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Absolute limiting efficiencies for photovoltaic energy conversion

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Abstract

The Detailed Balance Theory was used in the past by a number of authors to calculate the limiting efficiency of photovoltaic energy conversion. Values of 40.8% for optimum single gap devices and of 86.8% for infinite number of gaps were calculated for the maximum efficiencies of conversion of the radiation of the Sun, considered as a black body at a temperature of 6000 K. This work extends the generality of those results and introduces new refinements to the Theory: the cell absorptivity is justified to be equal to the emissivity under bias operation and under certain idealistic conditions, the optimization of the absorptivity is discussed and the concepts of *solid angle* and *energy* restriction are explained. Also, as a consequence of the review, new results arise: the maximum efficiency is found to be independent on the concentration and although the limiting efficiency of *optimum* devices is confirmed, the limiting efficiency previously established for *non-optimum* devices is found to have been underestimated under certain circumstances.

1. Introduction

The calculation of the limiting efficiencies of solar cells has already deserved a great amount of attention of the photovoltaic community. Since the publication of the paper by Shockley and Queisser [1] in 1961, *Detailed Balance Theory* has been extensively used to calculate the limiting theoretical conversion efficiency of photovoltaic solar cells when only radiative recombination losses are taken into account.

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Basically, the Detailed Balance Theory consists in establishing that the number of electrons extracted from a cell per unit of time as electrical current equals the difference between the number of photons absorbed and those emitted from the device. Since the absorbed photons can be related to the photogenerated current of the unbiased (short-circuited) device and the emitted photons to the operation voltage, the current–voltage relationship immediately follows and, from it, all the performance properties of the solar cell.

Originally, Shockley and Queisser established the limit for photovoltaic conversion efficiency to be 30%, for a device illuminated by black body (BB) radiation at 6000 K. The basis of the theory was retaken in 1967 by C.D. Mathers [2], generalizing the result to any solar or absorption spectrum. Thus, he obtained a limit of 31% for a solar cell under AM1 spectrum [3] illumination.

The basis of the Theory soon became useful not only as an approach to calculate the maximum efficiency that can be derived from one cell but also as a way to calculate the maximum efficiency that can be obtained from the Sun by photovoltaic energy conversion. The way to carry it out consisted of applying the Detailed Balance Theory to each of the individual cells of a system of devices each of them having a different bandgap and receiving the most appropriate part of the solar spectrum. The total power is then obtained by adding up the extracted power from each cell. Using this approach Henry [4] obtained in 1980 a limiting efficiency of 7% for a system of 36 cells, at a temperature of 300 K, illuminated with 1000 suns of AM1.5 (NASA/ERDA) spectrum [5]; and Parrot [6] obtained a value of 81%, in 1979, for a system illuminated by 10000 suns of a black body radiation at 5700 K.

These calculations were successively generalized, by increasing the number of cells to infinite, to calculate an absolute limit for the photovoltaic conversion, and by taking into account new aspects previously omitted. Thus, luminescent coupling between the cells of the stack was included by Pauwels and De Vos [7] in 1981, who, illuminating the cells at the highest possible concentration, obtained a limiting value of 86.8% for 6000 K black body radiation. Araújo and Martí [8], considered a different approach: the possibility of restricting the photons emitted from the cells in both energy and solid angle. They obtained essentially the same result, 86.3% for 5759 K black body radiation, for an infinite number of cells but their approach resulted in the highest calculated efficiencies for a *finite* number of devices and, in addition to that, it was obtained at any concentration if the emission angle was appropriately restricted. For a summary of the main results concerning the computation of the maximum conversion efficiency see Table 1.

As the study progressed, the *Detailed Balance Theory* showed also its usefulness as a guide for a better understanding of cell thermodynamics revealing how, at the maximum power operation point, the photovoltaic conversion was an irreversible process [9] and more specifically, how solar cells could be considered as endoreversible [10] engines (engines where all the irreversibilities are restricted to the coupling of the engine to the external world). In fact, it is very remarkable how essentially the same current–voltage relationship derived initially by Shockley and Queisser has been derived by Parrot [11] from pure thermodynamic approaches.

Table 1
Summary of the main results co
efficiency by means of the Detail
degrees. Cell temperature is 300

Authors	Ref.	Suns
Shockley and Queisser.	[1]	one
C.D Mathers.	[2]	one
Henry.	[4]	1000
Parrot.	[6]	10000
Pauwels De Vos.	[7]	max.
De Vos and Pauwels.	[9]	maximum
Araújo and Martí.	[8]	any

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Table 1
Summary of the main results concerning the computation of the maximum photovoltaic conversion efficiency by means of the Detailed Balance Theory. BB-T stands for black body radiation at T Kelvin degrees. Cell temperature is 300 K

Authors	Ref.	Suns	No. cells	Spectrum	Eff.	Comments
Shockley and Queisser.	[1]	one	one	BB-6000	30%	First basis of the Theory stabilised.
C.D Mathers.	[2]	one	one	AM1 [3]	31%	Generalization to any illumination spectrum.
Henry.	[4]	1000	32	AM1.5 [5]	72%	Application to multigap systems.
Parrot.	[6]	10000	∞	BB-5700	81%	Multigap systems. Stimulated emission discussed.
Pauwels De Vos.	[7]	max.	∞	BB-6000	86.8%	Multigap systems. Optimal solar cell structure discussed.
De Vos and Pauwels.	[9]	maximum	∞	BB-6000	86.8%	Multigap systems. Irreversibility of the photovoltaic conversion discussed.
Araújo and Martí.	[8]	any	∞	BB-5759	86.3%	Multigap systems. Maximum efficiency independent of concentration. Energy and angle restriction discussed.

In summary, the Detailed Balance Theory has revealed itself not only as a procedure for computing the maximum solar cell efficiency but also as a way for a better understanding of the photovoltaic solar energy conversion. Each of the computations or studies described above considered new aspects of the Theory previously missed or not fully exploited. This fact took the authors to the question of whether they had arrived or not at a point in which no further generalization and, consequently, no new limits could be established. Even more, the authors have recently heard of reported solar cells efficiencies which seem to be greater than "the limits" [12]. Although the results of [12] could not be reproduced [13] or interpreted [14] by other researchers and have already been questioned [15], it is worth on this point to ask ourselves questions as the following: How general and definitive these limiting efficiencies are? Is there still any possibility of increasing the limiting efficiencies? In some extent, the answer to these questions was anticipated in [8], but the authors want to give here a more detailed theoretical treatment and want to include new items that could not be treated in the limited frame of [8].

But to answer these questions it was found that the basis of the Detailed Balance Theory *game* had not been clearly established neither critically analyzed. Therefore, in this paper, the basic assumptions are reveiwed and a general formulation of the Detailed Balance Theory is established such that all the previous formulations can be derived from, particularly, the concepts of the restriction of the *solid angle* and the *energy* of the emitted photons. Finally, the authors conclude with the calculation of the absolute limits for photovoltaic solar energy conversion and the discussion of the optimization of the absorptivity of non optimum devices.

2. Generalized detailed balance theory

The *solar cell* is a device capable of absorbing the photons of the sunlight to produce free electron-hole pairs which can be extracted and made circulate through an external load that supports a positive voltage drop. In this way, the solar cell converts the energy of the sunlight into electrical energy or electricity. Thus, a solar cell consists basically of: (a) an absorbing medium, namely a semiconductor, which can be of any shape, occupying the volume V, bounded by a surface S, as shown in Fig. 1, and (b) specific regions where the quasi-fermi levels of the majority carriers (either electrons or holes) are in equilibrium with those of the metallic terminals, provided to extract the current and to support the external voltage (p^+ and n^+ regions).

For a given point on the illuminated surface and a given direction, the incident radiation is usually characterized by its spectral radiance R_P. For convenience, however, throughout this work we will refer to the *spectral photon flux*, b_P,

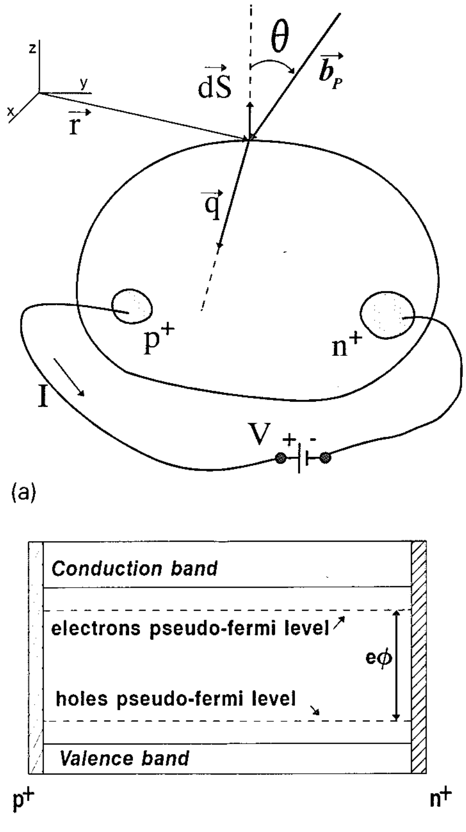

Fig. 1. (a) General sketch of the photon and carrier fluxes involved in the formulation of the generalized Detailed Balance Theory. (b) Sketch of a simplified geometry in one dimension showing uniform pseudo-fermi level splitting in the volume.

