Limiting Efficiency of Silicon Solar Cells

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Abstract—The detailed balance method for calculating the radiative recombination limit to the performance of solar cells has been extended to include free carrier absorption and Auger recombination in addition to radiative losses. This method has been applied to crystalline silicon solar cells where the limiting efficiency is found to be 29.8 percent under AM1.5, based on the measured optical absorption spectrum and published values of the Auger and free carrier absorption coefficients. The silicon is assumed to be textured for maximum benefit from light-trapping effects.

INTRODUCTION

SILICON IS uniquely favorable as a photovoltaic material. Not only is it one of the most abundant elements in the earth's crust, but it is also an elemental semiconductor whose bandgap is nearly an ideal match to the solar spectrum. Because of these and other favorable attributes of silicon, the ultimate limiting performance of silicon solar cells is a basic constant of nature that is of some interest, since it specifies a limit that cannot be exceeded by clever device design.

Two approaches have been taken to calculations of the limiting performance of silicon solar cells in the past. In the first approach [1]–[3], one calculates the efficiency as a function of bandgap for hypothetical semiconductors with step function optical absorptions and radiative recombination only. Then the limiting efficiency of silicon is taken to be the same as the hypothetical material with bandgap 1.12 eV. In the second approach [4], [5] a particular device structure is chosen such as an n or p diffused junction cell for example, and then the limiting performance of an optimized device is calculated from the known properties of silicon.

Both approaches have weaknesses. The first approach neglects Auger recombination, a fundamental loss mechanism that is comparable with radiative recombination in crystalline silicon, under one-sun illumination. In addition a step-function optical absorption is not necessarily a good approximation for the optical absorption of an indirect bandgap semiconductor such as silicon. The problem with the second device-based approach is that in focusing on a particular device structure one can build in device-dependent losses that could in principle be eliminated by more clever designs.

In this paper we calculate the limiting efficiency of silicon solar cells of variable thickness, based on the measured optical absorption of crystalline silicon. Auger recombination and free carrier absorption are included in addition to radiative recombination. All of these loss processes are fundamental properties of the material. The surfaces of the silicon are as-

sumed to be textured to fully randomize the incident sunlight for maximum enhancement of the optical absorption through light trapping and reabsorption of recombination radiation [6], [7]. The incident sunlight is assumed to occupy a large solid angle in the sky, appropriate to a nontracking flat-plate solar collector. Accordingly, the limiting efficiency calculated in this paper applies to the case of a full 2π-sr acceptance angle for incident light. For clarity of presentation we begin with a review of the efficiency in the radiative recombination limit, for semiconductor material with a step-function absorbance. Then we generalize the result to the case where the absorbance is a continuous function of photon energy and finally we specialize to silicon including free carrier absorption and Auger recombination.

STEP FUNCTION ABSORBANCE

We consider a slab of semiconductor material with a perfect antireflection coating on the front surface (zero reflectivity) and a perfect reflecting coating on the back surface (unity reflectivity) as shown in Fig. 1. The semiconductor material is assumed to be ideal in the sense that every photon absorption event produces a free electron–hole pair and every recombination event generates a luminescent photon. In this case, the condition for steady state is that for every solar photon that is absorbed, a luminescent photon must be reradiated to the surroundings or an electron–hole pair must be extracted as an electrical current in an external circuit. Of course this condition does not mean that every recombination event produces a photon that is lost to the outside. In general, the luminescent photons will have a high probability of being reabsorbed so that the electron–hole pair population will build up to the point where the reradiation balances the incoming solar flux.

