DETAILED DRIFT DIFFUSION MODEL FOR THE ANALYSIS AND DESIGN OF QUANTUM DOT SOLAR CELLS

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We propose a model for the simulation of quantum dot solar cells, based on drift-diffusion transport equations coupled with detailed rate equations of the quantum dots. Preliminary validation against literature experimental data is presented.

1. Introduction

One attractive concept for the realization of third generation solar cells is the Intermediate Band Solar Cell (IBSC) theoretically proposed in 1997 by Luque and Martì [1]. The basic structure can be regarded as a *p-i-n* junction where the intrinsic semiconductor hosts an intermediate energy band (IB) within its bandgap. High power conversion efficiency is attained by enhancing sunlight harvesting by sub-band gap photon absorption and at the same time by preserving the maximum energy that can be delivered by the photogenerated electrons to the external circuit, which is ultimately limited by the photoinduced IMREF splitting within the intrinsic semiconductor. This last condition requires IB and conduction band (CB) electrons to be out of equilibrium and thus must be sustained by photon absorption, i.e. the cell operation requires a two-photon absorption (TPA) process, or by impact ionization. On the other hand, band-to-band recombination processes between IB and CB turn to be detrimental since they tend to reestablish equilibrium between the two band populations, eventually causing a significant reduction of the achievable open circuit voltage (V_{oc}). Based on these considerations, an optimal IB solar cell has been theoretically identified, with a total bandgap of about 1.95 eV, split by the IB into two sub-bandgaps CB-IB=0.71 eV and IB-VB=1.24 eV [1]. Detailed balance analysis showed that such IBSC could provide a maximum efficiency (thermodynamic upper limit) of 63% under full concentration (i.e. 46000 suns) in contrast to the 40% of the *p-i-n* SC without IB. Very recently, it was also calculated that with an appropriate design of several IB levels in the hosting intrinsic region of the junction, it would be possible to reach a maximum efficiency of 74% [2].

To date, the practical realization of IBSC has been mainly pursued by including several layers of Quantum Dots (QDs) in the intrinsic region of a *p-i-n* junction. In particular, several examples of InAs/GaAs QDSC have been reported in the literature [3, 4, 5]. Despite the promising theoretical predictions, most of these devices [3, 4] have shown modest performance, with overall conversion efficiency sometimes even worse than their bulk counterpart; this has been at least partly attributed to the difference of the energy band gaps of the InAs/GaAs QDSC with respect to the optimum values predicted for the ideal IBSC. On the other hand, very recently InAs/GaAs QDSC with 50% increase of solar efficiency have been demonstrated [5], thus re-opening the debate on the effective potential of such a system material in the realization of IBSC.

Despite the strong research effort toward the realization of QDSCs, models proposed so far for IBSC [1] lack of a detailed description of the IB, usually treated as a zero-thickness energy band and neglecting transport. We believe that the absence of a detailed model accounting for the peculiar characteristics of the InAs/GaAs QD material prevents a deep understanding of the experimental results and a quantitative assessment of the many factors that affect the achievable efficiency. This is fundamental to find paths for the design and optimization of the devices. Two very debated and not yet understood points are for example

the reduction of V_{oc} [3] as well as the very slight increase of the short circuit current, which lead to a very limited increase of the power conversion efficiency with respect to the case without QDs [3]. From a more fundamental point of view it is not well understood if the QDs of the different layers must be really electronically coupled in the growth direction to form a mini-band and therefore approach the ideal IB foreseen by Martì [1] or if this coupling effect is unimportant [3]. The answer to this fundamental question is extremely important from the technological point of view because it is quite impossible growing QD layers so close to guarantee coupling without degrading the material quality, with the consequent increase of non-radiative recombination paths. Finally, the role of QD doping need to be clarified [5]. Even if there are already commercial softwares (e.g. APSYS [8]) with capabilities for the simulation of QDSC, it is quite difficult to use them for finding these answers, because the way the QD material is included is quite simplified and difficult to control.
In this work we present a drift-diffusion model for the study of QDSC including the detailed rate equations of the QDs [6] and accounting for the discrete band structure of the dots.

2. Numerical model

In Fig. 1a we present the typical structure of a QDSC [3]; it consists of a GaAs *p-i-n* junction with several InAs QD layers in the intrinsic region. The QDs are grown using Stranski-Krastanov self-assembling process and therefore result non uniform in size and composition. This leads to an inhomogeneous broadening of the absorption spectrum with the advantage of absorbing the photons at the longer wavelengths of the solar spectrum not absorbed by the bulk GaAs. In Fig.1b we show the band structure of the InAs QDs with the optical generation, capture and escape of the carriers. The QD band structure considered here consists of two states confined in the QD (ground state, GS, and excited state, ES) and a wetting layer (WL) state obtained by the low confinement of the higher energy states and by the thin InAs film that remains behind the QD during the growth. As shown in Fig.1b the photons absorbed by the QD can generate electron and hole pairs in the GS and/or in the ES. The generated pairs can then be lost due to radiative or non-radiative recombination or can escape out of the dots in the GaAs matrix and contribute to the photocurrent. The escape out of the QD can be thermal [3] and/or assisted by the absorption of another photon [1]. However it is important to remark that the existence of a significant TPA in InAs QDs at room temperature needs to be proved yet. We also include here the possible re-capture of the carriers in the GaAs matrix down to the QD states. This path, neglected in [1], can cause a reduction of the efficiency.

