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Recombination process in solar cells: Impact on the carrier transport

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Thickness of Si solar cells is being reduced below 200 µm to reduce costs and improve their performance. 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. Moreover, it is shown that in the conventional model the reverse-saturation current diverges (tends to infinity) in thin solar cells. 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.

1 Introduction Charge carrier transport underlies the electrical behaviour of any semiconductor device and, in particular, of solar cells. Despite the efforts made to correctly model such transport in semiconductors over the years, many questions still remain open. One of these open questions is how to model carrier recombination. The mathematical expression routinely used to model the recombination rate [1] is basically incorrect since it has recently been demonstrated that it violates Maxwell's equations, and hence a new corrected model must be developed [2]. This problem was partly addressed in previous works, [3]. 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 [4-8]. The last remark that must be made about the need for a correct modelling 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. In the present contribution we will discuss the importance of recombination in monocrystalline and amorphous solar cells in the framework of a general transport model in 1D [9, 10]. Our results show [11] that the new formulation corrects the inconsistencies found in the Shockley model [12] that is the basic one used in solar diodes modelling. Furthermore, recombination plays the key role to eliminate those inconsistencies in this model.

Since in general the set of Poisson and transport equations cannot be solved analytically, some simplifications must be introduced to obtain a closed-form solution. One approximation commonly used to solve this system of equations is the assumption of quasi-neutrality (QN) [10]. 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 modelling for many years, the role of space charge in the formation of the current-voltage (I−V) characteristic in a semiconductor is still controversial.

A very important question is the choice of the 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, e.g., [13]). Since in normal operation a current flows at the terminals, the 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 [14-16].

All the abovementioned issues need to be addressed when modelling semiconductor devices. Thin-film solar cells [11] are one of the strongest technologies in the steadily growing photovoltaic market [17]. In this paper we will address a very basic problem encountered when modeling cells with large values of the minority diffusion lengths.

2 Model description

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 and the Poisson equation (see [13], pp. 116-117):

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

$$\frac{\partial p}{\partial t} = g_p - \frac{1}{e} div\boldsymbol{j}_p - R_p , \tag{2}$$

$$div\boldsymbol{E} = \frac{4\pi}{\varepsilon}\rho , \tag{3}$$

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 ratio; $\boldsymbol{E}$ 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. (2) from (1), we obtain

$$e(g_n - g_p) + div(\boldsymbol{j}_n + \boldsymbol{j}_p) - e(R_n - R_p) = e\frac{\partial (n-p)}{\partial t} \tag{4}$$

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 [15]

$$div\boldsymbol{j} = div(\boldsymbol{j}_n + \boldsymbol{j}_p) = e\frac{\partial}{\partial t}(n - p + n_t) \tag{5}$$

where $\boldsymbol{j}$ is the total current and n_t is the concentration of electrons captured by the impurities. From Eq. (4) and (5), we obtain the following relationship:

$$g_n - g_p = R_n - R_p - \frac{\partial n_t}{\partial t} \tag{6}$$

As it follows directly from Eq. (6), the deviation of the concentration of the electrons trapped in the impurity level, δn_t, from its equilibrium value, n_t^0, 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. (6) it follows that:

$$R_n - R_p = g_n - g_p \tag{7}$$

In the case of a semiconductor that contains a concentration N_t of impurities, and assuming that the impurities follow Shockley-Read-Hall statistics, [1], the recombination rates R_n and R_p can be calculated (we are implicitly assuming thermal equilibrium between electrons, holes and phonons):

$$R_n = \alpha_n(T)n(N_t - n_t) - \alpha_n(T)n_1 n_t \tag{8a}$$

$$R_p = \alpha_p(T)pn_t - \alpha_p(T)p_1(N_t - n_t) \tag{8b}$$

Here, $\alpha_n(T)$ and $\alpha_p(T)$ 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. Below, 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. (7). Replacing n_t back in equations (8a) and (8b), the recombination rates R_n and R_p are finally obtained in terms of the concentrations of the excess of both kind of carriers (δn, δp), g_n, and g_p. Assuming a constant and uniform temperature across the sample, we obtain the following expression for n_t:

$$n_t = \frac{N_t\left(\alpha_n n + \alpha_p p_1\right) - g_n + g_p}{\alpha_p\left(p + p_1\right) + \alpha_n\left(n + n_1\right)} \tag{9}$$

