Maximum Efficiency of an Ideal Solar Cell Containing One and Two Intermediate Bands

Steven Jenks

May 30, 2008

Abstract

Introducing intermediate band(s) within the energy gap of the semiconductor could possibly increase efficiencies of solar cells. Photons with energy less than the band gap can contribute to the device output by using the intermediate band(s) as a 'ladder' to the conduction band. The present analysis shows the maximum efficiency an ideal solar cell containing one and two intermediate bands can achieve is 63.2% and 74.4%, respectively.

1 Introduction

The solar cell is a solid state device that converts light energy to electricity in a one step process that relies on the ideas of quantum mechanics. When light is absorbed in matter, depending on the material, electrons can excite to higher energy levels where they are able to move freely. The extreme case is when the electron can completely escape the surface of the metal after absorbing blue or ultraviolet light. This is known as the photoelectric effect and was described by Einstein in 1905 [1].

In a semiconductor, which has a band gap roughly ranging between 0.5 eV to 3.0 eV [2], a electron can be promoted to the conduction band if the absorbed photon has an energy greater than the band gap. The excited electron will decay very quickly (picoseconds) to the lowest available energy state in the conduction band due to the abundance of empty levels. This is called thermalization and happens through collisions with the lattice, giving up kinetic energy to produce phonons during the decay. Then in a much slower process, the electron will decay across the band gap to a vacant site in the valence band. A solar cell will take advantage of this slow process and have some asymmetry built in that pulls the electrons away to an external circuit before electrons can relax back down to the valence band. As they are pulled away, the extra energy is a potential difference which allows electrical work to be done.

One of the limitations of solar cells that can be readily observed is that low energy photons cannot excite electrons to the conduction band and hence external circuit. Intermediate bands take advantage of the lower energy photons by allowing the electrons to be

promoted to levels in the normally forbidden energy gap [3]. This is a muli-step or ladder approach to increase efficiency. It is shown that the maximum efficiency of a solar cell using one or two intermediate bands is greater than the single junction solar cell. The first step in this analysis is understanding the source.

2 The Source

The sun's radiation can be modeled as a black body, which by definition is a perfect absorber and emitter of light. Its properties are well known and in this section are only summarised. Specifically, the energy density of a black body is developed and the connection to its flux is discussed.

Energy density can be derived using the density of states, a, for photons with momentum between p and $p + dp$ in a cavity

$$\epsilon_{photon} = pc$$
$$a(p)dp = \frac{V}{h^3}g4\pi p^2 dp$$
$$a(\epsilon)d\epsilon = \frac{V}{h^3c^3}g4\pi\epsilon^2 d\epsilon$$

and using the mean occupation number.

$$\langle n_\epsilon \rangle = \frac{1}{e^{\epsilon/k_B T} - 1}$$

Combining the two, noting that the degeneracy $g = 2$ (polarization) and that the mean occupation number is multiplied by ϵ to give average energy, shows the energy density in range $d\epsilon$.

$$u(\epsilon)d\epsilon = \frac{8\pi\epsilon^2}{h^3c^3}\frac{\epsilon}{e^{\epsilon/k_B T} - 1}d\epsilon \tag{1}$$

The total energy density in a system is given by integrating the above equation over the over the desired range. Particle density can also be found by just combining the mean occupation number and density of states for photons.

$$n(\epsilon)d\epsilon = \frac{8\pi\epsilon^2}{h^3c^3}\frac{1}{e^{\epsilon/k_B T} - 1}d\epsilon \tag{2}$$

2.1 Angular Dependence of Radiation

Only a portion of the sun's radiation[1] is received by the earth and this is determined by the solid angle subtended by the sun from the earth. This will affect a solar cell's performance

---

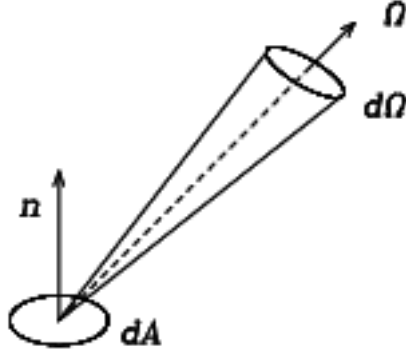[1]radiation refers to flux, energy per unit area per second.

Figure 1: Emitting black body where angle $d\Omega$ is an element of solid angle around the direction of emission

because it is only receiving a fraction of the sun's radiation. So, what exactly is the angular dependence of radiation and how much radiation does the earth receive because of it?

Figure 1 shows the segment, dA, of a black-body surface emitting radiation where $d\Omega$ is an element of solid angle around the direction of emission. A solid angle is defined by the mathematical equation, [4]

$$d\Omega = \frac{dA}{r^2} = sin\theta d\theta d\phi \tag{3}$$

If assuming planar symmetry, the radiation is resolved along the normal to the surface n (proportional to $cos\theta$). The angular dependence is determined by integrating over the angular ranges θ and ϕ

$$R \int_{\phi_1}^{\phi_2} \int_{\theta_1}^{\theta_2} cos\theta sin\theta d\theta d\phi = R \left(\frac{sin^2\theta_2 - sin^2\theta_1}{2} \right) (\phi_2 - \phi_1) \tag{4}$$

where R is the radiation independent of angular ranges. The emitted radiation passing through a hemisphere is just πR using $\theta_2 = \pi/2$, $\theta_1 = 0$, $\phi_2 = 2\pi$, and $\phi_1 = 0$. In most situations, ϕ will have the full range from 0 to 2π and θ_1 will most likely be 0 so that equation (4) will look like $F\pi R$, where $F = sin^2\theta_2$.

