Intermediate band solar cells: comparison with Shockley–Read–Hall recombination

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Intermediate band solar cells are characterized by the existence of a collection of energy levels in the middle of the, otherwise, conventional semiconductor bandgap. According to the standard Shockley–Read–Hall recombination theory, the states corresponding to these energy levels behave as non-radiative recombination centers and therefore, are detrimental to solar cell performance. Nevertheless, the theory of the intermediate band solar cells predicts and enhancement of the solar cell efficiency well above the limiting efficiency of single gap solar cells (63.2% vs 40.7%) when these levels exist. This paper clarifies the reasons.

The basic theory of the intermediate band solar cells (IBSCs) has been by now widely disseminated. In this paper, we will assume the reader is familiar with this theory and we will describe here again only those topics being convenient for the self-consistence of the paper. Were the reader not familiar with the theory and would wish to be so, we suggest he starts with Ref. [1], to find the original description of the model, to continue with Refs [2] to [3–6]. There he will find from refinements to the theory, such as the discussion of the influence of impact-ionization and Auger recombination mechanism on the performance of the cell, to thermodynamic analysis, discussion of the implementation of the IBSC with quantum dot technology and analyses of the influence of the overlap between absorption coefficients on the performance of cell.

Fig. 1 represents the simplified band diagram of an IBSC. The basic structure of this cell consists of an intermediate band material sandwiched between two ordinary semiconductors. The intermediate band material is a semiconductor like material but characterized by the existence of an intermediate band (IB) located within the, otherwise, conventional gap defined by the edges of the conduction band (CB) and valence band (VB). Theoretical efficiency improvement of IBSCs over conventional single and even tandems of two solar cells (63.2% vs 40.7% of single gap and 55.4% of a tandem) comes from two facts. First, current in the IBSC is enhanced because sub-bandgap photons can contribute to the photocurrent. This is because thanks to the IB, sub-bandgap photons, such as those labeled as „*1*“ and „*2*“ in Fig. 1, can now be absorbed to create one electron–hole pair. Second, the production of this extra current is made out without voltage degradation, that is, without the voltage being limited by any of the lowest sub-gaps, neither E_L nor E_H. Ultimately, this is due to the fact that carrier concentration in each band is described by its own quasi-Fermi level (ε_{FC}, ε_{FV} and ε_{FI} for the CB, VB and IB respectively), the output voltage being limited by the difference between the CB and VB quasi-Fermi levels. It is the voltage issue the one that must be emphasize the most because the solution to increase the photogenerated current of a solar cell could be, for example, just the use of a low bandgap energy semiconductor to manufacture it. In addition, to approach the IBSC limiting efficiency, electronic transitions to and from the IB must be of radiative nature (emitting one photon), the absorption coefficients governing these processes should not overlap when considered as a function of the photon energy, the IB must be half-filled with electrons (metallic) and ε_{FI} must remain clamped to its equilibrium position when the cell becomes excited.

However, the existence of energy levels within the semiconductor bandgap is traditionally considered as a source of non-radiative recombination, the so called Shockley–Read–Hall (SRH) recombination after the authors who first described the governing statistics [7,8]. Since the existence of non-radiative recombination degrades the performance of the cells, from this perspective, the existence of intermediate levels should be considered as an undersirable feature. On the contrary, the basic theory of the

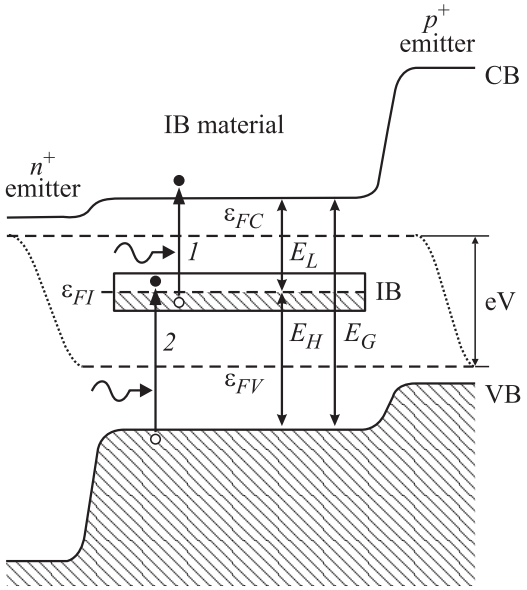

Figure 1. Simplified bandgap diagram of an intermediate band solar cell [5].

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IBSC pursues the existence of these levels and moreover, as mentioned, that the recombination processes to and from this band be of radiative nature.

Before explaining the reasons why the presence of intermediate energy levels within the semiconductor bandgap can lead to such a different behavior from the perspective of recombination (radiative vs non-radiative) we would like to point out that both frameworks (SRH and IBSC) assume the existence of three quasi-Fermi levels to rule the occupation probability out of the equilibrium in each of the existing group of states (conduction, intermediate and valence) in the semiconductor.

