Increasing the Efficiency of Ideal Solar Cells by Photon Induced Transitions at Intermediate Levels

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Recent attempts have been made to increase the efficiency of solar cells by introducing an impurity level in the semiconductor band gap. We present an analysis of such a structure under ideal conditions. We prove that its efficiency can exceed not only the Shockley and Queisser efficiency for ideal solar cells but also that for ideal two-terminal tandem cells which use two semiconductors, as well as that predicted for ideal cells with quantum efficiency above one but less than two. [S0031-9007(97)03454-6]

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Recent attempts have been made to increase the efficiency of solar cells by introducing an impurity energy level in the semiconductor band gap that absorbs additional lower energy photons [1–3]. The question has been raised [4,5] whether these cases have their efficiency limited too by the Shockley and Queisser (SQ) model [6] for ideal cells, as it is the case for conventional solar cells. In this paper an ideal solar cell with an intermediate energy level or band within the semiconductor gap is analyzed presenting an efficiency well above the one permitted by the SQ model. What we precisely mean by ideal solar cell is developed along the text in seven conditions labeled IC1 to IC7.

In Fig. 1 a band diagram of the structure we propose is presented. It contains the usual semiconductor valence band (VB) and conduction band (CB) but, in addition, there is an intermediate band (IB). Such an intermediate band (or level) is possible by several means (lone pair bands, low dimensionality superlattices, impurities, etc. [7]) although some of them may not comply with the required conditions.

We shall assume that, in addition to the common absorption of photons by electron transitions between the valence and the conduction band (process A_{CV}), absorptions with transitions between the valence band and the intermediate band (process A_{IV}), and between this band and the conduction band (process A_{CI}) may also take place. In this we follow an important early work of Wolf [8]. In most of the recent literature [1–5] only one of the last two processes was considered. Unlike Ref. [8] we consider that if the absorption processes occur, the opposite transitions with emission of photons also occur, as required by the detailed balance.

As in the SQ model, we shall assume that any irreversible mechanism is prevented, besides those inherent to the photovoltaic operation [9]. In particular, nonradiative transitions between any two of the three bands are forbidden (IC1), carrier mobilities are infinite (IC2), and Ohmic contacts are applied so that only electrons, no holes, can be extracted from the conduction band to form the external current, and only holes, no electrons, can be extracted from the valence band. No carrier can be extracted from the impurity band (IC3).

A consequence of the infinite carrier mobility is the constancy of the quasi-Fermi levels throughout the whole cell volume (currents are proportional to their gradients, the constant of proportionality comprising the mobility). We assume three separate quasi-Fermi levels, ϵ_{FV}, ϵ_{FI}, and ϵ_{FC}, one for each band.

In addition, we shall consider that the cell is thick enough to assure full absorption of the photons with enough energy to induce any one of the transitions described above (IC4). Furthermore, a perfect mirror must be located at the back of the cell (and elsewhere) so that the radiation generated in the cell by processes A_{CV}, A_{CI}, and A_{IV} can only escape by the front area of illumination (IC5). For simplicity this area is considered unity.

What we are going to do now is to determine the photons leaving the cell resulting from processes A_{CV}, A_{CI},

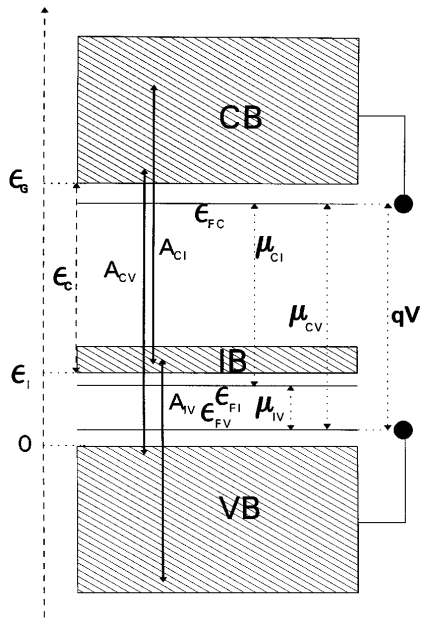

FIG. 1. Band diagram of a solar cell with an intermediate band.

