devices. Solar cells are one of the strongest technologies in the steadily growing photovoltaic market [24].

This paper reports on some unsolved basic problems encountered when modeling solar cells.

Let us note finally that the general theory [25–28] of another photothermal effect, Dember effect, is erroneous, which was shown recently [29, 30]. The correct theory bases on the same ideas that are presented below. It is interesting that the Dember photo-power induced by ultrashort laser pulses often significantly exceeds its steady-state value [31].

Other mechanisms of photoelectric phenomena based on the same physical conceptions are presented in Refs. [32, 33].

2. Problem statement

The commonly accepted electrical model for the current density–voltage characteristic (CVC) of an ideal p–n junction is [34]:

$$J = J_0(\mathrm{e}^{V/V_\mathrm{T}}-1), \tag{1}$$

where J is the diode current density, V is the bias voltage, V_T is the thermal voltage and J_0 is the reverse-saturation current density that for a long abrupt diode is

$$J_0 = V_\mathrm{T}\left(\frac{\sigma_\mathrm{p}^\mathrm{n}}{L_\mathrm{D}^\mathrm{n}} + \frac{\sigma_\mathrm{n}^\mathrm{p}}{L_\mathrm{D}^\mathrm{p}}\right). \tag{2}$$

Here $\sigma_\mathrm{n}^\mathrm{p}$ ($\sigma_\mathrm{p}^\mathrm{n}$) is the electron (hole) conductivity of minority carriers in the p-side (n-side) of a junction diode; L_D^n and L_D^p are, respectively, the electron and hole diffusion lengths of minority carriers in n- and p- sides defined as

$$\begin{aligned} L_\mathrm{D}^\mathrm{n} &= \sqrt{D_\mathrm{p}\,\tau_\mathrm{p}}\,, \\ L_\mathrm{D}^\mathrm{p} &= \sqrt{D_\mathrm{n}\tau_\mathrm{n}}\,, \end{aligned} \tag{3}$$

where D_n (D_p) is the electron (hole) diffusivity, and τ_n (τ_p) is the electron (hole) minority carrier lifetime.

Equation (1) may be rewritten for a solar cell under illumination as [35]

$$-J = J_0(\mathrm{e}^{V/V_\mathrm{T}}-1) + J_\mathrm{I}, \tag{4}$$

where J_I is the photocurrent, and J is additionally related to the generated voltage V through the external resistive load (R) in the circuit and the solar cell area (S) as shown in Fig. 1:

$$J = \frac{V}{RS}\,. \tag{5}$$

For the sake of simplicity, let us examine the photocurrent generated in the slab of the semiconductor of thickness L with the incident light at $x = 0$. J_I may be obtained as the integral of the light intensity across the device $I(x)$:

$$|J_\mathrm{I}| = e\alpha\beta\int_0^L I(x)\mathrm{d}x\,. \tag{6}$$

Here e is the absolute value of the electron charge, α is the absorption coefficient of light, and β is the quantum efficiency,

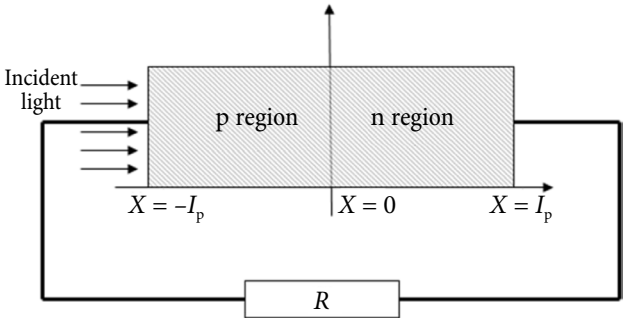

Fig. 1. Solar cell diode with an external resistor load.

$$\beta = \frac{\alpha - \alpha_0}{\alpha}, \tag{7}$$

where α_0 is the absorption coefficient on free carriers [36].

The light intensity inside the semiconductor slab will decrease following the law

$$I = I_0 e^{-\alpha x}, \tag{8}$$

where I_0 is the light intensity (number of incident photons per unit time and unit area) at the plane of the incident light ($x = 0$), and the carrier generation rate due to photon-absorption can be written as

$$g = (\alpha - \alpha_0)\, I_0 e^{-\alpha x}. \tag{9}$$

The set of Eqs. (4)–(9) may be extended or augmented with other equations for a finer modeling of a real technology [37], but this set constitutes the fundamental framework to describe the electrical behaviour of any diode-based solar cell.

Let us assume a one-dimensional problem for a single-diode solar cell such as the one given in Fig. 1. In this case from Eq. (4) we obtain the current–voltage characteristic (CVC) as shown in Fig. 2, left.

