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THE EFFECT OF DEPLETION LAYER RECOMBINATION ON SOLAR CELL EFFICIENCY

by

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Abstract

The power efficiency curves of photovoltaic solar cells are investigated as a function of the forbidden energy gap (E_g) and the current-voltage characteristic of the diode. Minority carrier injection, depletion layer recombination, and interface recombination terms are considered in models for the I-V characteristic. The collection efficiency for photons with energy between (E_g) and an upper energy cutoff (E_w) is assumed to be 100% and zero otherwise. Results are presented in terms of a single parameter related to the ratio of depletion layer width and minority carrier diffusion length. In particular it is found that increasing depletion layer recombination shifts the efficiency curves to larger values of the energy without changing the shape of the efficiency curve appreciably. This result is based on the Sah-Noyce-Shockley generation-recombination model, but it is believed that similar results would be obtained whenever the "quality factors" in the exponential energy gap and forward bias terms are equal.

Introduction

Loferski's classic 1956 paper is widely quoted in justifying the choice of particular semiconductors for solar cell applications.[1] The results of these calculations depend significantly on the model chosen for the solar cell's current-voltage characteristic. Loferski examined three models for this I-V characteristic. The first of these models is based on the minority carrier injection model and is given by

$$I_1 = 1.44\times10^8\, e^{-\frac{Eg}{kT}}\, e^{\frac{qV}{kT}} \quad \text{Amps/m}^2 \tag{1}$$

where Eg is the energy gap of the semiconductor, V is the applied forward bias voltage, and the multiplying factor is obtained by evaluating Shockley's expression using material parameters representative of silicon.[2] The second model is obtained by inserting an adjustable parameter f into eq. (1) to give

$$I_2 = 1.44\times10^8 f\, e^{-\frac{Eg}{kT}}\, e^{\frac{qV}{kT}} \quad \text{Amps/m}^2 \tag{2}$$

This parameter is convenient for scaling this one theoretical evaluation to match either experimental data or the combined effects of different assumptions about doping and material constants. The third model assumes

$$I_3 = Ae^{-\frac{Eg}{2kT}}\, e^{\frac{qV}{kT}} \tag{3}$$

where the multiplier A, or equivalently the choice of units, is not clear in Loferski's paper.

These models were reexamined for approximate AMO conditions assuming that the charge current equivalent to the total photon flux for photons with energy greater than E can be approximated by

$$I_S = \exp(6.9412 - 0.344E - .2515E^2) \quad \text{Amps/m}^2 \qquad (4)$$

where E is written in electron volts. This expression is a good global approximation to recent experimental data presented by Thekaekara[3] and greatly simplifies numerical evaluation and minimization routines. I_S and the numerical sum of Thekaekara's data differ by less than 5% for $0.7<E<3.0$eV. The photon flux per unit energy implied by Eq. (4) and Thekaekara's data agree to within 5% for 1.1<3.0eV. (Thekaekara's solar constant of 1350 Watts/m^2 is assumed in the efficiency calculations presented below instead of the underestimate of 1280 W/m^2 implied by Eq. (4).) Peak power output as a function of energy gap was determined by maximizing

$$P = V\left(I_S(Eg) - I_S(E_W) - I_n\right) \qquad (5)$$

with respect to the operating voltage V where P is the output power, I_n is an expression for the forward diode current, and source current expression $(I_S(Eg) - I_S(E_W))$ is equivalent to a collection efficiency of 100% for photons in the energy greater than the energy gap Eg and less than energy window E_W. The thermal energy kT/q was taken to be 26 meV in all cases.

Recalculation for Loferski's I_2 model (Eq. (2)) with E_W=3.8eV and with $f=10^2$ and $f=10^4$ is shown in Fig. (1). These f values were judged representative of wide bandgap semiconductors. Slight changes in these curves with respect to Loferski's Figure (9) are the result of more recent AMO spectrum data. The efficiency curves obtained using the I_3 model and A in Eq. (3) equal to 1 Amp/m^2 and 1 Amp/cm^2 are also included in Figure (1). Differences between the latter curve and the corresponding curve in Loferski's