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and A_{IV}. Photons are continuously emitted and absorbed inside the semiconductor but only when they leave the cell is a net electronic transition (towards the lower energies) produced. Accordingly, we shall establish equations of balance of electrons from which we shall obtain the solar cell current. This solar cell current is related to the splitting of the quasi-Fermi levels and consequently to the cell voltage. Hence an I-V equation will be obtained from which we shall calculate the cell efficiency.

Let us consider a mode of radiation—defined by a certain energy and photon direction (wave vector) when the electromagnetic field is developed in a set of plane waves—and ν be the number of photons in this mode. Let ζ be the distance along a ray associated with this mode from its entrance to the semiconductor ($\zeta = 0$) to its necessary [10] egress ($\zeta = 1$) by the front face after some reflections on the back mirror or, if the cell is textured, by total internal reflection on some of the front face facets. Let $h_{Ci,Vj} = h_{Vj,Ci}$ be a coefficient proportional to the element of matrix of the transition [11] from a certain state Ci in the conduction band to a certain state Vj in the valence band. Similarly let $h_{Ci,Ij} = h_{Ij,Ci}$ and $h_{Ii,Vj} = h_{Vj,Ii}$ be the coefficients for transitions between states in the conduction band and the intermediate band and between states in the intermediate band and the valence band, respectively. Let us also assume for generality that this photon mode has enough energy to induce all the three transitions A_{CV}, A_{CI}, and A_{IV}.

Let f_{Vi}, f_{Ii}, and f_{Ci} be the Fermi-Dirac functions for the electrons in the states Vi, Ii, and Ci, respectively, corresponding to each of the three bands considered. Taking into account the properties of the quantum mechanic harmonic oscillator [12], the variation of the number ν of photons in the mode when progressing along the ray is

$$\begin{aligned}\frac{d\nu}{d\zeta} &= \frac{n}{c}\sum_{i,j}[h_{Ci,Vj}(\nu+1)f_{Ci}(1-f_{Vj}) - h_{Vj,Ci}\nu f_{Vj}(1-f_{Ci})] \\ &+ \frac{n}{c}\sum_{i,j}[h_{Ci,Ij}(\nu+1)f_{Ci}(1-f_{Ij}) - h_{Ij,Ci}\nu f_{Ij}(1-f_{Ci})] \\ &+ \frac{n}{c}\sum_{i,j}[h_{Ii,Vj}(\nu+1)f_{Ii}(1-f_{Vj}) - h_{Vj,Ii}\nu f_{Vj}(1-f_{Ii})]. \end{aligned} \tag{1}$$

In each line the second term in brackets is the absorption of photons. The first term is their generation due to both spontaneous and stimulated emission. The sum refers to the different combination of states in the two bands involved producing emission or absorption of photons in the mode under study. The factor n/c (n, semiconductor index of refraction) is intended to convert a time rate into a space derivative.

After some mathematical handling, this equation may be written as

$$\frac{d\nu}{d\zeta} = \alpha_{\mathrm{CV}}(\nu_{\mathrm{CV}} - \nu) + \alpha_{\mathrm{CI}}(\nu_{\mathrm{CI}} - \nu) + \alpha_{\mathrm{IV}}(\nu_{\mathrm{IV}} - \nu) \tag{2}$$

