

# Considerations on the Solar Cell

By D. A. KLEINMAN

(Manuscript received September 1, 1960)

*The collection efficiency in solar cells is treated by a new method in which all the effects of the solar spectrum and the absorption curve are contained in a single function readily obtained by numerical integration. The method is illustrated by a detailed study of the effects of surface recombination, body recombination and junction depth in silicon cells. The method is also generalized to include built-in electric fields, and calculations are given for silicon. Sufficiently strong fields to improve the collection efficiency markedly can be produced in some compound semiconductors from a gradient in the energy gap. A discussion is given of the dependence of the collection efficiency on the absorption curve of the semiconductor. It is shown that silicon has a very favorable absorption curve in comparison with GaAs or InP. Finally, a treatment is given of the minority carrier collection in a two-junction cell, and calculations are presented for silicon. It is concluded that this structure may be important for cells with high energy gaps and short lifetimes.*

## I. INTRODUCTION

The considerations reported in this paper have been stimulated by the current interest in the solar battery as a power supply for instruments and transmitters in satellite and space probe vehicles. A number of space vehicles† have contained solar batteries with peak outputs ranging from several watts to several hundred watts. It has been demonstrated that solar battery power supplies are technically feasible, not only in space vehicles but also in terrestrial telephone systems.<sup>2</sup> For the latter type of application, however, the solar battery has been found to be not competitive economically with several other available power supplies.<sup>2</sup> However, it is highly advantageous for space vehicles because of its advanced development and commercial availability, light weight, reliability and long life. The long life is due not only to the ruggedness and permanence of its structure and the absence of moving parts or

---

† For a review of the use of solar batteries in space see Daniels.<sup>1</sup>

chemically unstable components, but also to its external and independent source of energy, the sun. The belts of particle radiation<sup>3</sup> recently discovered surrounding the earth may materially reduce the life of solar batteries carried into space.<sup>4,5</sup> We shall proceed with our discussion, however, on the assumption that the solar battery can survive the radiation.

The solar battery is an array of hundreds or thousands of individual cells called solar cells. Each cell is a semiconductor slab, typically  $1 \times 2$  cm, containing a p-n junction within a very small distance, typically  $2 \times 10^{-4}$  cm, of the illuminated surface. The front and back surfaces are fitted with "ohmic" contacts for making electrical connection, and the front surface may be specially treated to reduce its reflectivity.<sup>6</sup> Commercially available cells are made of silicon, and have efficiencies of up to 14 per cent for converting the solar radiation incident upon them into electric power.<sup>7</sup> Other methods now known for converting solar radiation are far less efficient.† Thermoelectric converters,<sup>9</sup> for example, on which considerable work has been done, can approach efficiencies of 1 per cent.

The solar cell was invented by Chapin, Fuller, and Pearson,<sup>10</sup> who briefly described its fabrication, its principles of operation, and the limitations on its efficiency. Due to the work of the inventors and later authors, notably Prince,<sup>11</sup> Pfann and Van Roosbroeck,<sup>12</sup> Cumerow,<sup>13</sup> Rittner<sup>14</sup> and Loferski,<sup>15</sup> the solar battery is well understood in terms of concepts familiar in electrical circuits and semiconductor physics.

High efficiency in a solar battery would be desirable in any application, but especially so in space vehicles. The value of the vehicle, launched at considerable expense, depends in large measure on the instruments and transmitters it carries and the power available for this equipment. At the same time, the more equipment that is carried, the less space and weight can be allowed for the power supply. Therefore, in the economy of space vehicles the solar battery should have the maximum possible efficiency irrespective of the costliness of the improvements.

The operation of the solar cell and the losses of efficiency can best be described in five steps:

(a) Radiation is incident upon the surface and some is *reflected* without entering the cell. This reflection can be a very important loss, since the reflectivity<sup>16</sup> of clean silicon is about 30 per cent in the wavelength range of interest (0.4 to  $1 \mu$ ), and other materials that might be used also have high reflectivities. In practice it is found that the processing in the manufacture of silicon cells leaves the surface with quite a low reflectivity.<sup>6</sup> A recent study<sup>16</sup> has shown that the best antireflection

† For a review of the utilization of solar energy, see Ref. 8, especially Vol. V.

treatments can increase the short circuit current of silicon solar cells by 20 to 25 per cent compared with clean surface cells. It is reasonable to expect that the reflection loss from any material that might be used in the solar cell could be minimized in the same way.