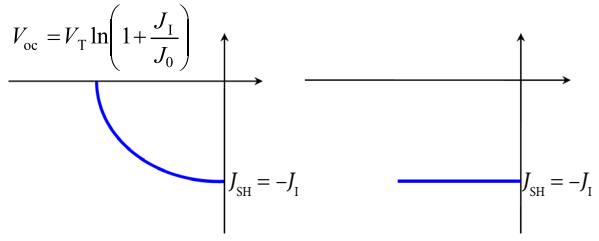

Fig. 2. J–V characteristic of an ideal solar cell with the short- and open-circuit expressions for the axis-intercept points V_{oc} and J_{SH}, respectively (left). J–V characteristic in the limiting case of a thin-film cell $l_{n,p} \ll L_D^{n,p}$ (right).

According to the values of diffusion lengths in Si (in a c-Si thin-film solar cell or in a-Si ones of nanometre dimensions [38]), the following inequality will hold:

$$l_{n,p} \ll L_D^{n,p}. \tag{10}$$

From Eq. (10) it follows that $L_D^{n,p} \to \infty$ and $\tau_{n,p} \to \infty$; therefore, recombination is negligible and according to Eq. (2) $J_0 \to 0$ and, moreover, from Eq. (4) the basic model leads to the unphysical result (see Fig. 2, right): $J \approx -J_I$, i. e. the p–n junction behaves as a current-source that translates photo-excitation into current at any value of the diode-voltage independently of the p–n junction properties.

If we have a long structure or a strong recombination rate ($L_D^{n,p} \to 0$ and $\tau_{n,p} \to 0$),

$$l_{n,p} \ll L_D^{n,p}, \tag{11}$$

according to Eq. (2) $J_0 \to \infty$ and, moreover, from Eq. (4) we obtain $V_{oc} = 0$.

From the above it follows that the framework of basic equations conventionally used to model solar cells fails [39]. Regardless of its apparent simplicity, since this framework constitutes the foundations of any electrical modeling of a solar cell diode, the discussed problem will persist in any other model that one can build, therefore it is crucial to identify the origin of the problem and modify the basic model to build a new framework free from unphysical errors. In this work we will present a new model and we will analytically show in a simple case that this new framework does not fail to correctly describe the solar cell.

3. Model description

The macroscopic description of the transport of non-equilibrium charge carriers is done with the continuity equations for the electron (j_n) and hole (j_p) current densities and the Poisson equation (PE) (see Ref. [20]):

$$\frac{\partial n}{\partial t} = g_n + \frac{1}{e}\mathrm{div}\boldsymbol{j}_n - R_n, \tag{12}$$

$$\frac{\partial p}{\partial t} = g_p - \frac{1}{e}\mathrm{div}\boldsymbol{j}_p - R_p, \tag{13}$$

$$\mathrm{div}E = \frac{4\pi}{\varepsilon}\rho, \tag{14}$$

where n and p are the local electron and hole concentrations (n_0 and p_0 are the equilibrium values); g_n and g_p are the electron and hole external generation ratios; E is the electric field; ρ is the bulk electrical charge; e is the hole charge; ε is the permittivity; and R_n and R_p are the electron and hole recombination rates. The above system of equations must be solved self-consistently on both sides of the p–n junction of the solar cell.

Subtracting Eq. (13) from Eq. (12), we obtain

$$e(g_n - g_p) + \mathrm{div}(\boldsymbol{j}_n + \boldsymbol{j}_p) - e(R_n - R_p) = e\frac{\partial(n-p)}{\partial t}. \tag{15}$$

Unless otherwise indicated, and with no loss of generality, in this paper we shall refer to a semiconductor that contains an impurity with a single energy level able to capture electrons. The charge conservation in this special case can be written as [40]

$$\begin{aligned}\mathrm{div}\boldsymbol{j} &= \mathrm{div}(\boldsymbol{j}_\mathrm{n} + \boldsymbol{j}_\mathrm{p}) \\ &= -\frac{\partial p}{\partial t} = e\frac{\partial}{\partial \mathrm{t}}(n - p + n_\mathrm{t}),\end{aligned} \tag{16}$$

where $\boldsymbol{j}$ is the total current and n_t is the concentration of electrons captured by the impurities. From Eqs. (15) and (16) we obtain the following relationship [8]:

$$g_\mathrm{n} - g_\mathrm{p} = R_\mathrm{n} - R_\mathrm{p} - \frac{\partial n_\mathrm{t}}{\partial t}. \tag{17}$$

As it follows directly from Eq. (17), the deviation of the concentration of the electrons trapped in the impurity level, δn_t, from its equilibrium value, $n_{0\mathrm{t}}$, depends on the deviations of the electron and hole concentrations from their own equilibrium values ($\delta n = n - n_0$, $\delta p = p - p_0$) through R_n and R_p, and on g_n, g_p and t.