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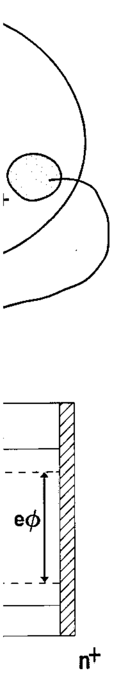

; involved in the formulation of the
d geometry in one dimension showing

($b_{\mathrm{P}} = R_{\mathrm{P}}/E$) defined as the number of incident photons per unit normal surface, time, energy, and solid angle. The spectral photon flux vary, as a general rule, with the energy of the photons and its actual distribution is related to that of the spectrum of the illumination source. In a quite general case, the radiation can reach the cell after being concentrated by optical means and, therefore, can also exhibit a dependence on the direction of the incident ray and must be characterized as a vector: $\boldsymbol{b}_{\mathrm{P}} = \boldsymbol{b}_{\mathrm{P}}(E,\boldsymbol{r},\boldsymbol{q})$. Here $\boldsymbol{r}$ represents the position vector and $\boldsymbol{q}$ is a unit vector parallel to the direction of the incidence of the ray (inside the semiconductor). Obviously, the total number of photons incident per unit of time and energy on the element $\mathrm{d}S$ of the surface, within an element $\mathrm{d}\Omega$ of the solid angle around a specified direction, may be expressed in the form

$$\mathrm{d}N_{\mathrm{ph}} = \boldsymbol{b}_{\mathrm{P}}\,\mathrm{d}\Omega\cdot\mathrm{d}\boldsymbol{S} = -b_{\mathrm{P}}\cos\theta\,\mathrm{d}S\,\mathrm{d}\Omega, \tag{1}$$

where θ is the angle formed between the direction of the ray and the normal surface vector. The minus sign arises from the usual convention of considering the emitted flux as positive. Similarly, all the photon fluxes within the semiconductor can be expressed in terms of a generalized spectral photon flux, $\boldsymbol{b}(E,\boldsymbol{r},\boldsymbol{q})$.

Within the frame of the Detailed Balance Theory, the only processes taken into account are:

(a) The fundamental band-to-band absorption of photons in the volume of the semiconductor to produce electron-hole pairs. This process can be characterized by its *spectral absorption rate* (number of absorbed photons per unit volume, energy and time), $a^{\mathrm{eh}}(E,\boldsymbol{r})$. The question to be addressed here is how many electron-hole pairs can be created by any absorbed photon. The generation of more than one pair becomes possible, for instance, for photons with energies high enough to generate excited electrons with sufficient energy to create a second electron-hole pair by impact ionization. However, the yield of the processes resulting in more than one electron for each absorbed photon is very low [16], and usually the assumption *each photon absorbed generates one, and only one, electron-hole pair* is assumed. Therefore, if a *generation rate* $G_n(\boldsymbol{r}) = G_p(\boldsymbol{r})$ (electron hole pairs per unit volume and second) is defined, it can be written

$$G_n(\boldsymbol{r}) = G_p(\boldsymbol{r}) = \int_E a^{\mathrm{eh}}(E,\boldsymbol{r})\,\mathrm{d}E. \tag{2a}$$

(b) The radiative recombination of electron-hole pairs resulting in the emission of photons that can be characterized by its *spectral emission rate* (number of emitted photons per unit volume, energy and time), $e(E,\boldsymbol{r})$. Again, the question is how many photons are emitted per each pair that recombines radiatively. Assuming that each *electron-hole pair radiative recombination produces one emitted photon*, the *radiative recombination rates*, $R_n^r(\boldsymbol{r}) = R_p^r(\boldsymbol{r})$, can be expressed in the form

$$R_n^r(\boldsymbol{r}) = R_{\mathrm{p}}^r(\boldsymbol{r}) = \int_E e(E,\boldsymbol{r})\,\mathrm{d}E. \tag{2b}$$

For steady state conditions and for any given energy, the photons leaving any volume V within the semiconductor through its surrounding surface S minus those entering the volume, must balance the net amount of photons resulting from the internal emission minus absorption processes in the volume V. Consequently, the following *spectral continuity equation for photons* can be written:

$$\int_S \boldsymbol{b}(E,\boldsymbol{s},\boldsymbol{q})\ \mathrm{d}\Omega \cdot \mathrm{d}\boldsymbol{S} = \int_V \left[e(E,\boldsymbol{r}) - a^{\mathrm{eh}}(E,\boldsymbol{r}) \right] \mathrm{d}V, \tag{3a}$$

where $\boldsymbol{b}(E,\boldsymbol{s},\boldsymbol{q})$ stands for the values of $\boldsymbol{b}$ on the surface S. By applying the Gauss theorem, Eq. (3a) can also be expressed in the following equivalent form:

$$\int_\Omega \nabla \cdot \boldsymbol{b}(E,\boldsymbol{r},\boldsymbol{q})\ \mathrm{d}\Omega = e(E,\boldsymbol{r}) - a^{\mathrm{eh}}(E,\boldsymbol{r}). \tag{3b}$$

For steady state conditions, the *continuity equations for electron and holes* are:

$$\nabla \cdot \boldsymbol{J}_n = -q\left[G_n(\boldsymbol{r}) - R_n(\boldsymbol{r}) \right], \qquad \nabla \cdot \boldsymbol{J}_p = q\left[G_p(\boldsymbol{r}) - R_p(\boldsymbol{r}) \right]. \tag{4}$$

Then, assuming that only electrons are extracted through the n^+-type regions and only holes through the p^+-type ones, the current extracted from the cell can be calculated by integrating any of Eqs. (4) for the whole volume of the device. Taking (2) and (3) into account, the following expression results:

$$I = -q\int_V \nabla \cdot \boldsymbol{b}(E,\boldsymbol{r},\boldsymbol{q})\ \mathrm{d}\Omega\ \mathrm{d}E\ \mathrm{d}V = -q\int_S \boldsymbol{b}(E,\boldsymbol{s},\boldsymbol{q}) \cdot \mathrm{d}\boldsymbol{S}\ \mathrm{d}\Omega\ \mathrm{d}E, \tag{5}$$

which states the very simple and, at the same time, very basic result of this Theory: *under detailed balance assumptions, the external outgoing current is q times the number of photons per unit time entering the volume V of the device through its surrounding surface S minus those leaving the same volume.*

The calculation of b, by solving (3b), needs some new knowledge about the absorption and emission (spontaneous and stimulated) processes. We considered here that they are described by the Einstein relationships [17] as follows:

(a) The absorption process is characterized by the *optical absorption* coefficient which relates the volume absorption rate to the photon flux. But as stimulated emission produces photons identical to the incident ones, the *absorption coefficient* of a semiconductor is, more precisely, related to the *net absorption rate*, $a^{\mathrm{eh}} - e^{\mathrm{st}}$, and is defined as

$$\mathrm{d}(a^{\mathrm{eh}} - e^{\mathrm{st}}) \equiv \alpha(E,\boldsymbol{r},\boldsymbol{q}) b(E,\boldsymbol{r},\boldsymbol{q})\ \mathrm{d}\Omega. \tag{6}$$

It must be emphasized that the absorption coefficient, α, corresponds only to processes involving electron transitions between the energy bands. The coefficient α so defined is not a pure material parameter but depends also on the operating conditions and can be negative if the stimulated emission rate, e^{st}, is higher than the absorption rate, a^{eh}. Particularly, if $q\phi(\boldsymbol{r})$ represents the quasi-fermi level split within the semiconductor, the absorption coefficient is a function of the form [18] $\alpha = \alpha[E,\phi(\boldsymbol{r}),\boldsymbol{q}]$. The dependence of α on the direction of the optical ray (on $\boldsymbol{q}$), stands for the possibility of anysotropies on the optical behavior of the material.

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(b) The spontaneous emission rate, e^{sp}, of photons due to recombinations between the electron and hole gases whose quasi-fermi levels are split by $q\phi(\boldsymbol{r})$ is given by [19]:

$$\mathrm{d}e^{\mathrm{sp}} \equiv \alpha[E,\phi(\boldsymbol{r}),\boldsymbol{q}]\, b_n(E,\phi)\ \mathrm{d}\Omega, \qquad b_n(E,\phi) \equiv \frac{2n^2E^2}{h^3c^2\left[\exp\left(\dfrac{E-q\phi}{kT}\right)-1\right]}, \tag{7}$$

where $b_n(E,\phi)$ is defined for any optical medium having n as refractive index. For the medium surrounding the cell (normally air) this photon flux will be denoted by $b_1(E,\phi)$.

By combining Eqs. (3b), (6) and (7) the following *spectral continuity differential equation for photons* results

$$\nabla \cdot \boldsymbol{b} + \alpha b = \alpha b_n, \tag{8}$$

and then, the current can be calculated by Eq. (5) or, equivalently, by

$$I = q \int_V \alpha(b - b_n)\ \mathrm{d}\Omega\ \mathrm{d}E\ \mathrm{d}V. \tag{9}$$

3. Solar cell operation characteristic

In equilibrium, $\phi = 0$, b is constant and the obvious solution of (8) is $b = b_n(E,\phi = 0) \equiv b_{n0}$, which corresponds to the illumination of the cell by the always present ambient at temperature T. But, for non-equilibrium conditions, Eq. (8) is coupled to the standard differential equations for electrons and holes in the semiconductor through the quasi-fermi level splitting ϕ. Thus, for the most general case, a set of differential equations must be solved, with the boundary conditions given by the known illumination at the device surface, $\boldsymbol{b}_p(E,\boldsymbol{s},\boldsymbol{q})$, and the known external biasing $V \equiv \phi_p$(p-contact) $-$ ϕ_n(n-contact). To find out a solution it is convenient to start with some approximation for $\phi(\vec{r})$, required to be inserted in the expressions of α and b_n. Then an iterative procedure must be used to approach the final solution.

Assuming that $\phi(r)$ is already known, one can make general considerations about the solution of Eq. (8) which deserve some comments. The solution can be expressed, by applying the superposition principle, as the addition of two terms, $b_{\mathrm{HM}} + b_{\mathrm{EM}}$, as follows:

- b_{HM}, is the solution of the homogeneous part of the differential equation ($\alpha b_n = 0$), obtained for the known external illumination (including that of the ambient). That is, no internal generation of photons is considered, which corresponds to a reverse biasing of the diode with an infinite voltage, and the differential equation deals only with the externally supplied photons.

