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LIMITING EFFICIENCY OF LDS SOLAR CELLS

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Abstract: An ideal solar energy converter can theoretically reach efficiencies up to 93%, when working reversibly. From first principles, photovoltaic converters based on a single p-n junction have an inherent limiting efficiency of 40%. The possibility to overcome this limit is discussed in the cases when the non-equilibrium carrier concentrations need to be described with more than 2 quasi-Fermi levels. The relevance to real systems like MQW solar cells is discussed. Model calculations indicate that a significant increase of the efficiency above the 40% limit is possible. The proposed framework presented here also clarifies the controversy on the limiting efficiency of MQW solar cells and related Low Dimensional Structures (LDS) converters. In the end, new designs are proposed in view of taking a better advantage of the potential of this kind of converters.

1- Introduction

Photovoltaic devices based on p-n junctions have demonstrated efficiencies of about 30% [1] (under concentration) and are limited to about 40% from theoretical considerations [2,3]. MQW (multiple quantum wells) solar cell designs have been proposed as a possibility to overcome this limitation [4]. Controversy has arisen about the actual possibility for this device to have efficiency beyond 40% when simulations yielded [5,6] much higher efficiencies. This discussion goes beyond the specific MQW cells problem, the question is to find the conditions under which the entropy production during the solar energy conversion can be minimised, so as to reach the highest efficiencies at the cost of a manageable complexity.

New insights on this problem, based on the taking into account of the specificities of the density of states in the MQW part of the device, are presented. It is shown that the usual assumption of local equilibrium of free electrons (resp. for holes) in the conduction band and the MQW states is not valid when these levels are only coupled by radiative recombination (i.e. it is not always possible to define a common quasi-Fermi level (QFL) for all free carriers of a given type). This results in an important overestimation of radiative recombination for such systems in the previous thermodynamic analysis [2,3] and thus an underestimation of the limiting efficiency. On the other side, the stimulated recombination can no longer be neglected in those devices when they are working close to their limiting efficiency, and the coupling between the Well states and the conduction and the valence band have a finite limit. Taking into account those two factors shows that efficiencies given in [4,5] are overestimated. We present arguments indicating that the improvement could be easier to materialize using other types of Low Dimensional Structures (LDS).

2- Approach

The model system is schematically represented on fig.1. The active region has a number of bands of delocalized states, instead of the 2 generally assumed in photovoltaic conversion. The framework, standard for the study of irreversible processes, is the detailed balance theory [8].

A realistic limit for efficiency for such systems must be based on the solution of the Boltzmann transport equation. This takes into account the microscopic reversibility of all the processes. This constitutes a complication compared to the 2 bands case, where the balance of photon and photogenerated carriers was enough to compute the efficiency. The limiting efficiency is obtained by assuming that radiative losses are predominant, as in previous studies [2,3,8]. For memory, we recall the usual assumptions: (a) Carrier Recombination and Generation are only radiative, (b) Each electronic transition is associated to only one photon emission or absorption, and one photon gives only one e-h⁺ pair, (c) All entering photons with an energy corresponding to a possible transition are absorbed (optical path $\gg 1/\alpha$, α is the absorption coefficient), (d) Carrier distributions can be described by a quasi-Fermi level (QFL) for each Band (intraband transitions much faster than interband).

Because of the increased complexity of the problem and to keep the physical insight, we will proceed here to further simplifications: (e) Carrier distributions are considered in the Boltzmann approximation, (f) The QFL are flat (diffusion

length \gg size of the active region), (g) Perfect collection of carriers (escape time from the active region much smaller than the radiative recombination time). Within this model, the Boltzmann equation can be solved in the relaxation time approximation and we obtained the formula (1,2). To get the meaning out of the equations, we will consider the most simple case, a "MQW" solar cell consisting of a conduction band, a valence band and a subband of the states due to the MQW.