Under stationary conditions, from Eq. (17) it follows that

$$R_\mathrm{n} - R_\mathrm{p} = g_\mathrm{n} - g_\mathrm{p}. \tag{18}$$

In the case of a semiconductor that contains a concentration N_t of impurities, and assuming that the impurities follow Shockley–Read–Hall statistics, [7], the recombination rates R_n and R_p can be calculated (we are implicitly assuming thermal equilibrium between electrons, holes and phonons):

$$R_\mathrm{n} = \alpha_\mathrm{n}(T)n(N_\mathrm{t} - n_\mathrm{t}) - \alpha_\mathrm{n}(T)n_1 n_\mathrm{t}, \tag{19a}$$

$$R_\mathrm{p} = \alpha_\mathrm{p}(T)pn_\mathrm{t} - \alpha_\mathrm{p}(T)\, p_1(N_\mathrm{t} - n_\mathrm{t}). \tag{19b}$$

Here $\alpha_\mathrm{n}(T)$ and $\alpha_\mathrm{p}(T)$ are the electron and hole capture coefficients, and n_1 (p_1) is the electron (hole) concentration when the Fermi level matches the activation energy of the impurity.

Further the temperature dependence of α_n and α_p will be omitted. Once R_n and R_p are available, n_t can be obtained using Eq. (18). Replacing n_t back in Eqs. (19), the recombination rates R_n and R_p are finally obtained in terms of n, p, g_n and g_p.

Assuming a constant and uniform temperature across the sample, we obtain the following expression for n_t:

$$n_\mathrm{t} = \frac{N_\mathrm{t}(\alpha_\mathrm{n} n + \alpha_\mathrm{p} p_1) - g_\mathrm{n} + g_\mathrm{p}}{\alpha_\mathrm{p}(p + p_1) + \alpha_\mathrm{n}(n + n_1)}. \tag{20}$$

By substitution of Eq. (20) in Eqs. (19) we obtain

$$R_\mathrm{n} = \frac{N_\mathrm{t}\alpha_\mathrm{n}\alpha_\mathrm{p}(np - n_0 p_0) + \alpha_\mathrm{n}(n + n_1)(g_\mathrm{n} - g_\mathrm{p})}{\alpha_\mathrm{p}(p + p_1) + \alpha_\mathrm{n}(n + n_1)}, \tag{21a}$$

$$R_\mathrm{p} = \frac{N_\mathrm{t}\alpha_\mathrm{n}\alpha_\mathrm{p}(np - n_0 p_0) - \alpha_\mathrm{p}(p + p_1)(g_\mathrm{n} - g_\mathrm{p})}{\alpha_\mathrm{p}(p + p_1) + \alpha_\mathrm{n}(n + n_1)}. \tag{21b}$$

It should be stressed that this result is valid for any level of excitation.

Let us now consider that the level of the excitation (generation) is weak, such that $\delta n \ll n_0$ and $\delta p \ll p_0$. In this case, the recombination rates and the excess of the electron concentration on the impurities reduce to

$$R_\mathrm{n} = \frac{\delta n}{\tau_\mathrm{n}} + \frac{\delta p}{\tau_\mathrm{p}} + \frac{\alpha_\mathrm{n}(n_0 + n_1^0)(g_\mathrm{n} - g_\mathrm{p})}{\alpha_\mathrm{n}(n_0 + n_1^0) + \alpha_\mathrm{p}(p_0 + p_1^0)}, \tag{22a}$$

$$R_\mathrm{p} = \frac{\delta n}{\tau_\mathrm{n}} + \frac{\delta p}{\tau_\mathrm{p}} - \frac{\alpha_\mathrm{p}(p_0 + p_1^0)(g_\mathrm{n} - g_\mathrm{p})}{\alpha_\mathrm{n}(n_0 + n_1^0) + \alpha_\mathrm{p}(p_0 + p_1^0)}, \tag{22b}$$

$$\delta n_\mathrm{t} = \frac{\alpha_\mathrm{n}(N_\mathrm{t} - n_1^0)\delta n - \alpha_\mathrm{p} n_\mathrm{t}^0 \delta p - g_\mathrm{n} + g_\mathrm{p}}{\alpha_\mathrm{n}(n_0 + n_1^0) + \alpha_\mathrm{p}(p_0 + p_1^0)}, \tag{22c}$$

where n_t^0, p_1^0 and n_1^0 are the equilibrium values of their respective magnitudes and $n_\mathrm{t} = n_\mathrm{t}^0 + \delta n_\mathrm{t}$.

Despite the time dimensions of τ_n and τ_p, these parameters cannot be straightforwardly identified with the lifetimes of the non-equilibrium carriers, contrary to what is widely used in semiconductor modeling: $R_\mathrm{n} = \delta n/\tau_\mathrm{n}$ and $R_\mathrm{p} = \delta p/\tau_\mathrm{p}$, where τ_n and τ_p are lifetimes [7, 20, 34].

