

01 Nov 1983

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Recommended Citation

C. Wu and R. M. Williams, "Limiting Efficiencies for Multiple Energy-Gap Quantum Devices," *Journal of Applied Physics*, vol. 54, no. 11, pp. 6721-6724, American Institute of Physics (AIP), Nov 1983.

The definitive version is available at <https://doi.org/10.1063/1.331859>

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Limiting efficiencies for multiple energy-gap quantum devices

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(Received 26 April 1983; accepted for publication 1 July 1983)

We have used a thermodynamic model to calculate theoretical limiting efficiencies for simple and multiple-gap solar cells. The limiting efficiency is 26% for a simple solar cell of hydrogenated amorphous silicon, operating at one Sun sensitivity. For a multiple gap cell made from hydrogenated amorphous silicon, together with a second cell, made from a material with lower band gap, it is 38%. The optimum band gap for the second material is 1.0 eV.

PACS numbers: 84.60.Jt, 85.30. — z, 05.70. — a

INTRODUCTION

To a good approximation, solar radiation can be treated as blackbody radiation from a source having a temperature T_s around 6000 K. Solar cells convert this heat to work. Therefore, they are heat engines, and their maximum working efficiency is determined by thermodynamic limitations. For a general kind of heat engine, the efficiency depends only on the source and receiver temperatures. We will consider problems for which the solar energy receiver temperature T_R is 300 K. Solar cells are further limited because they are quantum devices, having a forbidden energy gap, $E_g = h\nu_0$. They cannot make use of photons for which $h\nu < E_g$. When $h\nu > h\nu_0$, they can use only the fraction, $(h\nu_0/h\nu)$ of the photon energy. Thermodynamic discussions of heat engines often make use of the concept of infinitely slow, reversible operation. This concept cannot be used, even in principle, to describe solar cells. When the device properties are introduced, there is a substantial loss, at the maximum power point, due to recombination.

We are interested in the theoretical upper limit for the efficiency of hydrogenated amorphous silicon solar cells, and for multiple gap cells in which amorphous silicon makes up one part. For a simple cell, earlier estimates of 15% and 17% have been made,^{1,2} based on analyses of device performance. Several earlier discussions of solar energy conversion efficiency made use of the thermodynamic approach.²⁻⁹ Some of these treated solar cells and others did not. Some used the incident flux $f_w(\nu)$ of free energy, and others used the incident flux $f_u(\nu)$ of energy. All models have used an integration over the solar spectrum of the function

$$\int_{E_g}^{\infty} (Z/h\nu) f_{w(u)}(\nu) d\nu. \quad (1)$$

Landsberg and Tonge⁴ treated systems with no energy gap ($E_g = 0$) so that $Z = h\nu$. Buoncristiani, Byvik, and Smith⁹ treated quantum systems, $Z = E_g$, and used free energy flux $f_w(\nu)$. They did not include recombination losses in their calculation. Henry⁸ has used $Z = E_g$ and used the energy flux $f_u(\nu)$. However, he includes recombination losses.

THERMODYNAMIC MODEL

For a heat engine that does not have the quantum limitation, the efficiency limit is normally the Carnot efficiency η_{CAR} which, for this case, is

$$\eta_{CAR} = 1 - (T_R/T_S). \quad (2)$$

A more careful analysis of the properties of a radiative source^{3,4} shows that the maximum efficiency η_{max} is

$$\eta_{max} = 1 - 4X/3 + X^4/3, \quad (3)$$

where $X = T_R/T_S$. For the temperatures assumed above, $\eta_{max} = 0.93$, as compared with 0.95 for the Carnot efficiency.

LIMITING EFFICIENCY OF A THRESHOLD DEVICE

We will follow the analysis of Ref. 9, which is convenient for taking account of the band gap and for treating multiple gap cells. We assume that there is an ideally sharp absorption threshold, such that all photons, for which $h\nu > h\nu_0$, are absorbed and contribute part of the energy to useful work. No photons for which $h\nu < h\nu_0$ are absorbed. For the absorbed photons, the maximum energy that can actually be converted to work is E_g .

