

MINIMUM EFFECT OF NON-INFINITESMAL INTERMEDIATE BAND WIDTH ON THE DETAILED BALANCE EFFICIENCY OF AN INTERMEDIATE BAND SOLAR CELL

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ABSTRACT

This paper analyses the minimum deterioration of an intermediate band (IB) solar cell's conversion efficiency as a function of the IB's width. A central task in accomplishing this is to derive the emission spectrum of an IB material. The derivation is premised upon equilibria conditions and is derived under the stringent conditions that electronic transitions are limited to inter-band transitions coupled to photon emission or absorption. The resultant equilibrium emission spectrum is utilized to formulate expressions for the net photon flux and net power density absorbed by the IB material from a dual source solar geometry. Heuristic arguments are contrived to explain the relationship of the absorption coefficients and the absorptivity upon the conversion efficiency. Results indicate as the IB width increases, the conversion efficiency reduces to the limiting efficiency of a two-junction series-assembled tandem.

INTRODUCTION

In the present paper, the equations that govern the performance of the intermediate band solar cell (IBSC) are recast to include non-optimum solar concentration and non-infinitesimal IB width. In deriving these equations, the treatment of the chemical potential of radiation in equilibrium with a three-level system leads directly to the equilibrium emission spectrum itself. The results of this derivation are applied to calculate the minimum effect on the detailed balance efficiency limit of a non-infinitesimal intermediate band width under various solar concentrations. The remaining sections of this paper are ordered as follows. Next, are described the equilibria conditions upon which a detailed balance analysis of an IB material is made possible. This is followed by a discussion of the allowed radiative transitions within the IB material and the criterion for a detailed balance. This is followed by the presentation of the equilibrium emission spectrum. The subsequent section places the IB material into the familiar context of the dual source solar geometry allowing for the formulation of the net photon flux absorbed and the net power density absorbed by an IB material. After this comes a discussion of the effects of

the absorption coefficients and the absorptivity upon the power density generated by the IBSC. Finally, the optimum detailed balance efficiencies as a function of the width of the intermediate band is given, as well as a discussion of the results.

EQUILIBRIA CONDITIONS

In order to establish the density of photons in equilibrium with an electronic system, the equilibrium statistics of the electronic system itself must first be established. Fig. 1 illustrates the reduced band structure of an IB material. There are three bands: the valence band (VB), the conduction band (CB), and the intermediate band, which is located in between the former. The concentration of occupied electron states in the conduction band, $n_{e,C}(\varepsilon)$, intermediate band, $n_{e,I}(\varepsilon)$, and valence band, $n_{e,V}(\varepsilon)$, per volume and per energy interval $(\varepsilon, \varepsilon + d\varepsilon)$, follows Fermi statistics as:

$$n_{e,X}(\varepsilon) = D_{e,X}(\varepsilon) f_X(\varepsilon); \quad (1)$$

where X is an index indicating separately one of the following bands {CB, IB, VB}, and $D_{e,X}(\varepsilon)$ is the density of electron levels per volume per energy interval in the X band, and $f_X(\varepsilon)$ is a Fermi-Dirac function. Given that the electrons in a given band are in thermal equilibrium with the lattice (and the lattice is in thermal equilibrium with the terrestrial sink, which has temperature T_p) and in chemical equilibrium with each other, the probability of electron occupancy in the X band is governed by the electrochemical potential (quasi-Fermi energy) of the electrons in the band, η_X , as follows:

$$f_X(\varepsilon) = \left\{ \exp\left[\frac{(\varepsilon - \eta_X)}{kT_p}\right] + 1 \right\}^{-1}, \quad (2)$$

where k is Boltzmann's constant. Having established the equilibrium conditions of the electrons in the bands, the rates of electronic transitions may be formulated.

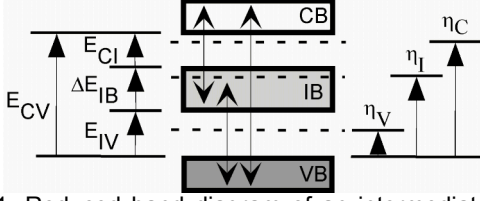


Fig. 1. Reduced band diagram of an intermediate band material. Band gaps are labeled as well as quasi-Fermi levels. Allowed inter-band radiative transitions are illustrated with double arrows. A photon's energy must be equal to or greater than the minimum separations between two bands to induce a transition between the bands.