- b_{EM}, is the solution of the complete differential equation, obtained for no external illumination (not even that of the ambient). That is, the device is in the dark, biased by the external voltage V, and the differential equation deals with the internally generated photons.

Once b_{HM} and b_{EM} are known, the current given by Eq. (9) can be re-expressed as

$$I = q\int_V \alpha b_{HM}\,\mathrm{d}\Omega\,\mathrm{d}E\,\mathrm{d}V - q\int_V \alpha(b_n - b_{EM})\,\mathrm{d}\Omega\,\mathrm{d}E\,\mathrm{d}V. \tag{10a}$$

The first integral represents the total volume absorption of the photons of the illumination source, and the second is the total amount of photons generated in the volume minus the total self absorption of these photons, in the same volume. Therefore, this last integral represents the net amount of internally generated photons and consequently must equal the total number of photons emitted through the external surface S. In other words, Eq. (10a) represents an alternative way of expressing the Detailed Balance Theory: *The external current is q times the number of illumination photons absorbed in the volume V minus the number of those internally generated photons which are emitted through the surface S.* This can sometimes be better represented by re-expressing (5) as

$$I = -q\int_{S^-} \boldsymbol{b}_{HM}(S)\cdot\mathrm{d}\boldsymbol{S}\mathrm{d}\Omega\,\mathrm{d}E - q\int_{S^-} \boldsymbol{b}_{EM}(S)\cdot\mathrm{d}\boldsymbol{S}\,\mathrm{d}\Omega\,\mathrm{d}E, \tag{10b}$$

where S^- is used to indicate that the integral is calculated through the inner side of the semiconductor surface.

3.1. Photogenerated current

The values of b_{HM} needed to evaluate the first integral of Eq. (10) depend ultimately on the illumination photon flux but not in a straightforward way since the flux at each point is also determined, in general, by the absorption properties in the semiconductor volume and the multiple reflections at its surface. To relax the complexity of the calculation and to gain in physical insight, we prefer to approach the calculation on the basis of the geometrical optics and the concept of “tube of rays”, illustrated in Fig. 8. Any beam of light, incident on the illuminated surface with a given orientation, follows a determined optical path inside the semiconductor. As shown in Fig. 8, the optical path will consist of multiple jumps, due to the reflection of the photons at the points where they strike the surfaces. In this case, for which the photon flux satisfies the homogeneous part of the differential Eq. (8), it is straightforward to obtain that: (a) the number of photons absorbed in each elemental jump (with length l_i, from S to S') is proportional to the total number of entering photons, and (b) the proportionality constant (the elemental absorptivity, a_i) depends only on the absorption coefficient, α, and on the length of the jump. The total absorption will be the addition of all the elemental absorptions but, as any initial value of an elemental jump can be related to the final value of the precedent one through the reflection coefficient, it is still

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possible to express the whole absorption as a function of the first initial value, which is related to the incident radiation at the surface. Therefore, the photogenerated current, (*q times the number of the illumination photons absorbed in the volume V*), I_{PH}, will be given by

$$I_{PH} = q \int_{S^-} a(E,s,\mathbf{q}) b_{HM}(E,s,\mathbf{q}) \cos\Theta \, d\Omega \, dE \, dS, \tag{11a}$$

where a is the *absorptivity*, a material dependent parameter through its dependence on α and on the reflection coefficient at the points where the rays strike the surface. As derived in the Appendix, the absorptivity is defined for each point of the surface and each direction of the incident ray. In this approach, $b_{HM}(E,s,\mathbf{q})$ is the photon flux entering the "tube of rays" due only to and related directly to the illumination.

For practical devices, the determination of the lengths of the optical paths (needed to calculate the absorptivity) not only depends on the orientation of the incident rays but also on the particular shape of the surface (flat, rough, pyramids, etc.) and on the geometry of the device and it is, therefore, a very difficult task. In spite of this fact, the expressions for the absorptivity corresponding to many useful light-trapping and light confining schemes have been obtained by a number of authors [20,21].

Concerning the calculation of limiting efficiencies, one can always think of ideal devices with regular surfaces which permits to consider the absorptivity as a magnitude with no dependence on the position. Additional simplifications can be applied to the dependence on the orientation considering an absorptivity at each point with cylindrical symmetry around the vector $d\mathbf{S}$ and, consequently, the dependence on the direction can be expressed as a function of θ only. This is the case of the common device geometry with flat surfaces and cylindrical symmetry as that shown in Fig. 1b and, therefore, for the rest of this work, we will always consider this kind of geometry with absorptivities of the form, $a = a(E,\theta,g)$, where g is some geometrical factor to characterize the influence of the volume and its shape. For instance, for an standard flat surface solar cell this parameter can be the thickness W. The total photogenerated current is then given by:

$$I_{PH} = q \int_{S^-} a(E,\theta,g) b_{HM}(E,s,\theta) \cos\theta \, d\Omega \, dE \, dS. \tag{11b}$$

The results (11) are referred to the internal side (semiconductor side) of the interface surface. At the surface S there is a change of optical medium: At one side, S^-, there is the semiconductor of refractive index n and at the other side, S^+, there is the surrounding optical medium with refractive index n_1. Assuming $n_1 = 1$ (air) for simplification, and taking energy conservation into account, the following relationship between the photon fluxes at both sides of the surface can be established:

$$[1 - r(E,\theta_1)] b_{HM}(E,S^+,\theta_1) \cos\theta_1 \, d\Omega_1 = b_{HM}(E,SU-,\theta) \cos\theta \, d\Omega, \tag{12a}$$

where $r(E,\theta_1)$ is the reflection coefficient of the incident light ray at the interface between the semiconductor and the surrounding medium and θ_1 and θ are the angles of incidence and refraction, respectively. Since these angles are related by the Fresnel's law,

$$\cos\theta_1\ \mathrm{d}\Omega_1 = n^2 \cos\theta\ \mathrm{d}\Omega, \tag{12b}$$

and (12a) becomes:

$$[1 - r(E,\theta_1)]n^2 b_{\mathrm{HM}}(E,S^+,\theta_1) = b_{\mathrm{HM}}(E,S^-,\theta). \tag{12c}$$

This means that if the incident radiation on S^+ is known and denoted by $b_{\mathrm{P}} \equiv b_{\mathrm{HM}}(E,S^+,\theta_1)$, the expression (11b) for the photogenerated current can be re-written as

$$\begin{aligned} I_{\mathrm{PH}} &= q\int_{S^-} A(g,E,\theta) n^2 b_{\mathrm{P}} \cos\theta\ \mathrm{d}\Omega\ \mathrm{d}E\ \mathrm{d}S \\ &= q\int_{S^+} A(g,E,\theta) b_{\mathrm{P}} \cos\theta_1\ \mathrm{d}\Omega_1\ \mathrm{d}E\ \mathrm{d}S, \end{aligned} \tag{13a}$$

where

$$A(g,E,\theta) \equiv [1 - r(E,\theta)]a(E,\theta,g). \tag{13b}$$

3.2. Diode or dark current

The evaluation of the second integral of Eq. (10) is not trivial in the most general case, due to the dependence on $\phi(\boldsymbol{r})$ of the internal generation of photons. Nevertheless, for the present study and without loss of generality, we can take advantage of the following important simplification: When calculating limiting efficiencies, the drift losses for the transport of current carriers within the semiconductor have to be neglected, which is equivalent to considering infinite mobility for electrons and holes and, therefore, flat quasi-fermi levels. In addition to this, to obtain maximum efficiency it is compulsory that $q\phi \geqslant V$ at any point, in order to have always a generation of carriers greater than the recombination. The consequence of the combination of these two requirements is that *the quasi-fermi level splitting, $q\phi$, must be constant inside the volume and therefore equal to qV*. Then $b_n[\phi(r)]$ will be a constant dependent on V, which will be denoted b_{nV}.

Now, a trivial solution of the complete differential Eq. (8) is $b_{\mathrm{EM}} = b_{nV}$, but this implies that no emission is possible, according to Eq. (10a). Physically, this solution stands for all possible optical paths that has no connection with the outside (they strike the surfaces with angles greater than the critical for total internal refraction). But for smaller angles, some emission will take place and, therefore, the inequality $b_{\mathrm{EM}}(S) < b_{nV}(S)$ holds at the surface points. Therefore, it is always possible to express the second integral of Eq. (10b) in the form

$$I_{\mathrm{LE}} = q\int_{S^-} [1 - r(E,\theta)] e(E,\theta,g) b_{nV}(E,V) \cos\theta\ \mathrm{d}\Omega\ \mathrm{d}S\ \mathrm{d}E, \tag{14}$$

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$\cos\theta \, \mathrm{d}\Omega \, \mathrm{d}S \, \mathrm{d}E$, (14)

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where the parameter e (less than unity) is introduced as the *emissivity*. In this way, e, like a, is defined for each point of the surface and each direction of the incident ray. The factor $[1 - r]$ is introduced to include, for each given orientation θ, at a time the emitted and its reflected ray, for each point of the interface surface. So the integral of Eq. (14) must be calculated considering only those rays approaching the surface from the inside.