The maximum work that can be done by a quantum device $f_w(\nu)$ is related to the flux of free energy into and out of the system. f_u and f'_u are the fluxes of energy into and out of the system, respectively. f_s and f'_s are the corresponding entropy fluxes. A loss term f'_s accounts for entropy generation within the system by processes such as carrier recombination.

$$f_w(\nu) = (f_u - T_R f_s) - (f'_u - T_R f'_s) - T_R f_s^i. \quad (4)$$

f_u and f_s represent the incoming radiation. They are the energy and entropy flux from a black-body source at the temperature of the sun and have the corresponding spectral distribution. The intensity corresponds to that at the earth's surface, not at the surface of the black body. Though the spectral distribution is determined by T_s , the solar energy receiver operates at T_R . Thus, it is T_R that appears in both the bracketed terms in Eq. (4). The terms enclosed by the second pair of brackets represent the black-body emission of the device operating at 300 K. For the time being we neglect the last term that gives the internal losses. This is needed for a proper discussion of solar cells and we will include it later.

The fraction $\Delta f_w(\nu)d\nu$ of work produced by the incoming radiation in the frequency range $d\nu$ is given by the function

$$\Delta f_w(\nu)d\nu = \frac{h\nu_0}{h\nu} f_w(\nu)d\nu. \quad (5)$$

The limiting efficiency $\eta(X, Y)$ is then

$$\eta(X, Y) = \frac{\int_{\nu_0}^{\infty} \Delta f_w(\nu) d\nu}{\int_0^{\infty} f_u(\nu) d\nu}. \quad (6)$$

Y is the threshold parameter, $Y = h\nu_0/kT_S$. The flux terms f_u and f_s can be evaluated from the Planck radiation law. Making the proper integrations, we can express Eq. (5) as

$$\eta(X, Y) = \frac{15}{\pi^4} Y \left[(1 - X)I_u(Y) + XI_F(Y) - X^3 I_F\left(\frac{Y}{X}\right) \right], \quad (7)$$

where

$$I_u(Y) = \sum_{n=1}^{\infty} \left(\frac{Y^2}{n} + \frac{2Y}{n^2} + \frac{2}{n^3} \right) e^{-nY} \quad (8)$$

and

$$I_F(Y) = -\frac{Y^2}{2} \ln(1 - e^{-Y}) - \frac{1}{2} \sum_{n=1}^{\infty} \left(\frac{Y^2}{n} + \frac{2Y}{n^2} + \frac{2}{n^3} \right) e^{-nY}. \quad (9)$$

Equation (7) was obtained in Ref. 9. Note that the temperature ratio $X = T_R/T_S$ is small since $T_S = 6000$ K and $T_R = 300$ K. The last term in Eq. (7) is negligible.

COMBINED EFFICIENCY FOR TWO DEVICES

Our main interest is to estimate the combined efficiency that can be achieved by adding a second solar cell, made from a material having a smaller band gap. We will first outline the formalism for this problem for a general threshold device, then introduce the modifications required to treat solar cells. We modify the above analysis by cutting off the integral at an upper energy equal to E_g for amorphous silicon. The integral then has a lower limit, $Y_i = h\nu_i/kT_S$, and an upper limit, $Y_f = h\nu_f/kT_S$. The efficiency $\eta(X, Y_i, Y_f)$ for a threshold device with both upper and lower cutoff energies is

$$\eta(X, Y_i, Y_f) = \eta(X, Y_i) - \frac{Y_i}{Y_f} \eta(X, Y_f). \quad (10)$$

The combined efficiency for the two devices together is then

$$\eta_i(X) = \eta(X, Y_i) = \left(1 - \frac{Y_i}{Y_f} \right) \eta(X, Y_f). \quad (11)$$