The existence of its own quasi-Fermi level to describe the occupation probability of the intermediate states is not usually sufficiently emphasized but it is true since, at some point in the development of the SRH theory, it is stated that the number of intermediate states (often also called *traps* or *defects* in the framework) being occupied by an electron, n_T, compared to the total number of states N_T, is given by [9]:

$$\frac{n_T}{N_T} = \frac{1}{1+\exp\left(\frac{E_T-\varepsilon_{FI}}{kT}\right)} = \frac{c_n N_T n + c_p N_T p_1}{c_n\left[n+n_i\exp\left(\frac{E_T-E_i}{kT}\right)\right]+c_p\left[p+n_i\exp\left(\frac{E_i-E_T}{kT}\right)\right]} \quad (1)$$

where no degeneracy has been assumed for the trap, E_T is the energy of the intermediate state, ε_{FI} is the trap quasi-Fermi level, k is the Boltzmann constant, T is the temperature, n and p are the electron and hole concentrations respectively, c_n and c_p are the electron and hole capture cross sections, n_i is the semiconductor intrinsic concentration and E_i is the semiconductor intrinsic level.

This fact is also illustrated by means of the example in Fig. 2. It shows the bandgap diagram of a forwarded biased $p-n$-junction and its corresponding quasi-Fermi levels, including the one related to the traps, ε_{FI}. The trap density, N_T, has been assumed uniform all over the $p-n$-structure and *much lower* than the doping density involved. The trap energy level, E_T, has been assumed located at the center of the bandgap. To emphasize further the need of a specific quasi-Fermi level associated to the occupation of the traps, one can realize that neither the electron quasi-Fermi level, ε_{FC}, nor the hole quasi-Fermi level, ε_{FV}, can rule the trap occupation ratio because the choice of any of them leads to opposite asseverations: the electron quasi-Fermi level, being located well above the trap energy level leads to a complete electron occupation of the traps while the hole quasi-Fermi level, being located well below, leads to its complete emptiness. Therefore, the existence of three different quasi-Fermi levels to explain the operation of the IBSC has not to be regarded as an awkward hypothesis of the IBSC theory: it has always been there, even in conventional semiconductor theory.

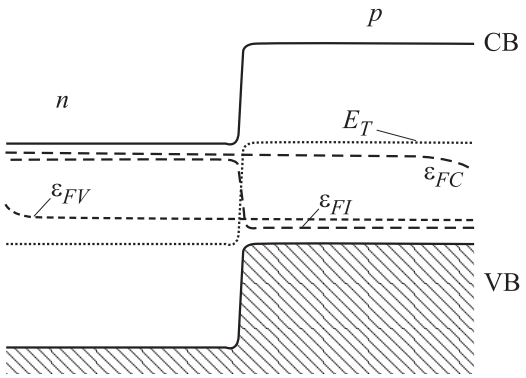

Figure 2. Bandgap diagram of a $p-n$-junction forward biased showing the electron, hole and trap quasi-Fermu levels (ε_{FC}, ε_{FV} and ε_{FI} respectively).

A couple of aspects of these *traps* are specific in the classic IBSC context. To explain them, it is convenient to define first what we understand by acceptor and donor like *traps*. Acceptor like traps become negatively charged when they capture an electron (its quasi-Fermi level is located then a few kT above E_T) remaining electrically neutral whether not (its quasi-Fermi level is then located below E_T). Donor like traps become positively charged when they give away an electron (quasi-Fermi level located below E_T) remaining neutral on the contrary (quasi-Fermi level located above E_T). Besides, whatever the type is, its density, in conventional devices in which their appearance is unintentional, is small and has a negligible contribution to the charge density when compared to the intentional doping contribution (usually characterized by concentrations well above $10^{16}\,\mathrm{cm}^{-3}$).

Hence, the two specific aspects regarding these *traps* (that shortly we will prefer call *band*), were they would have to play the role specified by the basic IBSC theory are, from one side, that they should have both acceptor and donor character. This means they become negatively charged when they capture an electron and positively charged when they release it (in other words, they become negatively charged when their quasi-Fermi level lays above E_T and positively charged when it does below). From the other side, their concentration should be, at least, of the order of magnitude of the CB and VB density of states [10]. The reason is the need of the IB to provide both positive as negative charge without significant displacement of the IB quasi-Fermi level so it can remain clamped to its equilibrium position as plotted in Fig. 1.

However, increasing the *trap* concentration, if they still behave non-radiatively, would only worsen the things. At this point is when we prefer to call this collection of intermediate levels *band* rather than *traps*. The term *band* is used to indicate that the intermediate quantum states have quantum properties no different from those of the CB and VB and, in particular, that they are of de-localized nature, that is, their wavefunction extends all over the crystal

lattice. This is a necessary condition for the transitions from and to the intermediate band to be of radiative nature [2].

To achieve this de-localization it is likely that the impurities have not to be placed randomly within the crystal lattice but ordered with a periodical pattern [11] or even better, that the intermediate band arises naturally from a given atomic crystal arrangement [12].