(b) The light enters the cell and some is absorbed by the intrinsic absorption process in which a hole-electron pair is created and a photon is destroyed.† The light absorbed in this way is the useful light in the solar cell. Light of wavelength longer than the intrinsic absorption edge cannot produce hole-electron pairs and is wasted in the solar cell. There is a further waste of energy when hole-electron pairs are produced by photons with more than the minimum required energy, since the excess energy is transferred in a very short time to the semiconductor lattice in the form of heat. These losses may be ascribed to the *spectrum* of solar radiation, since they would not occur if the radiation were monochromatic at the wavelength of the absorption edge. For silicon the losses due to the solar spectrum are about 53 per cent of the energy which enters the cell.<sup>15</sup> By choosing a semiconductor with a somewhat higher energy gap‡ this loss can be considerably reduced.<sup>13,14,15</sup> The energy gap is therefore very important in considering materials for the solar cell.§

(c) Some of the minority carriers produced by the light flow by diffusion to the p-n junction. These are the carriers which contribute to the output current of the cell. Other carriers diffuse away from the junction and *recombine* at the surface or deep inside the cell. The percentage of minority carriers which contribute to the current is called the *collection efficiency*. In a typical commercial silicon solar cell of 9 per cent over-all efficiency the collection efficiency is about 60 per cent.<sup>18</sup> Minority carrier recombination is, therefore, a serious loss of efficiency in the solar battery at the present time. From the spectral response<sup>6,10,18</sup> of silicon solar cells we can infer that the surface recombination velocity is very high, probably greater than  $10^5$  cm/second. From the analysis to be presented we can also infer that the body lifetime is about 10 microseconds, the diffusion length|| about  $10^{-2}$  cm. In high-purity silicon the lifetime can be several milliseconds<sup>20,21</sup> and with certain surface treatments the recom-

† For a review of the optical properties of semiconductors, see Hrostowski.<sup>17</sup>

‡ For the purposes of this paper the energy gap and the intrinsic absorption edge are essentially the same thing, except that the former is expressed as an energy while the latter is the equivalent photon wavelength.

§ We shall not consider in this paper composite cells such as those suggested by E. Jackson (Ref. 8, Vol. V), in which one attempts to reduce spectrum losses by stacking several thin cells of different energy gaps. Cells of this type appear to be somewhat impractical from the standpoints of mechanical construction and of providing a suitably matched electrical load.

|| Recently a measured value of  $\sim 5 \times 10^{-3}$  cm for the diffusion length has been reported by Vavilov, Smirnov and Patskevitch.<sup>19</sup>

bination velocity<sup>22</sup> can be as low as 40 cm/second. The recombination, therefore, is due almost entirely to the degradation<sup>20</sup> of surface and body lifetime that occurs in the manufacturing process. In compound semiconductors the recombination losses are likely to be considerably greater than in silicon. In gallium arsenide, for example, the lifetime seems at present to be of the order of a millimicrosecond.<sup>23</sup> In general, it appears difficult to obtain lifetimes greater than 0.01 or 0.1 microsecond in the compound semiconductors.†

(d) The diffusion maintains an excess concentration of minority carriers on both sides of the junction. The voltage developed by the solar cell is due to these excess concentrations of minority carriers. This voltage, however, is considerably less than the energy (in units of electron-volts) of a hole-electron pair in the semiconductor. The latter, for our purposes, may be taken to be the energy gap, which in silicon is 1.2 volts.<sup>25</sup> The voltage of a silicon solar cell in full sunlight under maximum power conditions is about 0.4 volts.<sup>10,18</sup> Therefore, the cell is able to convert only a portion of the energy stored as hole-electron pairs into electrical work. The loss may be referred to as the *junction loss*. The junction loss should vanish and the voltage should approach the energy gap when the minority carrier density approaches the majority carrier density, a limit corresponding to infinite light intensity. In the other limit of zero light intensity, the junction loss causes the efficiency of the solar cell to approach zero. According to the equivalent circuit point of view of Pfann and Van Roosbroeck,<sup>12</sup> the short-circuit current of the cell flows partly through the load and partly through the junction in the forward direction. The voltage and the junction loss therefore depend upon the forward current-voltage characteristic of the junction. The theory of p-n junctions<sup>26,27</sup> predicts that the forward current should decrease exponentially with increasing energy gap. Therefore, insofar as actual junctions obey the ideal junction theory, the junction loss can be reduced by increasing the energy gap. A number of authors<sup>13,14,15</sup> have considered the spectrum loss and junction loss as a function of energy gap. If all other losses are neglected, the maximum efficiency is obtained for an energy gap of about 1.6 volts.<sup>15</sup> It is now possible with mixed semiconductors<sup>24,28</sup> to obtain nearly any desired energy gap from 0.7 volt (germanium) to 2.4 volts (GaP), which completely covers the range of interest. It should be kept in mind that silicon p-n junctions show a large contribution to the current from thermal generation and recombination through traps in the junction region.<sup>29</sup> The short lifetimes in the compound semiconductors suggest that trap effects may be even more important in those

† Ref. 24, p. 58.



materials. Therefore, it may not be possible to obtain large reductions in the junction loss by increasing the energy gap.

