Charge separation in excitonic and bipolar solar cells — A detailed balance approach

Thomas Kirchartz [a], Uwe Rau [b,*]

[a] *Institut für Physikalische Elektronik, Universität Stuttgart, 70569 Stuttgart, Germany*
[b] *IEF5-Photovoltaik, Forschungszentrum Jülich, 52425 Jülich, Germany*

Abstract

A generalized solar cell model for excitonic and classical, bipolar solar cells is developed that describes the combined transport and interaction of electrons, holes and excitons. Both, conventional inorganic solar cells as well as organic solar cells, where excitons play a dominant role for energy transport, turn out to be special cases of this model. Due to the inclusion of photon recycling effects, the approach is compatible with the principle of detailed balance and the Shockley-Queisser limit. We show how varying the interaction between excitons and charge carriers as well as varying the respective mobilities of the different species changes the operation mode of the solar cell path between excitonic and bipolar.
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1. Introduction

The introduction of organic materials as photovoltaic absorbers in organic [1] or dye-sensitized [2] solar cells has raised questions whether or not these new types of devices can be described with the help of theories that initially have been developed for inorganic solid-state type devices usually provided with a pn-homo- or heterojuncion. In addition, the nano-scale mixture of different organic materials [3] has not only boosted the efficiencies of organic solar cells but also led to an apparent new type of solar cell, the bulk-heterojunction. Recently, it has been proposed to divide all solar cells into two classes, namely the classical inorganic solar cells and the 'excitonic' solar cells, embracing essentially all devices that use organic absorber materials [4,5].

The present paper proposes a model that allows us to describe virtually all single-absorber solar cells by an identical approach that will be published in more detail elsewhere [6]. For the bulk of the absorber, we use a set of differential equations for excitons, electrons, and holes that is coupled by the dissociation of excitons into an electron/hole pair and the recombination of this pair into an exciton. This approach is similar as in Refs. [7,8]. At the surfaces of the absorber, we allow for cross-dissociation of the exciton into an electron in the absorber and a hole in the contact and vice versa.

We also include in our approach the optical interaction (photon recycling) between the different regions in the device. As noted by Martì et al. [9], such a feature is necessary to make a microsopic transport theory consistent with the global detailed balance approach of Shockley and Queisser (SQ) [10]. Because the SQ-theory only accounts for the balance of photons entering or leaving the device photon recycling is imminent. To check the compatibility with the detailed balance approach, we verified with our calculations that in the limit of high mobilities for excitons, electrons and holes our model delivers the maximum efficiencies given by the SQ-theory as will be shown elsewhere [6].

The present paper concentrates on the carrier collection properties of the solar cells under short circuit conditions. We especially show that by changing the dissociation rate of excitons we can continuously tune the model from the excitonic range considered in Refs. [4,5] towards a situation where the solar cell works practically like a classical bipolar device.

2. Model

For simplicity, we restrict the photovoltaic action to the photogeneration of excitons and neglect that of free electron/

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* Corresponding author.
  E-mail address: u.rau@fz-juelich.de (U. Rau).

hole pairs. The radiative lifetime τ_{rx} of excitons is defined similar to that of charge carriers in a semiconductor [11] via

$$\tilde{c}/\tau_{rx} = \int \alpha_x(E)\phi_{bb}^{vol}(E)dE \qquad (1)$$

where $\tilde{c}$ denotes the concentration of excitons in thermal equilibrium, $\alpha_x(E)$ is the absorption coefficient resulting from the generation of excitons, E the photon energy, and $\phi_{bb}^{vol}(E)$ is the black body radiation per area into the full spherical angle 4π. Note at this point that, due to the finite cell thickness, a recombination event in the volume of the photovoltaic absorber does not necessarily lead to an emission of a photon from the surface of the solar cell. Instead the possibility of re-absorption of this photon by generation of another exciton has to be considered even in equilibrium [9]. In the present work, we use the computation scheme of Ref. [12] to involve this photon recycling effect into our calculations.