ELECTRONIC TRANSITIONS

In general electrons may transition from one state to another by both radiative means and non-radiative means. Precluding non-radiative transitions and precluding intra-band transitions, a photon mode within the energy interval $(\hbar\omega, \hbar\omega + d\hbar\omega)$ may only interact with an intermediate band material in one of nine ways: stimulated absorption of a photon by an electron causing an inter-band transition (VB \rightarrow IB; VB \rightarrow CB; IB \rightarrow CB), spontaneous emission of a photon caused by an electron spontaneously transitioning from a higher energy band to a lower energy band (CB \rightarrow IB; CB \rightarrow VB; IB \rightarrow VB), or stimulated emission of a photon caused by an inter-band transition of an electron already under the influence of a second photon (CB \rightarrow IB; CB \rightarrow VB; IB \rightarrow VB) [1]. With transitions limited to these nine cases, a detailed balance will exist when the rates of absorption equal to the rates of emission.

EMISSION SPECTRUM

Following through with the formalism of Würfel [2], these nine radiative processes lead to the equilibrium photon emission spectrum, $\dot{n}_\gamma(\hbar\omega)$, that is given per surface area per second per photon energy interval. The emission spectrum is the direct sum of three components: the emission spectrum of photons in equilibrium with the excitations between the IB and VB, $\dot{n}_{\gamma,IV}(\hbar\omega)$, excitations between the CB and IB, $\dot{n}_{\gamma,CI}(\hbar\omega)$, and excitations between the CB and VB, $\dot{n}_{\gamma,CV}(\hbar\omega)$. These are given mathematically as:

$$\dot{n}_{\gamma,XY}(\hbar\omega) = a(\hbar\omega) \frac{(\hbar\omega)^2}{4\pi^2 \hbar^2 c^3} \frac{\alpha_{XY}(\hbar\omega) f_{\gamma,XY}(\hbar\omega)}{\alpha_{IV} + \alpha_{CI} + \alpha_{CV}}; \quad (3)$$

where XY are indices indicating separately one of the following excitations {IV, CI, CV}, \hbar is Planck's constant, ω is the radian frequency of the photon, c is the vacuum speed of light, and $f_{\gamma,XY}$ are the Bose-Einstein distributions that describe the probability of photons in the mode as:

$$f_{\gamma,XY}(\hbar\omega) = \left\{ \exp\left[\frac{\hbar\omega - \mu_{\gamma,XY}}{kT_p}\right] - 1 \right\}^{-1}; \quad (4)$$

where $\mu_{\gamma,XY}$ is the equilibrium chemical potential of

photons emitted due to XY excitations and is equal to the difference between the electrochemical potentials of electrons in band X and band Y. The flux per photon interval is additionally written in terms of the absorptivity of the IB material, $a(\hbar\omega)$ as:

$$a(\hbar\omega) = \frac{[1 - R(\hbar\omega)] \left[1 - \exp\left(-\frac{[\alpha_{IV} + \alpha_{CI} + \alpha_{CV}]d}{\alpha_{IV} + \alpha_{CI} + \alpha_{CV}}\right) \right]}{[1 - R(\hbar\omega) \exp\left(-\frac{[\alpha_{IV} + \alpha_{CI} + \alpha_{CV}]d}{\alpha_{IV} + \alpha_{CI} + \alpha_{CV}}\right)]}; \quad (5)$$

and the absorption coefficients $\alpha_{IV}(\hbar\omega)$, $\alpha_{CI}(\hbar\omega)$, and $\alpha_{CV}(\hbar\omega)$ that are given mathematically as:

$$\alpha_{XY}(\hbar\omega) = \frac{\kappa}{c} \sum_{i,j} \left[\frac{M_{Xi,Yj}(\varepsilon_i, \varepsilon_j, \hbar\omega) D_{e,X}(\varepsilon_i) D_{e,Y}(\varepsilon_j)}{\times [f_Y(\varepsilon_j) - f_X(\varepsilon_i)] \delta(\varepsilon_j - \varepsilon_i, \hbar\omega)} \right]; \quad (6)$$

where κ is the dielectric constant of the IB material, $M_{Xi,Yj}(\varepsilon_i, \varepsilon_j, \hbar\omega)$ is a matrix element of momentum [3] and δ is the delta function. In equation (5), $R(\hbar\omega)$ is the reflectivity of the IB material's surface.