In equilibrium ($q\phi = 0$), the device is illuminated by and emits black body radiation, $b_{\mathrm{P}} = b_1$ and $b_{nV} = b_{n0}$. So, the external current is zero and, therefore, it must be $e = a$. For non equilibrium and the most general case, $b_n(S)$ will depend on the operation conditions through its dependence on $\phi(S,V)$ and so will depend the above defined e. On the contrary the only possible dependence of a on V is through α. Therefore, one can expect that in general $e \neq a$. However, it has to be remarked that for *constant* $\phi(\boldsymbol{r}) = V$, the equality $a = e$ still holds as it will be proved in the Appendix. Having this fact into consideration the calculation of Eq. (14) can be finally expressed as

$$I_{\mathrm{LE}} = q \int_{S^-} A(E,\theta,g) b_{nV}(E,V) \cos\theta \, \mathrm{d}\Omega \, \mathrm{d}E \, \mathrm{d}S. \tag{15}$$

In summary, the current–voltage equation of the solar cell can be calculated by combining Eqs. (13) and (15) and the calculations can be referred to the internal or to the external side of the interface surface. The resulting expressions are

$$I = q \int_{S^-} A(E,\theta,g) \left[n^2 b_P - b_n(E,V) \right] \cos\theta \, \mathrm{d}\Omega \, \mathrm{d}E \, \mathrm{d}S, \tag{16a}$$

or

$$I = q \int_{S^+} A(E,\theta,g) \left[b_P - b_1(E,V) \right] \cos\theta \, \mathrm{d}\Omega \, \mathrm{d}S, \tag{16b}$$

where the same notation has been used for the angles and solid angles, regardless of they are internal or external. Note, however, that when integrating on the surface S^+ the range on integration is $0 < \theta < \pi/2$ and that when integrating on S^-, θ varies between zero and the critical angle.

Eq. (16) has been reported before (see ref. [22], for instance). The generality given here is however much greater. In Ref. [22], an expression equivalent to Eq. (16b) and the assumption of $e = a$, as in equilibrium, are given without any demonstration. Here the validity of the expression (16) is linked to the case of constant quasi-fermi level splitting (which always holds for calculating limiting efficiencies) and the dependence of the absorptivity on orientation is also included.

4. Maximum photovoltaic conversion efficiency

Eq. (16) allows for the immediate computation of the delivered electric power P as $P(V) = I(V)V$. This power will be maximum for a certain value V_{m} satisfying

$$0 = \mathrm{d}P/\mathrm{d}V = I(V_{\mathrm{m}}) + V_{\mathrm{m}}[\mathrm{d}I/\mathrm{d}V]_{\mathrm{m}}, \tag{17}$$

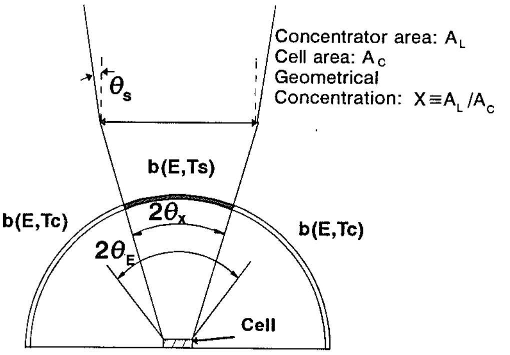

Fig. 2. Sketch illustrating the definition of the solid angles involved in the theory and the geometrical concentration concept, X.

which permits to obtain the maximum power point $[V_m, I(V_m)]$. Hence, the maximum power for a given absorptivity will be given by:

$$P_m = V_m q \int_{S^+} A(E,\theta,g)\left[b_P - b_1(E,V_m)\right] \cos\theta \, \mathrm{d}\Omega \, \mathrm{d}E \, \mathrm{d}S. \tag{18}$$

In general, the solar cell is illuminated by two external sources: the Sun and the ambient. To simplify the mathematics we will consider them as black body sources: the Sun, at a temperature T_s and the ambient, at temperature T_c. Additionally, we will consider that both of them illuminate with cylindrical symmetry each point of the device surface as sketched in Fig. 2. Into this scheme, the sun radiation reaches the cell within the solid angle $2\theta_X$. This solid angle can be equal to that subtended by the sun sphere, $2\theta_s$, or greater due to the use of optical concentrators. These two solid angles are related through the brightness conservation theorem for loss less concentrators which establishes, if we assume the concentrator surrounded by air, that

$$X \sin^2\theta_s = \sin^2\theta_X, \tag{19}$$

when the incident power is collected within an area X (concentration ratio) times the illuminated cell area.

On the other hand, photons are received from the ambient and emitted from the cell within the solid angle $2\theta_E$. In general, θ_E must be greater than or equal to θ_X and it has been considered equal to 90° by most of the authors in the past. In summary, the photon flux, b_P, incident on the cells according to the illumination configuration of Fig. 2 is

$$b_P(E,\theta) = \begin{cases} b(E,T_s) & \theta < \theta_X \\ b(E,T_c) & \theta > \theta_X \end{cases} \tag{20}$$

where

$$b(E,T) = \frac{2}{h^3c^2} \frac{E^2}{\exp(E/kT) - 1},$$

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n: $X \equiv A_L / A_C$

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which must be taken into account in Eqs. (16), (17) and (18) to calculate the maximum power. The photovoltaic conversion efficiency is defined here in the usual way as $\eta = P_m / P_X$ where P_X is the incident power received from the Sun that can also now be computed and is given by

$$P_X = \int E b(E,T_s) \cos\theta\ d\Omega\ dE\ dS = \sigma T_S^4 A_c \sin^2\theta_X = \sigma T_S^4 A_c X \sin^2\theta_s, \quad (21)$$

where σ is the Stefan–Boltzman constant and A_c is the illuminated area.

If the absorptivity $A = [1 - r(E,\theta)] a(g,E,\theta)$ is allowed to be engineered, then, to assure the highest delivering of power and conversion efficiency, it is clear from Eq. (18) that we have to assure that

$$[1 - r(E,\theta)] a(g,E,\theta) = 0 \quad \text{whenever } b_P(r,E,\theta) < b_1(E,V_m), \quad (22a)$$

in order to avoid a negative contribution to the integral in Eq. (19) and

$$[1 - r(E,\theta)] a(g,E,\theta) = 1 \quad \text{whenever } b_P(r,E,\theta) > b_1(E,V_m), \quad (22b)$$

in order to make the highest possible positive contribution to the same integral. The physical meaning behind the conditions expressed by Eqs. (22) is not other than this: Since absorption and emission are coupled processes, for achieving the maximum efficiency, the absorption of impinging photons should be avoided if it opens the via for the emission of photons that suppose a higher energy losses than the energy collection obtained by the absorption itself.

Condition (22a) requires as a necessary condition (although it might not be sufficient) to avoid the emission of light through the surfaces for those energies and solid angles not used for the incident radiation. The necessity of restricting the emission for certain energies and solid angles leads to the concepts of *energy* and *solid angle restriction* which are explained below. The benefits of avoiding the emission through the non illuminated surface are obvious and imply that all the dark surfaces of the solar cells should be perfect reflectors, $r(E,\theta) = 1$. The satisfaction of this condition will be assumed hereafter in this work and means that Eq. (16) together with Eq. (20) results in

$$I/A_c = J = q \int_0^{\theta_X} \int_{E_g}^{\infty} A(g,E,\theta) [b(E,T_s) - b_1(E,T_c,V)] \cos\theta\ d\Omega\ dE$$

$$- q \int_{\theta_X}^{\theta_E} \int_{E_g}^{\infty} A(g,E,\theta) [b_1(E,T_c,V) - b(E,T_c)] \cos\theta\ d\Omega\ dE. \quad (23)$$

The integration with respect to θ can be performed in the first place leading to the definition of the function

$$\Gamma(\theta,E,g) = 2\pi \int_0^{\theta} A(E,\vartheta,g) \cos\vartheta \sin\vartheta\ d\vartheta \leqslant 2\pi \sin^2\theta. \quad (24a)$$

Then, the efficiency of the cell can be written as

$$\eta = \frac{qV_\mathrm{m}}{\sigma T_\mathrm{s}^4 \sin^2\theta_X} \int_{E_g}^{\infty} \{\Gamma(E,\theta_X,g)[b(E,T_\mathrm{s}) - b(E,T_\mathrm{c})] - \Gamma(E,\theta_E,g) \times [b_1(E,T_\mathrm{c},V_\mathrm{m}) - b(E,T_\mathrm{c})]\}\,\mathrm{d}E, \tag{24b}$$

with V_m obtained by solving Eq. (17) that now can be written as

$$\int_{E_g}^{\infty} \{\Gamma(E,\theta_X,g)[b(E,T_\mathrm{s}) - b(E,T_\mathrm{c})] - \Gamma(E,\theta_E,g) \times [b_1(E,T_\mathrm{c},V_\mathrm{m}) - b(E,T_\mathrm{c})]\}\mathrm{d}E + - V_\mathrm{m}\int_{E_g}^{\infty} \Gamma(E,\theta_E,g) b_1'(E,T_\mathrm{c},V_\mathrm{m})\,\mathrm{d}E = 0. \tag{24c}$$

Eqs. (24) permit the calculation of the efficiency and show its functional dependence on E_g,θ_X,θ_E and g.

The question is: What is the highest possible efficiency? In the literature, the calculations of the limiting efficiencies have been based in the widely accepted assumption of making $A = 1$ (total absorption). However, there is no *a priori* reason for considering that the maximum efficiency results for this case. As it will be shown later, for a non optimum device it is possible to have a greater efficiency with $A < 1$ for some range of energies or solid angles.

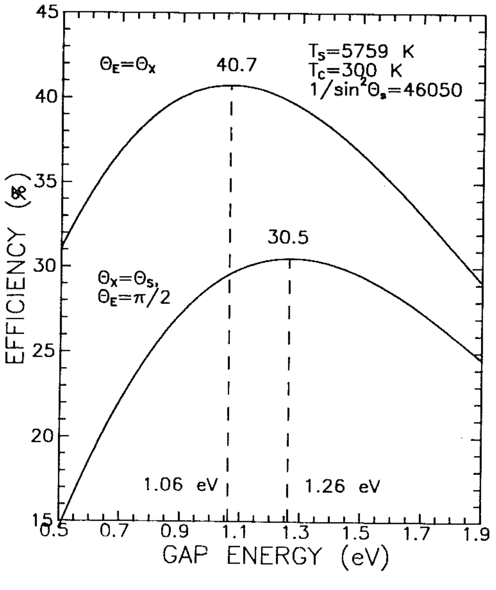

Fig. 3. Conversion efficiencies as a function of E_g for $A = 1$ and the two extreme cases given by Eq. (25).

