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Renewable Energy by Solar Cells with Intermediate Bands for Non-linear Solar Energy

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Abstract
An innovative method on solar energy is further studied and investigated by using intermediate bands within the energy gap of the semiconductor, in order to increase the efficiency of solar cells. Thus, the photons with energy less than the band gap could contribute to the output device by using the intermediate band or bands, in order to jump to the conduction band. Such a problem is reduced to the solution of a non-linear integral equation and for its solution a new and groundbreaking numerical method is proposed. Generally, in solar cells low energy photons can not excite electrons to the conduction band and then to the external circuit. Hence, intermediate bands get advantage of the lower energy photons by allowing the electrons to be promoted to levels in the usually forbidden energy gap. So, through the proposed multi-step approach, then the efficiency of the solar cell is increasing. By the current investigation we will show that the maximum efficiency of an ideal solar cell containing one and two intermediate bands will be 63 % and 75 %, respectively.

Key Word and Phrases
Solar Cells, Non-linear Integral Equation, Semiconductor, Intermediate Bands, Conduction Band, Valence Band, Electrons, Photons.

1. Introduction

Solar energy is produced when in the solar core of the sun thermonuclear fusion reactions occur unceasingly at millions of degrees and then they release huge quantities of energy in the form of electromagnetic radiations. Thus, some part of this solar energy reaches the outer area of the Earth's atmosphere with an average irradiance (solar constant) of about 1367 W/m^2, which varies as a function of the Earth-to-Sun distance and the solar activity. Moreover, by solar irradiance is meant the intensity of the solar electromagnetic radiation incident on a surface of one square meter [kW/m2]. This intensity is equal to the integral of the power associated to each value of the frequency of the solar radiation spectrum. So, when passing through the atmosphere, the solar radiation diminishes in intensity because it is partially reflected and absorbed. The radiation which passes through is partially diffused by the air and by the solid particles suspended in the air.

Consequently, when the sunlight is absorbed in the solar cell, depending on the material, then electrons can excite to higher energy levels and in this case they can move freely. In addition, the extreme case is when the electron can completely escape the surface of the metal after absorbing blue or ultraviolet light, known as the photoelectric effect. In the semiconductor, which has a band gap usually ranging between 0.5 eV to 3.0 eV, an electron can be promoted to the conduction band if the absorbed photon has an energy greater than the band gap. After following the above procedure, the excited electron will decay very quickly, at some picoseconds, to the lowest available energy state in the conduction band due to the abundance of empty levels. This physical phenomenon is called thermalization and happens through collisions with the lattice, giving up kinetic energy to produce photons during the decay.

In a much slower process, the electron will further decay across the band gap to a vacant site in the valence band. Then the solar cell takes 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, then the extra energy is a potential difference and this allows electrical work to be done.

On the other hand, a big problem occurring in solar cells is that low energy photons cannot excite electrons to the conduction band and then to the external electrical circuit. By using therefore intermediate bands in the solar cells, then these take advantage of the lower energy photons by allowing the electrons to be promoted to levels in the normally forbidden energy gap. Hence, by using the above muli-step approach, then the efficiency of the solar cells is increased too much. By the present research it will be shown that the maximum efficiency of a solar cell using one or two intermediate bands is much greater than the single solar cell.

Over the past years, several scientists have studied solar cells with intermediate bands, by using several methods. Among them the following publications will be mentioned: A. Luque and A. Marti [1], M.A. Green [2] - [4], R.P. Corkish, A.S. Brown and M.A. Green [5], J. Nelson [6], A. Luque, L. Cuadra L. and A. Marti [7], J. McDougall.and E.C. Stoner [8], J.S. Blakemore [9] and R.F. Tooper, E.W. Ng and C.J. Devine [10]. Besides, in order an intermediate band to be introduced in the semiconductor, three different ways can be used: (a) the direct synthesis of a material with an intermediate band, (b) the highly nanoporous materials approach, and (c) implementation using quantum dots. Only an experimental approach could show which of the above three methods would be ideal for using the intermediate band and increasing the efficiency of the solar cell.