(e) Finally there is the loss due to *resistance* of the very thin side of the junction next to the surface and of the contact to the surface. This resistance places a lower limit on the depth of the junction. Prince<sup>11</sup> has considered the optimum depth for silicon solar cells taking into account the resistance loss and the collection loss. In practice, the internal resistance of silicon cells<sup>11</sup> is between one and two ohms and the junction depth is between  $1 \times 10^{-4}$  and  $2 \times 10^{-4}$  cm. The elimination of resistance loss would increase the efficiency of a 9 per cent cell to about 11 or 12 per cent.<sup>18</sup> Unlike the other losses considered here, the resistance loss is not characteristic of the material used in the solar cell, and the methods for reducing it will be similar for any material.

It has been mentioned that the solar spectrum loss and the junction loss have been considered at some length. It is also well understood what to do about reflection and resistance. But the collection loss has not been thoroughly treated in the literature. Several calculations<sup>6</sup> have been made using the approach of Pfann and Van Roosbroeck.<sup>12</sup> This may be called the monochromatic method. Light of a certain wavelength, and therefore having a certain absorption coefficient in the material, enters the solar cell. Solutions are obtained in terms of elementary functions for the minority carrier density, taking into account diffusion, surface and body recombination, the generation of carriers by the light and the boundary conditions at the junction and at infinite depth. The solution gives a certain diffusion current into the junction which is the short-circuit current of the cell. This current must then be averaged over the wavelengths in the solar spectrum to obtain the collection efficiency. The averaging requires a tedious numerical integration, because the monochromatic current is a complicated function of the absorption coefficient, which is in turn a rapidly varying (measured) function of wavelength. The method is sound and can account in a satisfactory way for the collection efficiencies observed in solar cells.<sup>6</sup> The method is not well suited, however, for a systematic discussion of collection efficiency and no such discussion has been given. Several authors<sup>13,14,15</sup> have even argued that the collection efficiency can be considered unity in fundamental considerations on the solar battery, since lifetimes can be expected to increase as technology improves. A review of the history of the photovoltaic effect and its utilization has recently been given by Rappaport.<sup>30</sup>

In this paper we consider the collection efficiency more systematically by a more powerful method than the monochromatic method. This

method is based upon obtaining a function, called the *photodensity function*, which includes all the effects of the solar spectrum and the wavelength dependent absorption coefficient. This function is obtained by a relatively easy numerical integration over the solar spectrum. In terms of the photodensity function the solution can be obtained almost immediately to any solar cell collection problem in the approximation in which a single diffusion length describes the minority carriers. Illustrative calculations are presented for silicon solar cells showing how the collection efficiency depends on surface recombination velocity, junction depth and diffusion length. The method is readily generalized to include cases in which different diffusion lengths must be used for electrons and holes. Another generalization is presented which takes into account a "built-in" electric field in the region between the junction and the surface. It is shown that by the use of mixed semiconductors it should be possible to obtain sufficiently large built-in fields to increase the collection efficiency significantly. In ordinary silicon cells, however, one would not expect the field to be large enough to have much effect. The important question of which semiconductors should be best for solar battery applications, already much discussed<sup>11,13,14,15,30</sup> with respect to spectrum and junction losses, is taken up again from the point of view of the collection efficiency. It is pointed out that the absorption coefficient as a function of wavelength is very important in determining the collection efficiency. Silicon has an absorption curve of favorable shape, which in part accounts for its present superiority over other materials of more favorable energy gap. It is possible that for room-temperature use silicon will remain the best material, although higher-gap materials will certainly be needed for use at temperatures above 200°C. Finally, there is presented a discussion of cells containing two junctions to improve the collection efficiency. It is shown that in cells of comparatively low collection efficiency (<50 per cent), considerable improvement can be obtained by the use of a second junction. This construction may prove important in high gap cells which might otherwise have rather low collection efficiencies.