The luminescent emission spectrum of an optically or electrically excited semiconductor has the form of an ambient temperature black-body spectrum, multiplied by a coupling coefficient that is related to the optical density of the semiconductor, all scaled up by the factor $\exp[\mu/kT]$ determined by the internal chemical potential μ [8]. This chemical potential also determines the electron–hole pair population through the relation

$$np = n_i p_i \exp\left[\frac{\mu}{kT}\right] \tag{1}$$

where n_i and p_i are the equilibrium electron and hole populations at temperature T. In the absence of electron–hole concentration gradients, a good assumption for high electronic quality crystalline silicon under the conditions of interest here, μ will be a constant throughout the material. Furthermore it
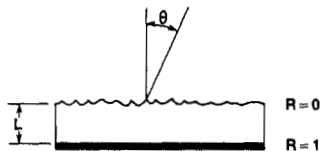
Fig. 1. Solar cell geometry considered in this paper, with zero-reflectivity textured front surface and unity reflectivity back surface.
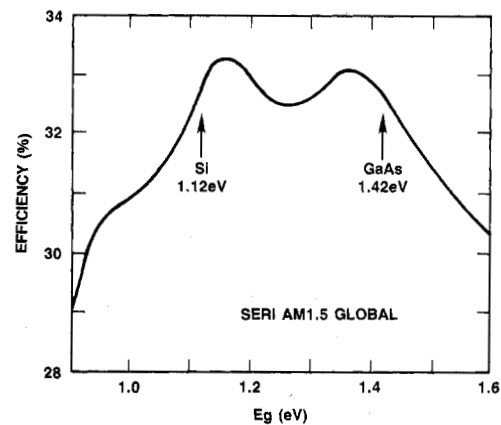

Fig. 2. Radiative recombination-limited efficiency of solar cells as a function of bandgap for materials with step-function optical absorption edges and the SERI AM1.5 global 37° solar spectrum [10].

follows from (1) that μ is equal to the separation between the electron and hole quasi-Fermi levels and hence it is also equal to the solar cell output voltage for a cell with ideal contacts and no internal concentration gradient.

The flux of black-body photons for a photon energy interval dE and solid angle $d\Omega$ is [9]

$$b_n(E, T) \, dE \, d\Omega = \frac{2}{h^3} \frac{n^2}{c^2} E^2 \exp\left(-\frac{E}{kT}\right) dE \, d\Omega \qquad (2)$$

where n is the index of refraction of the medium. The "one" in the denominator of the Bose-Einstein thermal occupation factor has been neglected. This approximation is valid in the limit $E_g - \mu > kT$ where E_g is the semiconductor's bandgap.

The flux of luminescent photons out of the top surface of a slab of semiconductor is most easily calculated from its reverse process, namely the rate at which black-body photons from the surrounding thermal bath are absorbed by the semiconductor. In the dark these two rates (emission and absorption) must be equal; under illumination the luminescent emission rate is equal to the dark emission rate multiplied by exp $[\mu/kT]$. The flux per unit area into the top surface of the semiconductor is

$$\int_0^{2\pi} \int_0^{\pi/2} b_1(E, T) \cos \Theta \sin \Theta \, d\Theta \, d\phi = \pi b_1(E, T) \qquad (3)$$

where Θ is the angle between the surface normal and the incident ray. We neglect radiative coupling through the back surface since it is assumed to be perfectly reflecting. Under illumination by the sun, the condition for steady state is that the total rate of photon emission be the same as the rate at which solar photons are absorbed, corrected for the fraction that is drawn off as current in the external circuit. Expressing the rates as currents

$$I_0 \exp\left(\frac{\mu}{kT}\right) = (1 - f) I_{sc} \qquad (4)$$

where the short-circuit current I_{sc} and the leakage current I_0 are defined by

$$I_{sc} = \int_0^\infty eS(E) \, a(E) \, dE$$

$$I_0 = e\pi \int_0^\infty b_1(E, T) \, a(E) \, dE \qquad (5)$$

where $S(E)$ is the solar spectrum, $a(E)$ is the absorbance of the semiconductor slab $(0 < a(E) < 1)$, and f is the fraction of the incident solar flux that is drawn off as current into the

external circuit. The absorbance is assumed to be independent of angle of incidence, a good assumption since light trapping necessitates internal angular randomization in any case.