Once generated, the excitons can dissociate into electrons and holes in the bulk of the absorber with a dissociation lifetime τ_{dx}. The dissociation of an exciton into an electron/hole pair and the recombination of this pair into an exciton are also interlinked by detailed balance and we have

$$R_x\tilde{n}\tilde{p} = \tilde{c}/\tau_{dx} \qquad (2)$$

where R_x is the recombination rate and $\tilde{n}$, $\tilde{p}$ denote the equilibrium concentrations of electrons and holes. Similarly, at the front or the back surface we allow for dissociation of an exciton into an electron in the respective junction and a hole that remains in the bulk of the absorber, as well as the complementary process, dissociation into a hole in the junction and an electron in the bulk. The rates for this type of charge separation that is thought to be the dominant one in excitonic solar cells are determined by the detailed balance relations

$$H_n\tilde{n}_j\tilde{p}_b = S_{xn}\tilde{c} \qquad (3)$$

and

$$H_p\tilde{n}_b\tilde{p}_j = S_{xp}\tilde{c} \qquad (4)$$

where $H_{n/p}$ are the cross recombination rates of electrons/holes in the junction with holes/electrons in the bulk of the absorber. The equilibrium concentrations of electrons and holes in the bulk/junction are denoted by $\tilde{n}_{b/j}$, $\tilde{p}_{j/b}$. The dissociation velocities S_{xn}/S_{xp} describe the probabilities that a free exciton dissociates into an electron (hole) in the contact and a hole (electron) in the bulk. An asymmetry in the values of S_{xn}/S_{xp} causes the selectivity of a contact for the dissociation of excitons much like an asymmetry of S_n/S_p causes the selectivity for free carriers.

The collection of free electrons and holes at the interface is determined by $S_n^*\tilde{n}_j = S_n\tilde{n}_b$ and $S_p^*\tilde{p}_j = S_p\tilde{p}_b$ where the rate constants $S_{n/p}$, $S_{n/p}^*$ again have the dimension of a (collection or injection) velocity. For the following computations, we set $\tilde{n}_j = \tilde{n}_b$, $\tilde{p}_j = \tilde{p}_b$, and, consequently, $S_{n/p}^* = S_{n/p}$.
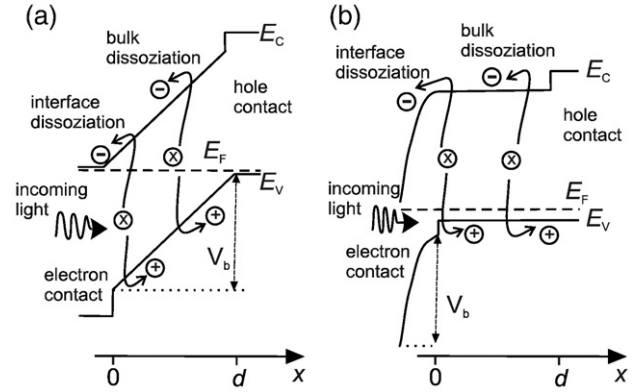

Fig. 1. Band diagrams for a pin-type (a) and a pn-type solar cell (b) with the conduction and valence band energy E_C and E_V as well as the equilibrium Fermi-energy E_F. The photovoltaic active absorber extends from coordinate $x=0$ (electron extracting contact) to $x=d$ (hole extracting contact). In case of the pin-type solar cell (a) the built-in voltage V_b drops across the undoped absorber, whereas for pn-type device (b) V_b is accommodated within a space charge region situated completely outside of the absorber. Schematically shown are the ways how photogenerated excitons dissociate into electron/hole pairs in the bulk of the absorber or at the interface to the electron extracting contact for both types of devices.

The motion of excitons in the bulk of the absorber is described by the continuity (diffusion) equation

$$D_x\frac{d^2}{dx^2}c = \frac{c}{\tau_{dx}} + \frac{c}{\tau_{rx}} - R_xnp - g_x \qquad (5)$$

where D_x is the diffusion constant for excitons and g_x their photogeneration rate. The continuity (drift-diffusion) equation for electrons reads

$$D_n\frac{d^2}{dx^2}n - F\mu_n\frac{d}{dx}n = R_xnp - \frac{c}{\tau_{dx}} \qquad (6)$$

and we have an analogous equation for the concentration p of free holes with the '−' sign in front of the electrical field F replaced by a '+'. The diffusion constants $D_{x/n/p}$ are linked to the mobilities $\mu_{x/n/p}$ by Einstein's relation $D_{x/n/p}=kT\mu_{x/n/p}/q$ where kT/q denotes the thermal voltage.

Note that in a pin type structure the electrical field F results from the difference between the built-in potential V_b (cf. Fig. 1a) and the applied external voltage V according to $F=(V_b-V)/d$ where d is the thickness of the intrinsic (undoped) absorber layer as sketched in Fig. 1a. Whereas in this pin solar cell the voltage dependence of the current voltage characteristics is exclusively determined by the electrical field F present in the intrinsic layer, no such field is present in a pn structure as sketched in Fig. 1b. The voltage dependence of this type of device is determined by the change of the minority carrier concentration $n_j=\tilde{n}_j\exp(qV/kT)$ that is available in the injecting contact.

3. Results

In order to focus on the charge separation mechanism in excitonic and bipolar solar cells, the following computations are