being

$$\begin{aligned} \epsilon &\doteq \epsilon_{Ci} - \epsilon_{Vj} = \epsilon_{Ci} - \epsilon_{Ij} = \epsilon_{Ii} - \epsilon_{Vj}, \\ \alpha_{\mathrm{CV}} &\doteq \frac{n}{c}\sum_{i,j} h_{Ci,Vj}(f_{Ci} - f_{Vj}); \qquad \nu_{\mathrm{CV}} \doteq \frac{1}{e^{(\epsilon-\mu_{\mathrm{CV}})/kT} - 1}; \qquad \mu_{\mathrm{CV}} \doteq \epsilon_{\mathrm{FC}} - \epsilon_{\mathrm{FV}}, \\ \alpha_{\mathrm{CI}} &\doteq \frac{n}{c}\sum_{i,j} h_{Ci,Ij}(f_{Ci} - f_{Ij}); \qquad \nu_{\mathrm{CI}} \doteq \frac{1}{e^{(\epsilon-\mu_{\mathrm{CI}})/kT} - 1}; \qquad \mu_{\mathrm{CI}} \doteq \epsilon_{\mathrm{FC}} - \epsilon_{\mathrm{FI}}, \\ \alpha_{\mathrm{IV}} &\doteq \frac{n}{c}\sum_{i,j} h_{Ii,Vj}(f_{Ii} - f_{Vj}); \qquad \nu_{\mathrm{IV}} \doteq \frac{i}{e^{(\epsilon-\mu_{\mathrm{IV}})/kT} - 1}; \qquad \mu_{\mathrm{IV}} \doteq \epsilon_{\mathrm{FI}} - \epsilon_{\mathrm{FV}}. \end{aligned} \tag{3}$$

The solution of Eq. (2) is

$$\begin{aligned}\nu(\zeta) &= \frac{\alpha_{\mathrm{CV}}\nu_{\mathrm{CV}} + \alpha_{\mathrm{CI}}\nu_{\mathrm{CI}} + \alpha_{\mathrm{IV}}\nu_{\mathrm{IV}}}{\alpha_{\mathrm{CV}} + \alpha_{\mathrm{CI}} + \alpha_{\mathrm{IV}}} \\ &\times [1 - e^{-(\alpha_{\mathrm{CV}}+\alpha_{\mathrm{CI}}+\alpha_{\mathrm{IV}})\zeta}] \\ &+ \nu(0)e^{-(\alpha_{\mathrm{CV}}+\alpha_{\mathrm{CI}}+\alpha_{\mathrm{IV}})\zeta}. \end{aligned} \tag{4}$$

In the case of reflections, the equation has to be solved for each straight line element of the path, putting as an initial condition the final situation in the preceding flight, because each flight involves a different photon mode (of the same energy) with different α's. However, in many cases the symmetry properties of the crystal wipe out the differences and the same α's are valid for the whole path.

The expression contains two terms. The latter reflects the progressive absorption of the photons in the mode that have entered the cell from the source. Full absorption (our condition IC4) means that the sum of the α's times l—the value of ζ when the ray leaves the cell—is large and the exponential becomes negligible. The former term shows the

progressive filling of the mode with photons emitted by the various emission mechanisms. Once ζ is big enough, the mode exhibits a constant population independent of ζ. In our case this population is fully developed when $\zeta = l$.

Such constant population is the average of the three Bose-Einstein functions ν_{CV}, ν_{CI}, and ν_{IV}, weighted by the absorption coefficients α_{CV}, α_{CI}, and α_{IV}. As an additional condition for high efficiency (IC6) we shall assume that for every range of energies only one of the three absorption lengths is important, so that a single Bose-Einstein function describes the population of photons escaping from the cell in every mode.

Thus (see Fig. 1), assuming that $\epsilon_I < \epsilon_C$, the photon population of each mode when escaping from the cell is 0 for $\epsilon < \epsilon_I$, ν_{IV} for the interval $\epsilon_I < \epsilon < \epsilon_C$, ν_{CI} for the interval $\epsilon_C < \epsilon < \epsilon_G$, and ν_{CV} for $\epsilon_G < \epsilon$.

The flux $\dot{N}$ of photons leaving the semiconductor associated with these distributions is well known because the distributions are those of thermodynamic equilibrium. It is given by [13]

$$\dot{N}(\epsilon_m, \epsilon_M, T, \mu) = \frac{2}{h^3 c^2} \int_{\epsilon_m}^{\epsilon_M} \frac{\epsilon^2 \, d\epsilon}{e^{(\epsilon-\mu)/kT} - 1}, \quad (5)$$

where proper intervals of integration and chemical potential are to be set, as described above. The temperature for each case is the crystalline network temperature T_a

We want to emphasize that, in spite of the distributions of the emitted photons being those of equilibrium, inside the semiconductor the photons are not in equilibrium as their populations are neither homogeneous nor isotropic.