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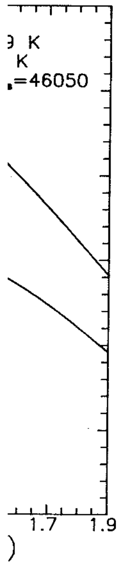

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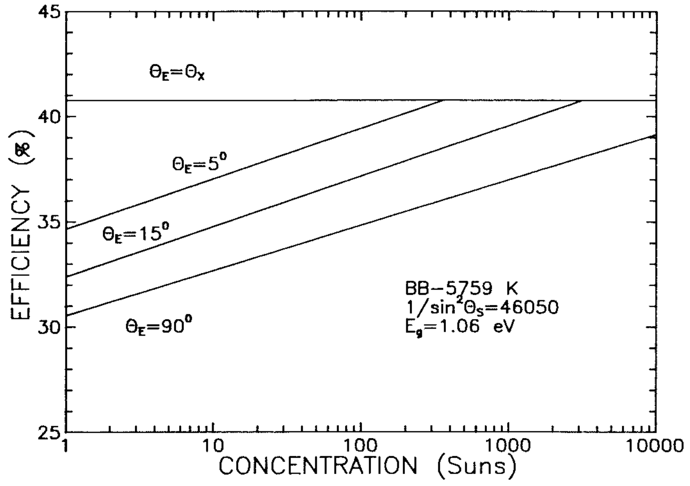

Fig. 4. Efficiency of the optimum photovoltaic material as a function of X and Θ_E.

Nevertheless, the calculations simplify a lot with $A = 1$ and, additionally, this particular case has a special significance as a theoretical reference. Because of this reasons the authors also give here a summary of some results for $A = 1$. Fig. 3 represents the computations for two extreme values of the parameters:

$$\theta_E = \theta_X \quad \text{and therefore } \Gamma_E = \Gamma_X = 2\pi \sin^2\theta_X, \tag{25a}$$

and

$$\theta_X = \theta_S \quad \text{and } \theta_E = \pi/2 \quad \text{and therefore } \Gamma_X = 2\pi \sin^2\theta_S, \qquad \Gamma_E = 2\pi. \tag{25b}$$

The relevance of these cases will be evident later. What is important to remark now is that all the efficiency versus E_g curves show a maximum for certain values of the bandgap and that the efficiency depends also on concentration (since, $\sin^2\theta_X = X \sin^2\theta_S$) and on the angle of emission. This dependence of η on X and θ_E is illustrated in Fig. 4 for the optimum photovoltaic material. Each value of η corresponding to any combination of values of X and θ_E has its representation in the triangle shown.

However, for an unfixed absorptivity A, the maximum value of the efficiency given by Eq. (24) will depend on the behavior of the total differential

$$\mathrm{d}\eta = \frac{\partial\eta}{\partial\theta_E}\mathrm{d}\theta_E + \frac{\partial\eta}{\partial E_g}\mathrm{d}E_g + \frac{\partial\eta}{\partial g}\mathrm{d}g + \frac{\partial\eta}{\partial\theta_X}\mathrm{d}\theta_X, \tag{26}$$

and the analysis of the partial derivatives will give us a complete insight of the general problem as it will become clear in the next paragraph.

5. Solid angle restriction and optimum photovoltaic device

By *optimum* device, the device is meant for which all the variables included in Eq. (26) have been optimized. Important physical concepts can be deduced from the particular analysis of each derivative in Eq. (26).

5.1. Analysis of the angle of emission θ_E: solid angle restriction concept

An expression to calculate the variation of η with the angle of emission can be derived directly from condition (17) and Eq. (23) to obtain

$$\begin{aligned}\frac{\partial\eta}{\partial\theta_E} &= \frac{V_m}{P_X}\frac{\partial I_m}{\partial\theta_E}\\ &= -\frac{V_m q\pi\,\sin(2\theta_E)}{\sigma T_s^4\,\sin^2\theta_X}\int_{E_g}^{\infty} A(E,\theta,g)\left[b_1(E,T_c,V_m)-b(E,T_c)\right]\,\mathrm{d}E, \qquad (27a)\end{aligned}$$

which is always negative because of the following reason: if temporally it is assumed that $qV_m < E_g$, it is straightforward to see that the illumination, $b(E > E_g,T_c)$, is always smaller than the emission due to the voltage V_m, $b_1(E > E_g,T_c,V_m)$; that is,

$$b(E,T_c) < b_1(E,T_c,V_m) \quad \text{for all } E > E_g > qV_m, \qquad (27b)$$

thus, the integrand will always be positive in Eq. (26) and, therefore, the derivative will always be negative. This means that there is no maximum value with respect to the variable under consideration but, instead, the power will always increase when θ_E decreases which is physically equivalent to reduce the luminescent emission from the cell. So, to obtain the greatest efficiency from the cell θ_E should be given its minimum value of θ_X to avoid the loss of energy produced by *the emission of photons outside the incident solid angle*. That is, we must have

$$\theta_E = \theta_X \quad \text{or } A(E,\theta,g) = 0 \quad \text{for all } \theta > \theta_X. \qquad (28)$$

We call this *the solid angle restriction*. From Eq. (24b) it follows that the efficiency in this case is given by

$$\eta = \frac{qV_m}{\sigma T_s^4\,\sin^2\theta_X}\int_{E_g}^{\infty}\Gamma(\theta_X,E,g)\{b(E,T_s)-b_1(E,T_c,V_m)\}\,\mathrm{d}E, \qquad (29)$$

together with Eq. (24c), necessary to calculate V_m.

5.2. Analysis of E_g: optimum gap

The maximum value of Eq. (29) with respect to E_g is given by the condition

$$0 = \frac{\partial\eta}{\partial E_g} \equiv \frac{V_m}{P_X}\frac{\partial I_m}{\partial E_g} \quad \text{or } \Gamma(\theta_X,E_g,g)\left[b(E_g,T_s)-b_1(E_g,T_c,V_m)\right] = 0, \qquad (30a)$$

which represents the condition of *optimum bandgap* for photovoltaic conversion. From here, it is straightforward to obtain the following expression relating V_m^{op} and E_g^{op} for the maximum efficiency point

$$V_m^{op} = \frac{E_g^{op}}{q}\left(1 - \frac{T_c}{T_s}\right). \tag{30b}$$

This relationship does not depend on the absorptivity and was also reported in Ref. [23], but the derivation presented here relates Eq. (30b) with the perfect solid angle restriction which means a generalization. Eq. (30b) together with Eq. (24c) conveniently particularized, permits the calculation of V_m^{op} and E_g^{op} for any given absorptivity.

5.3. Analysis of the absorptivity through the parameter g

In order to further increase the efficiency we can consider the geometrical factor g as the variable suitable to optimize the absorptivity, which implies that for the absolute maximum efficiency the derivative $\partial\eta/\partial g$ should also be made, if possible, equal to zero. This derivative is given by

$$\frac{\partial\eta}{\partial g} = \frac{V_m}{P_X}\frac{\partial I_m}{\partial g} = \frac{V_m}{P_X}\int_{E_g}^{\infty}\frac{\partial\Gamma(\theta_X,E,g)}{\partial g}\left[b(E,T_s) - b_1(E,T_c,V_m)\right]\,dE, \tag{31}$$

and it is always positive because of the following: Since according to Eq. (30a) $b(E_g,T_s) = b_1(E_g,T_c,V_m)$, the term within brackets in Eq. (31), $b(E,T_s) - b_1(E,T_c,V_m)$, will be always positive for the range of integration $E > E_g$. As $\partial\Gamma/\partial g$ is positive (A, and therefore Γ, is supposed to be an increasing function of g) it results that Eq. (31) always takes a positive value and, consequently, we can conclude that η increases with g. Therefore, the greatest maximum efficiency will be obtained when $\Gamma(g,E,\theta)$ is given its maximum value of $2\pi\sin^2\theta_X$ or, what is the same, A is given its maximum value of unity. Then, Eq. (29) results in

$$\eta = \frac{2q\pi V_m^{op}}{\sigma T_s^4}\int_{E_g^{op}}^{\infty}\left[b(E,T_s) - b_1(E,T_c,V_m^{op})\right]\,dE, \tag{32a}$$

where V_m^{op} and E_g^{op} are still related by the condition Eq. (24c) which now becomes

$$\int_{E_g^{op}}^{\infty}\left[b(E,T_s) - b_1(E,T_c,V_m^{op})\right]dE - V_m^{op}\int_{E_g^{op}}^{\infty} b_1'(E,T_c,V_m^{op})\,dE = 0, \tag{32b}$$

where $b_1' = \partial b_1/\partial V$.

5.4. Analysis of θ_X: maximum efficiency independent of the concentration

The solution of the set of Eqs. (30b)–(32b) results in values of V_m^{op} and E_g^{op} which are independent of θ_X and g. It follows then that the conversion efficiency given by Eq. (32a) also results independent of g and θ_X, and, therefore, independent of the concentration ratio, X. This permits to evaluate the optimum gap and

Table 2
Summary of results concerning the optimum photovoltaic device

Sun temperature: 5759 K	Optimum gap: 1.06 eV
Cell temperature: 300 K	Optimum efficiency: 40.7 %
Operation data:	
Photogenerated current, $I_{\mathrm{PH}} = 56.09$ mA/cm^2	
Voltage at maximum power point, $V_{\mathrm{m}} = 1.008$ V	
Current at maximum power point, $I_{\mathrm{m}} = 54.68$ mA/cm^2	

the efficiency as a function of the Sun and cell temperatures only. The authors have obtained the results which have been summarized in Table 2 for the optimum photovoltaic device.