Equation (4) is used to determine the sun's radiation as seen from earth. If the sun was directly overhead, a black body element on earth would see the sun at an angle of $\theta_s = sin^{-1}(r_{sun}/d_{es})$ with r_{sun} being the radius of sun and d_{es} being the distance from the earth's surface to the sun. The fraction of the sun's radiation reaching earth would then just be $F_s = (r_{sun}/d_{es})^2 = 2.16 \times 10^{-5}$ using $r_{sun} = 695,990$km and $d_{es} = 149,591,493$km. It is important to note that if the black body on earth receives radiation over a hemisphere, it will receive part of the radiation directly from the sun, $0 < \theta < \theta_s$, and the rest from the scattered or re-emitted radiation, $\theta_s < \theta < \pi/2$, this is shown in figure 2. For the purposes
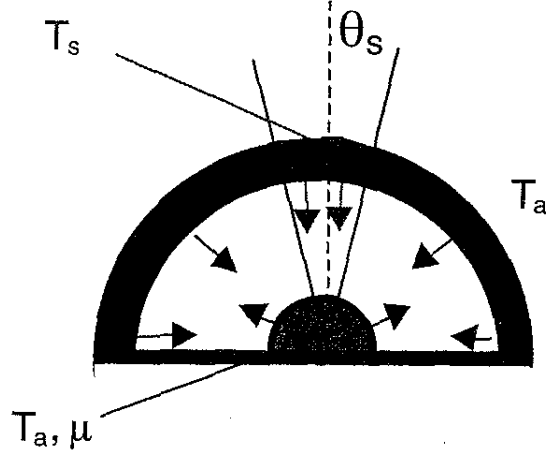
3

Figure 2: Flat plate black body receives radiation from the sun in the angular range $0 < \theta < \theta_s$. The plate will also receive ambient (scattered and re-emitted) radiation over the angular range $\theta_s < \theta < \pi/2$, this ambient radiation is assumed to behave like a black body as well.

of this paper, the scattered or re-emitted radiation will be referred to as ambient radiation that behaves just like a black body. If this angle, θ_s, is effectively increased through optics or through some other means, the black body is said to receive concentrated sunlight. When this angle is increased so the black body on earth **only** receives light from the sun, $\theta_s = \pi/2$, full concentration is achieved.

2.2 Fluxes

It is convenient when calculating efficiencies in solar cells to work with fluxes (per area per unit time) rather then energy or particle densities (per unit volume). This will become apparent in the next few sections. From dimensional analysis, one can observe that this can be achieved by multiplying by a velocity. In a black body cavity, the radiation is isotropic and moves at a velocity c. The fraction of photons $d\Omega/4\pi$ can be considered going in any direction to within an element of solid angle $d\Omega$ [5].

Now if we consider a hole of area dA and assume the hemisphere penetrates the cavity at a finite thickness dr, then the area dA subtends a solid angle $cos\theta dA/r^2$ from the point of view of the volume $r^2 sin\theta d\theta d\phi dr$. The amount of energy reaching this small hole, using $dr = cdt$, from the volume is just $cu_\epsilon cos\theta sin\theta d\theta d\phi dt dA$ and the total amount arriving per unit area per unit time is

$$\int_{\theta_1}^{\theta_2} \int_{\phi_1}^{\phi_2} cu_\epsilon cos\theta sin\theta \frac{d\theta d\phi}{4\pi}. \tag{5}$$

This is a very similiar expression to equation (4). If we assume, as before, the limits on angles $0 < \phi < 2\pi$ and $\theta_1 = 0$, the expression is just

$$= Fu_\epsilon \frac{c}{4} \tag{6}$$

4

with $F = sin^2\theta_2$. This is the conversion from energy density (per unit volume) to energy flux (per unit area per unit time). Similiar logic can be used to convert the photon density to photon flux and n_ϵ replaces u_ϵ in equation (6). Photon and energy flux are respectively

$$\dot{N} = \frac{2\pi F}{h^3 c^2} \int_{E_1}^{E_2} \frac{E^2}{e^{E/k_B T} - 1} dE \tag{7}$$

$$\dot{E} = \frac{2\pi F}{h^3 c^2} \int_{E_1}^{E_2} \frac{E^3}{e^{E/k_B T} - 1} dE \tag{8}$$

over the energy range E_1 and E_2. The energy flux is just power per unit area and for the purposes of this paper, we will call this power density. Efficiency of a solar cell can be calculated using the ratio of power density output by the cell to the power density received by the cell. The total power density from any black body can be calculated by integrating equation (8) over all energies. This gives the result $F\sigma_s T^4$, where σ_s is Stefan's constant.

$$\sigma_s = \frac{2\pi^5 k_B^4}{15 h^3 c^2}$$

This shows the power density depends only on the temperature of the black body. At the surface of earth's atmosphere, using the reduced F_s, the power density is 1353 W m^{-2}.