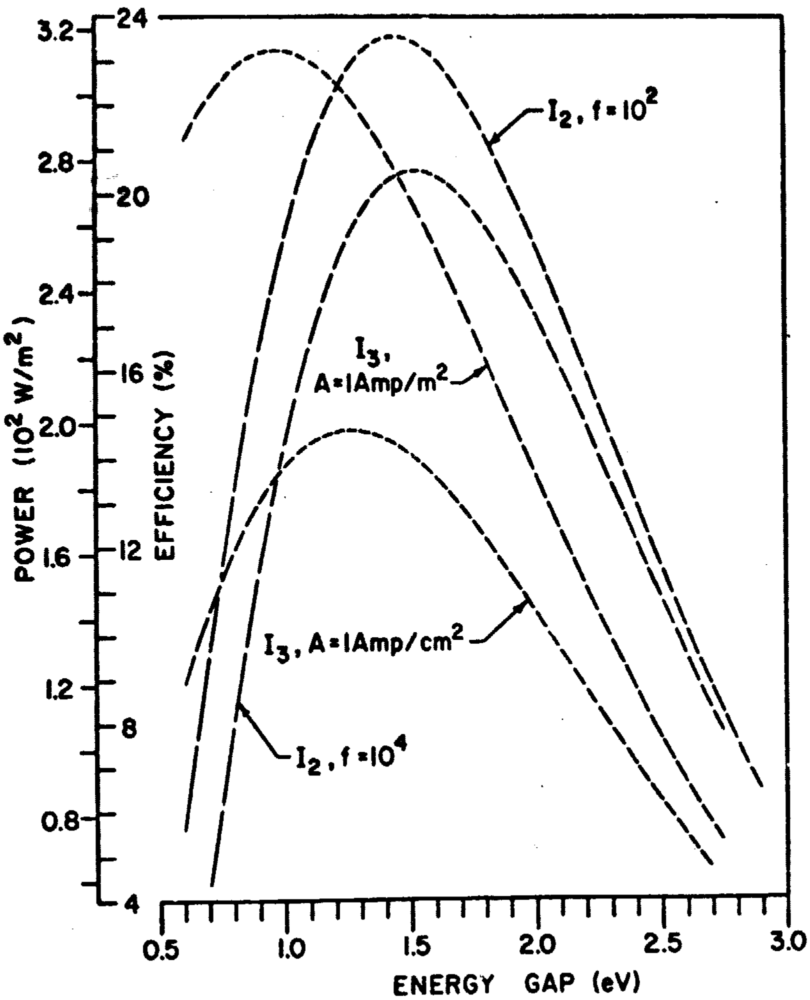

FIGURE 1

Maximum Power vs. Energy Gap. I_2 corresponds to the ideal diode current-voltage characteristic as written in Eq. (2); I_2, $f = 10^2$ is taken as the ideal diode limit for the remainder of this work. I_3 corresponds to the diode current-voltage characteristic given by Eq. (3); Loferski employed I_3, $A = 1$ Amp/cm^2 as an empirical model of real diodes.

Figure (7) can be accounted for by both differences in the AMO spectrum data and the fact that Eq. (4) underestimates the photon flux per unit energy in the 0.8 to 1.2eV energy range.

It would appear from the literature that it is generally accepted that the I_3 model predicts the behavior of generation-recombination dominated diodes with sufficient accuracy to permit selection of materials for solar cell applications.(1) In fact, Loferski's paper predates the generation-recombination paper of Sah, Noyce, and Shockley.(4) Loferski inserts a factor of two in the energy gap dependence of I_3 based on the experimentally observed temperature dependence of the reverse saturation of currents of silicon diodes.(5,1) Sah, Noyce, and Shockley's generation-recombination model indicates that the same factor of two should be inserted in the forward voltage dependence of I_3.(4) Although the minority carrier injection and generation recombination models are not sufficient to describe much of the experimental data, it can still be argued intuitively that the forward current model must be essentially symmetric in the applied electrostatic voltage and the diffusion voltage.

Results

The effect of generation-recombination processes was investigated using a current-voltage characteristic given by

$$I = qN\sqrt{\frac{D}{\tau}}\, e^{-\frac{Eg}{kT}} \left(e^{\frac{qV}{kT}}-1\right) + qN\,\frac{d}{\tau}\,\frac{kT}{(Eg-qV)}\, e^{-\frac{Eg}{2kT}} \left(e^{\frac{qV}{2kT}}-1\right) \quad (6)$$

where d is the depletion layer thickness, N is a characteristic density of states, the distinction between the diffusion potential and the energy gap is omitted, and diffusion coefficients and lifetimes of hole and electron minority carriers are assumed to be equal and independent of whether or not the region is depleted. Eq. (6) is an approximation to the diode current expression that is obtained by summing the minority carrier currents at the depletion layer midplane assuming that the majority carrier Fermi levels remain flat. Eq. (6) displays the general form of the more detailed expression given by Sah et al.[4] Eq. (6) can be rewritten as

$$I_4 = 1.44\times10^{10} \left\{ e^{-\frac{Eg}{kT}} \left(e^{\frac{qV}{kT}} - 1 \right) + \frac{kT}{(Eg-qV)} \frac{d}{L} e^{-\frac{Eg}{2kT}} \left(e^{\frac{qV}{2kT}} - 1 \right) \right\} \quad (7)$$

$$\text{Amps/m}^2$$

where L is the diffusion length and the multiplicative factor is chosen to be physically reasonable and conform to Loferski's I_{02} case for $f = 10^2$ in the limit of $d/L = 0$.

The current expression I_4 and $E_W = 3.8$eV was employed in Eq. (5) to yield the efficiency curves shown in Fig. (2). The d/L ratio was treated as a fixed parameter in these calculations. This phenomenological d/L ratio and the geometric d/L ratio can be related if the ratio of minority carrier lifetimes in the bulk and in the depletion layer are known. The curves demonstrate that the energy gap for peak response increases with increasing generation-recombination current while the width of response curve decreases slightly. This behavior is in contrast to the I_3 result which shows a shift of the peak to smaller energy gap and a broadening of the peak. There is no fundamental change in the shape of the response curve as the d/L ratio is changed from values where the diode current is dominated by minority carrier injection ($d/L \leq 10^{-4}$) to values where generation-recombination dominates ($d/L \geq 10^{-3}$).