An intriguing question when discussing the SRH recombination concerns about where the energy lost by an electron carrying out a transition goes. If it would go easily to a photon, we would not be discussing anything here: radiative recombination would already be granted.

To say the energy of the electron in the recombination process goes to phonons needs some comments. Phonons, the quantized vibrations of *lattice atoms*, have an energy in the range of a few tenths of meV [13]. Since the gaps E_L or E_H are in the range of several hundred of meV, the non-radiative transition of say one electron from the CB to the intermediate levels would require the simultaneous interaction with tenths (at least) of phonons. This simultaneous concurrence of such a number of phonons is considered extremely unlikely in a perfect crystal. Instead, the preferred figure is that in which the presence of the *trap* not only introduces strictly one energy level *in the middle* of the gap but also some *excited* electronic states and its *own vibration modes*, different from those of the lattice. Hence, in a first step, a CB electron is captured by the *trap*, that is, carries out a transition to one of the impurity excited electronic states (cascade model [9]). This state is usually localized. The impurity then captures the electron energy and momentum and vibrates. It can do so in one step because its vibration modes are not those of the lattice. Then, this energy is released to the lattice (lattice relaxation) through the emission (not simultaneous!) of the necessary number of phonons (multiphonon model [9]).

Hence, the solution to retake the unlikeness of an electron releasing its energy non-radiatively to the phonons, passes through the *blockade* of the two mechanisms just mentioned. And this solution, again, goes through the allocation of the impurities in a periodical pattern or, what is equivalent, to make them part of the crystal lattice itself. In this way they cannot vibrate freely any more but their vibrational modes should become those typical of a crystal lattice, that is, those whose energy is in the phonon energy range, a few tenths of meV. So, from one side they would again not be able to capture the energy of the electron in the first instance and, from another, as previously already mentioned, their energy spectra would be grouped into bands.

In the case the IBSC is engineered by means of quantum dots (QDs), this *blockade* of the capability of an electron to release its energy through phonons, although controversial [14] is known as the phonon-bottleneck effect. Physically, in the QD case, the intermediate band arises from the energy of the confined electrons in the dot. Remarkably, the dots are groups of thousands of atoms that again have certainly not the vibrational properties of single impurity atoms but likely, the vibrational properties of a lattice what again take us to the case that only phonons with energy of a few tenths of meV are available for electron energy releasing.

In summary, the IBSC and the SRH theory frameworks share the introduction of three quasi-Fermi levels to describe carrier occupation of the energy levels although in the case of the latest, this feature has not been commonly be made explicit in the literature. In addition, the IBSC theory assumes the recombination processes between bands being of predominantly radiative nature. There is nothing in the SRH theory against these processes being of radiative nature although for making them dominant, it will be required to blockade the possibility of energy transfer from the electrons to the phonons. This could be achieved, either by allocating the impurities periodically in the crystal lattice and therefore make them all constitute a new crystal, or possibly by using quantum dots to fabricate the intermediate band material.

References

[1] A. Luque, A. Martí. Phys. Rev. Lett., **78** (26), 5014 (1997).
[2] A. Martí, L. Cuadra, A. Luque. *Next Generation Photovoltaics*: *High Efficiency through Full Spectrum Utilization* (eds A. Martí, A. Luque), Series in Optics and Optoelectronics (IOP Publishing, Bristol, 2003).
[3] L. Cuadra, A. Martí, A. Luque. IEEE Trans. Electron. Dev., **51**, (2004).
[4] A. Luque, A. Martí, L. Cuadra. IEEE Trans. Electron. Dev., **50** (2), 447 (2003).
[5] A. Luque, A. Martí. Progr. Photovolt.: Res. Appl., **9** (2), 73 (2000).
[6] A. Luque, A. Martí, L. Cuadra. IEEE Trans. Electron. Dev., **48** (9), 2118 (2001).
[7] W. Shockley, W.T. Read. Phys. Rev., **87** (5), 835 (1952).
[8] R.N. Hall. Phys. Rev., **87** (2), 387 (1952).
[9] R. Pierret. Advanced Semiconductor Fundamentals, v. VI of Modular Series on Solid State Devices (eds R.F. Pierret, G.W. Neudeck), (Addison Wesley, Reading, 1989).
[10] A. Martí, L. Cuadra, A. Luque. In: Proc. 199th Electrochemical Society Meeting (The Electrochemical Society, Pennington, 2001) p. 46.
[11] B.K. Ridley. Quantum Processes in Semiconductors, Ch. 2 (Oxford University Press, Oxford, 1999), 4 edition.
[12] P. Wahnón, C. Tablero. Phys. Rev. B, **65**, 165 115, 1 (2002).
[13] *Handbook Series on Semiconductor Parameters*, ed. by M. Levinshtein, S. Rumyantsev, M. Shur. (World Scientific, Singapure, 1996) v. I, II.
[14] A.J. Nozik. *Next Generation Photovoltaics*: *High Efficiency through Full Spectrum Utilization* (ed. by A. Martí, A. Luque), Series in Optics and Optoelectronics (Institute of Physics Publishing, Bristol, 2003).

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