It has to be pointed out that, since $V_{\mathrm{m}} < E_g$, the stimulated emission is still not important and, therefore, the dependence of α on V is negligible and the above result must be considered as accurate without the need for any further precision. This result has been apparently reported before. However, its validity was unnecessary linked to the maximum concentration ($f = 1$ in the paper of Shockley and Queisser [1], $\theta_X = \pi/2$ or $X = X_{\max}$ in others), and it was intuitively stated that the maximum efficiency had to be computed with $A = 1$. While this is true, as demonstrated here, for the efficiency of the optimum photovoltaic device defined above, it is not necessarily true for *non-optimum* devices; in other words, devices for example with non optimum gap could achieve higher efficiencies with $A \neq 1$ and in consequence, previously established limiting efficiencies for materials with $E_g \neq E_g^{\mathrm{op}}$ would have been wrongly settled. In this respect, we disagree with a lot of published literature considering, without any further precision, that the condition $A = 1$ represents the condition for maximum achievable efficiency of any photovoltaic device. These ideas will be further explained in the next paragraph.

Finally, what is important to emphasize is that, *under the conditions of solid angle restriction, the conversion efficiencies do not depend on concentration and therefore, constitutes an absolute limit depending only on the sun and cell temperatures*. This means that the same maximum efficiency can be obtained at, say, $X = 1/\sin^2\theta_{\mathrm{s}}$ and $\theta_X = \pi/2$ (maximum concentration) as at $X = 1$ and $\theta_X = \theta_{\mathrm{s}}$ (one sun) as at any other intermediate concentration provided that the solid angle of emission is at any time restricted to $\theta_E = \theta_X$.

6. Limiting efficiencies of non optimum cells

As mentioned before, for values of the energy gap other than E_g^{op} and for $\theta_E > \theta_X$ it is not clear *a priori* if $A(E,\theta,g) = 1$ is the optimum value for the absorptivity. For example, it is obvious that any cell with $A < 1$ for $\theta > \theta_X$ is better. This reasoning leads at the end to the condition of solid angle restriction but, what the authors like to remark now is that, when there is no angle restriction, even real absorptivities with decreasing values as θ increases can be better than

1.06 eV
ency: 40.7 %

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the supposed ideal $A = 1$. For the case with angle restriction, and given the no dependency of the photon fluxes on θ, no extra benefit can be obtained from variations of A with θ, but some comments are still worthwhile with respect to the variation of the absorptivity with energy.

Let us first consider the possibility of engineering the absorptivity through the parameter g. To optimize g, the derivative $\partial\eta/\partial g$ should be made equal to zero, if possible. This derivative is given in the general case by

$$\frac{\partial\eta}{\partial g} = \frac{V_m}{P_X}\int_{E_g}^{\infty}\frac{\partial\Gamma_X}{\partial g}\left\{\left[b(E,T_s) - b(E,T_c)\right] - \frac{\partial\Gamma_E/\partial g}{\partial\Gamma_X/\partial g}\right.$$
$$\left.\times\left[b_1(E,T_c,V_m) - b(E,T_c)\right]\right\}\mathrm{d}E, \tag{33}$$

where $\Gamma_{E(X)} = \Gamma(\theta_{E(X)},E,g)$ has been used for simplification. *A priori*, it is not clear if this derivative can be made equal to zero for a finite value of g (and, therefore, a value of $A < 1$). We can go further: the condition of maximum efficiency, represented by Eq. (30) for $\theta_X = \theta_E$, can be generalized for any given value of θ_E, θ_X and g and the following general expressions relating V_m and E_g for the maximum point of each characteristic $\eta = \eta(E_g,\theta_E,\theta_X,g)$ are obtained

$$\left[b(E_g^{mx},T_s) - b(E_g^{mx},T_c)\right] - \frac{\Gamma_E}{\Gamma_X}\left[b_1(E_g^{mx},T_c,V_m^{mx}) - b(E_g^{mx},T_c)\right] = 0, \tag{34a}$$

or

$$V_m^{mx} = \frac{E_g^{mx}}{q}\left(1 - \frac{T_c}{T_s}\gamma\right),$$
$$\gamma = \frac{kT_s}{E_g}\ln\left[1 + \frac{\Gamma_E}{\Gamma_X}\left(\frac{1}{\exp(E_g/kT_s) - 1} + \frac{\Gamma_E/\Gamma_X - 1}{\exp(E_g/kT_c) - 1}\right)^{-1}\right]. \tag{34b}$$

Note that for $\theta_E = \theta_X$, $\gamma = 1$ and Eq. (34b) reduces to Eq. (30b), and that for $\theta_E > \theta_X$, $\gamma > 1$.

To go further, consider the case satisfying the condition

$$\frac{\partial\Gamma_E/\partial g}{\partial\Gamma_X/\partial g} = \frac{\Gamma_E}{\Gamma_X}. \tag{35}$$

This condition always satisfies for $\theta_E = \theta_X$, that is, for *solid angle restriction*, but it also satisfies for other practical devices as for example those for which the dependence of the absorptivity on the angle θ can be neglected. If Eq. (35) holds, then condition Eq. (34a) is equivalent to make the integrand of Eq. (33) equal zero for $E = E_g^{mx}$ and it is straightforward to verify that for $E > E_g$ the integrand is always positive. Therefore, the conclusions of the angle restriction case can be generalized to all the maximum efficiency points of the devices satisfying Eq. (35). That is, for maximum efficiency, $\Gamma(\theta_X,E,g)$ must be given its maximum value $2\pi\sin^2\theta_X$ or, what is the same, A must be given its maximum value of unity. The

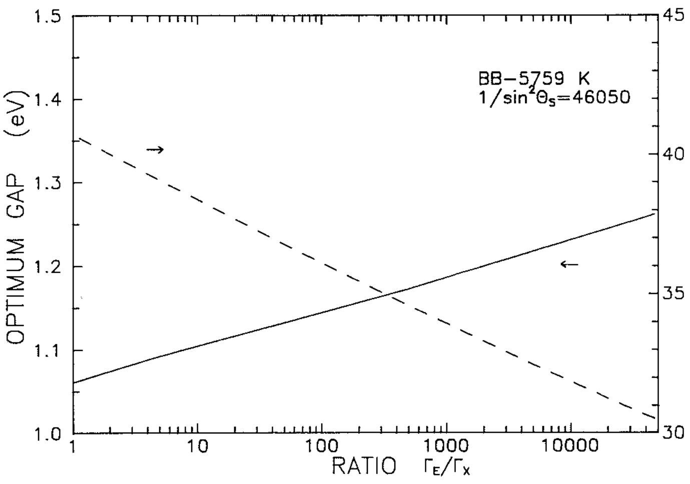

Fig. 5. (a) Optimum gap and maximum achievable efficiency as a function of the parameter ($\Gamma_E/\Gamma_X = \sin^2\theta_E/\sin^2\theta_X$).

optimum bandgaps and efficiencies can now be obtained from Eqs. (24) and (34) and are represented in Fig. 5.

Out of the maximum efficiency points, for devices with $E_g \neq E_g^{\text{mx}}$, there is still an energy E_{zc} for which the integrand of Eq. (33) is zero. The expression for E_{zc} is the same (34), considering the actual V_{m}, and it holds that for $E < E_{\text{zc}}$ the integrand is negative and for $E > E_{\text{zc}}$ is positive. For devices with $E_g > E_g^{\text{mx}}$ the derivative $\partial\eta/E_g < 0$ which implies that the integrand of Eq. (24b), which is the same as of Eq. (33), must be positive for $E = E_g$ and, therefore, $E_g > E_{\text{zc}}$ and, consequently, the integrand is positive for the whole integration interval of Eq. (33). Therefore, the greatest efficiency corresponds again to the maximum value of A of unity.

But for devices with $E_g < E_g^{\text{mx}}$, $\partial\eta/\partial E_g > 0$ which implies that the integrand is negative for $E = E_g$, then $E_g < E_{\text{zc}}$ and, therefore, the integrand in Eq. (33) will be negative for the interval (E_g, E_{zc}) within the range of integration and, therefore, it seems that some additional optimization of the absorptivity could be done. In the paragraphs that follows we comment some examples.

6.1. Finite thickness of the device

For instance, if one could have some $A(E,\theta,g)$ and, therefore, some $\Gamma(E,\theta,g)$ being smaller for the interval of energies with integrand negative than for the interval with integrand positive a greater value of the power would be found. In other words, if the emission of photons is unfavoured in the low range of energies, where the emission losses surpass the absorption gain, some increase of the

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Fig. 6. Efficiency as a function o
absorption coefficient of silicon

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$$\int_{E_g}^{\infty} \alpha \exp(-2\alpha W)$$

$$\times \left\{ \left[b(E,T_s) - b(\right. \right.$$

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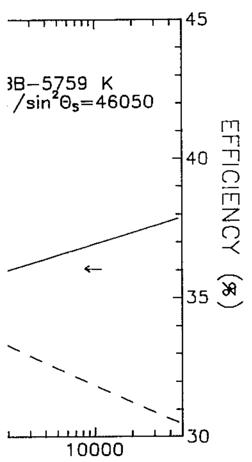

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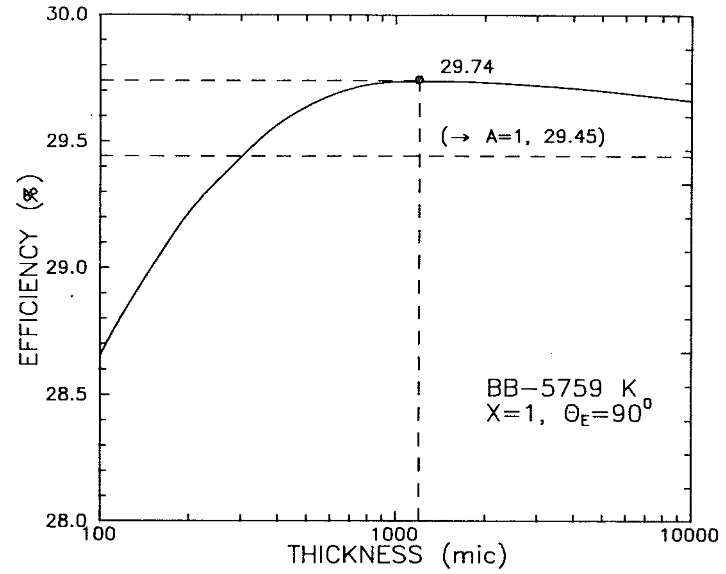

Fig. 6. Efficiency as a function of the thickness W as explained in text for a theoretical device with the absorption coefficient of silicon but ruled by radiative recombination.

efficiency could be expected. Such an asymmetry can be obtained for example by simply considering a finite thickness of the slab.