By substitution of Eq. (9) in Eq. (8a) and (8b) we obtain:

$$\begin{aligned} R_n &= \frac{\alpha_n\alpha_p N_t\left(np - n_0 p_0\right) + \alpha_n\left(n + n_1\right)(g_n - g_p)}{\alpha_n(n + n_1) + \alpha_p(p + p_1)} \\ R_p &= \frac{\alpha_n\alpha_p N_t\left(np - n_0 p_0\right) - \alpha_p(p + p_1)(g_n - g_p)}{\alpha_n(n + n_1) + \alpha_p(p + p_1)} \end{aligned} \tag{10}$$

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 $\delta n<<n_0$ and $\delta p<<p_0$. In this case, the excess of the electron concentration on the impurities reduces to

$$\begin{aligned} \delta n_t = &\frac{1}{\alpha_n(n_0 + n_1^0) + \alpha_p(p_0 + p_1^0)}\times \\ &\left[\alpha_n(N_t - n_t^0)\delta n - \alpha_p n_t^0 \delta p - g_n + g_p\right] \end{aligned} \tag{11}$$

where n_t^0, n_1^0 and p_1^0 are the equilibrium values of their respective magnitudes and $n_t = n_t^0 + \delta n_t$. By substitution of Eq.

(11) in Eq. (8a) and (8b) as before we obtain the following expressions for the recombination rates:

$$
\begin{aligned}
R_n &= \frac{\delta n}{\tau_n} + \frac{\delta p}{\tau_p} + \frac{\alpha_n\left(n_0 + n_1^0\right)\left(g_n - g_p\right)}{\alpha_n\left(n_0 + n_1^0\right) + \alpha_p\left(p_0 + p_1^0\right)} \\
R_p &= \frac{\delta n}{\tau_n} + \frac{\delta p}{\tau_p} - \frac{\alpha_p\left(p_0 + p_1^0\right)\left(g_n - g_p\right)}{\alpha_n\left(n_0 + n_1^0\right) + \alpha_p\left(p_0 + p_1^0\right)}
\end{aligned}
\tag{12}
$$

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 modelling: $R_n=\delta n/\tau_n$ and $R_p=\delta p/\tau_p$, where τ_n and τ_p are lifetimes [1, 12, 13].

In a non-degenerate semiconductor the following relationship holds:

$$
\frac{\tau_n}{\tau_p} = \frac{n_0}{p_0} \tag{13}
$$

From Eq. (15) it becomes clear that, in principle, both R_n and R_p are a function of the generation rates. This points to a strong coupling between the generation-recombination rates and the carrier densities across the sample.

3 New model for thin-film solar cells Let us assume once again that inequality $l_{n,p} << L_D^{n,p}$ holds ($L_D^{n,p}$ are the electron/hole diffusion lengths of minority carriers in n- and p- sides of a solar cell with lengths $l_{n,p}$ at each side of the junction), accordingly, in the solar cell recombination is negligible. Since volume recombination is negligible $R_n = R_p = 0$ and, therefore $g_n = g_p = g(x)$; i.e. the recombination is band-to-band.

Additionally, it can be shown that in absence of impurity recombination and under band-to-band generation the density of charge in any impurity level remains constant [18], under all the above conditions the QN approximation reduces to $\delta n = \delta p$. 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 (μ_n and μ_p) as [19]:

$$
\begin{aligned}
\delta n &= \frac{n_0}{T_0}\delta\mu_n \\
\delta p &= \frac{p_0}{T_0}\delta\mu_p
\end{aligned}
\tag{14}
$$

where the subscript 0 stands for equilibrium value of the magnitude, and using the QN approximation the following relationship between the deviations from equilibrium of the chemical potentials holds:

$$
\delta\mu_p = \frac{n_0}{p_0}\delta\mu_n \tag{15}
$$

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:

$$
I = \begin{cases} I_0 & -l_p < x < 0 \\ 0 & 0 < x < l_n \end{cases} \tag{16}
$$