By the present research, the problem by using intermediate bands in a solar cell, in order to increase its efficiency, will be reduced to the solution of non-linear integral equations. Thus, for the numerical solution of the above non-linear integral equations a special numerical method will be used.

Hence, the non-linear singular integral equations methods which were introduced by E.G.Ladopoulos [11] - [27] and were used successfully during the past years for the solution of several engineering problems of fluid mechanics, hydraulics, aerodynamics, solid mechanics, potential flows, petroleum engineering and structural analysis, are further extended by the present investigation for the solution of solar energy problems.

2. Modern Improvements of Energy and Photon Fluxes

Only a portion of sun's radiation is received by the earth, as 25 % is reflected by the atmosphere, 18 % is diffused by the atmosphere and finally 5 % is absorbed again by the atmosphere. Furthermore, 5 % of sun's radiation is reflected by the ground and 27 % is absorbed by the soil surface. So, a solar cell is receiving only a part of the sun's radiation.

As an introduction to the energy and photon fluxes analysis, consider the segment *dS* of a black body surface emitting radiation, with *dΩ* an element of solid angle around the direction of emission. Then, the solid angle can be given by the following relation:

$$d\Omega = \frac{dS}{r^2} = \sin\theta \, d\theta \, d\varphi \tag{2.1}$$

In addition, for the determination of sun's radiation as seen from earth, then the method which follows can be used. In general, consider planar symmetry and then the radiation is determined along the normal *n* to the surface.

Consequently, the angular dependence is calculated by integrating over the angular ranges θ and φ, as follows:

$$R\int_{\varphi_1}^{\varphi_2}\int_{\theta_1}^{\theta_2} \cos\theta \sin\theta d\theta d\varphi = R\left(\frac{\sin^2\theta_2 - \sin^2\theta_1}{2}\right)(\varphi_2 - \varphi_1) \tag{2.2}$$

where R denotes the radiation independent of angular ranges. For example the radiation passing through a hemisphere is equal to πR, by replacing $\theta_2 = \pi/2, \theta_1 = 0, \varphi_2 = 2\pi$ and $\varphi_1 = 0$ in eqn (2.2). Usually, φ ranges from 0 to 2π and $\theta_1 = 0$, which reduces (2.2) to $\sin^2\theta_2 \pi R$.

Normally, in order to calculate efficiencies in solar cells, it is preferred to work with fluxes. In addition, in a black body cavity the radiation is isotropic and moves with a velocity *c*. Then, photons $d\Omega/4\pi$ are moving in any direction within an element of solid angle $d\Omega$.

By considering further a hole of area dS and assuming that the hemisphere penetrates the black body cavity at a finite thickness *dr*, then the area dS has a solid angle $\cos\theta\, dA/r^2$ from the volume $r^2 \sin\theta\, d\theta\, d\varphi\, dr$. Hence, the total amount of energy arriving per unit area and per unit time is as following:

$$\int_{\varphi_1}^{\varphi_2}\int_{\theta_1}^{\theta_2} c\rho_\varepsilon \cos\theta \sin\frac{\theta d\theta d\varphi}{4\pi} = \frac{c\rho_e}{4\pi}\left(\frac{\sin^2\theta_2 - \sin^2\theta_1}{2}\right)(\varphi_2 - \varphi_1) \tag{2.3}$$

where ρ_ε denotes the energy density as given by the radiation law of Planck:

$$\rho_\varepsilon = \frac{8\pi\varepsilon^2}{h^3 c^3}\frac{\varepsilon}{e^{\varepsilon/kT} - 1} \tag{2.4}$$

in which c is the speed of light, ε photon's energy, h Planck's constant, T the temperature and k Boltzmann's constant.

So, by assuming, as before, that φ ranges from 0 to 2π and $\theta_1 = 0$, then (2.3) reduces to $\sin^2\theta_2 \frac{c\rho_e}{4}$. By following further a similar method, then the photon (particle) density n_e can be converted to photon flux, by replacing ρ_e with n_e.