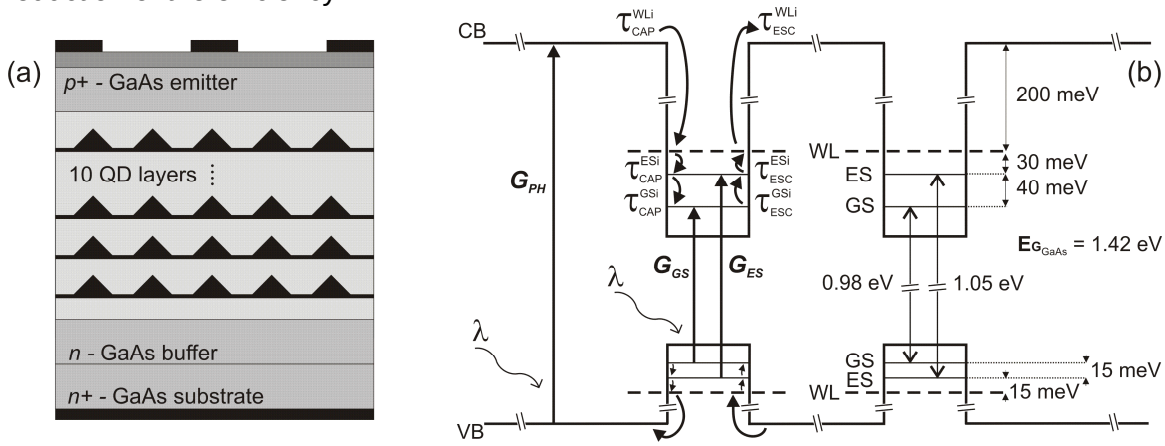

Fig.1. (a) Structure of the analyzed device; (b) Band diagram showing in detail the QDs confined states and all the involved processes.

The numerical model is based on the well-known drift-diffusion transport model of semiconductors, completed by the detailed rate-equations for carriers in the QDs. The optical absorption spectrum is calculated including the QD confined states in conduction and

valence bands and the inhomogeneous broadening of the emission line [6]. For electrons, the set of equations reads as follows:

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x}\left(\mu_n n E + D_n \frac{\partial n}{\partial x}\right) - R_{TOT} + G_{PH} - R_{N\,CAP}^{B\to WL} + R_{N\,ESC}^{WL\to B} \quad (1)$$

$$\frac{\partial n_{WL_i}}{\partial t} = R_{N\,CAP}^{B\to WL_i} - R_{N\,ESC}^{WL_i\to B} - R_{N\,CAP}^{WL_i\to ES_i} + R_{N\,ESC}^{ES_i\to WL_i} - R_{N\,CAP}^{WL_i\to GS_i} + R_{N\,ESC}^{GS_i\to WL_i} - R_{WL_i} \quad (2)$$

$$\frac{\partial n_{ES_i}}{\partial t} = R_{N\,CAP}^{WL_i\to ES_i} - R_{N\,ESC}^{ES_i\to WL_i} - R_{N\,CAP}^{ES_i\to GS_i} + R_{N\,ESC}^{GS_i\to ES_i} - R_{ES_i} + G_{PH\,ES_i} \quad (3)$$

$$\frac{\partial n_{GS_i}}{\partial t} = R_{N\,CAP}^{WL_i\to GS_i} - R_{N\,ESC}^{GS_i\to WL_i} + R_{N\,CAP}^{ES_i\to GS_i} - R_{N\,ESC}^{GS_i\to ES_i} - R_{GS_i} + G_{PH\,GS_i} \quad (4)$$

Equation (1) is the continuity equation for electrons in the bulk (B) GaAs, being E the electric field, and μ_n and D_n the electron mobility and diffusivity, related through the Einstein relation. The recombination rate R_{TOT} includes non-radiative, band-to-band and Auger processes in the bulk. G_{PH} is the photogeneration rate associated to the GaAs absorption of the solar spectrum. $R_{N\,CAP}$ is the capture rate from B down to the WL state; $R_{N\,ESC}$ is the escape rate in the opposite direction. Equation (2) is the rate equation for electrons in the wetting layer of the ith QD layer. Transitions between the WL and B, ES and GS are considered in this expression. R_{WL} is the non-radiative recombination rate in the WL. Equations (3) and (4) accounts for the capture and escape of the photo-generated electrons in the ES and GS within the ith QD layer. R_{ES} and R_{GS} are the non-radiative recombination rates, whereas G_{PHES} and G_{PHGS} are the photo-generation rates of electron-hole pairs into the ES and GS due to the QD absorption of solar photons. An example of the calculated QD absorption spectrum is shown in Fig. 2. The complete expressions associated to all the capture and escape rates are reported in [6]. Hole equations are fully analogous to the electron ones and are not specified here. The model is completed with the Poisson equation (5), which takes into account electron and hole densities in the bulk, WL, ES and GS from each of the QD layers, and the charges due to ionized impurities.

$$\frac{\partial E}{\partial x} = \frac{q}{\varepsilon}\left(p - n + N_d^+ - N_a^- + p_{WL_i} - n_{WL_i} + p_{ES_i} - n_{ES_i} + p_{GS_i} - n_{GS_i}\right) \quad (5)$$

Equations are numerically discretized through the Scharfetter–Gummel scheme in order to avoid oscillatory spatial behavior. The resulting system of nonlinear equations is finally solved through the Newton method [7].