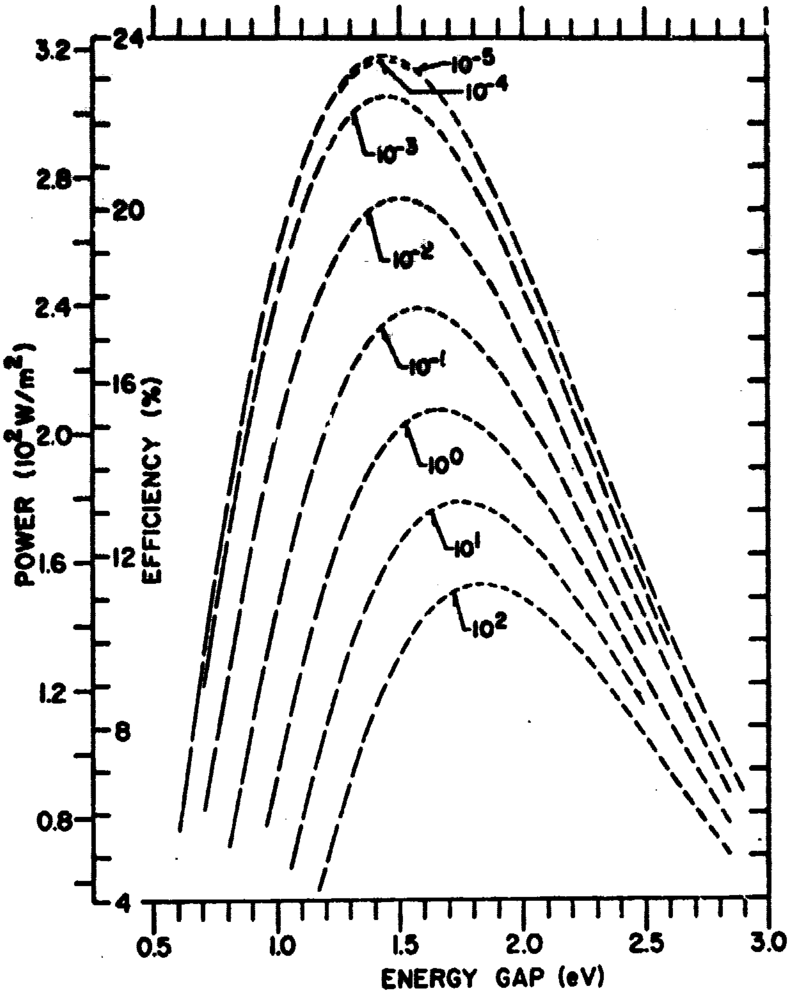

FIGURE 2

Maximum Power vs. Energy Gap where the current-voltage characteristic of the diode is given by Eq. (7), E_W = 3.8 eV. The curves are labelled by the value of the d/L parameter.

Recently there has been a great deal of interest in heterojunction solar cells. Many of the possible material pairings involve relatively large mismatches in lattice constants that in turn imply high interface recombination velocities.[6] The generic behavior of these cells can also be described using a phenomenological d/L parameter. (The assumption of 100% collection efficiency essentially requires that there be no band edge spike at the interface.) An expression of the form of Eq. (7) describes the heterojunction diode current in the limit where interface recombination can be neglected. In the limit in which the recombination at this interface is limited by diffusion across the depletion layer, the interface leads to a component of the forward diode current I_I of the form

$$I_I = qN \frac{D}{d} \left(\frac{Eg-qV}{kT}\right) e^{-\frac{Eg-qV}{kT}} \tag{8}$$

Including interface recombination in the forward current expression and assuming 100% collection efficiency is mathematically consistent if the electrostatic field at the interface is high enough. Inserting Eq. (8) into Eq. (6) yields

$$I_5 = 1.44\times10^{10} \left\{\frac{1}{2}\left(1+\left(\frac{L}{d}\right)\left(\frac{Eg-qV}{kT}\right)\right) e^{-\frac{Eg}{kT}} \left(e^{\frac{qV}{kT}} -1\right) + \left(\frac{d}{L}\right)\left(\frac{kT}{Eg-qV}\right) e^{\frac{Eg}{2kT}} \left(e^{\frac{qV}{2kT}} -1\right)\right\} \quad \text{Amps/m}^2 \tag{9}$$

where interface recombination and minority carrier injection contributions have been weighted equally. This weighting is directly related to the relative doping of the window and active layers. The derivation of Eq. (8) and Eq. (9) rests on the same assumptions as