If we substitute the output voltage V for the chemical potential μ, then (4) can be rewritten as a current-voltage relationship for the solar cell

$$I = I_{sc} - I_0 \exp\left(\frac{eV}{kT}\right) \qquad (6)$$

from which the maximum output power can be obtained from a numerical solution for the maximum value of the I-V product. The cell efficiency is then the maximum output power divided by the total energy flux from the sun.

For purposes of comparison with the calculations below, based on the actual absorption of silicon, we have calculated the solar cell efficiency as a function of energy gap E_g, assuming that the absorbance in (5) is a step function (zero for $E < E_g$ and unity for $E > E_g$.). The result of the calculation, based on the AM1.5 global, 37° tilt, solar spectrum with total power 97 mW recommended by SERI [10], is shown in Fig. 2 for energy gaps in the vicinity of the maximum efficiency. Notice that the limiting efficiencies for both Si ($E_g = 1.12$ eV) and GaAs ($E_g = 1.42$ eV) are close to the maximum and that at least for the solar spectrum chosen, the Si bandgap is marginally more favorable than the GaAs bandgap.

ABSORBANCE FOR CONTINUOUSLY VARYING ABSORPTION COEFFICIENT

In all real materials the absorbance will always be a continuous function of photon energy. For a slab of material with thickness L and specular surfaces as in Fig. 1, the absorbance is equal to $1 - \exp(-2\alpha L)$, where α is the optical absorption coefficient and the factor of two accounts for the double pass due to the reflecting back surface. It is possible, however, to increase the absorbance substantially in materials with index $n > 1$, with nonspecular textured surfaces [6]. In this case incident light is deflected away from the angle of incidence at one or both interfaces and is trapped inside the material. The light remains trapped until it is either absorbed or scattered back into the escape cone. In the limit that the absorption is
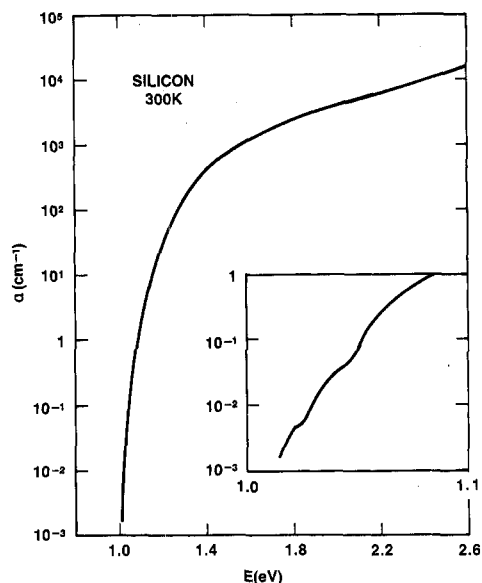
Fig. 3. Optical absorption coefficient of silicon at 300 K in the vicinity of the band edge [12].
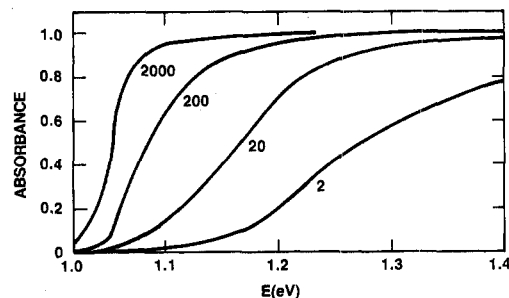