The maximum value of η_i is for $Y_i = Y_{i-\max}$ as determined by the condition

$$\left(\frac{\partial \eta_i(X, Y_i)}{\partial Y_i} \right)_{Y_{i-\max}} = 0. \quad (12)$$

INTERNAL LOSSES AND RADIATIVE RECOMBINATION

For a solar cell, we must take account of internal losses. The cell must operate under an internally generated forward bias. A forward current flows in the junction or barrier around which the cell is built. The magnitude of this current is determined by the rate of recombination of the carriers that produce the current. The slowest recombination mechanism is that due to radiative emission. The rate of this process determines the minimum loss. When the solar cell is at equilibrium in the dark, with the terminals shorted, there is a

very small recombination rate, just equal to the thermal generation rate for carriers. This is too small to be a significant loss. However, when the cell is operating, the number of free carriers in the junction is many orders of magnitude larger than the dark equilibrium number. The recombination rate is correspondingly higher, and is a significant limitation to the ultimate efficiency.

The rate of recombination depends strongly on the voltage V developed across the load. We can take account of the effect of radiative recombination by showing that photons having energies $h\nu > E_g$ do not contribute the quantity E_g to the work done by the device. Instead they contribute a smaller quantity W which we will discuss in detail.

For this discussion, it is convenient to reformulate the previous analysis so that we can express the solar cell efficiency using the number of "useful photons," $\tilde{N}(E_g)$, for which $h\nu > E_g$. We distinguish this from the total number $N(E_g)$ of photons for which $h\nu > E_g$. This distinction arises because it is the flux of free energy $f_w(\nu)$ rather than the flux of energy $f_u(\nu)$ that relates directly to the work that can be done by the device. $\tilde{N}(E_g)$ is given by

$$\tilde{N}(E_g) = \int_{E_g}^{\infty} \frac{f_w(\nu)}{h\nu} d\nu. \quad (13)$$

Using the Planck radiation formula, together with Eq. (2), we can rewrite Eq. (13) as

$$\tilde{N}(E_g) = A \left[(1 - X)I_u(Y) + XI_F(Y) - X^3 I_F\left(\frac{Y}{X}\right) \right], \quad (14)$$

where

$$A = 2\pi(kT_S)^3(R_S/R_0)^2/h^3c^2 \quad (15)$$

and R_S/R_0 is the ratio of the radius of the sun to that of the earth's orbit. Equation (14) is to be compared with the total number of photons $N(E_g)$ with $h\nu > E_g$, given by

$$N(E_g) = \int_{E_g}^{\infty} \frac{dN(\nu)}{d\nu} d\nu = A \cdot I_u(Y), \quad (16)$$

where $dN(\nu)/d\nu$ is the number of photons in the frequency range $d\nu$ at ν . The difference between $\tilde{N}(E_g)$ and $N(E_g)$ goes into the generation of heat or reradiated energy. This can be seen in Fig. 1. Equation (6) can then be rewritten as

$$\eta(X, Y) = E_g \cdot \tilde{N}(E_g) / \int_0^{\infty} N(E_g) dE_g. \quad (17)$$

We note that the denominator of Eq. (6) is

$$\int_0^{\infty} f_u(\nu) d\nu = \int_0^{\infty} N(E_g) dE_g. \quad (18)$$

The meaning of $\eta(X, Y)$ in Eq. (17) can be understood graphically by considering the I - V relationship. The denominator is the total area under plot of $eN(E_g)$ as a function of E_g/e , where e is the electron charge. The numerator is the rectangular area bounded by the current $I = e\tilde{N}(E_g)$ (A/cm²) and the voltage $V = E_g/e$ (V) of the I - V curve, as shown in the figure. In Ref. 8, an expression similar to Eq. (17) was used, except that $\tilde{N}(E_g)$ was replaced by $N(E_g)$. An energy difference was used, rather than a free energy difference. The difference is small except in the limit of a multigap cell made