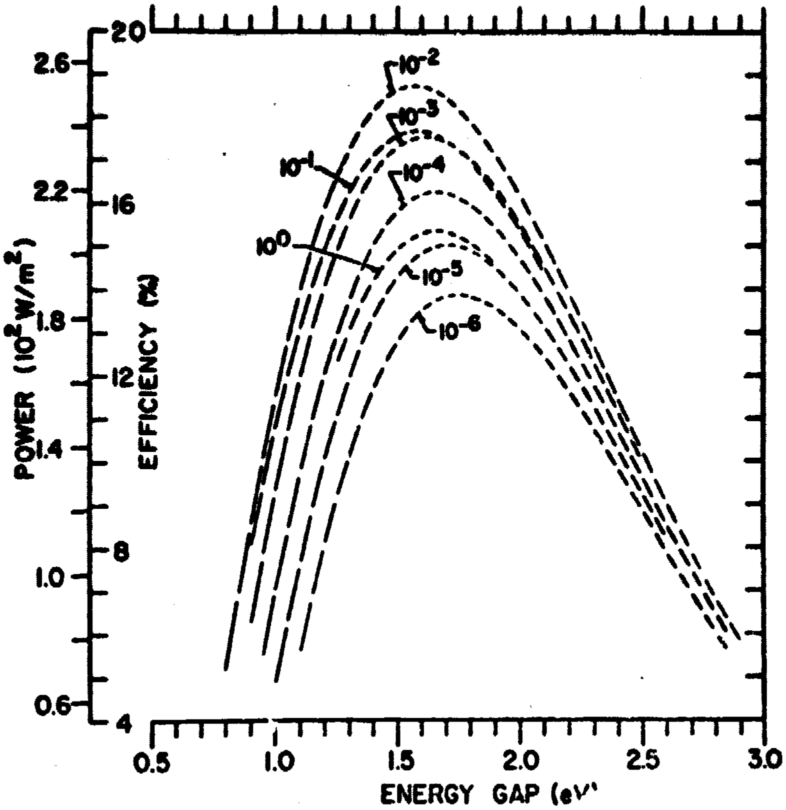

FIGURE 3

Maximum Power vs. Energy Gap for front surface illuminated heterojunction or Schottky diode. The energy window is 3.8 eV and the surface recombination velocity is infinite. The diode current expression is given by Eq. (9) and the curves are labelled by the value of the d/L parameter.

those employed in obtaining Eq. (6).

The result of maximizing Eq. (5) using the diode current expression I_5 and assuming 100% collection for photon energies E such that $Eg \leq E \leq 3.8eV$ and no collection otherwise is shown in Fig. (3). This model corresponds to the case of either a heterojunction with a wide gap window layer or a Schottky diode. I_5 is dominated by depletion layer recombination for $d/L > 10^{-1}$ and the efficiency curves are identical to the corresponding curves in Fig. (2) so the curves for $d/L = 10^{-1}$, 10^{0}, and 10^{1} are included in Fig. (3) only for reference. The term in Eq. (9), corresponding to minority carrier injection into the active layer bulk, does not play a significant role for any d/L value. Minority carrier injection does become significant if the relative weight of interface recombination term in Eq. (9) is less than 10^{-4}.

Similar variations in the efficiency curves with respect to variation of the d/L parameter are obtained if high energy cutoff E_W is changed to lower values. In these cases Eq. (5) would represent the behavior of a heterojunction cell where the window layer has an energy gap E_W, there is no interface spike, and absorption in the window does not contribute to the output power. Simultaneous maximization of the power output with respect to the energy gap of the active layer and the d/L parameter with the energy window fixed is obtained at a d/L value of $1.5\text{-}2.0\times10^{-2}$ independent of the energy window. This numerical result is due to the particular relative weighting of interface and depletion layer recombination implied by Eq. (9). Making d/L either larger or smaller than this optimum value reduces the peak efficiency, shifts the energy gap Eg for peak efficiency to larger values, and narrows the efficiency curve slightly. Reducing d/L below its optimum cuts the peak efficiency at a rate of 1 to 1.25% per decade. Increasing d/L above its optimum value cuts the peak efficiency at a rate of 2 to 2.5% per decade. If d/L is a decade or more larger than the optimum value, interface recombination current becomes negligible and the efficiency becomes independent of the recombination velocity assumption.

The diode current expression given by Eq. (9) can be minimized trivially with respect to d/L. If this minimized current is used in evaluating the maximum power output versus Eg for fixed E_W, it is found that the optimum d/L versus Eg varies from 3×10^{-2} to 1×10^{-2} between small and large Eg values, respectively. (These small and large Eg values are vaguely defined as the Eg values at which the efficiency falls to the neighborhood of 4%.) This variation of d/L is small enough that the minimized form of Eq. (9) is sufficient for preliminary estimates of the solar cell potential of particular material pairings. The results of this evaluation are shown in Fig. (4). These results do depend on the relative doping of the window and active layers. If, for example, the doping of the active layer can be reduced by approximately one decade and all of the characteristics are shifted upward by approximately one percent. The "best case" analogue of the data presented in Fig. (4) is shown in Fig. (5). The data in Fig. (5) assumes that the only mechanism for forward diode current flow is minority carrier injection into the active layer. Both depletion layer and interface recombination currents are assumed to be negligible. The dominant result of eliminating both of these currents is a three to five percent improvement in the peak efficiency for all E_W values of conceivable interest. The Eg value for peak efficiency at fixed E_W is also reduced by .pproximately 0.1 eV.