Fig. 4. Absorbance as a function of thickness for slabs of silicon in which the light is fully randomized. The numbers indicate the slab thickness in micrometers.
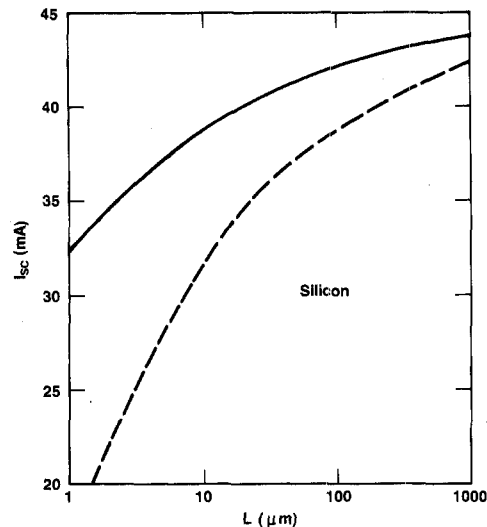

Fig. 5. Short-circuit current as a function of silicon thickness for material with textured surfaces (solid line) and specular surfaces (dashed line), based on the SERI AM1.5 global 37° tilt solar spectrum, with 97-mW/cm² total power [10].

negligible and the scattering surfaces randomize the light inside the semiconductor it can be shown that the light-trapping effect increases the mean path length for a light ray inside the material from $2L$ to $4n^2L$ [7]. A sufficient condition for the light to be randomized is that the multiple scattering surfaces behave as Lambertian surfaces [11] when averaged over some appropriate length scale which may be as large as n^2L.

In this case, in the weakly absorbing limit ($\alpha L < 1$) the light intensity is uniformly distributed inside the semiconductor, which is assumed to be thick compared to a wavelength of the radiation. Since the average light ray experiences many reflections with variable path lengths before it escapes, the escape rate can be regarded as a continuous process proceeding at the rate $1/4n^2L$ in units of per internal path length. Similarly the absorption process proceeds at a rate equal to α, the absorption coefficient, in the same units. It follows that the probability per unit internal path length for a photon to be absorbed is a ratio of competing rates, namely the rate at which absorption takes place divided by the rate at which absorption plus escape through the loss cone takes place. The absorption probability is the same as the absorbance or

$$a(E) = \frac{\alpha(E)}{\alpha(E) + \dfrac{1}{4n^2L}} \qquad (7)$$

for $\alpha L \ll 1$. Since $4n^2$ is large (50 at the band edge of silicon), (7) is a good approximation to the absorbance even for $a(E)$ as large as 0.9. Above this value, the true absorbance approaches unity more rapidly (exponentially) with large α than predicted by (7); however, since the approximate expression is already close to unity at this point the discrepancy is not significant. The expression in (7) for the absorbance together with (5) can be used to calculate the limiting efficiency for any semiconductor material in which radiative recombination is the dominant recombination mechanism.

In Fig. 3 we show the optical absorption coefficient of silicon in the vicinity of the band edge [12]. In Fig. 4, we show

the absorbance as a function of photon energy calculated by substituting the absorption data of Fig. 3 into (7) for four different silicon thicknesses. The index of refraction as determined experimentally from the reflectivity at 1.1 eV, gave $4n^2 = 50$. For convenience in this paper we take $4n^2$ to be a constant equal to 50 in the wavelength range of interest.

EFFICIENCY OF SILICON SOLAR CELLS

From Fig. 4 we note that the absorption threshold for silicon shifts by about 0.2 eV to higher energy as the silicon sheet thickness decreases from 2000 to 2 μm. This shift in the absorption threshold can be converted into a thickness dependent short-circuit current by numerical evaluation of the I_{sc} integral in (5). The calculated short-circuit current as a function of silicon thickness is shown in Fig. 5 for material with textured surfaces, based on the absorbance in (7), and for material with specular surfaces based on the absorbance $a(E) = 1 - \exp[-2\alpha(E)L]$. In both cases the front and back surfaces are assumed to have zero and unity reflectivity respectively. From Fig. 5 we note that the light-trapping effect is particularly important for thin samples. Incidentally, the strong thickness dependence of the absorption threshold points out the inadequacy of the assumption that $E_g = 1.1$ eV in silicon solar cell calculations.