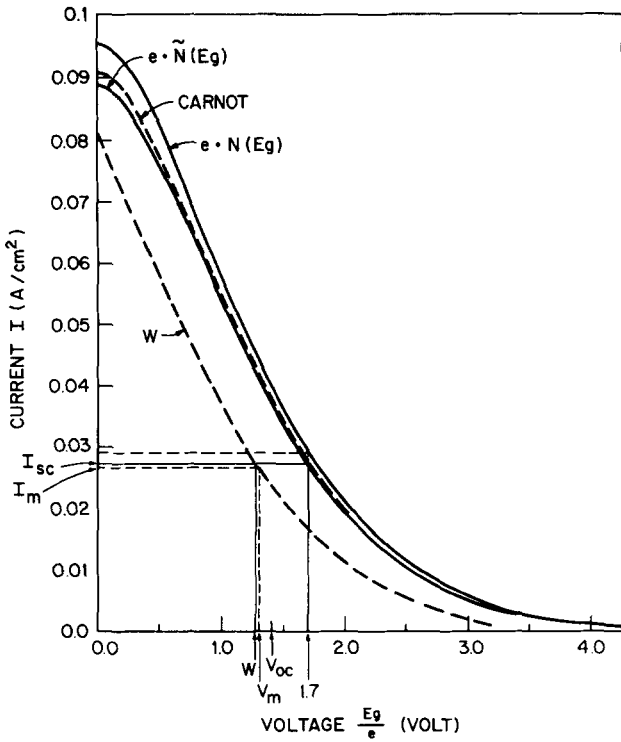


FIG. 1. Spectrum of solar photons. The curves represent the photon flux for an intensity of 1 Sun, expressed as a current density. $N(E_g)$ is the total flux of photons having energies $\geq E_g$ as a function of E_g . $\tilde{N}(E_g)$ shows the flux, cf. "useful photons," as defined by the thermodynamic analysis in the text. The curve labelled "Carnot" corresponds to the efficiency expression in Eq. (2). Curve W takes account of radiative recombination which can be expressed as a lower effective output per photon. The rectangular areas (solid lines) at the lower left express the output work of a solar cell with band gap $E_g = 1.7$ eV. The smaller solid rectangle ($I_{sc} \times W$) is with radiative recombination loss and the larger solid rectangle ($I_{sc} \times E_g$) is without the loss. The maximum power point (I_m, V_m) is indicated by the smaller dotted rectangle. The larger dotted rectangle (the horizontal line above I_{sc} and the vertical line at 1.7 eV) is the equivalent area used by Henry (Ref. 8) who used incident energy as compared to free energy (the large solid rectangle).

up of many individual components. In this case, use of the energy flux leads to a limiting efficiency of 100%, which is not physically correct.

From conventional device analysis⁸ the radiative recombination current density I_{rad} can be written

$$I_{rad} = B \cdot \exp[(eV - E_g)/kT_R], \quad (19)$$

where

$$B = e(n^2 + 1)/4\pi c^2 \text{ (A/cm}^2\text{)} \quad (20)$$

and n is the refractive index. The total current density I consists of three terms: $I_{ph} = e\tilde{N}(E_g)$, from the useful photons; I_{th} , the thermal radiation current; and I_{rad} as given by Eq. (19).

$$I(V) = I_{ph} + I_{th} - I_{rad}(V), \quad (21)$$

where I_{th} is obtained by setting $V = 0$ in Eq. (19). At the open circuit voltage, $I(V_{oc}) = 0$ so that

$$eV_{oc} = kT_R \ln[1 + e\tilde{N}(E_g)/I_{th}]. \quad (22)$$

The maximum power point (I_m, V_m) can be obtained by setting $d(IV)/dV = 0$.

$$eV_m = eV_{oc} - kT_R \ln(1 + eV_m/kT_R). \quad (23)$$

The maximum power is then

$$P_m = I_m V_m = eV_m \left(\frac{1 + I_{th}/e\tilde{N}(E_g)}{1 + kT_R/eV_m} \right) \tilde{N}(E_g). \quad (24)$$