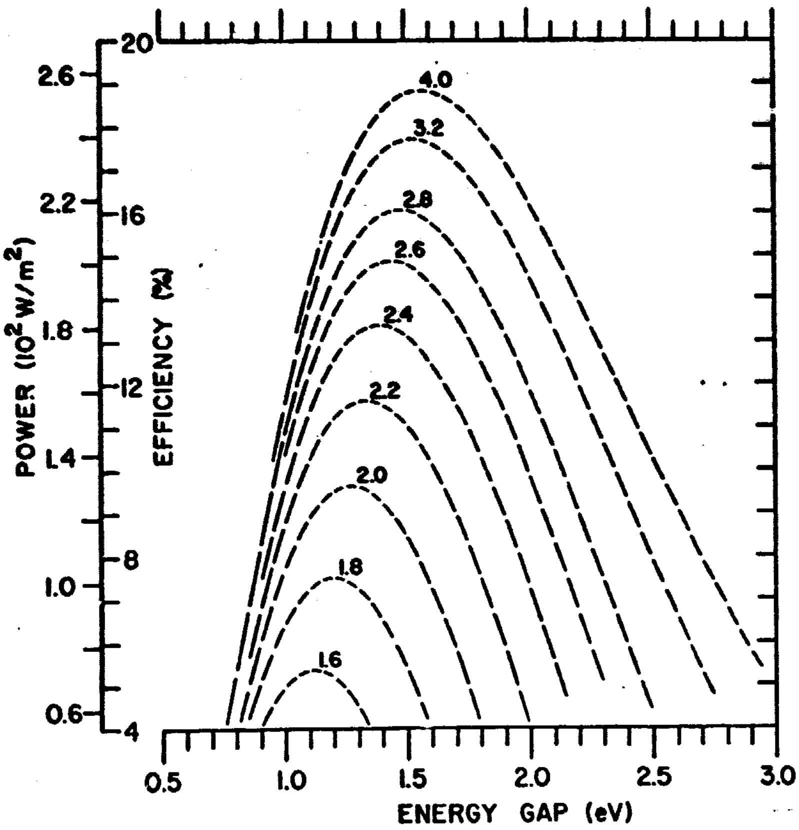

FIGURE 4

Maximum Power vs. Energy Gap for heterojunctions with an infinite interface recombination velocity. The current expression given by Eq. (9) was minimized with respect to d/L and the curves are labelled with the value of the energy window in eV.

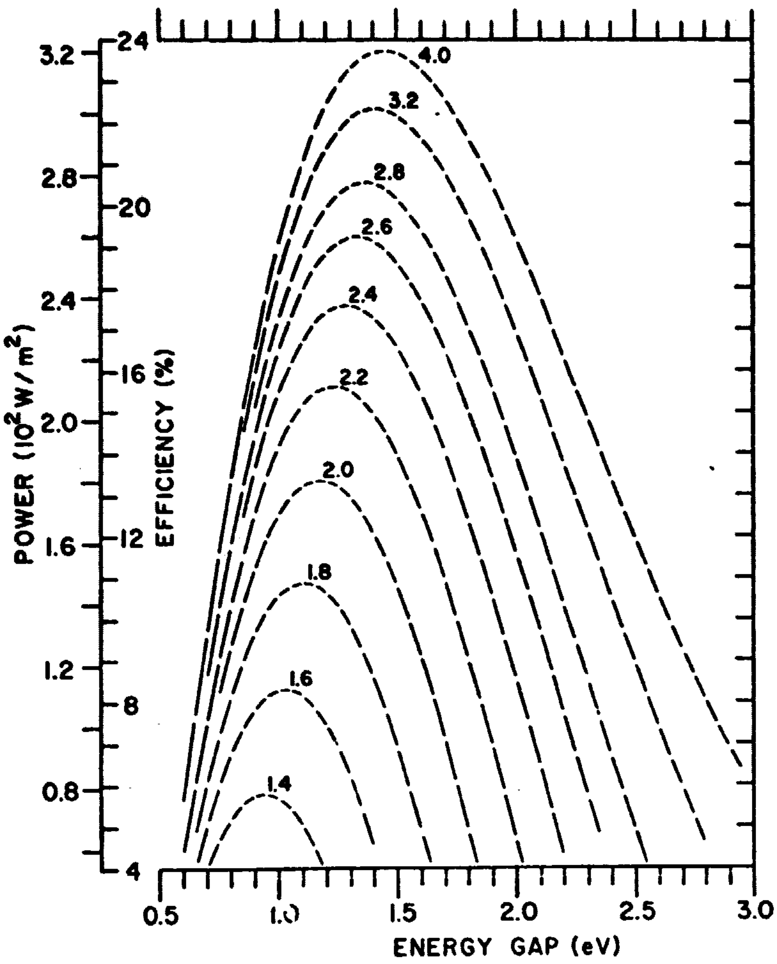

FIGURE 5

Maximum Power vs. Energy Gap for heterojunctions with an interface recombination velocity of zero and no depletion layer recombination. The ideal diode expression was obtained by eliminating the appropriate terms from Eq. (9) and the curves are labelled by the value of the energy window in eV.

Discussion

A generic description of the power efficiency behavior of photovoltaic solar cells has been presented. The models include the generation-recombination component of forward diode current according to the Sah-Noyce-Shockley theory,[4] and the results are presented in terms of the ratio of the depletion layer thickness to the minority carrier diffusion length. If variations of this d/L parameter are considered to be due to variations in d via changes in the doping of an abrupt junction structure, there is a simultaneous variation in the density factor that is buried in the 1.44×10^{10} Amps/m^2 multiplier that is not included in the calculation. Variations in d can also be affected by tailored doping profiles within the depletion layer and this procedure would not lead to a simultaneous effect on the multiplier. If variations in d/L are due to changes in L via changes in the minority carrier lifetime, there is a simultaneous effect on the diffusion velocity factor $\sqrt{D/\tau}$ in the multiplier which is also ignored in the calculation. These changes in the multiplier are neglected in order to preserve a one-parameter formalism. The results of changes in the multiplier can be estimated by the shift of the efficiency curves shown in Fig. (1) (I_2, $f = 10^2$ and $f = 10^4$).