3   Radiative Transition Rates

When dealing with an ideal solar cell and its limiting efficiency, only radiative recombination is considered. This is the first condition of an ideal solar cell. Therefore, electronic transition rates are described by first order pertubation theory and *Fermi's Golden rule*. Fermi's rule formally states that the transition probability per unit time is the following [6],

$$\frac{2\pi}{\hbar} |\langle f | H | i \rangle|^2 \delta(E - E_f + E_i) \tag{9}$$

where the bracket term is the matrix element coupling the inital and final states. The delta function ensures energy conservation. In order to develop the transition rate, we need to multiply by the probability that the initial state is occupied f_i and by the probability the final state is unoccupied $(1 - f_f)$. Mathematically this looks like

$$r_i \rightarrow r_f = \frac{2\pi}{\hbar} |\langle f | H | i \rangle|^2 \delta(E - E_f + E_i) f_i (1 - f_f)$$

and when the final state starts to partially fill up then there will be some probability that there will be a transition back to the initial state. Symmetry ensures this is the same matrix element that governs the transition from initial to final state [6].

$$r_f \rightarrow r_i = \frac{2\pi}{\hbar} |\langle i | H | f \rangle|^2 \delta(E + E_f - E_i) f_f (1 - f_i)$$

These radiative transition rates prove very useful in the solar cell. To illustrate, an important conclusion can be reached by considering a semiconductor with a valence and conduction band exposed to light. There are three types of radiation events that can occur between the two bands:

- A photon can excite an electron from the valence band to the conduction band.

- A photon can stimulate the relaxation of an electron from the conduction band to the valence band through the emission of another photon.

- An electron can spontaneously emit a photon and relax from the conduction band to the valence band.

The first two items are closely related because a photon causes either event, distinguished only by the occupation probabilities of the two levels. Therefore, it is natural to combine the two into a net absorbtion $r_{v\to c} - r_{c\to v}$

$$r_{abs} = \frac{2\pi}{\hbar} \left| \langle c | H | v \rangle \right|^2 \delta(E - E_c + E_v) n \cdot (f_v - f_c)$$

where n is the number density of photons with energy E, f_v is the probability there is an electron in valence band (E_v), and f_c is the probability there is an electron in the conduction band (E_c). The probability associated with an electron in the solar cell material is governed by the Fermi-Dirac distribution function that has the following form

$$\frac{1}{e^{(E-E_F)/k_B T} + 1}$$

where E_F essentially is the Fermi energy (the energy at which all the states are filled at absolute zero). Now here is the second assumption of the ideal solar cell and one that greatly simplifies solar cell physics in general. When the cell is exposed to light or some applied bias, both the electrons and holes (vacancy left behind from electron) are disturbed from their equilibrium. The electron population in the conduction band and hole population in the valence band rise above their normal equilibrium. This disturbance causes the electrons and holes to relax in what is called quasi-thermal equilibrium. This causes the Fermi energy level to split and electrons in the conduction band settle to a chemical potential (E_{F_n}), while the electrons in the valence band settle to a different chemical potential (E_{F_p}). They are both assumed to be constant in each band. Using the quasi-thermal equilibrium condition the two probabilities, f_v and f_c, are just;

$$f_v = \frac{1}{e^{(E_v - E_{F_p})/k_B T} + 1} \tag{10}$$

$$f_c = \frac{1}{e^{(E_c - E_{F_n})/k_B T} + 1} \tag{11}$$

Spontaneous emission isn't caused by a photon so it will just have the form,

$$r_{sp} = \frac{2\pi}{\hbar} \left| \langle c | H | v \rangle \right|^2 \delta(E - E_c + E_v) f_c \cdot (1 - f_v).$$

6

In a steady-state process, all three processes must balence so $r_{abs} = r_{sp}$.

$$n \cdot (f_v - f_c) = f_c \cdot (1 - f_v)$$

Solving this equation for n (Complete derivation in Appendix A) shows that

$$n = \frac{1}{e^{(E-\mu)/k_B T} - 1}$$

$$\mu = E_{F_n} - E_{F_p}$$

$$E = E_c - E_v$$

which is the quasi-equilibrium occupation function for photons and can be used in conjunction with photon density of states to determine the number of emitted photons from the cell device.

4   Analysis

The efficiency of the solar cell is the ratio of power output delivered from the cell to the power output produced by the sun incident on the cell. The power from the sun has already been shown to be 1353 W m^{-2} which was calculated using equation (8). The task now lies to determine the power output delivered from the solar cell.

A circuit delivers a power density that is described by the equation $P = J \cdot V$, with J being current density at a certain voltage V. So the task is reduced to finding the current density at a certain voltage that delivers maximum power. This can be found using what has been developed so far and assumptions made about the solar cell. The assumptions are as follows:

1. Both the sun and solar cell behave like a black body that operates at temperatures T_s and T_a respectively (cell is assumed to be at ambient temperature).