By comparing Eq. (24) with the numerator of Eq. (17), where the useful power $P = E_g \tilde{N}(E_g)$, we find that, when we take account of radiative recombination, the threshold factor is reduced from E_g to W , where

$$W = eV_m [1 + I_{th}/e\tilde{N}(E_g)] / [1 + kT_R/eV_m]. \quad (25)$$

This is equivalent to saying that the limiting efficiency in Eq. (6) is now modified to

$$\eta_{rad}(X, Y) = \int_{E_g}^{\infty} \frac{W}{h\nu} f_w(\nu) d\nu / \int_0^{\infty} f_u(\nu) d\nu, \quad (26)$$

where the numerator of Eq. (26) is the same as P_m in Eq. (24). The useful fraction of the free energy difference is reduced from its value ($E_g/h\nu$) in Eq. (6) to the value ($W/h\nu$) in Eq. (26).

It is instructive to consider two of the important fundamental loss processes in a solar cell and how they are related to the terms in Eq. (4). One of these processes is the thermalization of hot electrons and holes. When $h\nu > E_g$, the photo-generated carriers have excess energy ($h\nu - E_g$) above the minimum E_g needed to create an electron-hole pair. The excess energy corresponds to the usual kinetic energy of a free particle in motion. Due to electron-phonon coupling, the excess energy is rapidly converted into energy of lattice vibrations. This corresponds to damping of the motion of a free particle by a viscous medium. Energy is conserved, but entropy increases. A fraction $(h\nu - E_g)/h\nu$ of the available work $f_w(\nu)$ in Eq. (4) appears as an increase in entropy, given by the last term in Eq. (4):

$$\left(\frac{h\nu - E_g}{h\nu} \right) f_w(\nu) = T_R f_s^i. \quad (27)$$

The other loss process that we must consider is recombination. When we do this, the result in Eq. (27) must be modified. The operating solar cell is a diode under forward bias. Under these conditions, some of the carriers generated by the incident light are lost through recombination. There are several possible mechanisms for recombination, most involving defects or impurities in the material. These can, in principle, be reduced to arbitrarily low levels by increasing the perfection of the material. The process of radiative recombination takes place in a perfect material and cannot, in principle, be reduced to arbitrarily low levels. The effect of radiative recombination can be treated as an effective lowering of E_g , as we have done in Eq. (25). When we take account of this loss, then the following equation, taking account of both thermalization losses and radiative recombination, replaces Eq. (27):

$$\left(\frac{h\nu - w}{h\nu} \right) f_w(\nu) = T_R f_s^i. \quad (28)$$

For amorphous silicon solar cells, $n = 3.6$; $E_g = 1.7$ eV; $X = 0.05$. For the ideal device we have $eV_{oc} = 1.411$ eV and $eV_m = 1.309$ eV. W then is equal to 1.284 eV. The limiting efficiency is then $\eta_{rad} = 0.264$, when radiative recombina-