In a non-degenerate semiconductor, the following relationship holds:

$$\frac{\tau_\mathrm{n}}{\tau_\mathrm{p}} = \frac{n_0}{p_0}. \tag{23}$$

From Eqs. (22) it becomes clear that, in principle, both R_n and R_p are functions of the generation rates. This points to a strong coupling between the generation–recombination rates and the carrier densities across the sample.

Because all the problems mentioned above exist in a linear region of CVC, too, we will study only the last region.

4. Model for low injection

From the previous section, it follows that by assuming linear conditions (low generation), uniform temperature ($T = T_0$) across the sample, and stationary conditions in the region under study, the system of Eqs. (12) and (13) can be rewritten as (see Eqs. (22))

$$\begin{aligned}\mathrm{div}\, j_\mathrm{n} &= e\left(\frac{\delta n}{\tau_\mathrm{n}} + \frac{\delta p}{\tau_\mathrm{p}}\right) \\ &+ e\left(\frac{\alpha_\mathrm{p}(n_0 + n_1^0)g_\mathrm{p} + \alpha_\mathrm{p}(p_0 + p_1^0)g_\mathrm{n}}{\alpha_\mathrm{n}(n_0 + n_1^0) + \alpha_\mathrm{p}(p_0 + p_1^0)}\right),\end{aligned} \tag{24a}$$

$$\operatorname{div} j_{\mathrm{p}} = -e\left(\frac{\delta n}{\tau_{\mathrm{n}}} + \frac{\delta p}{\tau_{\mathrm{p}}}\right) - e\left(\frac{\alpha_{\mathrm{n}}(n_0 + n_1^0)g_{\mathrm{p}} + \alpha_{\mathrm{p}}(p_0 + p_1^0)g_{\mathrm{n}}}{\alpha_{\mathrm{n}}(n_0 + n_1^0) + \alpha_{\mathrm{p}}(p_0 + p_1^0)}\right). \tag{24b}$$

We shall use the variation in magnitudes, not the magnitudes themselves, and in this way we can separate and remove the equilibrium contributions. In a general case, for a non-degenerate semiconductor, in a linear approximation δn and δp can be written in terms of the variations in their respective chemical potentials as [41]

$$\delta n = \frac{n_0}{T_0}\delta\mu_{\mathrm{n}}, \tag{25a}$$

$$\delta p = \frac{p_0}{T_0}\delta\mu_{\mathrm{p}}. \tag{25b}$$

Both Eqs. (25a) and (25b) are related to the definition of the Fermi quasi-levels for electrons and holes. Let us consider, for the sake of simplicity, that the current flux only takes place in the x direction. The current densities can then be calculated as

$$j_{\mathrm{n}} = -\sigma_{\mathrm{n}}\frac{\mathrm{d}\delta\psi_{\mathrm{n}}}{\mathrm{d}x}, \tag{26a}$$

$$j_{\mathrm{p}} = -\sigma_{\mathrm{p}}\frac{\mathrm{d}\delta\psi_{\mathrm{n}}}{\mathrm{d}x}, \tag{26b}$$

where σ_{n} (σ_{p}) is the electrical conductivity of electrons (holes), and $\delta\psi_{\mathrm{n}}$ ($\delta\psi_{\mathrm{p}}$) is the variation in the electrochemical potential (or quasi-Fermi level) of the electrons (holes):

$$\delta\psi_{\mathrm{n}} = \delta\phi - \frac{\delta\mu_{\mathrm{n}}}{e}, \tag{27a}$$

$$\delta\psi_{\mathrm{p}} = \delta\phi + \frac{\delta\mu_{\mathrm{p}}}{e}, \tag{27b}$$

where $\phi = \phi_0 + \delta\phi$ is the electrical potential, and ϕ_0 is the electrical potential in equilibrium (built-in potential). Using Eqs. (24a), (24b), and (26), we obtain

$$-\sigma_{\mathrm{n}}\frac{\mathrm{d}^2\delta\psi_{\mathrm{n}}}{\mathrm{d}x^2} = e\left(\frac{\delta n}{\tau_{\mathrm{n}}} + \frac{\delta p}{\tau_{\mathrm{p}}}\right) + e\left(\frac{\alpha_{\mathrm{n}}(n_0 + n_1^0)g_{\mathrm{p}} + \alpha_{\mathrm{p}}(p_0 + p_1^0)g_{\mathrm{n}}}{\alpha_{\mathrm{n}}(n_0 + n_1^0) + \alpha_{\mathrm{p}}(p_0 + p_1^0)}\right), \tag{28a}$$

$$-\sigma_{\mathrm{p}}\frac{\mathrm{d}^2\delta\psi_{\mathrm{p}}}{\mathrm{d}x^2} = -e\left(\frac{\delta n}{\tau_{\mathrm{n}}} + \frac{\delta p}{\tau_{\mathrm{p}}}\right) - e\left(\frac{\alpha_{\mathrm{n}}(n_0 + n_1^0)g_{\mathrm{p}} + \alpha_{\mathrm{p}}(p_0 + p_1^0)g_{\mathrm{n}}}{\alpha_{\mathrm{n}}(n_0 + n_1^0) + \alpha_{\mathrm{p}}(p_0 + p_1^0)}\right). \tag{28b}$$