2. Only radiative transitions occur.

3. All photons above energy gap are absorbed.

4. Quasi-Fermi energy levels are constant and $\mu = qV$ [7].

5. There is only one electron-hole pair created per photon.

6. Radiation generated by the cell can only escape through front surface.

7. Full concentration of the sun is received.

First, let us define the function $\dot{N}(E_1, E_2, T, \mu)$,

$$\dot{N}(E_1, E_2, T, \mu) = \frac{2\pi}{h^3 c^2} \int_{E_1}^{E_2} \frac{E^2}{e^{(E-\mu)/k_B T} - 1} dE \qquad (12)$$

which is very similiar to equation (7). It is a generalized form of the photon flux for a black body and will be used to determine the current density due to the incoming and outgoing photon fluxes between the energy levels E_1 and E_2. This might seem strange at first because current is associated with the flow of electrons. However using the assumptions above, we can determine the current density through a detailed balance of photons.

We know that all the photons with energy greater then energy gap, E_g, are absorbed in the cell and will create one electron-hole pair (assumptions 3 and 5). All the photons with energy less then the energy gap are not absorbed in the cell. Therefore, the absorbed photon flux in the cell will equal the excited electrons in the conduction band. This absorbed photon flux is $\dot{N}(E_g, \infty, T_s, 0)$ over the entire hemisphere (assumption 7), which was determined in section 2.2.

However, a number of photons will be emitted through the processes described in section 3, and electrons (same number of emitted photons) will recombine with holes in the valence band. These electrons will not contribute to the current. The emitted photons can be calculated to be $\dot{N}(E_g, \infty, T_a, \mu)$ over the entire hemisphere (assumption 6). The chemical potential of radiation, μ, comes from quasi-equilibrium occupation function determined in section 3 and is equal to qV (assumption 4). Excited electrons will lose extra kinetic energy through repeated collisions with the lattice producing phonons while they decay to lower energy states in the conduction band. This will continue to occur until they are in thermal equilibrium with the lattice temperature, T_a. This is why the emitted photons are released at the ambient temperature. The net electrons (absorbed photon flux minus emitted photon flux) will be pulled away to the external cicuit where the potential energy allows electrical work to be done.

The total current density through the device can be determined by the net electron flux multiplied by q,

$$J = q[\dot{N}(E_g, \infty, T_s, 0) - \dot{N}(E_g, \infty, T_a, qV)] \qquad (13)$$

The output power density is given by $P(V) = V \cdot J(V)$, observing that it is a function of E_g and V. For each value of E_g there will be some V in the range from 0 to E_g that will maximize the output power density. Figure 3 shows the efficiency results using the outline described above. From the figure, the maximum efficiency occurs when there is a band gap of 1.1 eV at about 41%. This seems to make sense because if the energy gap in the cell was to large, then a good portion of the photons would not be absorbed and efficiency would decrease. If the energy gap was too small, then most photons would be absorbed but a good portion of the their energy would be wasted through thermalization and phonon generation, efficiency would decrease.
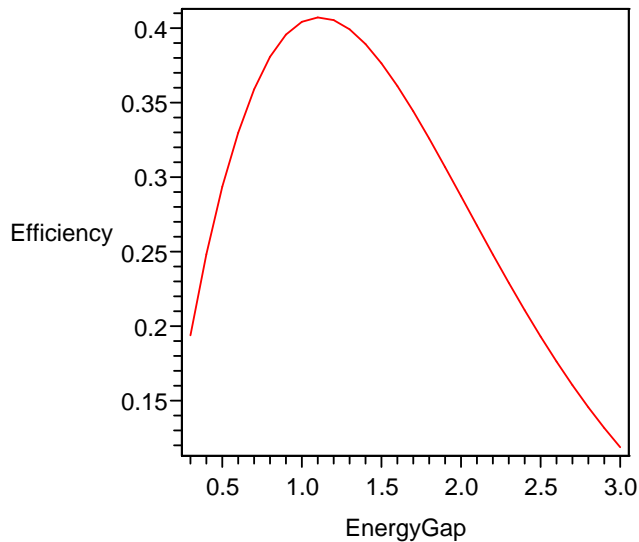
Figure 3: Limiting efficiency of single gap solar cell (in eV) at full concentration. $T_s = 6000K$ and $T_a = 300K$

5   3-Band Analysis

If some of the low-energy photons could be absorbed (infrared) and used in a solar cell, the efficiency would increase. One way to do this is to introduce an intermediate band in between the forbidden band gap to give a total of three bands in the semiconductor. Figure 4 shows a detailed diagram of what the structure should look like and figure 5 shows an equivalent but general 3-band structure with the possible electronic transitions. It has the valence band (VB), conduction band (CB), and the new intermediate band (IB). Transitions can occur between the valence and conduction bands (A_{CV}), between valence and intermediate bands (A_{IV}), and between intermediate and conduction bands (A_{CI}). We assume that stimulated emission, spontaneous emission, and stimulated absorbtion can occur in all transitions.