Introducing increasing amounts of generation-recombination current to an otherwise ideal, minority carrier injection diode reduces the peak efficiency, shifts the energy gap for peak efficiency, and narrows efficiency curves very slightly. An increase in the diode current multiplier and/or a decrease in insolation leads to an additional increase in the energy gap for peak as well as a decrease in output power and output power efficiency. In addition, an examination of Fig. (2) indicates that degradation due to generation-recombination current is far more severe on the low energy gap side of the ideal diode peak than it is on the high energy side. All of these arguments suggest that materials for solar cells should preferably have energy gaps in the 1.4 eV to 1.8 eV range rather than in the 1.0 eV to 1.4 eV range. In practice these arguments must be weighed against any additional difficulties in doping or achieving comparable diffusion lengths in the wider gap materials.

The efficiency curves for heterojunctions with negligible interface recombination velocities are identical to those for homojunctions. Addition of an infinite surface recombination velocity implies the existence of a d/L value that maximizes the power efficiency. This ratio does depend on the relative doping of the window and active layers but is essentially independent of the energy gap and the energy window. The approximately equal doping case implied by Eq. (9) leads to an optimum d/L value of $1.5\text{-}2\times10^{-2}$. It could be argued that this represents a practical lower limit on the geometric d/L ratio (depletion layer thickness/bulk diffusion length). Figures (2) and (3) for d/L values greater than 10^{-2} are virtually identical indicating that the recombination velocity is relatively unimportant in the practical limit. This result no longer is obtained if the minority carrier lifetime is much longer in the depletion layer than it is in the bulk or if the active layer is more heavily doped than is the window.

REFERENCES

1.) J. J. Loferski, J. Appl. Phys. 27, 777 (1956).

2.) W. Shockley, Bell System Tech. J. 28, 435 (1949).

3.) M. P. Thakaekara, "Solar Energy Data Workshop - 1973," p. 86, (Ed. C. Turner), U. S. Government Printing Office, Washington, D.C., NSF-RANN-74-062.

4.) C. T. Sah, R. N. Noyce, and W. Shockley, Proc. IRE 45, 1228 (1957).

5.) H. Kleinknecht, and K. Seiter, Z. Phyisk Bd 139, 599 (1954).

6.) A. L. Fahrenbuch, V. Vasilchenko, F. Buch, K. Mitchell, and R. H. Bube, Appl. Phys. Lett. 25, 605 (1974).

Appendix I.

Figure (6.) shows the analogue of figure (3) for E_W=2.4 eV; i.e., a heterojunction cell with a window of 2.4 eV, variable active layer energy gap and d/L ratio, and an infinite interface recombination velocity. Figure (7.) describes the same situation except that the interface recombination is assumed to be zero. These curves can be used to predict the solar cell possibilities of heterojunctions employing CdS or $CuGaS_2$ windows. In particular, the CuIn Se_2/CdS, 12% efficiency solar cell reported by Shay, Wagner, and Kasper [7.] approaches the theoretical efficiency for this material if the interface recombination velocity is, in fact, infinite. Their short circuit current suggests that they obtained a collection efficiency close enough to 100% throughout the Eg to E_W band to make the present calculation appropriate. The sharp drop in photocurrent near the open circuit voltage and the crossover with respect to the silicon characteristic suggests dominance of interface recombination current. Finally, comparison with figure (6.) & (7.) suggests that the only way of improving the performance of this pair is by reducing the interface recombination velocity.

Some improvement in performance is possible if the InP-CdS pairing investigated by Wagner, Shay, Bachmann, and Buehler is pursued as an alternative.[8] The relative merits of these two pairs depend on the interface recombination velocities for these two pairs. The formalism for determining over what interface recombination velocity range the pair performance changes from the results presented in figure (6.) to those presented in figure (7.)