The preceding equation can also be used for the photons coming from the Sun by using the solar temperature T_s and putting 0 for the chemical potential. By doing so we implicitly admit that the cell illumination is isotropic. This is another condition (IC7) for maximum efficiency. It is achieved if we use an ideal concentrator, of zero absorptance, that sends the luminescent photons escaping from the cell somewhere inside the solar disk. Such a concentrator has to have a geometrical concentration of, at least, the ratio of the sun distance to the sun radius, that is 46 000.

According to our outline let us now calculate, by a balance of electrons, the current I delivered to an external load. This current leaves the semiconductor by the valence band (positive contact) and returns by the conduction band (negative contact), which involves a flow of electrons leaving this band of value I/q (q, electron charge). Thus, looking at the conduction band,

$$I/q = [\dot{N}(\epsilon_G, \infty, T_s, 0) - \dot{N}(\epsilon_G, \infty, T_a, \mu_{\mathrm{CV}})] + [\dot{N}(\epsilon_C, \epsilon_G, T_s, 0) - \dot{N}(\epsilon_C, \epsilon_G, T_a, \mu_{\mathrm{CI}})]. \quad (6)$$

This current is delivered at a voltage that equals the quasi-Fermi levels splitting of the two bands involved [6], that is, $qV = \mu_{\mathrm{CV}}$.

As no current is extracted from the intermediate band,

$$\dot{N}(\epsilon_I, \epsilon_C, T_s, 0) - \dot{N}(\epsilon_I, \epsilon_C, T_a, \mu_{\mathrm{IV}}) = \dot{N}(\epsilon_C, \epsilon_G, T_s, 0) - \dot{N}(\epsilon_C, \epsilon_G, T_a, \mu_{\mathrm{CI}}). \quad (7)$$

For a given value of the external voltage, this equation, together with

$$qV = \mu_{\mathrm{CI}} + \mu_{\mathrm{IV}} = \mu_{\mathrm{CV}} \quad (8)$$

[see Eq. (3) or Fig. 1], allows for the calculation of all the chemical potentials. With this knowledge, and using Eq. (6), the I-V curve and the power delivered IV can be calculated. As in normal cells, this power presents a maximum. The efficiency is the result of dividing this maximum power by the power σT^4 (σ, Stefan-Boltzmann constant) delivered by the Sun on the cell illuminated area (with concentrated sunlight).

In Fig. 2 we present the maximum efficiency achievable with this structure vs the intermediate band position ϵ_I. This curve is obtained by selecting an ϵ_I and then taking arbitrary values of ϵ_G and calculating the maximum power for each one. Only the highest value of these maxima is retained and, once divided by the incoming power, it is drawn in the curve. The corresponding value of ϵ_G is also displayed in the figure.

The efficiency corresponding to the SQ model, without intermediate band, using a back mirror and an ideal concentrator [14], is also represented in Fig. 2. The cell with intermediate band presented in this paper can reach an efficiency of 63.1% instead of the 40.7% which is the SQ model limit.

If only one of the radiative links of the intermediate band is absent, the cell proposed here shall behave like the SQ cell. In effect, as no electron is extracted from the intermediate band to the external circuit (condition IC3) the transitions to and from the band remaining radiatively linked balance out.