Using Eqs. (23) and (25), system (28) becomes

$$\frac{\mathrm{d}^2\delta\psi_{\mathrm{n}}}{\mathrm{d}x^2} = \frac{\tau_{\mathrm{M}}^{\mathrm{n}}}{\tau_n l_{\mathrm{n}}^2}(\delta\psi_{\mathrm{n}} - \delta\psi_{\mathrm{p}}) + \frac{e}{\sigma_{\mathrm{n}}}\left(\frac{\alpha_{\mathrm{n}}(n_0 + n_1^0)g_{\mathrm{p}} + \alpha_{\mathrm{p}}(p_0 + p_1^0)g_{\mathrm{n}}}{\alpha_{\mathrm{n}}(n_0 + n_1^0) + \alpha_{\mathrm{p}}(p_0 + p_1^0)}\right), \tag{29a}$$

$$\frac{\mathrm{d}^2\delta\psi_{\mathrm{p}}}{\mathrm{d}x^2} = -\frac{\tau_{\mathrm{M}}^{\mathrm{n}}}{\tau_n l_{\mathrm{n}}^2}(\delta\psi_{\mathrm{n}} - \delta\psi_{\mathrm{p}}) - \frac{e}{\sigma_{\mathrm{p}}}\left(\frac{\alpha_{\mathrm{n}}(n_0 + n_1^0)g_{\mathrm{p}} + \alpha_{\mathrm{p}}(p_0 + p_1^0)g_{\mathrm{n}}}{\alpha_{\mathrm{n}}(n_0 + n_1^0) + \alpha_{\mathrm{p}}(p_0 + p_1^0)}\right). \tag{29b}$$

Here $\tau_{\mathrm{M}}^{\mathrm{n}}$ is the dielectric relaxation time for electrons, and l_{n} is the Debye length for the electrons [14]. It immediately follows from Eqs. (29) that since the sub-system of two equations for the electrochemical potentials is explicitly independent of the electrical potential, the PE is decoupled from Eqs. (29). The fact that the PE can be decoupled from the transport equations is very important.

Let us recall that the calculation of current density in a semiconductor only involves the derivative of the electro-chemical potential and no other magnitudes (see Eqs. (26)). The physical meaning of Eqs. (28) is that under linear conditions the electrochemical potentials for holes and electrons can be obtained, ignoring the spatial distributions of other relevant magnitudes such as carrier concentrations and the electrical potential. From this it immediately follows that neither the Poisson equation nor its boundary conditions (BCs) are necessary to obtain the electrochemical potentials and, eventually, the current density. It must be highlighted that this important result has been obtained without any additional hypothesis such as QN. Evidently, to obtain the distributions of the quantities n, p and ϕ, the Poisson equation must be solved with appropriate BCs. All these quantities exhibit strong variations over distances of the order of the Debye length. Nevertheless, since the pairs n and ϕ or p and ϕ exhibit the same dependence on the Debye length, this dependence cancels out when calculating the electrochemical potentials. Since ψ_{n} and ψ_{p} do not depend on the Debye length, the current density and the resistance in a semiconductor sample may not be influenced by the bulk space charge on a distance comparable to the Debye's length at the contacts. In fact, a compensation of the influence of the bulk charge layer on the electric and chemical potentials takes place through the cancellation of the drift and diffusion currents originated by, on the one hand, the non-equilibrium built-in electric field and, on the other hand, the heterogeneity of the carrier concentration in

the bulk charge layer. This is in conflict with the results reported in Refs. [13, 14].

5. BCs for semiconductor structures

The challenge in elaborating boundary conditions for solar cells lies in the fact that, on the one hand, BCs must be sufficiently universal, and, on the other, that they must comprise all fundamental effects introduced by the interfaces.

Let us consider the BCs widely used for a contact with surface recombination. It is a common practice [20,42–44] to model at the contact the electric current flowing through it for electrons as $j_n = s_n\,\delta n_s$ (where j_n is the density of the electron current; s_n is the surface recombination rate; and δn_s is the concentration of nonequilibrium carriers at the interface). These BCs are only physically correct in open circuits since there is no effective carrying of charge through the boundary; the total current is caused solely by surface recombination, as can be verified trivially if one sets $s_n = 0$. However, as a matter of fact, the use of these BCs is extended to closed circuit conditions with no physical support [44, 45]. As a result, the equations obtained for the CVC characteristic of solar cells as well as the value obtained for the photoelectromotive force appear to be incorrect.