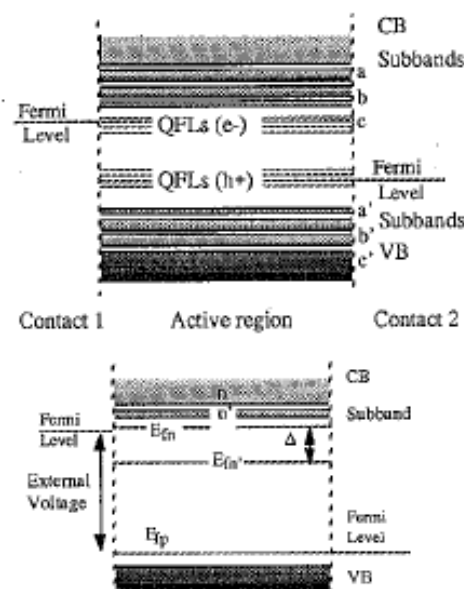


Fig. 1: Schematic representation of the band diagram of the model system. Top: full model; bottom: simplified 3-level system.

3- Results on the efficiency

3.a. The photogenerated current

In the following, T_s and T_c are respectively the sun (6000K) and the cell (300K) temperatures, f_w is the solar concentration factor ($f_w = 1$ at the maximal concentration), E_a and E_c are the bottom energy of the subband and of the conduction band respectively (energies with respect to the top of the valence band), $Q(E_1, E_2, T)$ is the flux of photon having an energy $h\nu$, $E_1 < h\nu < E_2$, emitted by a black body source of temperature T , we simplify the notation in $Q(E, T)$ for E_2 infinite. The exact form of the Q function can be found in many references and textbooks [2,3,8].

The photogenerated current is then:

$$I_{ph} = q [f_w \cdot Q(E_a, T_s) + (1 - f_w) \cdot Q(E_c, T_c)] \quad (1)$$

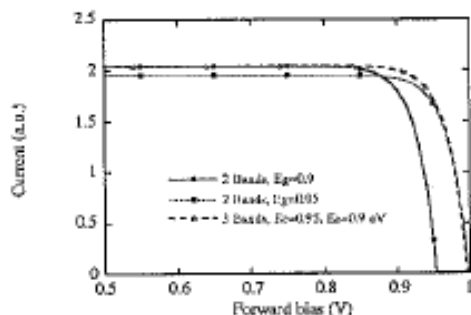


Fig. 2: I-V curves under illumination ($f_0=1$) of two normal p-n junctions with $E_g=0.9$ and 0.95 eV and (dotted line) of the idealised MQW solar cell made with the 2 materials.

E_a is the closest distance between 2 levels. That is, since we assumed a perfect absorption (corresponding also to an emissivity of 1) and a perfect collection efficiency, the photocurrent is the same as the one given by a 2-band cell, with the same degree of perfection.

3.b. The dark current

We give directly the result of the computations, within the stated approximations, when the subbands are all packed together near the conduction CB, or the valence band VB, (levels a, b, c, ... or a', b', c' in fig.1, ...) only, to get a reasonable formula, let us, to fix the ideas, consider a bare VB and a "dressed" CB :

$$I_d(V) = q \cdot Q(E_b, T_c) \left[\exp\left(\frac{qV}{kT_c}\right) - 1 \right] + q \cdot \sum_i Q(E_i^*, E_i^*, T_c) \left[\exp\left(\frac{q(V - \Delta_i)}{kT_c}\right) - 1 \right] \quad (2)$$

This formula shows that, as could be expected, the effects of the subbands are cumulative. That is why it is enough to consider one "incremental" cell in what follows.

The subbands are numbered by i , the bottom of the subband i is E_a^i and its top is E_b^i , Δ_i is the difference between the QFL of the electron in the CB and in the subband i , $\Delta_i = E_{fn} - E_{fi}$. As explained above we will now focus on the 3 level case, for which:

$$I_d(V) = q \cdot Q(E_b, T_c) \left[\exp\left(\frac{qV}{kT_c}\right) - 1 \right] + q \cdot Q(E_a, E_b, T_c) \left[\exp\left(\frac{q(V - \Delta)}{kT_c}\right) - 1 \right] = q \cdot Q(E_a, T_c) \left[\exp\left(\frac{qV}{kT_c}\right) - 1 \right] + q \cdot Q(E_a, E_b, T_c) \left[\exp\left(-\frac{q\Delta}{kT_c}\right) - 1 \right] \exp\left(\frac{qV}{kT_c}\right) \quad (3)$$

That is, the 2 different writings show that the 3-band cell has a dark current intermediate between the high band gap ($E_g=E_b$) and the low ($E_g=E_a$) band gap corresponding 2-bands cells, as a comparison with Shockley's formula shows immediately (Δ has to be >0 because the weak generation-recombination term between CB and the subband and the large amount of states in the CB compared to the subband). This is illustrated in figure 2.