The effect will be better illustrated with a numerical example: assume an imaginary material with the absorption coefficient of silicon given in Ref. [24] and a device of width W with a perfect back reflector and a perfect front antireflecting coating so that the absorptivity is given by $A = 1 - \exp(-2\alpha W)$, now W being the geometrical factor ($W \equiv g$). Eq. (33) reduces in this case to

$$\int_{E_g}^{\infty} \alpha \exp(-2\alpha W) \times \left\{ [b(E,T_s) - b(E,T_c)] - \frac{\sin^2\theta_E}{\sin^2\theta_X} [b_1(E,T_c,V_m) - b(E,T_c)] \right\} \mathrm{d}E = 0, \tag{36}$$

from which it results that the optimum value for the thickness $W = 1200$ μm, and then the efficiency $\eta = 29.74\%$, which is greater than the corresponding for $A = 1$ which is 29.45%, as we wanted to demonstrate. Fig. 6 plots the efficiency of this imaginary device versus the thickness W. It has to be mentioned that these results would not apply strictly to silicon because in our ideal material only radiative recombination taken into account while in actual silicon, Auger recombination can become the limiting recombination process.

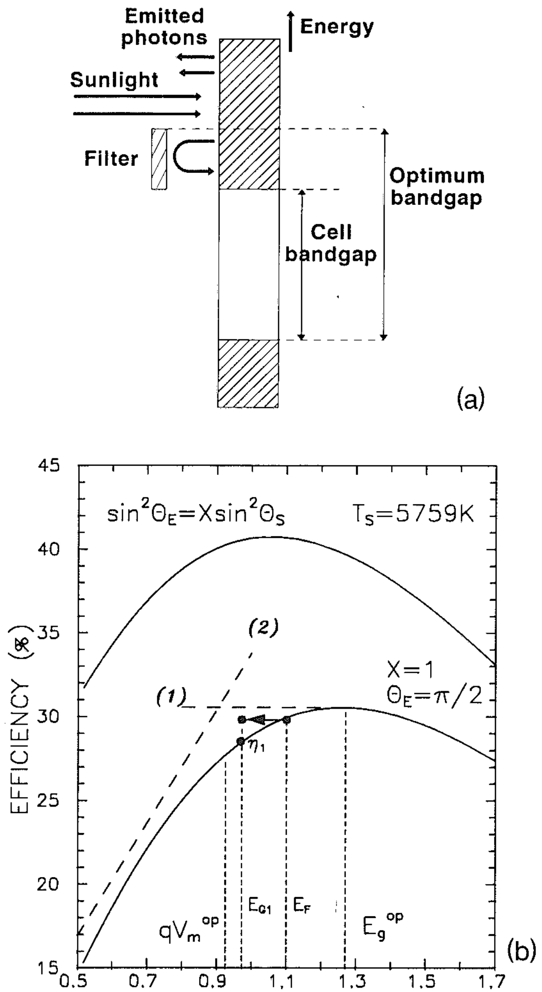

Fig. 7. (a) Sketch of a high energy photon pass filter and cell energy gap. (b) Efficiency as a function of the gap energy for the cases labelled in the figure. Dashed lines represent the expected increase in efficiency by energy restriction of emitted photons. See text for more details.

6.2. Use of high pass filters

Nevertheless, a better optimization would demand to make $A = 0$ for all or, at least, part of the interval $E_g < E < E_{zc}$. This can be achieved by using a high pass filter, as shown in Fig. 7a. Consider, for example, a device with hemispheric emission, bandgap E_{g1} and $\eta = \eta_1$ (Fig. 7b). Because of the use of a filter E_F the device apparently behaves exactly the same as a single gap cell with $E_g = E_F$, since its I–V characteristic is in all equal to Eq. (23). Now the recalculation of E_{zc}

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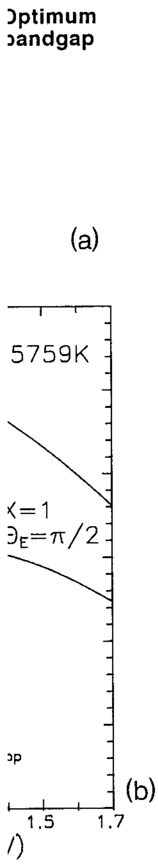

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would again result in a $E_{\mathrm{F}} < E_{\mathrm{zc}}$ which would demand a new filter to further improve the efficiency, in an iterative process that ends in $E_{\mathrm{F}}^{\mathrm{op}} = E_g^{\mathrm{mx}}$ and would imply $A = 1$. That is, from the mathematics of Eq. (24b) it seems that any cell with $E_g < E_g^{\mathrm{mx}}$ could be converted into a device with the maximum efficiency by the use of the appropriate filter. From the physics, however, we can see that such a situation is impossible because it can lead to $qV_{\mathrm{m}} > E_g$ which would produce a stimulated emission higher than the absorption and, therefore, $\alpha(E,V)$, $A[\alpha(E,V)]$ and $b_1(E,V)$ would result negative and the device would enter in a regime of rapidly increasing losses which prevent qV_{m} from being greater than about E_g [25].

For non optimum devices, however, for which $V_{\mathrm{m}} \ll E_g$ it is possible to draw more power of a given material by the use of filters. That is the case, for example, of any solar cell with hemispheric emission ($\theta_E = \pi/2$) allowed. Any of these cells with $E_g > qV_{\mathrm{m}}^{\mathrm{op}}$ can be converted in a device with the efficiency η^{mx}, by using a high pass filter with $E_{\mathrm{F}} = E_g^{\mathrm{mx}}$ (Fig. 7b, line 1). For cells with $E_g < qV_{\mathrm{m}}^{\mathrm{op}}$, an approximated upper bound for this efficiency increment can be calculated by limiting the maximum operation voltage V_{m} to E_g/q (Fig. 7b, line 2).

6.3. About the use of monolithic heterostructures

For $E_g > E_g^{\mathrm{mx}}$, a counterpart of the use of high pass filters for $E_g < E_g^{\mathrm{mx}}$ can be devised. It consists in the use of an embedded absorbing region introducing an absorbing edge lower than E_g. This can be achieved, for example, by sandwiching a semiconductor between two regions of a higher gap material. These structures are, in fact, multigap devices, but we are interested now in those monolithic versions that can be treated in practice as single material devices.

For such structures, the various regions are optically connected in series but are connected in parallel from the electrical point of view and this connection imposes that their quasi-fermi levels are equally split (in a quantity $= qV$) in all the regions and, therefore, limited by the lower gap in order to prevent this zone to enter the stimulated recombination regime. As a result, it must be said that the efficiency of this device cannot be higher than that of the lower gap cell working alone. But, given a solar cell made of a material with a bandgap greater than that of the maximum efficiency point, it would be possible to use embedded absorbing regions with lower absorbing gaps to approach the behavior and, therefore, the efficiency of the cell with the bandgap E_g^{mx}.

The use of embedded absorbing regions providing intermediate levels in the bandgap or quantum wells has attracted an increasing attention in the last few years [14,26–29] These concepts can possibly produce efficiency improvements on the practical efficiency of the corresponding baseline cells, but from the point of view of the limiting efficiencies, it is the opinion of the authors that these cells must obey the same limitations commented above and, therefore, will not be able to give efficiencies greater than the η^{mx} given in this work. This is in disagreement with affirmations given in Refs. [12,26]. Thus, the small increment, with respect to the detailed balance maximum, calculate in Ref. [29] for the quantum well solar cell is not feasible within the approximations (the omission of the stimulated recombination, for instance) of the Detailed Balance Theory [30].

7. Conclusions

This work began with the idea of reviewing and generalizing the Detailed Balance Theory when applied to the computation of the maximum achievable efficiency for photovoltaic energy conversion by a single gap solar cell. Hence, the basic assumptions involved in the Theory are remarked, the Theory is formulated for an arbitrarily shaped solar cell and the absorptivity is reasoned to be equal to the emissivity even under no equilibrium conditions for the case of constant quasi-fermi level splitting.

As a result of this review:

(a) The maximum theoretical efficiency is confirmed: 40.7% for the Sun assumed as a black body at 5759 K.

(b) The maximum efficiency is found to be independent on the concentration providing that the *angle of emission* of radiative photons is strictly restricted to the angle of the illumination photon flux.

(c) It is proved that the common assumption that considers that for achieving maximum efficiency it is necessary the total absorption of the incident photons can be wrong for *non-optimum* devices.

(d) Previously computed limiting efficiencies for materials with lower gap than the optimum have been underestimated. The theoretical efficiency of these devices increases if the concept of *energy restriction* is applied.

(e) It is pointed out that the limiting efficiencies of solar cells manufactured with innovative ideas (quantum wells, impurity photovoltaic effect) cannot overpass the limiting efficiencies confirmed here.