A significant step towards addressing this issue can be found in Ref. [21], where a method for constructing BCs that correctly takes into account the recombination in the transition layer when an electric current flows (closed circuit condition) is offered. Actually, the boundary between two media of the structure is the transition layer 3 of the thickness δ, where the parameters of sample 1 continuously turn into the parameters of sample 2 [46]. One can consider the thickness of this layer 3 to be zero if one is not interested in the microscopic processes in the layer. In this case, the scattering mechanisms in this layer become surface scattering mechanisms.

The experimental proofs of these surface scattering mechanisms [47, 48] make it possible to suggest the occurrence of the surface kinetic coefficients, which are different from the bulk ones.

However, in that paper BCs were formulated only for the continuity equations, and the BCs to the Poisson equation were not discussed at all. This aspect was explored in the papers [22, 23]. Each paper was tracking how the BCs change depending on whether the QN approach was invoked. A general system of BCs was formulated that is suitable for research into stationary transport processes in any structure of semiconductors and metals in various combinations within the framework of the continuity equations. BCs are presented for the general case of a contact between a solid (this contact is considered as a "free-surface" in a broad sense) and the vacuum under nonequilibrium conditions. Finally, the case of a hetero-contact between two conducting media under a current flow is addressed and it is found that BCs for open-circuit conditions are a limiting case when the current flow is set to zero. In all the considered cases the changes occurring in the BCs if the QN approach is invoked are carefully studied. Since these BCs were obtained based on the fundamental physical features of carrier transport, the suggested BCs can also be successfully used in other methods of the theoretical treatment of carrier transport; for example, while modeling physical devices with the Monte Carlo technique [45].

6. New model for thin-film solar cells

Let us assume once again that inequality of Eq. (10) holds and, accordingly, in the solar cell recombination is negligible. The macroscopic description of the transport of non-equilibrium charge is done with the continuity equations for the electron ($\boldsymbol{j}_n$) and hole ($\boldsymbol{j}_p$) current densities (see Eqs. (12), (13)).

In a stationary case and one-dimensional problem along the x-direction, normal to the p–n junction plane as in Fig. 1, these equations become

$$\frac{\mathrm{d}j_n}{\mathrm{d}x} = e(R_n - g_n), \tag{30a}$$

$$\frac{\mathrm{d}j_p}{\mathrm{d}x} = -e(R_p - g_p)\cdot \tag{30b}$$

Since volume recombination is negligible, $R_n = R_p = 0$, and, accordingly, $g_n = g_p = g(x)$; i. e. the generation is band-to-band and the continuity equations reduce to

$$\frac{\mathrm{d}j_n}{\mathrm{d}x} = -eg(x), \tag{31a}$$

$$\frac{\mathrm{d}j_p}{\mathrm{d}x} = eg(x). \tag{31b}$$

Additionally, it can be shown that in the absence of recombination and under band-to-band generation the density of charge in any impurity level remaining constant [39], under all the above conditions the QN approximation reduces to $\delta n = \delta p$. Using the QN approximation, the following relationship between the deviations from the equilibrium of the chemical potentials holds (see Eqs. (25)):

$$\delta\mu_p = \frac{n_0}{p_0}\delta\mu_n. \tag{32}$$

In order to further simplify the mathematical problem, while ensuring no loss of generality of the physical one, we will assume a step-like profile for the light absorption instead of the model in Eq. (8):

$$I = \begin{cases} I_0 & -l_\mathrm{p} < x < 0 \\ 0 & 0 < x < l_\mathrm{n}. \end{cases} \tag{33}$$

Using Eqs. (9) and (33) we may write the continuity Eqs. (31) as

$$\begin{aligned} \frac{\mathrm{d}j_\mathrm{n}^\mathrm{p}}{\mathrm{d}x} &= -eg_0, & \frac{\mathrm{d}j_\mathrm{p}^\mathrm{p}}{\mathrm{d}x} &= eg_0, \\ \frac{\mathrm{d}j_\mathrm{n}^\mathrm{n}}{\mathrm{d}x} &= 0, & \frac{\mathrm{d}j_\mathrm{p}^\mathrm{n}}{\mathrm{d}x} &= 0. \end{aligned} \tag{34}$$