3.c. The open circuit voltage and the efficiency

The eqs (1) & (3) allow the computation of V_{oc} through a transcendental equation. But if we expand Δ in a series of powers of V (external voltage), since $\Delta=0$ when $V=0$, we get $\Delta=m \cdot V + \dots$. Keeping only the first term:

$$V_{oc} = \frac{kT}{q} \left[1 + \frac{m \cdot Q(E_a, E_b, T_c)}{Q(E_a, T_c)} \right] \ln \left(\frac{Q(E_a, T_c)}{Q(E_b, T_c)} \right) \quad (4)$$

That is, V_{oc} is larger than the one of the 2-bands cell with $E_g=E_a$. The eqs (1) & (3) allow also the computation of the efficiency. We have plotted the efficiency as a function of the low band gap in fig.3. The efficiency is above the reference efficiency of a 2-bands cell, giving at most a 2.5% absolute increase in efficiency, with an incremental band of width 0.025 eV.

4- Relevance to experimental systems and prospective structures

To understand how far the previous analysis can help us to see whether such improvement were experimentally observed in the studied MQW solar cells, we have to put side by side the theoretical conditions given in 2- with the known material parameters of the III-V used in the structures. As expected, the fastest of the time constants (≈ 1 ps) in the system concerns the thermalization of carriers via phonon scattering within each of the bands of levels, which justifies the operational definition of a common QFL for the carriers in these states. A second condition, also promisingly enough satisfied, was related to the collection efficiency. The measured escape times (< 40 ps [9]) are much smaller than the radiative recombination time (≈ 10 ns [10]) which ensures an escape probability close to unity, as assumed above. A third condition was that radiative recombination would dominate over non radiative ones, which is also realized, according to [10]. The departure of experimental systems from our assumptions is most likely to arise because the transit time⁸ is \approx or $>$ relaxation time to the subband (≈ 10 ps). This fact has the important consequence, which was never stressed to our knowledge, that an important carrier exchange takes place between the subband and the conduction band, i.e. the QFL separation is small (small value of m in eq. (4)), with an important consequence on the efficiency gain (the absolute gain in efficiency is 2.5% at $m=0.03$, but only 0.2% at $m=0.01$). In the end, the effects could be present, but faint. For instance, on the one hand the measured V_{oc} could exceed what would be obtained if a complete relaxation to the subband [9] was assumed. On the other hand, the measured efficiencies never got close to the theoretical limit.

How could the situation be improved? Increasing the relaxation time can be done in principle by using structures of lower dimensionality (Q-dots or Q-wires arrays) restricts the number of relaxation paths and gives more stringent selection rules for the transitions because of the quantification of the moment in more directions. Decreasing the transit time can be done in Low dimensional anisotropic structures like MQW by having the carriers flowing in the direction of the highest mobility as on Fig.4. In principle perpendicular wells would do as well (with a good light trapping), but growing lateral superlattices on misoriented substrates has already been realised [11].

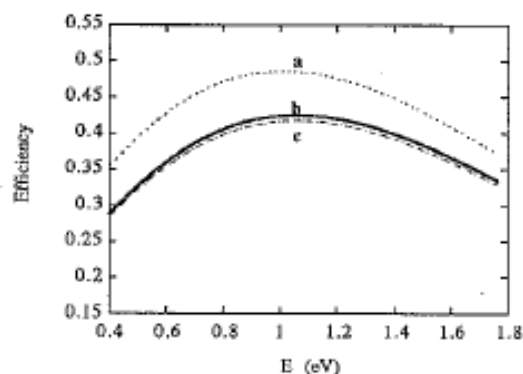


Fig. 3: Efficiency of an idealised MQW cell (b) as a function of the lower bandgap material when the width of the incremental band is kept at 0.025 eV. For comparison, the Nominal efficiency, (a), (when the fill factor is taken as 1), and the efficiency of the standard 2 bands devices (c).