Using similiar arguments as before, we can assume that each level has constant quasi-Fermi levels, ϵ_{FV}, ϵ_{FI}, ϵ_{FC} [3]. In order to use the same analysis as the 2-band system, the following assumptions are made:

1. Both the sun and solar cell behave like a black body that operates at temperatures T_s and T_a respectively (cell is assumed to be temperature of ambient).

2. Only radiative transitions occur between all the bands.

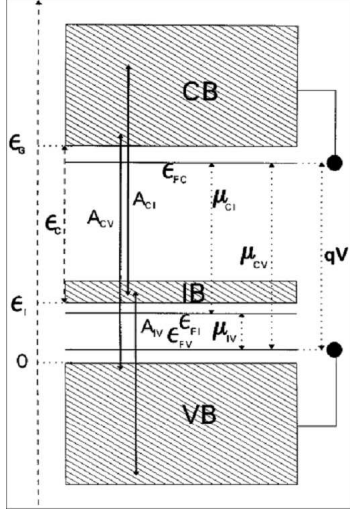3. All photons are absorbed that have energy greater then the band gap.

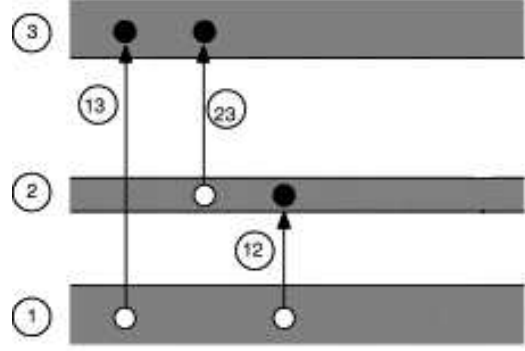Figure 4: Solar cell with intermediate band.

Figure 5: This is a 3-Band Diagram with the possible electronic transitions (reverse transitions aren't shown but do occur). The VB corresponds to band 1, CB corresponds to band 3, and IB corresponds to band 2.

4. No high energy photons are used for low energy transitions.

5. Quasi-Fermi energy levels are constant.

6. There is only one electron-hole pair created per photon.

7. Radiation generated by the cell can only escape through front surface.

8. Full concentration of the sun is received.

9. No carriers are extracted from the intermediate band. Electrons are only fed to the external circuit from the conduction band.

Now we are in position to determine the current density throughout the cell using the same outline as before

$$
\begin{aligned}
J = q[\dot{N}(E_g, \infty, T_s, 0) - \dot{N}(E_g, \infty, T_a, \mu_{CV})] + \\
q[\dot{N}(E_C, E_g, T_s, 0) - \dot{N}(E_C, E_g, T_a, \mu_{CI})]
\end{aligned}
\tag{14}
$$

$$
E_g = E_C - E_V
$$

$$
\mu_{CV} = \epsilon_{FC} - \epsilon_{FV}
$$

$$
\mu_{CI} = \epsilon_{FC} - \epsilon_{FI}
$$

$$
\mu_{IV} = \epsilon_{FI} - \epsilon_{FV}
$$

and once again the current is delivered at a voltage that is equal to the Fermi-level splitting between the conduction and valence band, $\mu_{CV} = qV$. The first part of this equation is
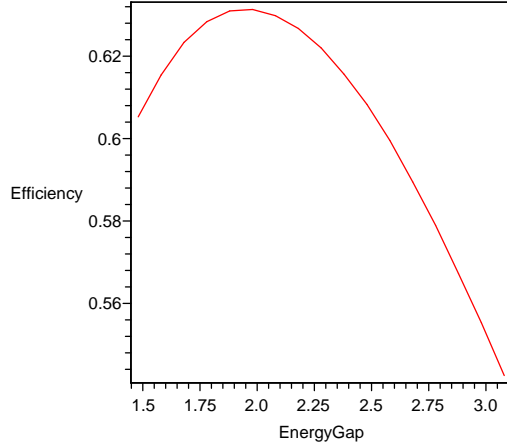
Figure 6: Limiting efficiency of 3-band solar cell (in eV) at full concentration. $T_s = 6000K$ and $T_a = 300K$

the current generated from those electrons excited from the valence to the conduction band, while the second part is the current generated from those electrons excited from the intermediate to conduction band. However because there is no current extracted from the intermediate band, we have to balance the flux and satisfy the equation

$$\dot{N}(E_C, E_g, T_s, 0) - \dot{N}(E_C, E_g, T_a, \mu_{CI}) = \dot{N}(E_I, E_C, T_s, 0) - \dot{N}(E_I, E_C, T_a, \mu_{IV}). \quad (15)$$

In order to solve the above equation, the relationship between μ_{CI} and μ_{IV} has to be determined. This can be seen from figure (4)

$$qV = \mu_{CV} = \mu_{CI} + \mu_{IV}. \quad (16)$$

Using the two equations (17) and (18), all the chemical potentials can be solved.

The maximum efficiency can be determined by selecting an energy gap, E_g, and scan through values of E_C that maximize the power. Remember that for each specific set of energy configurations, the constraint equations have to be solved to find the chemical potentials. This was done and the code can be found in the appendix. Figure (6) shows the results with the energy gap (eV) and efficiency. The maximum efficiency of the intermediate band is around 63.1% and this occurs when $E_g = 1.94$, $E_C = 1.23$, and $E_I = 0.71$. The intermediate band cell presents a higher efficiency then the normal single juntion cell.