As long as the electron–hole pairs and photons interconvert

by absorption and radiative recombination and no other processes are allowed, the only loss mechanism in the solar cell is the luminescent emission from the semiconductor, required by thermodynamics. In real semiconductors other loss mechanisms always exist. For example photons can be absorbed by free carriers, which in turn dissipate the energy to heat by interaction with the lattice. This absorption is denoted by $\alpha_1(E)$ to distinguish it from the absorption process $\alpha_2(E)$ which generates electron–hole pairs. It follows from the arguments given in the preceeding section that the absorbance in (7) for electron–hole pair generation should be replaced by

$$a_2(E) = \frac{\alpha_2(E)}{\alpha_2(E) + \alpha_1(E) + \dfrac{1}{4n^2 L}} \qquad (8)$$

in the presence of free carrier absorption. The hot carriers are assumed to dissipate their excess energy to photons. The spectrum of light radiated by the electron–hole pairs in equilibrium at T with an external thermal bath is given by $a_2(E) b_1(E, T)$ through detailed balance arguments. Likewise, the spectrum of the light radiated from the semiconductor to an internal black body is $a_2(E) b_n(E, T)$.

The condition for steady state in the photon population can now be written down

$$\int_{\mathrm{Vol}} Rnp \, dV = \left[\iiint_{\mathrm{Vol}} \alpha_1(E) \, a_2(E) \, b_n(E, T) \, dE \, dV \, d\Omega \right.$$

$$+ \iiint_{\mathrm{Vol}} \alpha_2(E) \, a_2(E) \, b_n(E, T) \, dE \, dV \, d\Omega$$

$$\left. + \iiint_{\mathrm{surf}} a_2(E) \, b_n(E, T) \, dE \, dS \, d\Omega \right] \exp\left[\frac{\mu}{kT}\right]. \qquad (9)$$

The left-hand side is the rate at which photons are generated through radiative recombination and the right-hand side is the rate at which they are lost. R is the radiative recombination rate coefficient. Following the arguments given in the preceeding section the surface integral can be converted into a volume integral as follows:

$$\int_{\mathrm{surf}} dS \to \frac{1}{4n^2 L} \int_{\mathrm{Vol}} dV$$

With this substitution (9) reduces to

$$Rnp = \exp\left[\frac{\mu}{kT}\right] \iint \alpha_2(E) \, b_n(E, T) \, dE \, d\Omega \qquad (10)$$

which is the fundamental detailed balance relationship between the absorption coefficient and the radiative recombination rate. Equation (10) could have been written down from first principles [13]; our derivation confirms that the expression for the absorbance given in (8) is the correct one. In fact, we might have started with (10) as the basic assumption and then solved for the absorbance (8) by requiring consistency be-
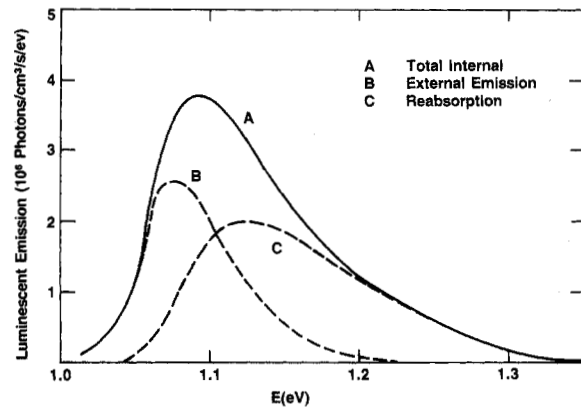

Fig. 6. Spectral dependence of the luminescent emission rate for a 100-μm-thick slab of roughened silicon in thermal equilibrium at 300 K.

tween (9) and (10). A numerical integration of (10) gives $R = 2.1 \times 10^{-15}$ cm³/s in agreement with [13].