The photon flux and the energy flux over the energy range E_1 and E_2 can be given by the following relations, respectively:

$$\dot{N} = \frac{2\pi \sin^2\theta_2}{h^3 c^2}\int_{E_1}^{E_2}\frac{E^2}{e^{E/kT} - 1}dE \tag{2.5}$$

and:

$$\dot{E} = \frac{2\pi \sin^2\theta_2}{h^3 c^2}\int_{E_1}^{E_2}\frac{E^3}{e^{E/kT} - 1}dE \tag{2.6}$$

As the energy flux is power per unit area, then the power density will be used. Hence, the efficiency of a solar cell can be calculated by using the ratio of the power output by the cell, to the power density received by the cell.

Then, from (2.6) follows that the power density from a black body is equal to :

$$\dot{E} = \sigma_S \sin^2\theta_2 T^4 \tag{2.7}$$

with σ_S Stefan's constant:

$$\sigma_S = \frac{2\pi^5 k^4}{15 h^3 c^2} \tag{2.8}$$

At the surface of the earth's atmosphere follows that the power density is equal to 1353 W/m^2. The next step is the determination of the power output from the solar cell.

Thus, the power density *P* which is delivered by an electric circuit is equal to:

$$P = J \cdot V \tag{2.9}$$

where J denotes the current density at a certain voltage *V*. Then, the main problem is to find the current density at a certain voltage *V*, which can deliver the maximum power.

The generalized form of a photon flux for a black body, is given by the following non-linear integral equation:

$$\dot{N}(E_1, E_2, T, \mu) = \frac{2\pi}{h^3 c^2} \int_{E_1}^{E_2} \frac{E^2}{e^{(E-\mu)/kT} - 1} dE \tag{2.10}$$

in which μ denotes the chemical potential of radiation :

$$\mu = qV \tag{2.11}$$

with q the magnitude of the charge of an electron.

Furthermore, (2.10) will be used in order to determine the current density because of the incoming and outgoing photon fluxes between the energy levels E_1 and E_2. In general, all the photons with energy greater than energy gap E_g are absorbed in the cell and will create an electron-hole. Also, all the photons with energy less than the energy gap are not absorbed in the cell. So, the absorbed photon flux in the cell will be equal to the excited electrons in the conduction band. Such an absorbed photon flux is denoted by $\dot{N}(E_g, \infty, T_{sun}, 0)$, with T_{sun} the temperature of the sun.

On the other hand, some of the photons will be emitted from the solar cell and thus electrons will recombine with some holes in the valence band. The above electrons will not contribute to the current. In addition, the power of the emitted photons will be equal to $\dot{N}(E_g, \infty, T_{cell}, \mu)$. Then, the net electrons (absorbed photons minus emitted photons) will be used to the external electrical circuit, in order electricity to be produced.

Consequently, the current density produced by the solar cell can be given as follows :

$$J = q\left[\dot{N}(E_g, \infty, T_{sun}, 0) - \dot{N}(E_g, \infty, T_{cell}, qV\right] \tag{2.12}$$

and the output power density is equal to:

$$P(E_g, V) = qV\left[\dot{N}(E_g, \infty, T_{sun}, 0) - \dot{N}(E_g, \infty, T_{cell}, qV\right] \tag{2.13}$$

from which finally follows that the output power density is a function of E_g and *V*.

3. Modern Improvements for Three Band Solar Cell

In order the efficiency of a solar cell to be increased, then some of the low energy photons should be absorbed and used in the above cell. Hence, in order such an action to be effected, then an intermediate band should be included between the forbidden band gap, to give a total number of three bands in the semiconductor. The new solar cell should therefore have a valence band (VB), a conduction band (CB) and the new intermediate band (IB).

Transitions can occur between the valence and conduction bands, the valence and intermediate bands and the intermediate and conduction bands. Additionally, let us consider that each band has constant quasi-Fermi levels $\varepsilon_{FV}, \varepsilon_{FIn,} \varepsilon_{FC}$ [1]. Then, the same method will be followed as for the two band solar cell analysis, as described in the previous section.