RADIATIVE EXCHANGE AND THE SOLAR GEOMETRY

Due to the solar geometry, in general, photons will be exchanged with two distinct sources. Within a solid angle Ω the IB material will exchange photons with the Sun, whose photon distribution, $f_{\gamma,S}$, is described by temperature $T = 6000$ K and chemical potential $\mu = 0$. Within the remainder of the outward facing hemisphere, due to the elements comprising the Earth's atmosphere, the IB material exchanges photons with the Earth, whose photon distribution, $f_{\gamma,P}$, is described by temperature $T = 300$ K and chemical potential $\mu = 0$. Due to its higher temperature, the Sun emits more photons within the range $(\hbar\omega, \hbar\omega + d\hbar\omega)$ than the Earth, and therefore a larger power density may be absorbed by the IB material by preferentially exchanging photons with the Sun as opposed to the Earth. With the use of optical devices the solid angle may be given as the product of a geometrical dilution factor, D , and a geometrical concentration factor, C [1]. A perfect reflector is placed on the underside of the IB material to limit the emission of photons.

The net particle flux absorbed by the IB material from the sources is the sum of net flux absorbed due to electronic excitations between the IB and VB, $\dot{N}_{\gamma,IV}$, between the CB and IB, $\dot{N}_{\gamma,CI}$, and between the CB and VB, $\dot{N}_{\gamma,CV}$. These terms are given individually as:

$$\dot{N}_{\gamma,XY} = \int_0^\infty \left[\frac{(\hbar\omega)^2}{4\pi^2 \hbar^2 c^3} \frac{a(\hbar\omega) \alpha_{XY}(\hbar\omega)}{\alpha_{IV} + \alpha_{CI} + \alpha_{CV}} \times \left(CD [f_{\gamma,S} - f_{\gamma,XY}] + (1 - CD) [f_{\gamma,P} - f_{\gamma,XY}] \right) \right] d\hbar\omega \quad (7)$$

Meanwhile the net power density absorbed by the IB material from the sources, \dot{W} , is the sum of net power

density absorbed due to electronic excitations between the IB and VB, \dot{W}_{IV} , between the CB and IB, \dot{W}_{CI} , and between the CB and VB, \dot{W}_{CV} . These terms are given individually as the product of the net photon flux absorbed and the difference between the chemical potentials of the bands involved in the excitations. They are given mathematically as:

$$\dot{W}_{IV} = \mu_{\gamma,IV} \dot{N}_{\gamma,IV}; \dot{W}_{CI} = \mu_{\gamma,CI} \dot{N}_{\gamma,CI}; \text{ and } \dot{W}_{CV} = \mu_{\gamma,CV} \dot{N}_{\gamma,CV} \quad (8)$$

In steady state, the net rate of electron generation per area within the IB caused by IB-VB excitations, $J_{IV} = q\dot{N}_{\gamma,IV}$, and CB-IB excitations, $J_{CI} = q\dot{N}_{\gamma,CI}$, must balance, for there is no path allowing the injection or extraction of carriers to/from the IB by external means. The above statements in conjunction with the ultimate efficiency hypothesis [4], which states, in part, that each net photon absorbed creates one electron-hole pair, allows the electrical power density generated by the IBSC, \dot{W}_{IBSC} , to be written as:

$$\dot{W}_{IBSC} = \mu_{\gamma,CV} (\dot{N}_{\gamma,IV} + \dot{N}_{\gamma,CV}) = \mu_{\gamma,CV} (\dot{N}_{\gamma,CI} + \dot{N}_{\gamma,CV}); \quad (9)$$

where the relationship $\mu_{\gamma,CV} = \mu_{\gamma,CI} + \mu_{\gamma,IV}$ is taken into account as well as the condition of net electron balance in the IB:

$$J_{CI}(\mu_{CI}/q) = J_{IV}(\mu_{IV}/q). \quad (10)$$

SPECTRAL SELECTIVITY

This section specifies the conditions that lead to an optimization of electrical power generation. For optimum power generation an ideal spectral selectivity may be assumed. The ideal spectral selectivity is a generalization of the ultimate efficiency hypothesis as follows. Each photon with energy $\hbar\omega$ that is greater than or equal to the minimum band-gap will produce one electronic charge q . Further, the voltage at which that electronic charge is produced is the largest of the set $\{E_{AB}\}$ divided by q , where the elements of $\{E_{AB}\}$ are the elements of set $\{E_{XY}\}$ that meets the criterion $E_{XY} \leq \hbar\omega$.