Using Eq. (16) and $g_0 = \alpha I_0$ we may write the continuity equations, (1)-(2), as

$$
\begin{aligned}
\frac{dj_n^p}{dx} &= -eg_0 \quad ; \quad \frac{dj_p^p}{dx} = eg_0 \\
\frac{dj_n^n}{dx} &= 0 \quad ; \quad \frac{dj_p^n}{dx} = 0
\end{aligned}
\tag{17}
$$

Superscripts in current densities in Eqs. (17) denote the doping type of the region. The current densities may be written as [10]:

$$
\begin{aligned}
j_n^n &= -\sigma_n^n\left(\frac{d\delta\varphi^n}{dx} - \frac{1}{q}\frac{d\delta\mu_n^n}{dx}\right) \\
j_p^n &= -\sigma_p^n\left(\frac{d\delta\varphi^n}{dx} + \frac{1}{q}\frac{d\delta\mu_p^n}{dx}\right) \\
j_n^p &= -\sigma_n^p\left(\frac{d\delta\varphi^p}{dx} - \frac{1}{q}\frac{d\delta\mu_n^p}{dx}\right) \\
j_p^p &= -\sigma_p^p\left(\frac{d\delta\varphi^p}{dx} + \frac{1}{q}\frac{d\delta\mu_p^p}{dx}\right)
\end{aligned}
\tag{18}
$$

where we introduced the electric potential (φ). To solve Eq. (17) with Eqs. (14), (15) and (18), we need to determine and impose enough boundary conditions at the semiconductor interfaces [16]. We will assume ideal metallic (ohmic) contacts placed at x=-l_p and at x=l_n, therefore the excess of carries are null:

$$
\begin{aligned}
\delta n^p\left(-l_p\right) &= \delta p^p\left(-l_p\right) = 0 \\
\delta n^n\left(l_n\right) &= \delta p^n\left(l_n\right) = 0
\end{aligned}
\tag{19}
$$

And, accordingly to Eq. (22), we obtain the following four boundary conditions for the chemical potentials at the metal-semiconductor contacts:

$$
\begin{aligned}
\delta\mu_n^p\left(-l_p\right) &= \delta\mu_p^p\left(-l_p\right) = 0 \\
\delta\mu_n^n\left(l_n\right) &= \delta\mu_p^n\left(l_n\right) = 0
\end{aligned}
\tag{20}
$$

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

$$
\begin{aligned}
\delta\varphi^p\left(-l_p\right) &= 0 \\
\delta\varphi^n\left(l_n\right) &= V
\end{aligned}
\tag{21}
$$

At the interface of the two semiconductor regions, since there is no recombination, we may write two additional boundary conditions at x=0, [14]:

$$\begin{aligned} j_n^n(0) &= j_n^p(0) \\ j_p^n(0) &= j_p^p(0) \end{aligned} \tag{22}$$

Assuming, for simplicity, absence of both surface recombination and surface resistivity at x=0, we can write two additional boundary conditions:

$$\begin{aligned} \delta\varphi^p(0) - \frac{\delta\mu_n^p(0)}{q} &= \delta\varphi^n(0) - \frac{\delta\mu_n^n(0)}{q} \\ \delta\varphi^p(0) + \frac{\delta\mu_p^p(0)}{q} &= \delta\varphi^n(0) + \frac{\delta\mu_p^n(0)}{q} \end{aligned} \tag{23}$$

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 (Eq. (18)) and obtain the solution:

$$j\left(\frac{l_n}{\sigma_p^n}\frac{l_p}{\sigma_n^p}\right) + V\left(\frac{l_p}{\sigma_n^p} + \frac{l_n}{\sigma_p^n}\right) + \frac{qg_0}{2}\left(\frac{l_p^2 l_n}{\sigma_n^p\sigma_p^n}\right) = 0 \tag{24}$$

In the third term of Eq. (24) we may identify the photocurrent density created under illumination:

$$J_I = \frac{qg_0}{2} l_p \tag{25}$$

Since we may re-write Eq. (24) as

$$J_I + V\left(\frac{l_p}{\sigma_n^p} + \frac{l_n}{\sigma_p^n}\right)\left(\frac{\sigma_n^p\sigma_p^n}{l_p l_n}\right) = -j \tag{26}$$