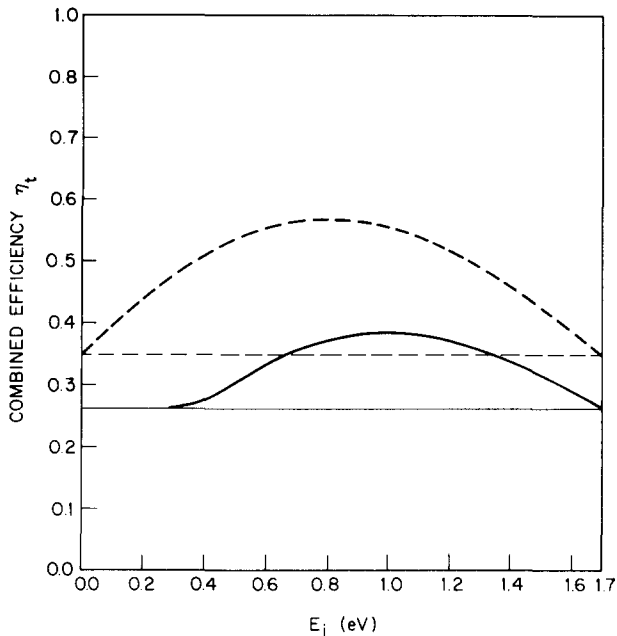


FIG. 2. Limiting efficiencies for a multigap device. One material has a band gap of 1.7 eV, and the second material has a smaller band gap E_i . Limiting efficiency is plotted as a function of E_i . Upper curve: general threshold device. Lower curve: solar cells. The dotted curves are for the case without radiative recombination. The combined efficiency peaks at about $E_i = 0.8$ eV with $\eta_t = 0.565$. When the radiative recombination loss is taken into consideration (solid curves) the peak moves to $E_i = 1.0$ eV with $\eta_t = 0.38$.

ation is taken into account. This is shown graphically on the I - V curve in Fig. 1. The ideal fill factor is $f = (I_m V_m)/(I_{sc} V_{oc}) = 0.910$.

MULTIPLE GAP SOLAR CELLS

We now consider two solar cells, made from materials having different band gaps. The light transmitted by the material having the higher band gap is absorbed by the material with lower band gap. For this case, Eq. (11) becomes

$$\eta_i(X) = \eta_{rad}(X, Y_i) = (1 - W_i/W_f)\eta_{rad}(X, Y_f). \quad (29)$$

We get W_i and W_f from Eq. (25) by inserting the values for E_i and E_f . Figure 1 shows W as a function of E_g . W is about 0.4 eV smaller than E_g over most of the range shown.

Figure 2 shows the combined efficiency for a system of two solar cells, made from materials having different band gaps. One band gap E_f is 1.7 eV for hydrogenated amorphous silicon. The combined efficiency is shown as a function of the band gap E_i of the second material. The optimum value for E_i is approximately 1.0 eV, giving a combined efficiency $\eta_t = 0.383$. η_t is nearly constant over the range 0.8–1.2 eV for E_i . By extending this concept from two solar cells to an arbitrarily large number of different cells, each operating over a narrow spectral range, it can be shown that the full area under the $W(E_g)$ curve can be converted to useful work.

SUMMARY AND CONCLUSIONS

The use of a system of two solar cells, made from materials having different band gaps, raises the theoretical limiting efficiency from 26% to 38%. One way to use this calculation is to assume that both components of the solar cell could be developed to achieve actual efficiencies that are the same fraction of the ideal limiting efficiency. Current best efficiency¹⁰ is 10% for hydrogenated amorphous silicon solar cells. Adding a second cell with smaller band gap, having the same ratio of actual to theoretical efficiency, would give a combined efficiency of 14.6%. For the second material the band gap could be anywhere in the range 0.8–1.2 eV. One possible material in this range is amorphous tin-silicon alloy,¹¹ which can be made with a band gap of 1.1 eV, and has some of the other properties needed for a solar cell.

For the present discussion we consider only the simplest configuration for a composite solar cell. It consists of two individual cells, made of different materials. One material has a band gap of 1.7 eV, and the other has a band gap of 1.1 eV. The two cells are arranged to be optically in series, but not electrically connected to each other. Light is incident on the higher band-gap material which absorbs light for which $h\nu > 1.7$ eV. The remaining light passes through and is incident on the lower band-gap material which absorbs light for $h\nu$ is between 1.1 and 1.7 eV. The power generated by the separate cells is then combined or utilized in a suitable way.

We have used the value 1.7 eV for the band gap of hydrogenated amorphous silicon in this calculation. This depends somewhat on material preparation and composition, and a different value might be appropriate for certain specific cases. There are also conceptual reasons why a different specific value for the band may need to be considered.¹² Where there is a band tail of states in the forbidden gap, some of these can contribute to light absorption and transport. The idealized model for the band gap needs to be modified somewhat to take account of these properties.

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