6 Flux Integral

The flux integral, equation (12), is an important role in solving for the limiting efficiency of solar cells using the approach outlined in the previous sections. Therefore, some discussion is appropriate in order to get real results. This integral is part of a class of integrals called

Bose-Einstein integrals that are seen throughout physics. Therefore much effort has been taken in studying the properties and solutions. In this case, only solutions are desired. The general form is the following,

$$g_v(\eta) = \frac{1}{\Gamma(v+1)} \int_0^\infty \frac{E^v dE}{e^{E-\eta} - 1} \tag{17}$$

and $\Gamma(v)$ is the gamma function. Now it may be shown that $g_v(\eta)$ (when $\eta < 0$) can be turned into [8–10]

$$g_v(\eta) = \sum_{r=1}^\infty \frac{e^{r\eta}}{r^{v+1}}. \tag{18}$$

This series can be evaluated by using only a finite number of terms and bounding the error [5].

$$g_v(\eta) = \sum_{r=1}^{m-1} \frac{e^{r\eta}}{r^{v+1}} + \Delta \tag{19}$$

$$\Delta = \frac{e^{m\eta}}{m^{v+1}[1 - (\frac{m}{m+1})^{v+1}e^\eta]} \tag{20}$$

In the present analysis, the flux integral has finite limits so this integral expansion is incomplete. Using a similiar expansion, the integral

$$I_v(\eta, \epsilon) = \frac{1}{\Gamma(v+1)} \int_\epsilon^\infty \frac{E^v dE}{e^{E-\eta} - 1} \tag{21}$$

can be turned into

$$I_v(\eta, \epsilon) = \sum_{r=1}^\infty \frac{e^{r(\eta-\epsilon)}}{\Gamma(v+1)} \left(\frac{\epsilon^v}{r} + \frac{v\epsilon^{v-1}}{r^2} + \frac{v(v-1)\epsilon^{v-2}}{r^3} + \dots \right) \tag{22}$$

Noticing that there are finite number of terms it is compactly put into the form

$$I_v(\eta, \epsilon) = \sum_{k=0}^v \frac{\epsilon^{v-k} g_k(\eta - \epsilon)}{(v-k)!}. \tag{23}$$

where, $g_k(\eta - \epsilon)$ is equation (20). If both limits are finite, as is the case with some of the integrals evaluated, then this summation can be extented to the following form,

$$I_v(\eta, \epsilon_1, \epsilon_2) = \sum_l^2 \sum_{k=0}^v (-1)^{l+1} \frac{\epsilon_l^{v-k} g_k(\eta - \epsilon_l)}{(v-k)!}. \tag{24}$$

These approximations to the integrals can be implemented in code with minimal difficulty. For example, to evaluate equation (14) we need to get the integral into a form similiar to equation (23). This is done with the substitution $x = E/k_B T_a$ and $\eta = qV/k_B T_a$.

$$\dot{N}(E_g, \infty, T_a, qV) = \frac{2\pi(kT_a)^3}{h^3 c^2} \int_{E/kT_a}^\infty \frac{x^2 dx}{e^{x-\eta} - 1}$$
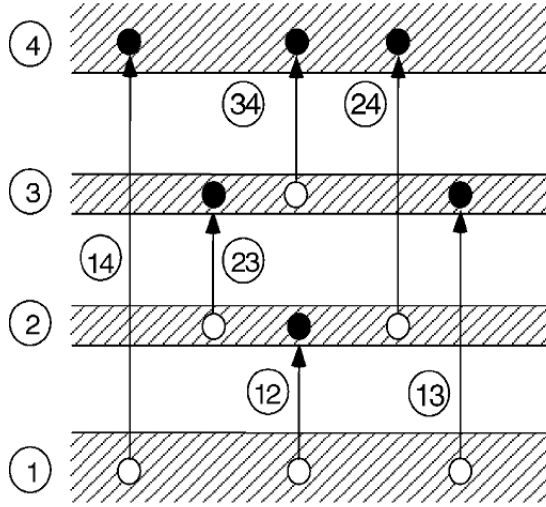
Figure 7: 4-Band Diagram

It turns into

$$\dot{N}(E_g, \infty, T_a, qV) = \frac{2\pi(kT_a)^3}{h^3 c^2} \cdot \Gamma(3) \cdot I_2(qV/kT_a, E/kT_a) \tag{25}$$

and now this is in a form that can be utilized by a computer.

7 Finding Chemical Potentials

Before proceding with the analysis of the 4-band solar cell (2 intermediate bands), it is necessary to discuss the algorithm used to find the chemical potentials. Since the intermediate band is thermally isolated, the flux into the band has to equal the flux out of the band. This was a constraint equation introduced in the analysis of the 3-band solar cell. Combined with the other constraint, equation (18), all the chemical potentials can be found for every band configuration.

