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INCLUDING EXCITONS IN SEMICONDUCTOR SOLAR CELL MODELLING

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Abstract

Excitonic effects are introduced in standard semiconductor device modelling of solar cells. Previous work by the groups of Green and of Zhang is extended here to also include field dependent exciton dissociation in the space charge layer (SCL) of a n^+p diode, and exciton surface dissociation or charge transfer at the contact or at the junction. A clear result is that it is possible to apply the standard semiconductor device modelling frame to situations where excitons are dominant. Even when there is only exciton (and no free *eh*) generation an almost ideal short circuit current can be collected when there is sufficient exciton dissociation, either at an interface, or in the bulk, or in the SCL. The possible application of this model to organic solar cells is briefly explored.

Key words: solar cell, exciton, modelling

1. Introduction

Excitons are marginally important in classical semiconductor device physics, and their treatment is not included in standard solar cell modelling. However, in organic semiconductors and solar cells, the role of excitons is essential, as the primary effect of light absorption is exciton generation, and free electrons and holes are created by exciton dissociation. While there is a vast literature on the exciton related materials properties in organic solar cells, a quantitative description which relates excitonic phenomena to the final solar cell output is lacking. First steps to include excitons in inorganic semiconductor solar cell modelling were presented by Green [1][2][3] and Zhang [4] for silicon solar cells; later, other inorganic solar cells where studied with the same model, e.g. CdTe in [5]. This model was restricted to an analytic treatment of the quasi-neutral *p*-region (QNR) of a one sided n^+p junction, and exciton dissociation and recombination was considered only in the *p*-bulk, and assumed to be uniform. We will here extend this model to cover more realistic solar cell structures: we will include the space charge region (SCL) and the non-uniform bulk dissociation of the excitons therein (caused by field enhanced dissociation), and the occurrence of exciton surface dissociation and recombination at the contacts and at the junction. As we assume a preset hole concentration throughout the cell, and a given electric field in the SCL, our model is still not general, but it covers most real semiconductor situations. The applicability of this extended model to organic solar cells will be briefly discussed.

2. Solar cell modelling including excitons

We will denote electrons, holes and excitons with the subscript *e*, *h* and *x*, respectively. We will limit ourselves to a one-dimensional analysis.

2.1 Exciton transport and dynamics

The total optical absorption G is due to the generation of free electron-hole pairs (fraction f_{eh}) and of excitons (fraction f_x). Other absorption mechanisms will be neglected, thus $f_{eh} + f_x = 1$. In inorganic semiconductors, $f_x \cong 0$, except at low temperatures in a narrow wavelength region around the band gap energy, $\lambda\ \hat{}\ \ \lambda_g = h\nu / E_g$. In organic materials, the dominant absorption is by excitons, and hence $f_x \cong 1$ for all absorbed wavelengths. We take a simple monomolecular form for the direct recombination (or annihilation) of excitons:

$$U_x = \frac{1}{\tau_x}\left(n_x - n_{x0}\right) \tag{1}$$

where τ_x is the exciton lifetime. Excitons also can dissociate and convert to a free electron-hole pair, with a net conversion rate $C_{x/eh}$ (this corresponds to $-U_{eh/x}$ in the notation of [1] and [4])

$$C_{x/eh} = b\left(n^* n_x - n_e n_h\right) \tag{2}$$

where b (in cm^{3}s^{-1}) describes the strength of the exciton binding and n^* is an appropriate constant, with the dimension of concentration (thus in cm^{-3}). In equilibrium, detailed balance requires this net rate $C_{x/eh}$ to be zero; this defines the equilibrium exciton concentration $n_{x0} = n_i^2 / n^*$, occurring also in Eq. (1). Since excitons do not carry charge, their transport is by diffusion:

$$J_x = -D_x \frac{dn_x}{dx} \tag{3}$$

2.2 Basic model

In the basic model of Green [1] and Zhang [4], only minority carriers in the quasi-neutral p-region of a one-sided n^+p junction are considered: the problem is reduced to finding the electron concentration $n_e(x)$ and the exciton concentration $n_x(x)$ in the range $0 \le x \le x_0$ in the structure of Fig. 1. Since the QNR is field-free, also the electron current is solely by diffusion, and the problem is formulated as a set of two coupled differential equations for the two unknown functions $n_e(x)$ and $n_x(x)$:

$$D_e \frac{d^2 n_e}{dx^2} = U_{eh} - C_{x/eh} - f_e G \tag{4}$$

$$D_x \frac{d^2 n_x}{dx^2} = U_x + C_{x/eh} - f_x G \tag{5}$$

where we note that the exciton to *eh*-pair conversion is a generation term for the electrons and a recombination term for the excitons. In [1] and [4], a simple low-level injection approximation is used for the electron recombination U_{eh}:

$$U_{eh} = \frac{1}{\tau_e}\left(n_e - n_{e0}\right) \quad \text{where} \quad n_{e0} = \frac{n_i^2}{N_A} \tag{6}$$

and N_A is the uniform acceptor doping in the *p*-QNR. Further, it is assumed that the hole concentration (needed in Eq. (2)) is constant in the *p*-QNR, $n_h = N_A$, and that the binding parameter b is constant over the field-free QNR. Under these assumptions, Eqs. (4) and (5) are linear and can be solved analytically with standard techniques [1]. As an infinitely wide *p*-QNR is assumed in [1] and [4], both $n_e(x)$ and $n_x(x)$ tend to zero when $x \to \infty$, and no special boundary conditions are needed at the *p*-contact. At the SCL-edge ($x = 0$), the usual Shockley boundary condition for electrons is used, $n_e(0) = n_{e0} \exp(qV/kT)$, where V is the applied voltage. For the excitons, Green [1] uses $n_x(0) = n_{x0}$ corresponding to zero exciton recombination at the SCL-edge (Eq. (1)), whilst Zhang [4] uses $n_x(0) = n_e(0) N_A / n^* = n_{x0} \exp(qV/kT)$, corresponding to zero exciton to *eh* conversion at $x = 0$ (Eq. (2)). Both compute the electric current $J(V)$ in the diode by summing the electron and exciton particle current at the edge of the SCL:

$$J(V) = q\left[J_e(x = 0; V) + J_x(x = 0; V)\right] \tag{7}$$

The appropriateness of these boundary conditions will be discussed in the next section.

2.3 Extensions to the basic model

Eq. (7) implicitly assumes that the current in the diode is dominated by the electrons in the *p*-QNR (which holds for a one-sided n^+p junction), and that all excitons in the SCL convert to free *eh* pairs, whose electron contributes to the current. In order to check out this latter assumption, one has to extend the Green-Zhang model to include the SCL. To include drift of electrons in the SCL, Eq. (4) has to be replaced by

$$D_e \frac{d^2 n_e}{dx^2} + \mu_e \frac{d}{dx}\left(n_e E\left(x\right)\right) = U_{eh} - C_{x/eh} - f_e G \tag{8}$$

Also, the recombination U_{eh} no longer takes the simple form of Eq. (6), but should be replaced by a Shockley-Read-Hall expression, e.g.

$$U_{eh} = \frac{1}{\tau_e} \frac{n_e n_h - n_i^2}{n_e + n_h + 2n_i} \tag{9}$$

where we assumed for simplicity an equal lifetime for electrons and holes, and one trap level at midgap. Due to this Eq. (9), the set of differential equations (8) and (5) becomes non-linear. Also, the electric field $E(x)$ is related to the electric charge by the Poisson equation. These two complications preclude an analytic treatment, and the problem has to be solved numerically. To avoid needless numerical complications, we confine our attention to electrons and excitons only (assuming a constant E_{Fp} also in the SCL, thus for $-W \le x \le x_0$), and we assume a preset field distribution $E(x)$

$$E\left(x\right) = E_m \frac{|x|}{W}, \text{SCL: } -W \le x \le 0 \quad \text{and} \quad E\left(x\right) = 0, \text{QNR: } 0 \le x \le x_0 \tag{10}$$

where the maximum field E_m and the depletion width W follow from the standard abrupt depletion approximation, e.g. [6]. With these simplifying assumptions, the electrostatic potential $\Phi(x)$ and the hole concentration $n_h(x)$ are easily calculated. If the assumptions were relaxed, one would have to solve a set of four differential equations for the concentrations to find $n_e(x)$, $n_h(x)$, $n_x(x)$ and $\Phi(x)$.