Superscripts in current densities in Eqs. (34) indicate the doping type of the region. The current densities may be written as [15]

$$j_\mathrm{n}^\mathrm{n} = -\sigma_\mathrm{n}^\mathrm{n}\left(\frac{\mathrm{d}\delta\varphi^\mathrm{n}}{\mathrm{d}x} - \frac{1}{e}\frac{\mathrm{d}\delta\mu_\mathrm{n}^\mathrm{n}}{\mathrm{d}x}\right), \tag{35a}$$

$$j_\mathrm{p}^\mathrm{n} = -\sigma_\mathrm{p}^\mathrm{n}\left(\frac{\mathrm{d}\delta\varphi^\mathrm{n}}{\mathrm{d}x} + \frac{1}{e}\frac{\mathrm{d}\delta\mu_\mathrm{p}^\mathrm{n}}{\mathrm{d}x}\right), \tag{35b}$$

$$j_\mathrm{n}^\mathrm{p} = -\sigma_\mathrm{n}^\mathrm{p}\left(\frac{\mathrm{d}\delta\varphi^\mathrm{p}}{\mathrm{d}x} - \frac{1}{e}\frac{\mathrm{d}\delta\mu_\mathrm{n}^\mathrm{p}}{\mathrm{d}x}\right), \tag{35c}$$

$$j_\mathrm{p}^\mathrm{p} = -\sigma_\mathrm{p}^\mathrm{p}\left(\frac{\mathrm{d}\delta\varphi^\mathrm{p}}{\mathrm{d}x} + \frac{1}{e}\frac{\mathrm{d}\delta\mu_\mathrm{p}^\mathrm{p}}{\mathrm{d}x}\right), \tag{35d}$$

where we introduced the electric potential φ. To solve the Eqs. (34) with Eqs. (25), (32) and (35), we need to determine and impose enough boundary conditions at the semiconductor interfaces [21–23]. We will assume ideal metallic (ohmic) contacts placed at $x = -l_\mathrm{p}$ and at $x = l_\mathrm{n}$, therefore the excess of carries is null:

$$\delta n^\mathrm{p}(-l_\mathrm{p}) = \delta p^\mathrm{p}(-l_\mathrm{p}) = 0,\ \delta n^\mathrm{n}(l_\mathrm{n}) = \delta p^\mathrm{n}(l_\mathrm{n}) = 0. \tag{36}$$

According to Eq. (36), we obtain the following four boundary conditions for the chemical potentials at the metal–semiconductor contacts:

$$\delta\mu_\mathrm{n}^\mathrm{p}(-l_\mathrm{p}) = \delta\mu_\mathrm{p}^\mathrm{p}(-l_\mathrm{p}) = 0,\ \delta\mu_\mathrm{n}^\mathrm{n}(l_\mathrm{n}) = \delta\mu_\mathrm{p}^\mathrm{n}(l_\mathrm{n}) = 0. \tag{37}$$

Two additional boundary conditions may be imposed on the electric potential at the same metal–semiconductor contacts:

$$\delta\varphi^\mathrm{p}(-l_\mathrm{p}) = 0,\ \delta\varphi^\mathrm{n}(l_\mathrm{n}) = V. \tag{38}$$

At the interface of the two semiconductor regions, since there is no recombination, we may write two additional boundary conditions at $x = 0$ [23]:

$$j_\mathrm{n}^\mathrm{n}(0) = j_\mathrm{n}^\mathrm{p}(0), \quad j_\mathrm{p}^\mathrm{n}(0) = j_\mathrm{p}^\mathrm{p}(0). \tag{39}$$

Two more boundary conditions are [21]

$$\delta\varphi^\mathrm{p}(0) - \frac{\delta\mu_\mathrm{n}^\mathrm{p}(0)}{e} = \delta\varphi^\mathrm{n}(0) - \frac{\delta\mu_\mathrm{n}^\mathrm{n}(0)}{e}, \tag{40a}$$

$$\delta\varphi^\mathrm{p}(0) + \frac{\delta\mu_\mathrm{p}^\mathrm{p}(0)}{e} = \delta\varphi^\mathrm{n}(0) + \frac{\delta\mu_\mathrm{p}^\mathrm{n}(0)}{e}. \tag{40b}$$

Using the obtained boundary conditions from the continuity of the Fermi quasi-levels it is straightforward to solve the linear system of equations for the current densities (Eqs. (34), (35)) and obtain the solution:

$$J\left(\frac{l_\mathrm{n}}{\sigma_\mathrm{p}^\mathrm{n}}\frac{l_\mathrm{p}}{\sigma_\mathrm{n}^\mathrm{p}}\right) + V\left(\frac{l_\mathrm{p}}{\sigma_\mathrm{n}^\mathrm{p}} + \frac{l_\mathrm{n}}{\sigma_\mathrm{p}^\mathrm{n}}\right) + \frac{eg_0}{2}\left(\frac{l_\mathrm{p}^2}{\sigma_\mathrm{n}^\mathrm{p}}\frac{l_\mathrm{n}}{\sigma_\mathrm{p}^\mathrm{n}}\right) = 0. \tag{41}$$