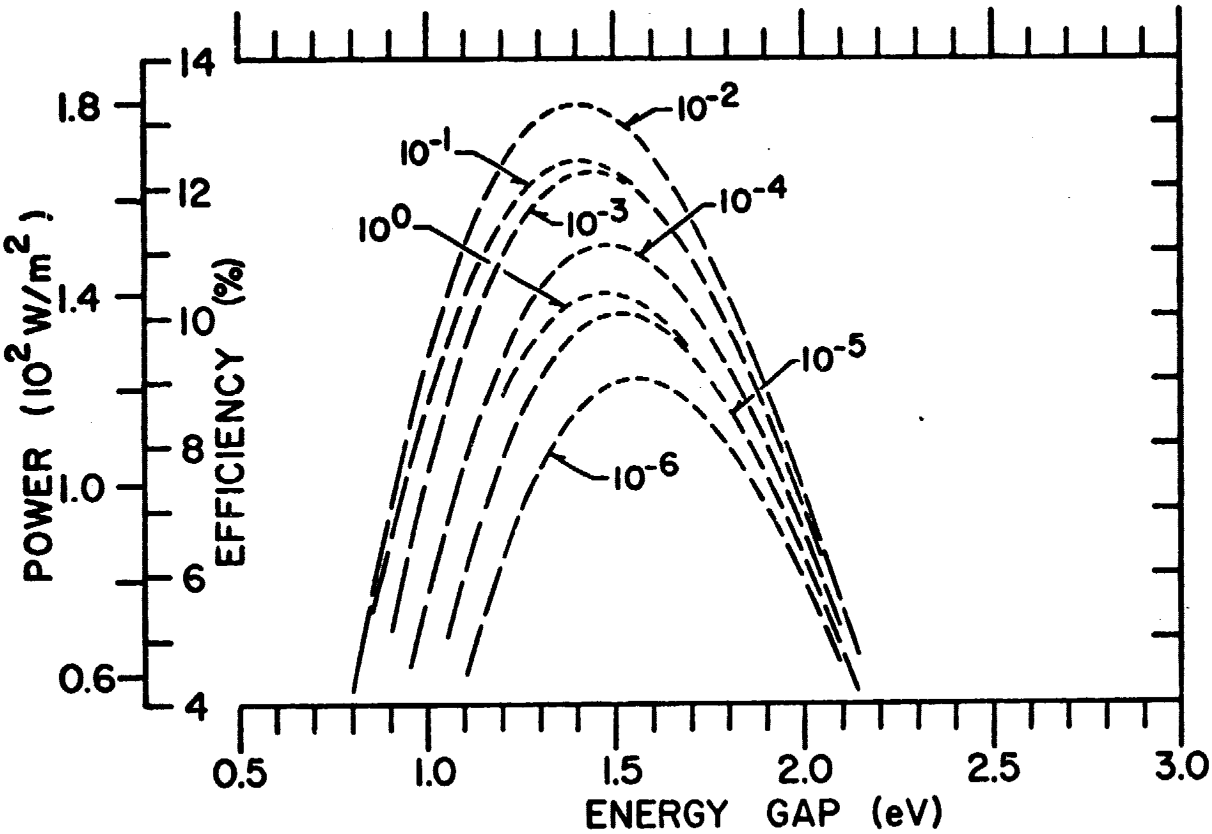

FIGURE 6

Maximum Power vs. Energy Gap for front surface illuminated heterojunction or Schottky diode. The energy window is 2.4 eV and the surface recombination velocity is infinite. The diode current expression is given by Eq. (9) and the curves are labelled by the value of the d/L parameter.

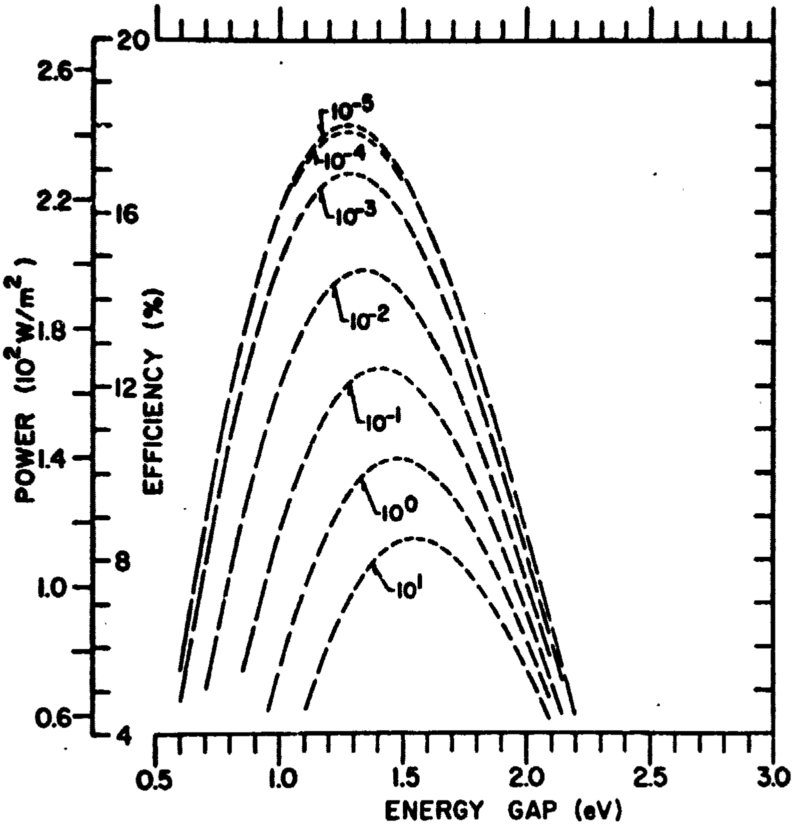

FIGURE 7

Maximum Power vs. Energy Gap where the current-voltage characteristic of the diode is given by Eq. (7), $E_W = 2.4$ eV. The curves are labelled by the value of the d/L parameter.

has been set up but the calculations have not been performed.

As a matter of principle, it would be better to choose active layers on the high side of the peak performance energy gap (1.4 eV to say 1.8 eV in this case.) Although Eg in this range cannot yield optimum performance, deterioration of performance because of less than ideal materials is far less severe on this side of the peak. The dollars invested in material preparation per watt of power delivered could be substantially lower.

7.) J.L. Shay, S. Wagner, and H.M. Kasper, Appl. Phys. Lett. 27, 89 (1975)

8.) S. Wagner, J.L. Shay, K.J. Bachmann, and E. Buehler, Appl. Phys. Lett. 26, 229 (1975)

APPENDIX II

Gärnter calculated the collection efficiency of front surface illuminated heterojunction solar cells as

$$\eta = P(0)\left\{\left(1-e^{-\alpha d}\right) + \frac{\alpha L}{1+\alpha L}\, e^{-\alpha d}\right\} \tag{10}$$

where P(0) is the probability that a photon of given energy E will reach the interface at $x = 0$, α is the absorption coefficient for this photon in the active layer substrate, d is the depletion layer thickness, and L is the diffusion length in the field-free substrate.[9] P(0) was taken to be unity for $E_g < E < E_W$ and zero elsewhere in the text; the term in braces was taken to be unity. The term in parentheses in Eq. (10) corresponds to unity collection efficiency for carriers generated in the depletion layer. The second term in braces corresponds to collection in the field-free active layer assuming that this layer is thick enough to affect complete absorption and that back surface recombination can be neglected; the coefficient reflects the competition between the bulk recombination time and the time required for minority carriers to diffuse back to the depletion layer.