Our model, though still containing simplifications, allows studying effects that were neglected in the basic model. We model the field enhancement of exciton dissociation (e.g. [7]) by introducing a non-uniform binding parameter b in the SCL:

$$b(x) = b\left[E(x)\right] \tag{11}$$

Next, we treat the boundary conditions more carefully. The electron concentration at the junction is set to the donor density in the n^+ region: $n_e(-W) = N_D$. For the other boundaries, we relate the particle current to the surface recombination and conversion. Thus, e.g. at $x = x_0$:

$$J_e(x_0) = S_e\left(n_e(x_0) - n_{e0}\right) - b_s\left(n_x(x_0) - n_{x1}\right) \tag{12}$$

$$J_x(x_0) = S_x\left(n_x(x_0) - n_{x0}\right) + b_s\left(n_x(x_0) - n_{x1}\right) \tag{13}$$

Here S_e and S_x are the normal definitions for surface recombination velocity. E.g. $S_e \to \infty$ corresponds to an ohmic contact, and $S_e = 0$ to a perfectly passivated surface. In the absence of the conversion terms in b_s, one sees that $S_x = 0$ is appropriate for excitons, since we assume that an exciton cannot *as such* pass a semiconductor-metal contact. The terms in b_s describe a simple form of surface conversion of excitons to free *eh* pairs: this term is a generation term for electrons, and a recombination term for excitons. Normally we expect $n_{x1} = n_{x0}$, the equilibrium exciton concentration, but the more general formulation allows e.g. to totally exclude the 'back reaction', i.e. surface association of *eh* pairs to excitons, by simply putting $n_{x1} = 0$. In our simplification of the 'no holes-diode', the terms in b_s can also describe charge transfer: surface dissociation of the exciton to a free electron in the *p*-semiconductor and a hole transferred to the material contacting the semiconductor at $x = 0$. At the n^+p junction, thus at $x = -W$, we take a boundary condition for the excitons like Eq. (13).

2.4 Numerical solution

The set of differential equations (8) and (5) and the boundary conditions (12) and (13) are discretised with the 'exponentially fitted scheme' [8], and solved with the Newton-Raphson method. Since the electron equation (8) depends on the exciton concentration n_x, and the exciton equation (5) depends on the electron concentration n_e via the conversion term $C_{x/eh}$, a Gummel iteration scheme [8] between the two equations is applied. The boundary conditions (12) and (13) need special care in case of a high surface conversion velocity $b_s \to v_{th}$, since they reduce to one single equation $n_x(x_0) = n_{x1}$ when $b_s \to \infty$ (indeed, the thermal velocity v_{th}

has to be considered as an 'infinitely high' value of the surface velocities S_e, S_x and b_s). A second, independent boundary condition however can be found by eliminating b_s from (12) and (13):

$$S_e\left(n_e\left(x_0\right)-n_{e0}\right)+S_x\left(n_x\left(x_0\right)-n_{x0}\right)+D_e\frac{dn_e}{dx}\left(x_0\right)+D_x\frac{dn_x}{dx}\left(x_0\right)=0 \tag{14}$$

The assumption of a non-uniform $b(x)$ does not complicate the numerical implementation. Care is needed to define the discretisation mesh, since there can be a large difference in size between the SCL width W, the QNR width x_0 and the absorption depth $1/\alpha$.