The electron–hole pair recombination can take place non-radiatively even in the absence of defect-mediated Shockly–Read–Hall type recombination. The most important mechanism of this type is Auger recombination. Auger recombination takes place at a rate given by $C_n n^2 p + C_p p^2 n$ where C_n and C_p are Auger coefficients. The condition for steady state in the electron–hole population, including Auger recombination is

$$Rnp + C_n n^2 p + C_p p^2 n$$

$$= \exp\left(\frac{\mu}{kT}\right) \iint \alpha_2(E) \, a_2(E) \, b_n(E, T) \, dE \, d\Omega$$

$$+ \frac{I_{\mathrm{sc}}}{eL}(1 - f) \qquad (11)$$

where the right-hand side includes I_{sc}/eL, the volume rate of generation of electron–hole pairs by the sun, and an integral which corresponds to the rate at which electron–hole pairs are regenerated through absorption of the recombination radiation.

The reabsorption process competes with luminescent emission from the surface of the semiconductor to the surroundings. This loss process proceeds at a rate given by the third term on the right-hand side of (9). In Fig. 6 we show the spectral dependence of the loss rate through external emission compared with the spectral dependence of the reabsorption rate. The solid line is the total internal emission spectrum given by $\alpha_2(E) \, b_n(E, T)$, and the broken lines marked B and C are the integrands of (9), third term and second term, respectively, all for a 100-μm-thick sample. Note in Fig. 6 that reabsorption and external emission are about equally probably for a luminescent photon (see Fig. 9), and that the loss is primarily from low-energy photons.

There has been some uncertainty in the literature in the past as to the correct experimental values for the Auger coefficients in silicon [14]. Experimental measurements of these quantities are difficult because of complications from heavy doping effects and surface recombination. However, we are interested in the simpler case where the silicon is intrinsic or, so lightly doped that $n = p$ under illumination. In this case, measurements of the bipolar Auger coefficient $C = C_n + C_p$ are available by a technique that is insensitive to surface re-

combination [15]. The result is $C = 3.88 \times 10^{-31}$ cm^6 s^{-1}. For the free carrier absorption coefficient we use $\alpha_1 = \alpha_n + \alpha_p = 5.5 \times 10^{-18}$ n(cm^{-1}) appropriate for a band-edge photon where n is the electron density [16]. The wavelength dependence of the free carrier absorption is neglected in the narrow wavelength region of interest near the band-edge.

Equation (11) can now be simplified with the help of (10) and the above mentioned assumptions that $n = p$ and that α_1 is independent of wavelength. The result is

$$\left(\alpha_1 + \frac{1}{4n^2 L}\right) \exp\left(\frac{\mu}{kT}\right) \iint a_2(E)\, b_n(E, T)\, dE\, d\Omega + Cn^3$$

$$= \frac{I_{sc}}{eL}(1 - f) \tag{12}$$

where there is now one term on the left-hand side for each of the three loss processes namely free carrier absorption, radiative emission and Auger recombination. This equation can be solved for the chemical potential μ (output voltage), since $np = n_i p_i \exp[\mu/kT]$. In principle, (12) is a nonlinear integral equation since the absorbance $a_2(E)$ depends in a nonlinear way on the carrier density through the free carrier absorption. In practice the free carrier absorption is a small effect and can be neglected in a first trial solution and then iterated once for self-consistency.

In the absence of free carrier absorption, (12) has the form

$$I_0 \exp(x) + eL\, Cn_i^3 \exp\left(\frac{3x}{2}\right) = I_{sc}(1 - f) \tag{13}$$

where $x = eV/kT$, and I_0 and I_{sc} are defined in (5). The open-circuit voltage is the solution of (13) with $f = 0$; the maximum output power is the maximum value of the product xf (multiplied by $I_{sc} kT/e$) where f is a function of x through (13). The maximum output power is obtained from a numerical solution for the root of the equation $d(xf)/dx = 0$. This solution is then iterated to include free carrier absorption self-consistently. Free carrier absorption turns out to be negligible except for the thickest samples. It is interesting that Auger recombination increases the fill factor over the case for radiative recombination only. At open circuit, the Auger recombination is the dominant loss mechanism. At the maximum power point radiative losses are about 20 percent of the losses due to Auger recombination.

