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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.

Keywords: 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 [1–3] and Zhang [4] for silicon solar cells; later, other inorganic solar cells where studied with the same model, e.g. CdTe in Ref. [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, $\lambda \lesssim \lambda_g = hv/E_g$. 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:

$$U_x = \frac{1}{\tau_x}(n_x - n_{x0}) \qquad (1)$$

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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 [1,4])

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

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 Refs. [1,4], a simple low-level injection approximation is used for the electron recombination U_{eh}:

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

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 Refs. [1,4], 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:

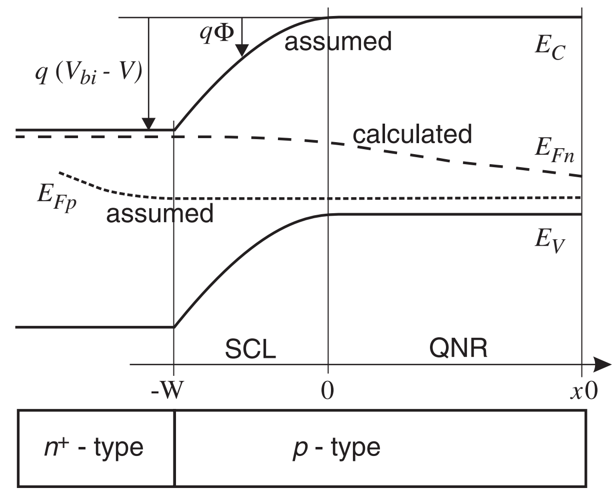

Fig. 1. Schematics of a one-sided p^+n-junction. The space charge layer (SCL) extends from $x=-W$ to $x=0$. The quasi-neutral region (QNR) extends from $x=0$ to $x=x_0$.

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

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

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

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 Eqs. (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 $E(x)$

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