3. Results and discussion

Our final goal is to create a numerical model based on standard semiconductor physics, which is applicable to organic solar cells. Therefore we check whether a full short circuit current density (i.e. corresponding to the illumination intensity; in Fig. 2, $\alpha \to 0$, and G_0 is adjusted to set $J_{L\text{ideal}} = 20$ mA/cm^2) can be obtained when the light is generating excitons only, thus if $f_x = 1$ and $f_e = 0$. This can only be the case if there is an appreciable exciton to *eh* conversion rate at some place in the cell. In Fig. 2, J_L is plotted for some exciton dissociation parameters. For surface dissociation at the contact ($x = x_0$), we varied b_s between $b_{s\text{low}} = 10^{-2}$ cms^{-1} and $b_{s\text{high}} = 10^7$ cms^{-1}. For homogeneous bulk dissociation we varied b between $b_{\text{low}} = 10^{-16}$ cm^{3}s^{-1} and $b_{\text{high}} = 10^{-7}$ cm^{3}s^{-1}. For field enhanced bulk dissociation, we kept $b = b_{\text{low}}$ in the QNR, and assumed an exponential dependence $b\left(E\right)=A\exp\left(E/E_0\right)$ in the SCL; the constants A and E_0 were chosen to set $b(0) = b_{\text{low}}$, and $b(-W) = b_{\text{max}}$, and b_{max} was varied from b_{low} to b_{high}. Fig. 2 clearly proves that a decent J_L is obtained as soon as one of the exciton dissociation parameters is high enough. The threshold values are approximately: $b_s = 10^4$ cms^{-1} for surface dissociation, $b = 10^{-10}$ cm^{3}s^{-1} for uniform bulk dissociation, and $b_{\text{max}} = 10^{-8}$ cm^{3}s^{-1} for our assumed form of field enhanced dissociation in the SCL. These threshold values apply to the case where the other dissociation parameters have their low value, thus being inactive. For none of the curves, the ideal short circuit current is reached. This is due to a too low value of the diffusion lengths, compared to the cell thickness. In Fig. 3, the curves are recalculated for a hypothetical case with very long diffusion lengths L_e = L_x = 1000 µm. This clearly illustrates that $J_{L\mathrm{ideal}}$ is reached as soon as one of the dissociation mechanisms is strong enough. The threshold values obviously depend on L_e and L_x. The influence of the diffusion lengths L_e and L_x is further illustrated in Fig. 4, where both are varied in case that only the exciton surface dissociation is high ($b_s = 10^7$ cms^{-1}), and the bulk dissociation is low (uniform $b = 10^{-16}$ cm^{3}s^{-1} in SCL and QNR). It can be seen on Fig. 4 that both L_e and L_x must be rather high, i.e. a few times the diode QNR thickness x_0, to obtain the ideal short circuit current $J_{L\mathrm{ideal}}$. This is plausible, since the excitons generated in the SCL and QNR must first diffuse to the back contact at x_0, where they dissociate, and then, as electrons, diffuse back to the SCL to be collected and contribute to the current. For the parameters used in Fig. 4, the electron diffusion is slightly more critical than the exciton diffusion. This applies to the situation of Fig. 4, where the exciton dissociation occurs at $x = x_0$; the arguments have to be adapted slightly when it occurs in the bulk, or near the junction ($x = 0$) (no illustration).

4. Possible application to organic solar cells

An obvious difference between inorganic and organic semiconductors is the exciton binding energy Δ: it is small ($\Delta \cong 25$ meV $\cong kT$ at room temperature) for e.g. Si, but substantial larger for organic materials (e.g.$\Delta \cong 300$ meV $\cong 12\ kT$). As a result, in organics, the exciton is more stable: excitons are the particles generated by illumination, and they only dissociate to free carriers in a high field region, or at the contact with a suitable neighbour molecule, where the one of the carriers is injected ('transferred'). These phenomena are described in our model by a field dependent bulk dissociation constant $b(E)$ and by a surface dissociation rate b_s.

The increased value of Δ has a large influence on the other exciton related parameters, as suggested in [1][4]: the parameter n^* in Eq. (2) is thermally activated with Δ, and thus would decrease, at room temperature, by a factor of about $e^{11} \cong 6\ 10^4$, and the equilibrium exciton concentration n_{x0} would increase with the same factor. The enhancement of the bulk dissociation in an electric field is well documented (e.g. it increases with one or two orders of magnitude when E increases from 10^5 V/cm to 10^6 V/cm [7]), and also is the enhanced transfer of charge from an exciton dissociating at the tangent point of two neighbouring molecules [7]. However these phenomena are treated in different terms, and it is not possible to extract suitable values of the parameters $b(E)$ and b_s in organic molecules. Therefore we kept these as running parameters, to show their influence in qualitative terms.