Hence, the current density produced by the three band solar cell can be given as follows:

$$J = q\left[\dot{N}(E_g, \infty, T_{sun}, 0) - \dot{N}(E_g, \infty, T_{cell}, qV\right] + q\left[\dot{N}(E_C, E_g, T_{sun}, 0) - \dot{N}(E_C, E_g, T_{cell}, \mu_{CIn}\right]$$

$$E_g = E_C - E_V$$

$$\mu_{CV} = \varepsilon_{FC} - \varepsilon_{FV} \tag{3.1}$$

$$\mu_{CIn} = \varepsilon_{FC} - \varepsilon_{FIn}$$

$$\mu_{InV} = \varepsilon_{FIn} - \varepsilon_{FV}$$

where E_C and E_V denote the energy in the conduction and valence band, respectively.

Moreover, the chemical potential of radiation between the valence and the conduction bands is equal to:

$$\mu_{CV} = qV \tag{3.2}$$

and also μ_{CV} can be given by the formula:

$$\mu_{CV} = \mu_{CIn} + \mu_{InV} \tag{3.3}$$

From (3.1) it can be seen that the total current is the sum of the current generated from the electrons which are excited from the valence to the conduction band and the current generated from the electrons excited from the intermediate to the conduction band.

On the contrary, as there is no current extracted from the intermediate band, then the flux has to be balanced and so the following relation should be satisfied:

$$\begin{aligned} &\dot{N}(E_C, E_g, T_{sun}, 0) - \dot{N}(E_C, E_g, T_{cell}, \mu_{CIn}) = \\ &\dot{N}(E_{In}, E_C, T_{sun}, 0) - \dot{N}(E_{In}, E_C, T_{cell}, \mu_{InV}) \end{aligned} \tag{3.4}$$

By using therefore eqs (3.1) to (3.3), then the maximum efficiency can be calculated, by selecting an energy gap E_g, and then check through values of E_C in order the power to be maximized..

4. Modern Improvements for Four Band Solar Cell

The efficiency of a solar cell can be further increased. So, a four band cell could be used, by putting two intermediate bands between the energy gap, instead of one, as in the previous studied case of a three band cell. The new solar cell should have therefore a valence band (VB), a conduction band (CB) and the two new intermediate bands (IB1 and IB2).

Thus, transitions can occur between the valence and conduction bands, the valence and intermediate bands and the intermediate and conduction bands. Furthermore, consider that each band has constant quasi-Fermi levels $\varepsilon_{FV}, \varepsilon_{FIn1}, \varepsilon_{FIn2}, \varepsilon_{FC}$ [1]. Then, the same method will be followed as for the three band solar cell analysis, as described in the previous section.

The current density produced by the four band solar cell is equal to:

$$J = q\left[\dot{N}(E_g, \infty, T_{sun}, 0) - \dot{N}(E_g, \infty, T_{cell}, qV)\right] + q\left[\dot{N}(E_C, E_g, T_{sun}, 0) - \dot{N}(E_C, E_g, T_{cell}, \mu_{CIn1}\right] + \\ + q\left[\dot{N}(E_C, E_g, T_{sun}, 0) - \dot{N}(E_C, E_g, T_{cell}, \mu_{CIn2})\right]$$

$$E_g = E_C - E_V$$

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

$$\mu_{CIn\,1} = \varepsilon_{FC} - \varepsilon_{FIn\,1}$$

$$\mu_{CIn\,2} = \varepsilon_{FC} - \varepsilon_{FIn\,2}$$

$$\mu_{In\,1V} = \varepsilon_{FIn\,1} - \varepsilon_{FV}$$

$$\mu_{In\,2V} = \varepsilon_{FIn\,2} - \varepsilon_{FV}$$

$$\mu_{In\,1In\,2} = \varepsilon_{FI\,n\,1} - \varepsilon_{FIn\,2}$$

(4.1)

where E_C and E_V denote the energy in the conduction and valence band, respectively.

The chemical potential of radiation between the valence and the conduction bands is equal to:

$$\mu_{CV} = qV \tag{4.2}$$

and μ_{CV} can be further given by the relation:

$$\mu_{CV} = \mu_{CIn2} + \mu_{In2In1} + \mu_{In1V} \tag{4.3}$$

Beyond the above, following relations should exist:

$$\begin{aligned} \mu_{VIn2} &= \mu_{VIn1} + \mu_{In1In2} \\ \mu_{In1C} &= \mu_{In1In2} + \mu_{In2C} \end{aligned} \tag{4.4}$$

Thus, as could be seen from (4.1), the total current is the sum of the current generated from the electrons which are excited from the valence to the conduction band and the current generated from the electrons excited from the two intermediate bands to the conduction band.