As shown in Fig. 2, the absorption and emission of photons is allowed at the band edges. All photons absorbed by an IB material contribute a quantity of useful work that is less than the energy of the photon itself. This is because $\mu_{\gamma,XY}$ is always less than E_{XY} , which is the minimum photon energy that allows an energy transfer of magnitude $\mu_{\gamma,XY}$. Within the detailed balance method, a transition may be assumed to be prevalent as long as there is a non-zero probability of the transition occurring. Thus, if at the band edges, the absorption coefficients are small, it may still be assumed to be prevalent. In practice this can be justified if the optical path length is large enough.

Beginning with a brief discussion of a single junction solar cell, the remainder of this section presents these concepts with more mathematical rigueur. The conversion

efficiency of a photovoltaic material depends heavily upon the absorption coefficient(s) and the absorptivity of the material. For a single junction solar cells, the highest efficiencies will be found for a well-defined band-gap of value E_g and an equilibrium chemical potential, μ_{γ} , wherewith $f_{\gamma,S} + f_{\gamma,P} - f_{\gamma,C}(\mu_{\gamma})$ is always positive for all $\hbar\omega \geq E_g$. Further, given $f_{\gamma,S} + f_{\gamma,P} - f_{\gamma,C}(\mu_{\gamma})$ is always positive for all $\hbar\omega \geq E_g$ then a unitary absorptivity for all $\hbar\omega \geq E_g$ would tend to be most efficient, so as to make the best of a good situation.

In the case of an IBSC, the efficiency will tend to be large if for all photons in the range $(\hbar\omega, \hbar\omega + d\hbar\omega)$, $\alpha_{XY}(\hbar\omega)$ is zero for $[f_{\gamma,S} + f_{\gamma,P} - f_{\gamma,XY}(\mu_{\gamma,XY})]\{\hbar\omega\} < 0$ and non-negative for $[f_{\gamma,S} + f_{\gamma,P} - f_{\gamma,XY}(\mu_{\gamma,XY})]\{\hbar\omega\} \geq 0$. Under these provisions, because irreversible entropy generation increases monotonically with $(\hbar\omega - \mu_{\gamma,XY})/kT$ [2], to make the best of a good situation:

$$\sum_{i=\{XY\}} \alpha_i(\hbar\omega) = \begin{cases} \alpha_{IV}(\hbar\omega) & \text{for } E_{IV} \leq \hbar\omega < E_{CI} \\ \alpha_{CI}(\hbar\omega) & \text{for } E_{CI} \leq \hbar\omega < E_{CV} \\ \alpha_{CV}(\hbar\omega) & \text{for } E_{CV} \leq \hbar\omega \end{cases}, \quad (11)$$

$$a(\hbar\omega) = \begin{cases} 0 & \text{for } 0 \leq \hbar\omega < E_{IV} \\ 1 & \text{for } E_{IV} \leq \hbar\omega \end{cases}; \quad (12)$$

where it is assumed that $E_{IV} < E_{CI}$ and it is taken into account, from Fig. 1 and equation (6), that the absorption coefficient α_{XY} is necessarily zero for $\hbar\omega < E_{XY}$ and non-negative for $\hbar\omega \geq E_{XY}$. The result is equivalent to what Luque and Martí postulate [5].

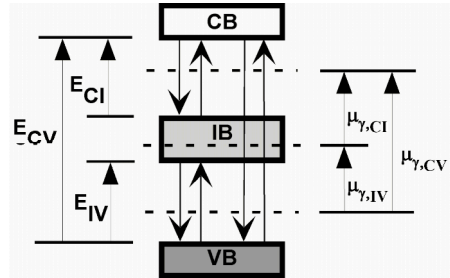


Fig. 2. Reduced IBSC band diagram illustrating generation (upward arrows) and recombination (downward arrows) events.