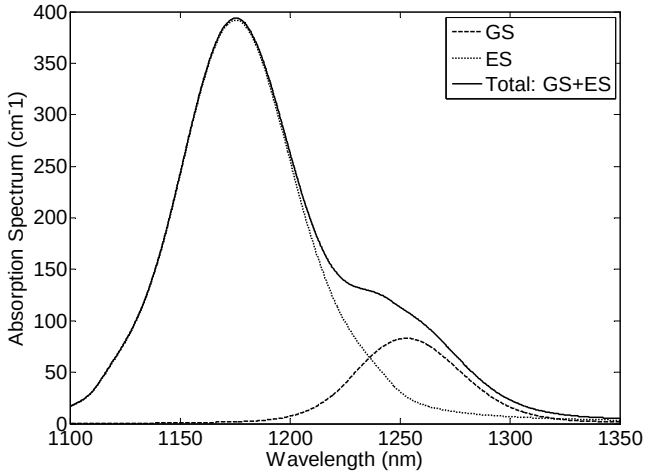

Fig. 2. Absorption spectrum due to the GS and ES of a QD layer.

3. Preliminary results

In order to validate the model, we have chosen some reference structures similar to those reported in [3]; the scheme is shown in Fig.1a. In particular we considered two SC: one without QDs (ie: only GaAs *p-i-n* junction) and the other one with 10 QD layers in the intrinsic region and a dot density of $4x10^{10}$ cm^{-2} per layer.

Fig. 3*a* shows a comparison between the external quantum efficiency of both simulated devices. These results are qualitatively in agreement with the experimental measurements published in the literature [3, 4]. It can be seen the extended absorption range exhibited by the QD solar cell, associated to the absorption spectrum of the QDs. Due to the small size of the QDs of this example there is only the GS confined in the QDs with a peak absorption wavelength at 1000 nm.

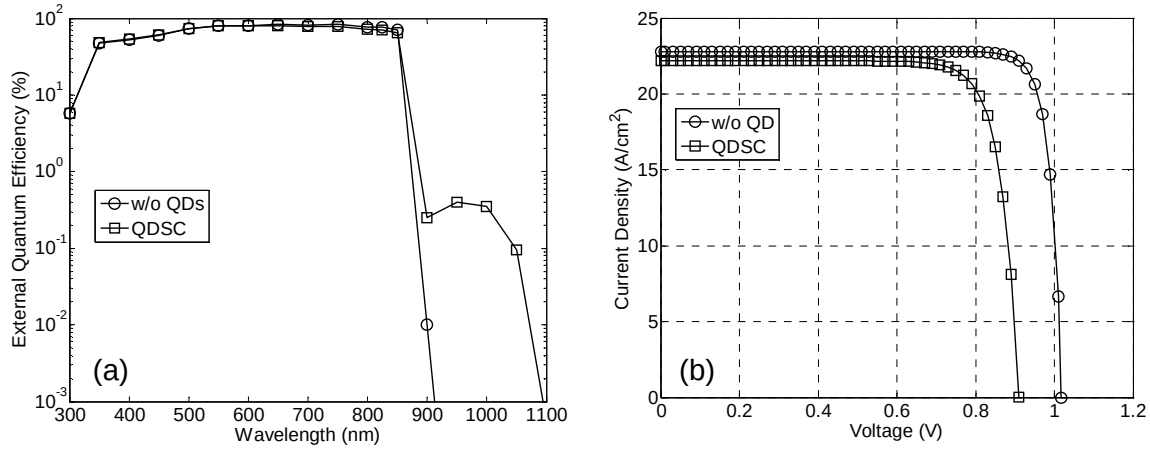

Fig. 3. (a) External quantum efficiency of the simulated SC with and without QDs; (b) I-V characteristics of simulated devices under 1 sun AM1.5G solar spectrum.

These same structures have also been simulated with the commercial software APSYS [8] in order to get reference I-V curves to be compared with the model developed. The calculated I-V are shown in Fig.3b and will be used for comparison with the results obtained by the drift diffusion model we developed. Fig. 3b highlights a significant unwanted reduction of the V_{OC} voltage as reported in [3]. Our purpose is to use our "home-made" simulator to better understand this effect and eventually propose a proper design configuration that does not change the V_{OC}.

4. Conclusions

We have described a detailed drift diffusion model for QDSC; the results obtained by the model will be compared with reference results obtained by commercial software. The model will be used to understand the role of QDs in IBSC.

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