The maximum solar cell efficiency is shown in Fig. 7 as a function of silicon thickness for $T = 300$ K and $n_i = p_i = 1.45 \times 10^{10}$ cm^{-3} [17]. We note that the combined effect of the actual optical absorption spectrum, Auger recombination and free carrier absorption is to bring the efficiency of silicon down from 32.9 percent on the basis of Fig. 2 to a peak value of 29.8 percent, for silicon about 100-μm thick. Table I shows the operating parameters for the 100-μm cell. Also shown in Fig. 7, for reference, is the purely radiative efficiency limit when Auger recombination and free carrier absorption are neglected. Fig. 8 shows the open-circuit voltage as a function of cell thickness for the purely radiative case and for the case where we include Auger recombination and free carrier absorption. At open circuit, Auger recombination is the dominant
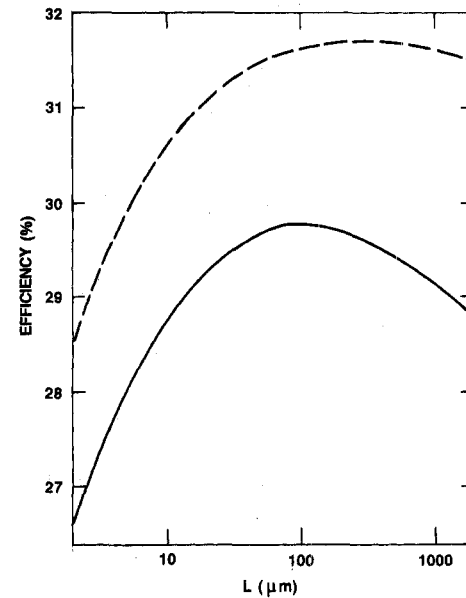

Fig. 7. Efficiency of silicon solar cells as a function of thickness for textured cells with back reflectors. The top curve includes only radiative recombination and the bottom curve includes Auger recombination and free carrier absorption in addition to radiative recombination as discussed in the text.
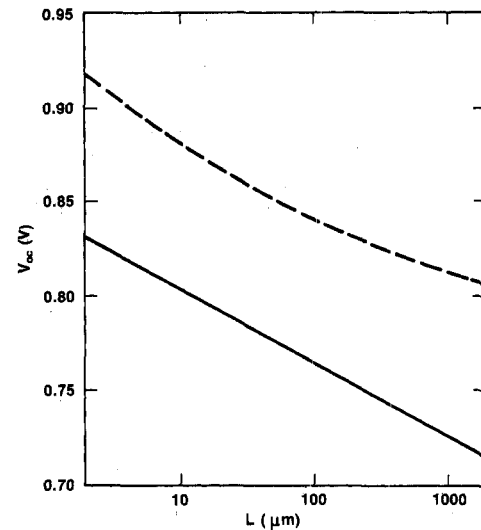

Fig. 8. Open-circuit voltage as a function of cell thickness for radiative recombination only (dashed line) and for radiative, Auger, and free carrier absorption (solid line).

TABLE I
OPERATING PARAMETERS OF OPTIMUM (100 μm) SILICON SOLAR CELL

V_{oc}	=	769 mV
I_{sc}	=	42.2 MA/cm^2
FF	=	0.890
$V_{MAX\ PWR}$	=	703 mV
Efficiency	=	29.8%

loss mechanism. Fig. 9 summarizes the loss processes in the optimum 100-μm solar cell at the operating point.