Equation (10) can be recast in terms of a material parameter equal to αL and d/L geometry parameter identical in form to the d/L parameter used in developing the power efficiency in the text. Eq. (10) is an increasing function of d/L for all d/L if this is done. Eq. (10) must be modified to include depletion layer recombination in order to obtain the correct asymptotic form for the collection efficiency in the limit of very wide depletion layers.

This can be achieved by multiplying the right hand side of Eq. (10) by a worst case approximation to the probability that a minority carrier will travel halfway across the depletion layer without recombining, i.e.,

$$\eta' = \eta e^{-\frac{t_{tr}}{\tau}} \tag{11}$$

where t_{tr} is the transit time and τ is the lifetime in the depletion layer. If the assumptions of constant mobility and of spatially independent lifetime are made in addition to the assumptions of equal electron hole parameters, equation (11) becomes

$$\eta' = P(o) \exp\left\{-\frac{1}{2}\frac{kT}{(E_g-qV)}\left(\frac{d}{L}\right)^2\right\}$$

$$\times \left\{1 - \frac{1}{1+\alpha L}\exp\left(-(\alpha L)\left(\frac{d}{L}\right)\right)\right\} \tag{12}$$

This is a rather good approximation to more glorified expressions except that it neglects interface recombination. Figure 8 shows Eq. (12) for the case of $P(0)=1$ and $kT/2(E_g-qV)=1/80$; this is reasonable for generation-recombination limited diodes for all Eg and solar flux levels of practical interest. This figure represents the collection efficiency of some experimental data reasonably well.(8) Figure 8 does not include the effect of interface recombination which reduces the collection efficiency substantially for αL values greater than ten. Figure 8 does show that the collection efficiency can be improved substantially by choosing d/L correctly if αL falls in the range $0.1 < \alpha L < 10$. Unfortunately, the optimum d/L for collection

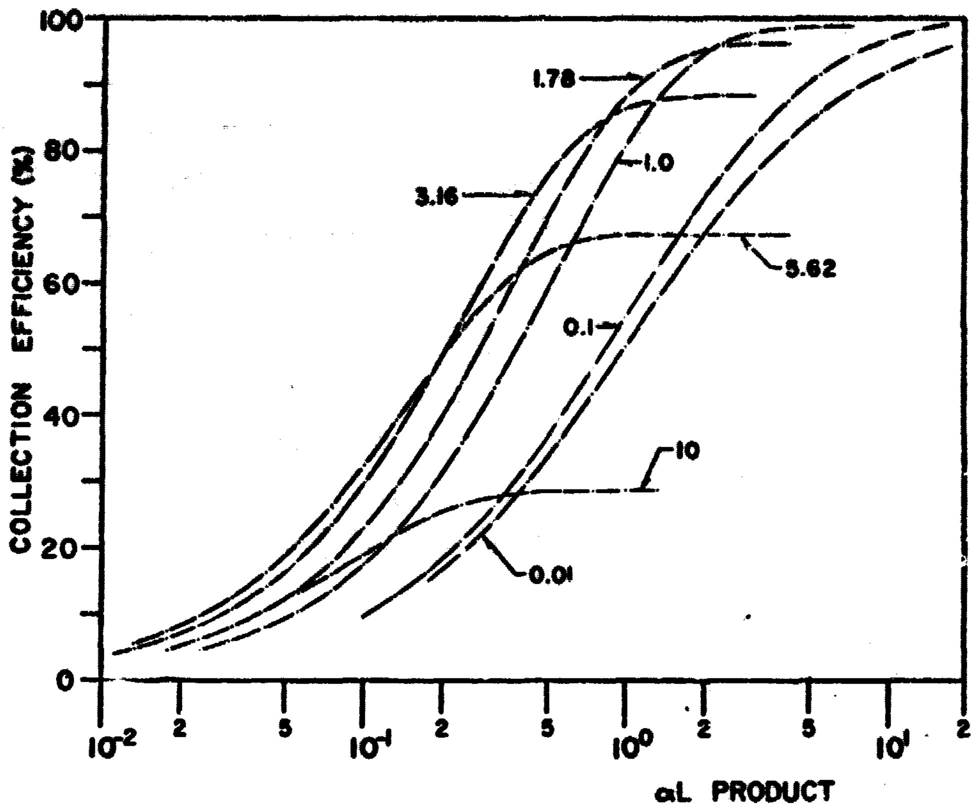

FIGURE 8

Collection Efficiency vs. αL according to the approximate Eq. (12) assuming $\frac{[illegible]-qV}{kT} = 40$. The curves are labelled by the value of the d/L ratio.

efficiency ($0.3 \lesssim d/L \lesssim 3.0$) and the optimum d/L for power efficiency assuming unity collection efficiency ($0.01 \lesssim d/L \lesssim 0.1$) do not coincide. In any event, a detailed optimization with respect to d/L should include both collection efficiency and power efficiency effects simultaneously.

9.) W.W. Gärtner, Phys. Rev. 116, 84 (1959).