This is a main result of this work, identifying the second terms in the left-hand side of Eq. (26) as the saturation current density, j_0, we obtain a new expression for the current density j_0:

$$j_0 = \left(\frac{l_p}{\sigma_n^p} + \frac{l_n}{\sigma_p^n}\right)\left(\frac{\sigma_n^p\sigma_p^n}{l_p l_n}\right) V_T \tag{27}$$

j_0 for a long abrupt diode in classical theory, [12], is:

$$j_0 = V_T\left(\frac{\sigma_p^n}{L_D^n} + \frac{\sigma_n^p}{L_D^p}\right) \tag{28}$$

σ_n^p (σ_p^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:

$$\begin{aligned} L_D^n &= \sqrt{D_p\tau_p} \\ L_D^p &= \sqrt{D_n\tau_n} \end{aligned} \tag{29}$$

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

This new expression does not exhibit an unphysical behaviour ($j_0 \to \infty$) in thin-film solar cells. It can be trivially verified that the x-intercept point (V_{oc}) of the current-voltage characteristic 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 J −V is not properly obtained, but the framework of transport equations and boundary conditions can be solved numerically to study any real solar cell diode.

4 Conclusions Solar cells rely on photo-generation of charge carriers in p-n junctions and their subsequent recombination in the quasineutral regions. A number of basic issues concerning the physics of the operation of solar cells still remain obscure.

In this paper we briefly discussed some of those unsolved basic problems: need for not unphysical models of the carrier recombination and revision of the QN concept. In conventional solar cells recombination of photogenerated 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 behavior 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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References

[1] P.T. Landsberg, Recombination in Semiconductors (Cambridge University Press, Cambridge, 1991).
[2] I.N. Volovichev, G.N. Logvinov, O. Yu. Titov, and Yu.G. Gurevich, J. Appl. Phys. **95**, 4494 (2004).
[3] Yu.G. Gurevich and I.N. Volovichev, Phys. Rev. B **60**, 7715 (1999).
[4] L. Kronik and Y. Shapira, Surf. Sci. Rep. **37**, 1 (1999).
[5] W.M. Saslow, Phys. Rev. Lett. **76**, 4849 (1996).
[6] C.E. Korman and I.D. Mayergoyz, J. Appl. Phys. **68**, 1324 (1990).
[7] A. Konin, Semicond. Sci. Technol. **18**, L17 (2003).
[8] M. Krcmar and W. Saslow, Phys. Rev. B **65**, 233313 (2002).

[9] Yu.G. Gurevich, G.N. Logvinov, J.E. Velaquez, and O. Titov, Sol. Energy Mater. Sol. Cells **91**, 1408 (2007).
[10] Yu.G. Gurevich, J.E. Velazquez-Perez, G. Espejo-Lopez, I.N. Volovichev, and O.Yu. Titov, J. Appl. Phys. **101**, 23705 (2007).
[11] J.E. Velazquez-Perez and Yu.G. Gurevich, Int. J. Photoenergy **2011**, 976063 (2011).
[12] J. Singh, Semiconductor Devices: Basic Principles (Wiley, New York, 2000).
[13] K. Seeger, Semiconductor Physics (Springer, Berlin, Germany, 1985).
[14] O. Yu. Titov, J. Giraldo, and Yu.G. Gurevich, Appl. Phys. Lett. **80**, 3108 (2002).
[15] I.N. Volovichev, J.E. Velazquez-Perez, and Yu.G. Gurevich, Solid-State Electron. **52**, 1703 (2008).
[16] I.N. Volovichev, J.E. Velazquez-Perez, and Y.G. Gurevich, Sol. Energy Mater. Sol. Cells **93**, 6 (2009).
[17] A.M.A. Green, J. Mater. Sci. **18**, S15 (2007).
[18] J.E. Velázquez-Pérez and Y.G. Gurevich, in: Proc. 25th European Photovoltaic Solar Energy Conference and Exhibition/5th World Conference on Photovoltaic Energy Conversion, Valencia, Spain, September 2010.
[19] Yu.G. Gurevich, G.N. Logvinov, I.N. Volovichev, G. Espejo, O. Yu. Titov, and A. Meriuts, Phys. Status Solidi B **231** 278 (2002).