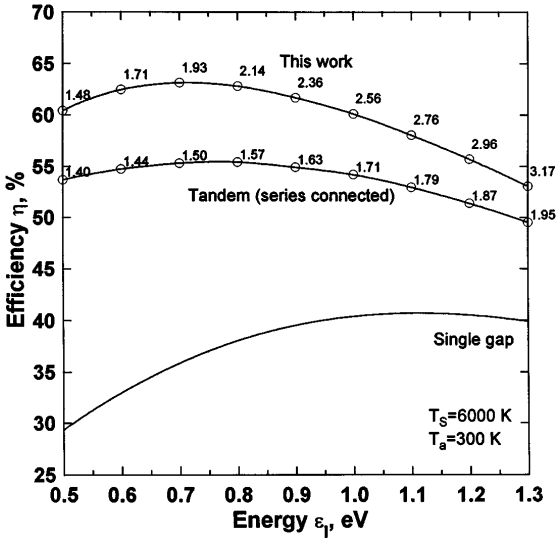

FIG. 2. Efficiency limit for a solar cell with an intermediate band and for a two-terminal ideal tandem cell, in both cases vs the lowest band gap ϵ_I, and for a cell with a single band gap. The corresponding values of the highest band gap in cells with intermediate band (E_G) and in tandem cells (E_C), for maximum efficiency, are also presented.

It has to be underlined that tandem cells, whose development effort for high efficiency is significant today, can exceed the SQ model efficiency. In Fig. 3 we show the diagram of a two-terminal tandem cell using two semiconductors. The semiconductor of higher band gap is located at the top and the one of lower band gap at the bottom, separated—to avoid photonic coupling—by an ideal filter reflecting the photons of energy above ϵ_C (and transmitting the rest). A perfect mirror at the rear and an ideal concentrator are also used. The equations governing this system are

$$I/q = \dot{N}(\epsilon_C, \infty, T_s, 0) - \dot{N}(\epsilon_C, \infty, T_a, \mu_{\mathrm{CI}}) \qquad (9)$$

[instead of Eq. (6)] and Eqs. (7) (with ∞ in place of ϵ_G, not defined in Fig. 3) and (8) (without the last equality referring to μ_{CV}, not defined either). The curve of best efficiencies is also presented in Fig. 2 and shows poorer results: The highest efficiency in this case is only 55.4%, below the 63.1% mentioned above.

The reason for this poorer performance is that in the tandem cell structure two photons are needed to deliver one electron to the external circuit. In other words, the overall quantum efficiency is $\frac{1}{2}$. In the single band gap cell with intermediate band the same applies to the low energy photons [see the terms in the second brackets of Eq. (6)] unable to transfer the free energy necessary to produce the external voltage. However, for the most energetic photons (terms in the first brackets) only one photon is needed to deliver one electron and, therefore, the overall quantum efficiency is above $\frac{1}{2}$.

It is of interest here to make a comparison with the Auger effect cells allowing for a quantum efficiency higher than one [15,16]. Excluding values of the quantum efficiency higher than two, the maximum efficiency is more or less the same as the one obtained in the two-terminal tandem cell with two semiconductors, which is 55.4%. However, it is lower than the one obtained with our intermediate band gap structure.

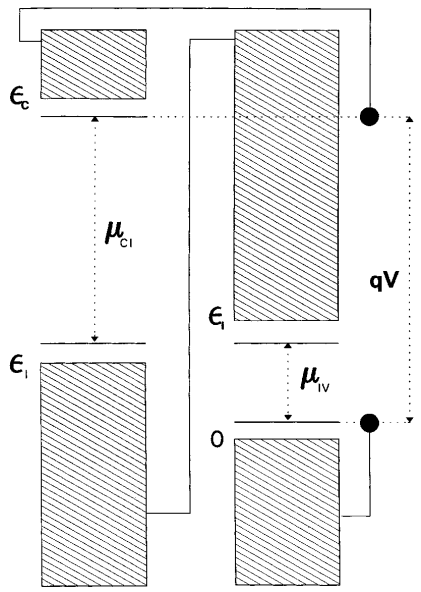

FIG. 3. Band diagram of a two-terminal tandem cell.

Indeed, this paper, aimed to obtain limits, deals with highly ideal structures. However, a recent theoretical study [17], with realistic parameters, has shown that Si cells might experience real, although minor, improvement by the impurity level due to indium.

In summary, we can state that a cell with an intermediate band gap has an efficiency limit higher than the SQ model, if the intermediate band gap is radiatively connected with the two bands: of valence and of conduction. Moreover—putting aside multiple (more than two) semiconductor tandems or multiple pair-generation processes—this ideal structure shows better performances than any other ideal structure of similar complexity known today.

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