The nanometer size and the complicated geometry or morphology in bulk heterojunction solar cells constitutes a major obstacle to apply standard semiconductor device modelling to organic solar cells. One way out is to treat this cell as an infinite network of small, nanometer sized 'unit cells', as was done in [9] for solar cells based on nano-structured TiO_2. It can be expected that the major conclusion of our work on planar semiconductor cells will remain valid: the cells will work when there is enough exciton dissociation (wherever this be in the cell) and when both the electron and the exciton diffusion lengths exceed the unit cell thickness. There are indications that L_x can be very small in organic materials (down to a few nm), and thus the size of the unit cell, defined by the morphology of the donor/acceptor blend, will be extremely important. Another way to model bulk heterojunction solar cells is to treat the blend as one 'effective medium' (e.g. [10]). The surface dissociation b_s in the nano-units that constitute the effective medium, will translate into an effective bulk dissociation rate b. The framework to include the exciton generation and dissociation effects, including the field dependence $b(E)$, has been given in the previous section. Both approaches, the network approach and the effective medium approach, are equivalent when suitable parameters are chosen [11]. The effective medium approach has the advantage that it can be directly implemented (but for the exciton effects, at present) in a standard solar cell device simulation programme like SCAPS [12].

5. Conclusions

In this work, we extended the standard semiconductor device modelling of solar cells to include excitonic effects. The work of Green and Zang was extended to also include field dependent exciton dissociation in the SCL, and surface dissociation or charge transfer at the interfaces. Our numerical simulations for Si cells show that the cells can work decently, even if the light generates only excitons and no free *eh* pairs. The conditions are that there is enough exciton dissociation (wherever this is in the cell) and that both the electron and the exciton diffusion lengths exceed the unit cell thickness. This model is applicable to organic bulk heterojunction solar cells, provided that suitable values for the parameters involved can be found.

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Figure captions

Fig. 1 Schematics of a one-sided p^+n-junction. The space charge layer (SCL) extends from $x = -W$ to $x = 0$. The quasi-neutral region (QNR) extends from $x = 0$ to $x = x_0$.

Fig. 2 Short circuit current under uniform illumination ($\alpha \rightarrow 0$), generating excitons only ($f_x = 1$), for varying exciton dissociation parameters: surface dissociation at contact b_s: low = 10^{-2} cms^{-1}, high = 10^{7} cms^{-1}; bulk dissociation b: low = 10^{-16} cm^{3}s^{-1}, high = 10^{-7} cm^{3}s^{-1}; field enhanced dissociation $b(E)$ in SCL: $b = b_{\text{low}}$ for $x > 0$ and exponentially increasing towards junction ($x = -W$). Curve (1): b varying and b_s = low. Curve (2): b varying and b_s = high. Curve (3): $b(E)$ varying and b_s = low. Curve (4): b_s varying and b = low. Curve (5): b_s varying and b = high. The horizontal axis is normalised to the high value of the varying parameter. Other parameters are: $L_e = L_x = x_0 = 50$ μm and $S_e = S_x = 0$.

Fig. 3 Short circuit current under uniform illumination, equivalent to $J_{L\text{ideal}} = 20$ mA/cm^2. The diffusion lengths are: $L_e = L_x = 1000$ μm. All other parameters and the labelling of the curves are as in Fig. 2.

Fig. 4 Influence on J_L of the diffusion lengths L_e and L_x. The exciton surface dissociation at $x = x_0$ is high ($b_s = 10^7$ cm/s), and the bulk dissociation is low (uniform $b = 10^{-16}$ cm^3/s in SCL and QNR). The other parameters are as in Fig. 2 and in Fig. 3. Curve (1): L_e varying and $L_x = 10$ μm. Curve (2): L_e varying and $L_x = 1000$ μm. Curve (3): L_x varying and $L_e = 10$ μm. Curve (4): L_x varying and $L_e = 1000$ μm.