In the computer code, equation (18) is substituted into the constraint equation involving the flux. However, this isn't your typical equation that can be solved algebraically since it involves many terms from the summation and exponentials involving the chemical potentials. Therefore, all the terms are put on one side of the equation so that it becomes a root finding exercise using one dimensional numerical techniques. Newton, bisection, or secant methods are all appropriate to use.

8 4-Band Analysis

In the 4-band solar cell, there are two intermediate bands in between the energy gap instead of one as in the 3-band system. Figure 7 shows the band set up with the electronic

transitions (reverse transitions do occur but not shown) and for simplicity each band is labeled with a number. The conduction band is number 4, valence band is number 1, and the two intermediate bands are 2 and 3. A similiar analysis is used with the same assumptions [11], but the difference being there are more variables and more equations to solve.

In the 3-band analysis there were three types of absorbtions that could occur. They were $E_I < E < E_C$, $E_C < E < E_g$, and $E > E_g$ with E being the photon energy. If there are N-bands, it can be shown that there will be $N \cdot (N-1)/2$ absorbtions. Using this, a 4-band system will have 6 types of absorbtions (shown in figure (4)). With these come more constraint conditions:

1. The current entering band 2 must equal the current leaving band 2 ($J_{12} = J_{23} + J_{24}$) and the current entering band 3 must equal the current leaving band 3 ($J_{23} + J_{13} = J_{34}$). This is due to the fact that no current is extracted from the intermediate levels.

2. The quasi-Fermi level μ_{13} must equal the sum of the quasi-Fermi levels $\mu_{12} + \mu_{23}$. The quasi-Fermi level μ_{24} must equal the sum of the quasi-Fermi levels $\mu_{23} + \mu_{34}$. Finally and as before, the quasi-Fermi level $\mu_{14} = qV$ must equal the sum of the quasi-Fermi levels $\mu_{12} + \mu_{23} + \mu_{34}$.

The same general approach to find all the chemical potentials (total of 6) is used except this time a two dimensional numerical root finding algorithm is needed. Newton's method is appropriate as it can be extended in multiple dimensions.

8.1 Newton's Method in One-Dimension

The idea of the method in one-dimension is to find the local tangent line for the function $y = f(x)$ and use the zero of this line ($y(x) = 0$) as the next approximation to the zero of the function [12]. Mathematically the tangent line is

$$y(x) = f(x_i) + f_x(x_i)(x - x_i)$$

where $f_x(x_i)$ is the derivative of the function evaluated at the guess x_i. Substituting $y(x) = 0$ will give the next iteration.

$$x_{i+1} = x_i - \frac{f(x_i)}{f_x(x_i)} \tag{26}$$

If the derivative cannot be analytically determined (as in our case) it can be done numerically.

$$f_x(x_i) = \frac{f(x_i + \delta) - f(x_i)}{\delta} \tag{27}$$

8.2 Newton's Method in Multi-Dimensions

This is easy to extend in multi-dimensions, x coordinate is replaced by the vector $\mathbf{x} = (x_1, x_2, \ldots, x_n)$, the guess x_i is replaced by the vector $\mathbf{x}_i = (x_{1i}, x_{2i}, \ldots, x_{ni})$, the function f is repaced by the vector $\mathbf{f} = (f_1, f_2, \ldots, f_n)$, and the derivative f_x is replaced by $\nabla = (\frac{\partial}{\partial x_1}, \frac{\partial}{\partial x_2}, \ldots, \frac{\partial}{\partial x_n})$. In two-dimensions, using the coordinates x and y for simplicity, we get two simultaneous equations

$$f_1(x_i, y_i) + \frac{\partial f_1(x_i, y_i)}{\partial x}(x - x_i) + \frac{\partial f_1(x_i, y_i)}{\partial y}(y - y_i) = 0$$

$$f_2(x_i, y_i) + \frac{\partial f_2(x_i, y_i)}{\partial x}(x - x_i) + \frac{\partial f_2(x_i, y_i)}{\partial y}(y - y_i) = 0$$

and they can be solved using Cramers rule.

$$\begin{bmatrix} \frac{\partial f_1(x_i,y_i)}{\partial x} & \frac{\partial f_1(x_i,y_i)}{\partial y} \\ \frac{\partial f_2(x_i,y_i)}{\partial x} & \frac{\partial f_2(x_i,y_i)}{\partial y} \end{bmatrix} \cdot \begin{bmatrix} x - x_i \\ y - y_i \end{bmatrix} = \begin{bmatrix} -f_1(x_i, y_i) \\ -f_2(x_i, y_i) \end{bmatrix}$$

$$x - x_i = \frac{f_2 \frac{\partial f_1}{\partial y} - f_1 \frac{\partial f_2}{\partial y}}{\frac{\partial f_1}{\partial x} \cdot \frac{\partial f_2}{\partial y} - \frac{\partial f_1}{\partial y} \cdot \frac{\partial f_2}{\partial x}} \tag{28}$$

$$y - y_i = \frac{f_1 \frac{\partial f_2}{\partial x} - f_2 \frac{\partial f_1}{\partial x}}{\frac{\partial f_1}{\partial x} \cdot \frac{\partial f_2}{\partial y} - \frac{\partial f_1}{\partial y} \cdot \frac{\partial f_2}{\partial x}} \tag{29}$$

$$x_{i+1} = x_i + (x - x_i) \tag{30}$$

$$y_{i+1} = y_i + (y - y_i) \tag{31}$$

These equations were implemented into the code to find all the chemical potentials for each specific energy band configuration.