On the other hand, as there is no current extracted from the two intermediate bands, then the current entering band 1 must be equal to the current leaving band ($J_{VIn1} = J_{In1In2} + J_{In1C}$) and the current entering band 2 must be equal to the current leaving band ($J_{In2C} = J_{In1In2} + J_{VIn2}$).

5. Numerical Calculation of the Non-linear Flux Integral Equation

For the numerical calculation of the non-linear flux integral equation, a special method will be used. This numerical method will be based on the Bose-Einstein integrals.

Thus, consider the following integral equation:

$$f_u(y) = \frac{1}{\Gamma(u+1)} \int_0^{\infty} \frac{F^u dF}{e^{F-y} - 1} \tag{5.1}$$

where $\Gamma(u)$ denotes the gamma function.

Then, we will show that when $y<0$, eqn (5.1) can be approximated by the relation:

$$f_u(y) = \sum_{r=1}^{\infty} \frac{e^{ry}}{r^{u+1}} \tag{5.2}$$

The above series can be calculated by using only a finite number of terms and bounding the error: [4]

$$f_u(y) = \sum_{r=1}^{m-1} \frac{e^{ry}}{r^{u+1}} + \Delta \tag{5.3}$$

$$\Delta = \frac{e^{my}}{m^{y+1}\left[1 - (\frac{m}{m+1})^{u+1} e^{y}\right]} \tag{5.4}$$

In addition, by using a similar method, then the integral equation:

$$G_u(y,\varepsilon) = \frac{1}{\Gamma(u+1)} \int_{\varepsilon}^{\infty} \frac{F^u dF}{e^{F-y} - 1} \tag{5.5}$$

can be approximated by the function:

$$G_u(y,\varepsilon)=\sum_{r=1}^{\infty}\frac{e^{r(y-\varepsilon)}}{\Gamma(u+1)}\left(\frac{\varepsilon^u}{r}+\frac{u\varepsilon^{u-1}}{r^2}+\frac{u(u-1)\varepsilon^{u-2}}{r^3}+..........\right) \tag{5.6}$$

Furthermore, eqn (5.5) can be written as following:

$$G_u(y,\varepsilon)=\sum_{k=0}^{u}\frac{\varepsilon^{u-k}f_k(y-\varepsilon)}{(u-k)!} \tag{5.7}$$

where $f_k(y-\varepsilon)$ is given by (5.3).

On the contrary, if both limits are finite, which is the usual case of the integrals under study, then the above summation can be extended by the formula:

$$G_u(y,\varepsilon_1,\varepsilon_2)=\sum_{l}^{2}\sum_{k=0}^{u}(-1)^{l+1}\frac{\varepsilon_l^{u-k}f_k(y-\varepsilon_l)}{(u-k)!} \tag{5.8}$$

The above outlined numerical method will be used for the calculation of the integral equations used in two- three - and four - band solar cell analysis.

Thus, the application of the new numerical method to a two-band solar cell analysis, for $T_{sun}=6000^o K$ and $T_{cell}=300^o K$, shows that the maximum efficiency occurs when there is a band gap of 1.1 eV at about 40 % (Figure 1).