Using these arguments, the limiting efficiency of the IBSC is settled at 63.2% [6, 7] and the minimum degradation of efficiency conversion is determined as well [8]. The next section presents the optimum detailed balance efficiencies of an IBSC with non-infinitesimal IB width.

NON-INFINITESMAL INTERMEDIATE BAND WIDTH

This section presents the results of detailed balance calculations that illustrate the minimum deterioration of the

efficiency as a function of the IB width, ΔE_{IB} . For each value of E_{IB} , the optimum efficiency is found by utilizing an optimization routine that treats E_{IV} and E_{CI} as freely varying parameters. Fig. 3 shows the optimum efficiency as a function of ΔE_{IB} . The efficiency, ω , as calculated in the standard way:

$$w = \dot{W} / (\sigma C D T_s^4); \quad (13)$$

where σ is the Stefan-Boltzmann constant.

The results indicate the following. As initially shown by Brown *et. al.* [7], the efficiency limit occurs when ΔE_{IB} is 15 meV. Further, the efficiency at this value is close to the absolute limit (63.8%) of three electrically isolated junctions operating in tandem [9]. As the value of ΔE_{IB} increases the optimum efficiency decreases until stabilizing at 55.5%. Further, upon stabilizing at ΔE_{IB} equal to 6 eV, the optimum efficiency and the band-gaps E_{IV} and E_{CI} are those of an optimized two-junction tandem electrically assembled in series [10]. This indicates that as ΔE_{IB} increases, the power absorbed from the sources due to electronic excitations between the CB and VB steadily decreases. Ultimately, they offer no contribution whatsoever as there are relatively few photons in the solar spectrum at such high energies. The degeneration of an IBSC into a two-junction solar cell is due to the stringent condition that there are no intra-band transitions. Though the detailed balance method allows this, it is not realistic for such large band widths.

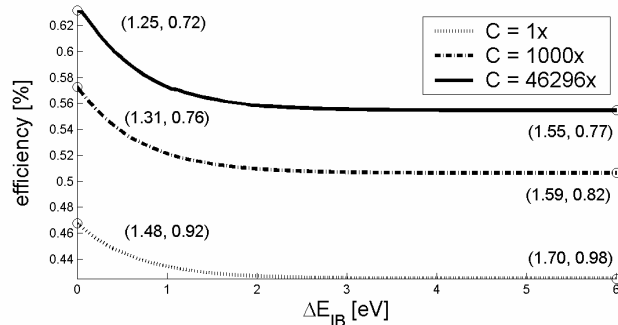


Fig. 3. Effect of E_{IB} on efficiency. For each value of E_{IB} , E_{IV} and E_{CI} are allowed to vary in order to find the optimum efficiency. For each endpoint, the optimized (E_{IV} , E_{CI}) are provided in eV.

CONCLUSIONS

This paper examines the effect of a non-infinitesimal intermediate band width on the detailed balance efficiency of an intermediate band solar cell. In order to accomplish this, two specific tasks are performed: the equilibrium emission spectrum is derived and the power density absorbed by the intermediate band photon converter is derived. The derivation of the equilibrium emission spectrum is restricted to the stringent case where all electronic transitions are coupled to a radiative process. The derivation precludes non-radiative transitions and precludes intra-band transitions. Within this stringent

framework, it is found that the emission spectrum is the direct sum of three components: one for each of the allowed inter-band electronic transitions. The emission spectrum is utilized to formulate expressions for the net photon flux and net power density absorbed by the IB material from a dual source solar geometry.

The results of detailed balance calculations for maximum solar concentration indicate that when the IB width is infinitesimal, the IBSC conversion efficiency is 63.2%, which is near to the limit of a three-junction tandem (63.8%). The novel result given in this paper is that as the width of the IB increases, the optimum efficiency does not go to zero with increasing, but saturates to the efficiency and band gaps of an optimized two-junction serially-connected tandem (55% efficiency with bandgaps: 1.55 eV and 0.77 eV). This result is physically unrealistic, for in the extreme the band structure approximates that of a black body. In order to obtain more comprehensive results, the inclusion of intra-band transitions within the intermediate band should be considered. With the inclusion of intra-band transitions, the conversion efficiencies would tend to degrade from those results presented here.

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