8.3 Results

The maximum efficiency can be determined by selecting the energy gap, E_g, and scan through the various energy band configurations that maximize the power. As before, for each energy band configuration the chemical potentials were determined from Newton's method in two dimensions. The maximum efficiency for the two intermediate bands was determined to be 74.4%. This occurs when the band configuration is $E_g = 2.48$, $E_{34} = 1.00$, $E_{23} = 0.91$, and $E_{12} = 0.57$.

9 Future Work

It was shown that introducing one and two intermediate bands will increase the maximum efficiency of a single junction solar cell. Now with the general outline, we can try to extrapolate the absolute maximum efficiency for the N-band approach as N$\to \infty$. This will put a ceiling on the approach and a comparison can be made to limiting efficiencies of other solar designs.

One of the main assumptions in the solar cell device is that only radiative recombination is present, however no mention was made if this was ever possible. If non-radiative recombination (Shockley-Read-Hall, multi-step, etc.) is taken into account, it would be interesting to see how the efficiency would be effected or what kind of recombination would dominate.

The main goal of calculating theorical efficiencies is to show the potential a particular design might possess. However, if the design cannot be put into practice then it is only an idea. In the analysis shown in this paper, no mention is made of how an intermediate band could be introduced in the semiconductor. The current research aiming to put this idea into practice involves three approaches [13]; (1) the direct synthesis of a material with an intermediate band, (2) the so-called highly nanoporous materials approach, and (3) implementation using quantum dots. It would be extremely beneficial to determine which one of these methods (or any) present the most promise by determining a 'real' efficiency for each one.

Appendix A

Derivation of Quasi-Equilibrium Occupation Function for Photons

$$
\begin{aligned}
n &= \frac{f_c(1 - f_v)}{f_v - f_c} \\
f_c(1 - f_c) &= \frac{e^{E_v - E_{F_p}/k_B T}}{(e^{E_c - E_{F_n}/k_B T} + 1)(e^{E_v - E_{F_p}/k_B T} + 1)} \\
f_v - f_c &= \frac{e^{E_c - E_{F_n}/k_B T} - e^{E_v - E_{F_p}/k_B T}}{(e^{E_c - E_{F_n}/k_B T} + 1)(e^{E_v - E_{F_p}/k_B T} + 1)} \\
\frac{f_c(1 - f_v)}{f_v - f_c} &= \frac{e^{E_v - E_{F_p}/k_B T}}{e^{E_c - E_{F_n}/k_B T} - e^{E_v - E_{F_p}/k_B T}} \\
&= \frac{1}{e^{E - \mu/k_B T} - 1} \\
E &= E_c - E_v \\
\mu &= E_{F_n} - E_{F_p}
\end{aligned}
$$

Appendix B

Programs for calculating maximum efficiency for 3 and 4 band solar cells (in ANSI C)

References

[1] C.A. Moyer R.A. Serway, C.J. Moses. *Modern Physics*. Thomson Learning, Singapore, 1997.

[2] Jenny Nelson. *The Physics of Solar Cells*. Imperial College Press, London, 2003.

[3] A. Luque and A. Marti. Increasing the efficiency of ideal solar cells by photon induced transitions at intermediate levels. *Physical Review Letters*, 78(26), 1997.

[4] H.J. Weber G.B. Arfken. *Mathematical Methods for Physicists*. Harcourt, San Diego, 2001.

[5] Martin A. Green. *Third Generation Photovoltaics*. Springer, New York, 2006.

[6] L.E. Ballentine. *Quantum Mechanics: A Modern Development*. World Scientific, Singapore, 1998.

[7] W. Shockley and H.J. Queisser. Detailed balance limit of efficiency of p-n junction solar cells. *Journal of Applied Physics*, 32(3), 1961.

[8] J. McDougall and E.C. Stoner. The computation of fermi-dirac functions. *Phil. Trans. Roy. Soc. Lond.*, A.237(67), 1938.

[9] J.S. Blakemore. Approximations for fermi-dirac integrals, especially the function $F_{1/2}(\eta)$ used to describe electron density in a semiconductor. *Solid-State Electronics*, 25(11), 1982.

[10] R.F. Tooper E.W. Ng, C.J. Devine. Chebyshev polynomial expansion of bose-einstein functions of orders 1 to 10. *Mathematics of Computation*, 23(107), 1969.

[11] R.P. Corkish A.S. Brown, M.A. Green. Limiting efficiency for a muli-band solar cell containing three and four bands. *Physica E*, 14, 2002.

[12] R.W. Hamming. *Numerical Methods for Scientists and Engineers*. Dover, New York, 1962.

[13] A. Luque L. Cuadra, A. Marti. Present status of intermediate band solar cell research. *Thin Solid Films*, 451-452, 2004.