Throughout the above discussion we have ignored surface recombination. This is one of the most important loss mecha-
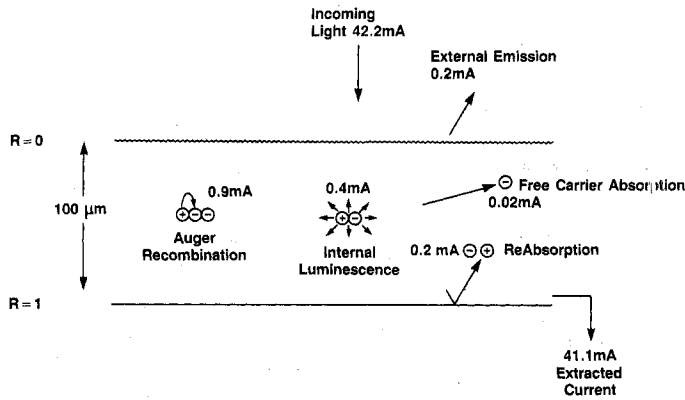
Fig. 9. Summary of the relative magnitudes of the various radiative and other loss processes in the optimum 100-μm cell at the maximum power point.

nisms in conventional unpassivated p-n junction solar cells. In principle, surface recombination can be eliminated by suitable surface passivation treatments. For example, with surface oxidation, surface recombination velocities as low as 5 cm/s have been observed in silicon [18]. In a 200-μm-thick cell this degree of surface passivation gives a surface recombination rate that is ten times worse than the bulk Auger recombination at the maximum power point. In all cells, better surface passivation is required. Even so, a solar cell cannot be completely passivated with SiO_2, since then current could not be extracted. Conductive (n or p type) passivating contacts are required. The development of such contacts is a major obstacle to the practical realization of efficiencies as high as those predicted in this paper for silicon.

We have not included the band gap narrowing due to plasma screening effects [19]. The magnitude of this effect is small at the injection levels for the operating point of the optimum solar cell thickness. The model of Lanyon and Tuft [19] gives the largest effect compared to other models, which nevertheless amounts to only 3.4 mV for the optimum solar cell.

Thus far we have neglected the effect of the carrier concentration gradients that are required inside the cell to collect the current. For the peak efficiency case (100-μm Si thickness) a 1-percent difference in carrier concentration across the cell is sufficient to drive the short-circuit current. This concentration gradient has a negligible effect on the efficiency. However, for a 2000-μm cell, the carrier concentration has to change by a factor of two across the cell in order to maintain a diffusion potential sufficient to drive the short-circuit current. This built-in potential drop will decrease the output voltage by of order kT/e and decrease the limiting efficiency in Fig. 7 for large L. Although internal concentration gradients will not affect the peak efficiency in Fig. 7 they will cause the efficiency to drop more rapidly for large L than indicated in Fig. 7.

CONCLUSIONS

The limiting efficiency of crystalline silicon solar cells has been calculated as a function of silicon thickness, for hypothetical solar cells in which only the fundamental loss mechanisms, radiative recombination, Auger recombination, and free carrier absorption are operative. The radiative recombination rate is calculated from the measured optical absorption spectrum for silicon [12]. The absorption spectrum together with a SERI AM1.5 global solar spectrum were used to determine the short-circuit current. The surfaces of the silicon are assumed to be textured so that the incident sunlight is randomized inside the semiconductor in order to take maximum advantage of light-trapping in the high index of refraction semiconductor. The result of the calculation is a maximum theoretical efficiency of 29.8 percent, for cells about 100-μm thick. This efficiency is close to the 32.9-percent limiting efficiency for an ideal radiative recombination limited solar cell with a step-function optical absorption edge at the bandgap of crystalline silicon (1.12 eV).

The calculation in this article applies to crystalline silicon. In order to apply this approach to a direct gap material like GaAs it would be necessary to consider thin-film periodic texturing as discussed by Sheng et al. [20], a much more complicated problem.

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