Figure 1

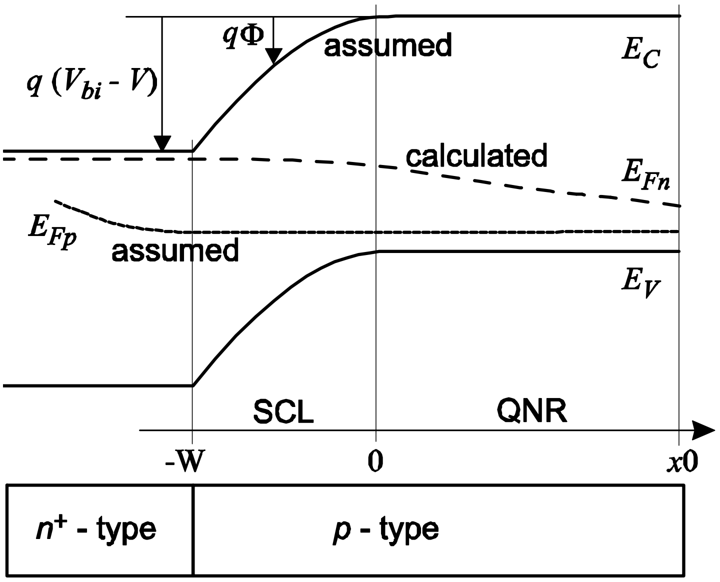
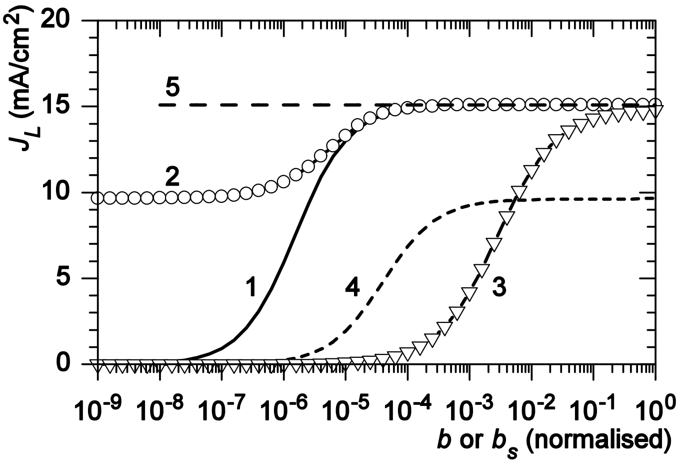

$q\Phi$
assumed
E_C
$q\,(V_{bi} - V)$
calculated
E_{Fn}
E_{Fp}
assumed
E_V
SCL
QNR
-W
0
x0
n^+ - type
p - type

Figure 2


J_L (mA/cm^2)
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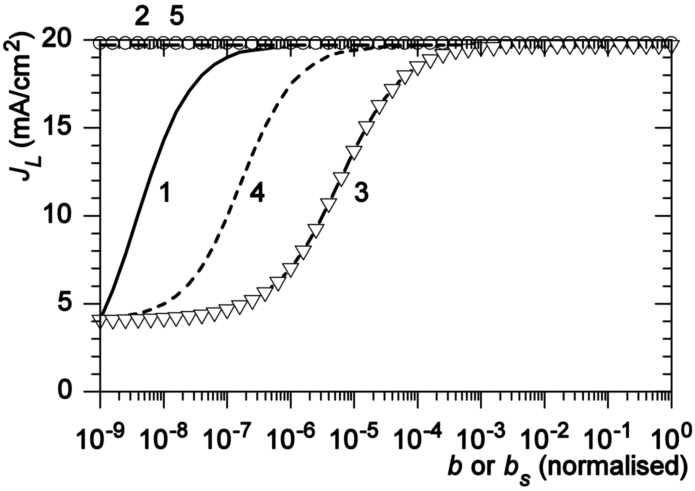
b or b_s (normalised)

Figure 3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10^{-1}
10^{0}
b or b_s (normalised)

Figure 4