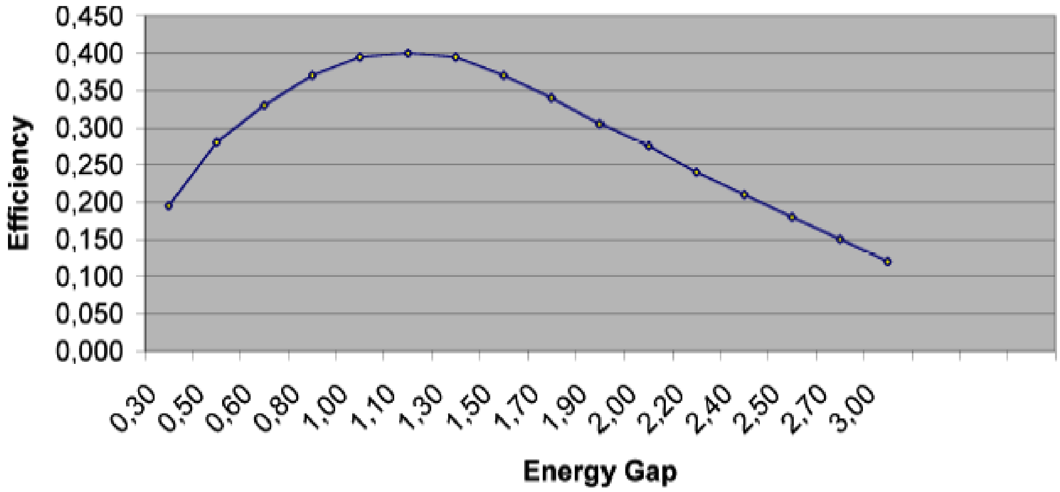

Fig. 1 Efficiency of a Single Solar Cell (in eV) at full concentration.

Additionally, the application of the new numerical method to a three-band solar cell analysis, shows that the maximum efficiency occurs when there is a band gap of 1.95 eV at around 63 % (Figure 2).

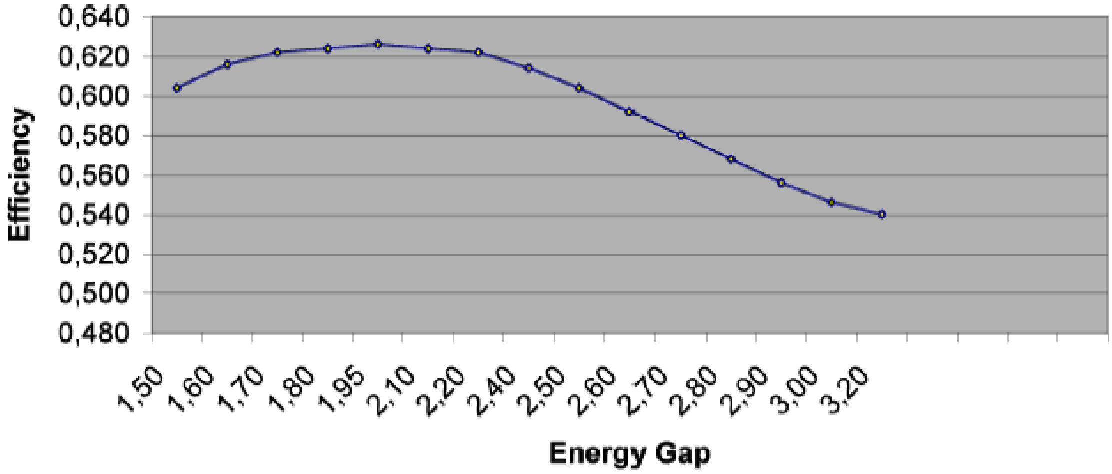

Fig. 2 Efficiency of a Three-Band Solar Cell (in eV) at full concentration.

Finally, for a four-band solar cell the maximum efficiency occurs for a band gap of 2.40 eV at around 75 %.

5. Conclusions

A leading technology has been further improved by using intermediate bands within the energy gap of the semiconductor in order to increase the efficiency of solar cells. Consequently, photons with energy less than the band gap can contribute to the output device by using the intermediate band or bands, in order to jump to the conduction band. Such a problem was reduced to the solution of *non-linear integral equations* and for their evaluation a special numerical method has been proposed.

Thus, it was shown, that for a three-band solar cell the efficiency is increased to 63 %, while for a four-band solar cell the efficiency is increased to 75 %. We propose for future research the investigation of the absolute maximum efficiency of a multi-band solar cell, for *n* bands. Consequently, a ceiling can be put to the determination of the maximum efficiency of a multi-band ideal solar cell. This will help the future plans of the international solar cells industry.

The proposed method was based on the idea, that in solar cells low energy photons can not excite electrons to the conduction band and then to the external circuit. So, the use of intermediate bands is giving advantage of the lower energy photons by allowing the electrons to be promoted to levels in the usually forbidden energy gap. As a result, through the above multi-step approach, then the efficiency of the solar cell is increasing.

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