Appendix

It has been advanced in the text, see Eq. (15) that, for constant pseudo-fermi level splitting ($\Phi = V$), the relationship $e = a$ holds as in equilibrium. This is demonstrated in the following paragraphs by directly computing the values of the *emissivity* and the *absorptivity*.

(a) Absorptivity at the surface element dS

Each beam of rays of light entering the volume of the device through the surface element dS will produce an optical path ("tube of rays") in its travelling inside the semiconductor as that illustrated in Fig. 8a. As no photons can escape through the lateral surfaces of a tube of rays, the number of photons absorbed in each elemental jump (with length l_i, from S to S') is equal to the number of photons entering the tube at S minus those leaving the tube at S'. By choosing an

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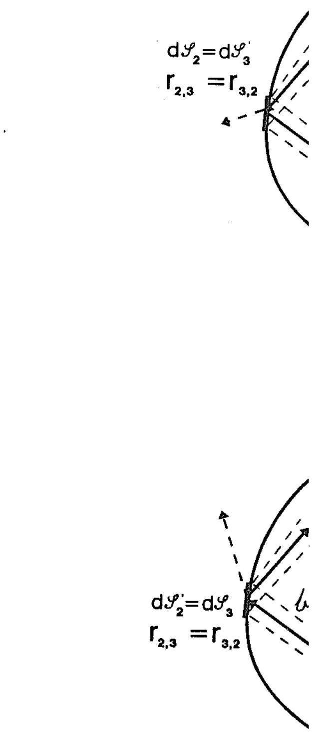

Fig. 8. Illustration of the

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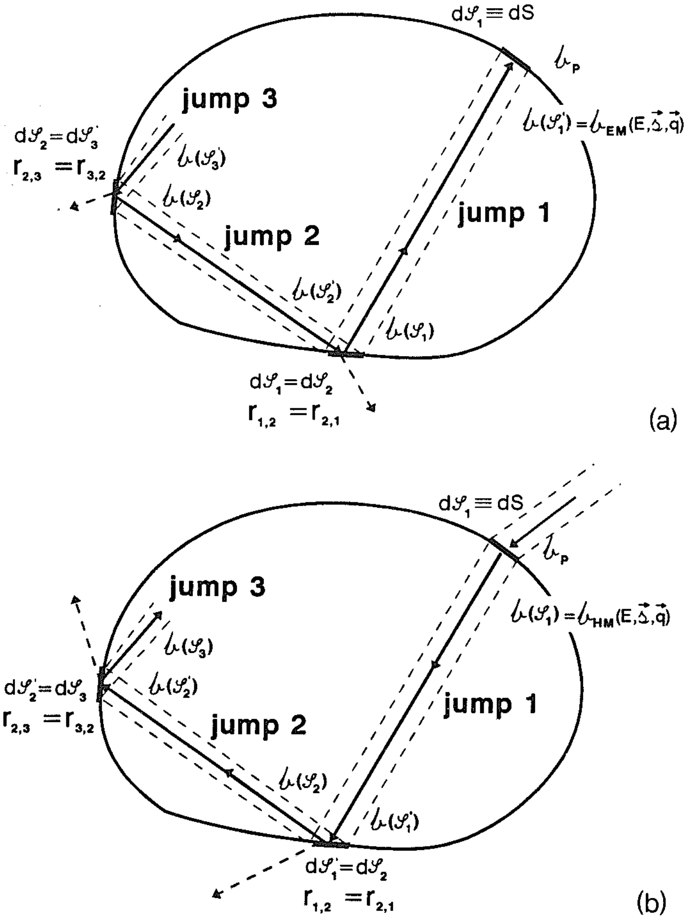

Fig. 8. Illustration of the optical paths for the (a) absorption and (b) emission of photons.

axis of coordinates following the rays, the differential Eq. (8) becomes one-dimensional and the corresponding homogeneous part can be written as:

$$\frac{\mathrm{d}b}{\mathrm{d}z} + \alpha b = 0, \qquad \text{with } b(0) = b(S_i), \tag{A1}$$

which has the following general solution:

$$b(z) = b(S_i)\exp(-\alpha z). \tag{A2}$$

Therefore, the photons absorbed in the volume V_i of the i-jump of the *tube of rays* will be

$$\int_{V_i} \alpha b \, \mathrm{d}\Omega \, \mathrm{d}V = a_i b(S_i) \, \mathrm{d}E \quad \text{with } a_i \equiv 1 - \exp(-\alpha l_i), \tag{A3}$$

and where $\mathrm{d}\epsilon = \cos\theta_i \, \mathrm{d}S_i \, \mathrm{d}\Omega_i$ is the *etendue*, which is constant along the optical path.

The initial value of the flux at any elemental jump, $b(S_i)$, can be related to the final value of the precedent jump, $b(S'_{i-1})$, through the reflection coefficient, $r_{i-1,1}$ at the $\mathrm{d}S'_{i-1} \equiv \mathrm{d}S_i$ elemental surface. And the final value, $b(S'_{i-1})$, can be related to the initial value, $b(S_{i-1})$, of the same jump through the absorptivity. Thus

$$b(S_i) = r_{i-1,i} b(S'_{i-1}) = r_{i-1,i}(1 - a_{i-1}) b(S_{i-1}). \tag{A4}$$

Proceeding in this way, it is still possible to express $b(S_i)$, and, consequently, the absorbed photons in the i-jump, as a function of the first initial value, which is related to the incident radiation at the semiconductor inner surface, here denoted as $b(S_1)$.Hence,

$$\text{Absorption}(i) \equiv a_i r_{i-1,i} b(S_1) \prod_1^{i-1} r_{k-1,k}(1 - a_k) \mathrm{d}\epsilon, \tag{A5}$$

for $i > 1$ and where $r_{0,1} \equiv 1$. Obviously, absorption(1) $= a_1$.

The total absorption will be the addition of all the elemental absorptions. Therefore, the photogenerated current (*q times the number of the illumination photons absorbed in the whole volume of the tube of rays*), $\mathrm{d}I_{\mathrm{PH}}$, will be given by

$$\mathrm{d}I_{\mathrm{PH}} = qab(S_1) \cos\theta \, \mathrm{d}S \, \mathrm{d}\Omega \, \mathrm{d}E, \tag{A6a}$$

with

$$a = a_1 + \sum_2^N a_i r_i \prod_1^{i-1} (1 - a_k) r_{k-1,k}, \tag{A6b}$$

where N is the number of jumps in the whole optical path. This number can be finite, if there is a point where $r = 0$ at the end of the path, or infinite if $r \neq 0$ at any point. The *absorptivity*, a, so defined is a material dependent parameter through its dependence on α and on the reflection coefficient at the points where the rays strike the surface. The absorptivity is defined for each point of the surface and each direction of the incident ray.

(b) Emissivity at the surface element dS

Within the same tube of rays defined by the illumination photons, and for the case of constant b_{nV}, the photon flux b_{EM} satisfies the differential equation

$$\frac{\mathrm{d}}{\mathrm{d}z}(b_{nV} - b_{\mathrm{EM}}) + \alpha(b_{nV} - b_{\mathrm{EM}}) = 0, \tag{A7}$$

$$(b_{nV} - b_{\mathrm{EM}})(0) = b_{nV} - b_{\mathrm{EM}}(S_i).$$

In this equation, as z increases, the path of the rays is followed in opposite direction to the case of the absorptivity (See Fig. 8b). Concerning the variable $b_{nV} - b_{\mathrm{EM}}$, Eq. (A7) is mathematically the same as (A1) and, therefore, has a

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straightforward solution which leads to the following relationship between the emitted fluxes at the end (S') and at the beginning (S) of the i-jump:

$$b_{EM}(S'_i) = (1 - a_i) b_{EM}(S_i) + a_i b_{nV}, \tag{A8}$$

where a_i is the same absorptivity for the path i defined before. Again, the initial value of the flux at any elemental jump, $b_{EM}(S_i)$, can be related to the final value of the precedent jump, $b_{EM}(S'_{i+1})$, through the reflection coefficient, $r_{i+1,i}$, at the $dS'_{i+1} \equiv dS_i$ elemental surface. Therefore, it is possible to express the photon flux, $b_{EM}(S'_1)$, emerging out of the "tube of rays" through the elemental surface of the first jump, as a function of a value at the starting point, located a number (finite or infinite) of elemental jumps before. After some mathematical manipulation the result can be arranged as follows

$$b_{EM}(S'_1) = b_{nV}\left[a_1 + \sum_2^N r_{i,i-1} a_i \prod_1^{i-1}(1 - a_k) r_k\right] + b_{EM}(S_N) \prod_1^N (1 - a_i) r_{i,i-1}. \tag{A9}$$

But the second term of this expression is always zero because at least one of the following cases will always hold: (a) For a finite number of jumps, $r_{N,N} - 1 = 0$ (and therefore $b_{EM}(S_N) = 0$) or (b), for and infinite number of jumps, the factorial product of an infinite number of factors all of them less than unity is also zero. In summary, it results

$$b_{EM}(S'_1) = e b_{nV} \quad \text{with } e = a_1 + \sum_2^N r_{i,i-1} a_i \prod_1^{i-1} (1 - a_k) r_k, \tag{A10}$$

and given that $r_{i-1,i} = r_{i,i-1}$ it finally results that

$$e = a, \tag{A11}$$

as we wanted to prove.

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R. Pal, K.K. C

Department of Material

Abstract

CuInSe$_2$ films with differen
three source evaporation tech
depleted grains. Photoconduc
170–370 K. The data at low
boundary trapping model wi
height in dark varied within 0
1.18. The variation of the bar
range 10–75 mW/cm^2 was an
under various illumination lev

1. Introduction

Among the different cha
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the preparation of CIS fil
deposition conditions, such
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CIS films along with their d
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* Corresponding author.

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