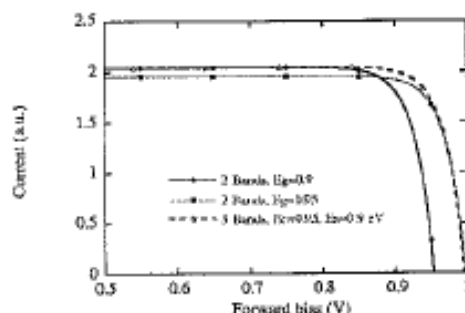


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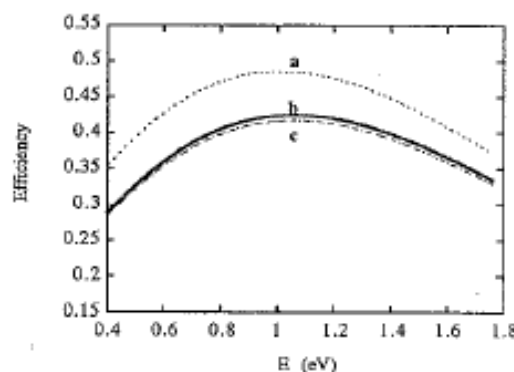
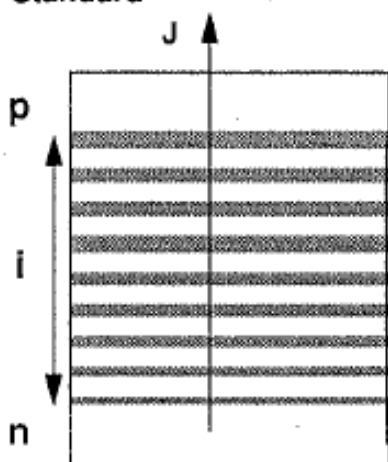


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Standard



Inclined

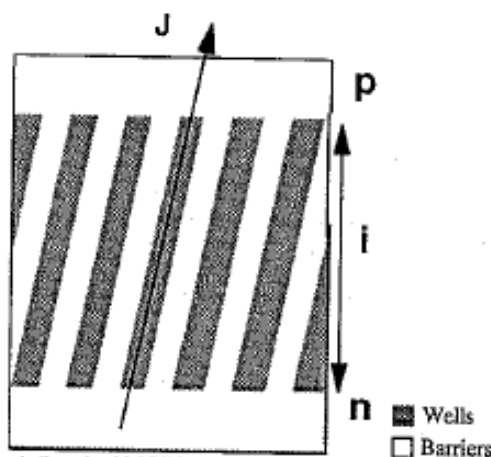


Fig. 4: Standard MQW structure (top) and lateral superlattice for an improved transport of the carriers. The arrow shows the direction of the current.

Conclusions

The limiting efficiency of multi-quantum well solar cells can exceed the one of single band gap solar cells in the radiative recombination limit after optimization. This limiting efficiency is intermediate between the one given in [2,3] and the ones given in [5,6], provided the restrictions on relaxation processes are stringent enough to prevent complete thermalization of the mobile electrons (holes).

A functional equation, allowing for the optimization of the efficiency by tailoring the density of states of the MQW region, can be derived from the condition of optimal efficiency (the density of states and the transition probabilities enter this equation), and this is one of our future prospects. The development of a more general framework should also have some use in the research on photodetectors and LED, since they are basically the same devices as solar cells but operated in a different regime.

Material and structures still have to be optimized in order to take full advantage of the effect. Investigations are under progress to get a more accurate description of real systems and to find the sensitivity of the gain in conversion efficiency with the physically relevant material parameters.

Acknowledgements

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References and Notes

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