In the third term of Eq. (41) we may identify the photocurrent density created under illumination:

$$J_\mathrm{I} = \frac{eg_0}{2} l_\mathrm{p}. \tag{42}$$

Since we are under a small voltage/current – linear approximation – with the aim of obtaining an analytical closed form for the CVC (Eq. (41)), we must compare the obtained equation with the linearization of Eq. (4):

$$J_\mathrm{I} + V\left(\frac{J_0}{V_\mathrm{T}}\right) = -J. \tag{43}$$

By rewriting Eq. (41) in a similar form we obtain

$$J_\mathrm{I} + V\left(\frac{l_\mathrm{p}}{\sigma_\mathrm{n}^\mathrm{p}} + \frac{l_\mathrm{n}}{\sigma_\mathrm{p}^\mathrm{n}}\right)\left(\frac{\sigma_\mathrm{n}^\mathrm{p}\sigma_\mathrm{p}^\mathrm{n}}{l_\mathrm{p} l_\mathrm{n}}\right) = -J. \tag{44}$$

This is the main result of this model; identifying the second terms in the left-hand side of Eqs. (43) and (44) we obtain a new expression for the current density J_0:

$$J_0 = \left(\frac{l_\mathrm{p}}{\sigma_\mathrm{n}^\mathrm{p}} + \frac{l_\mathrm{n}}{\sigma_\mathrm{p}^\mathrm{n}}\right)\left(\frac{\sigma_\mathrm{n}^\mathrm{p}\sigma_\mathrm{p}^\mathrm{n}}{l_\mathrm{p} l_\mathrm{n}}\right) V_\mathrm{T}. \tag{45}$$

This new expression does not exhibit an unphysical behaviour ($J_0 \to \infty$) in thin-film solar cells (Fig. 2, right). Figure 3 gives the two axis intercept points (V_oc and J_SH) of the CVC, it can be trivially verified

that the x intercept point (V_{oc}) will remain at a finite value independently of the minority carriers diffusion lengths at each side of the junction and the diode dimensions. Since the analytical model presented in this paper was obtained by a linearization of the full model and some other approximations have been used to simplify the mathematical problem, the large-signal CVC is not properly obtained (Fig. 3) but the framework of transport equations and boundary conditions can be solved numerically to study any real solar cell diode.

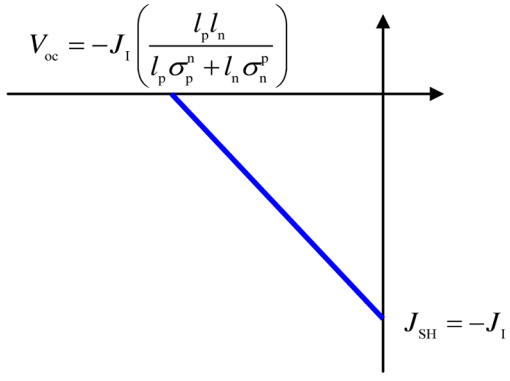

Fig. 3. J–V characteristic of an ideal thin-film solar cell with the new expression for the x axis intercept point V_{oc}.

7. Conclusions

In this work, we report the results concerning the fundamental equations of charge carrier transport in semiconductor structures. We discuss a modeling of the recombination terms in the charge transport equations that respects the charge conservation law. Under a low level of carrier generation (linear regime), the recombination rate can be expressed as a linear combination of the variation of the carrier concentrations δn and δp. Only in one particular situation can a lifetime, τ, be defined: in QN conditions provided that $\delta n_t \ll \delta n$, δp ($\delta n = \delta p$, $\tau^{-1} = \tau_n^{-1} + \tau_p^{-1}$).

Explicit calculation of the charge variation was carried out within the framework of Shockley–Read–Hall statistics. The study of space charge in non-equilibrium has been addressed. It has been demonstrated that the bulk space charge established on distances of the order of the Debye length cannot influence the CVC of a device in the linear regime. It was found that in general the quasineutrality condition cannot be written as $\delta n = \delta p$. It should be emphasized that for the first time a recombination rate that depends on the electron and hole generation rates is presented. This result is of paramount importance for the correct modeling of solar cells.

It was shown that in the linear approximation CVC depends on nonequilibrium carriers (J_0).

In conventional solar cells, recombination of photo-generated charge carriers plays a major limiting role in the cell efficiency. High quality thin-film solar cells may overcome this limit if the minority diffusion lengths become large as compared to the cell dimensions, but, strikingly, the conventional model fails to describe the cell electric behaviour under these conditions. A new formulation of the basic equations describing charge carrier transport in the cell along with a set of boundary conditions is presented. An analytical closed-form solution is obtained under a linear approximation. In the new framework given, the calculation of the open-circuit voltage of the solar cell diode does not lead to unphysical results.

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