## II. FORMULATION OF THE PROBLEM

If the concentration of minority carriers is small compared to the concentration of majority carriers, the equation describing the production, diffusion, and recombination of minority carriers is

$$D \frac{d^2 n}{dx^2} - \frac{n}{\tau} + \int_0^{\lambda_g} N(\lambda) \alpha(\lambda) e^{-\alpha x} d\lambda = 0. \quad (1)$$

In (1),  $n(x)$  is the excess minority carrier concentration over the equilibrium concentration. In a typical case the maximum value of  $n(x)$  is of the order  $10^{12} \text{ cm}^{-3}$ , so that the validity of (1) is assured. The diffusion constant  $D$  and lifetime  $\tau$  will be assumed to apply to all minority carriers whether holes on the n-side or electrons on the p-side of the junction. This assumption should lead to no serious error in silicon, but might have to be modified for some of the III-V semiconductors because of the relatively low mobility of the holes.<sup>†</sup> The integral term in (1) represents the production of minority carriers by light with a photon distribution  $N(\lambda)$  in a material with absorption coefficient  $\alpha(\lambda)$  and intrinsic absorption edge  $\lambda_g$ . The total flux of photons capable of producing hole-electron pairs is

$$N = \int_0^{\lambda_g} N(\lambda) d\lambda. \quad (2)$$

We shall neglect reflection completely and identify  $N(\lambda)$  with the solar photon spectrum with respect to wavelength.<sup>‡</sup> The total effective photon flux is  $N = 3.3 \times 10^{17} \text{ cm}^{-2} \text{ sec}^{-1}$  for silicon.<sup>§</sup> The boundary conditions to be imposed on  $n(x)$  are

$$n(\infty) = 0, \quad n'(0) = (s/D)n(0), \quad (3)$$

where  $s$  is the recombination velocity of the surface. A solution of (1) and (3) over the whole domain  $0 \leq x < \infty$  represents the minority carrier density in a homogeneous illuminated semiconductor.

If we now locate a junction at depth  $x = a$ , additional boundary conditions must be satisfied at the junction. In general, these will relate the minority carrier densities on each side of the junction to the operating voltage of the cell. The simplest case is the short-circuit condition, in which the voltage is zero.<sup>||</sup> For this case the excess carrier densities must vanish on each side of the junction.<sup>26,27</sup> The boundary conditions for the short-circuit condition are therefore

$$n(a) = 0. \quad (4)$$

<sup>†</sup> Ref. 24, p. 12.

<sup>‡</sup> Details on the solar spectrum are given by Ref. 31. See also Ref. 15.

<sup>§</sup> This number, obtained from Ref. 31, is in substantial agreement with the plot of  $\int_0^{\lambda_g} N(\lambda) d\lambda$  in Ref. 15. We are considering the solar radiation in space just outside the earth's atmosphere.

<sup>||</sup> We neglect voltage drops due to internal resistance. This causes no loss of generality, since an arbitrary resistance can be included in the equivalent circuit. In the presence of resistance, (4) corresponds to a small forward bias externally applied to the cell. The statement following (4) remains valid, and one identifies this maximum diffusion current, not the short-circuit current, with the current generator.

This corresponds to the maximum current which can be drawn from the cell; smaller currents correspond to nonvanishing values of  $n(a)$  on both sides of the junction. However, we may regard any solution of (1) corresponding to arbitrary operating conditions as the *superposition* of the short-circuit solution and an appropriate solution of the homogeneous equation

$$D \frac{d^2 n}{dx^2} - \frac{n}{\tau} = 0. \quad (5)$$

According to p-n junction theory,<sup>26,27</sup> these solutions are just those associated with forward currents in an unilluminated p-n junction. The superposition of solutions for the minority carrier density is therefore equivalent to superposing the short-circuit current with an appropriate forward current in the junction. If  $I_g$  is the short-circuit current and  $I_f$  the forward current, the current in the external circuit is  $I_g - I_f$ , in accordance with the equivalent circuit of Pfann and Van Roosbroeck.<sup>12</sup>

The collection problem, therefore, is to calculate the short-circuit solution from (1) and (4) and from this the diffusion current density at the junction, taking into account the contributions from each side. The collection efficiency then is given by

$$Q_1 = DN^{-1} ( |n'(a-) | + |n'(a+) | ), \quad (6)$$

with the subscript "1" indicating that the expression applies to cells with a single junction. In a many junction cell  $Q_n$  would be a sum of terms of the form (6).

The equivalent circuit for a solar cell with load therefore consists of a current generator  $I_g$  connected to a junction and a load in parallel, with the currents  $I_f$  flowing in the junction (forward) and  $I_f - I_g$  in the load. Pfann and Van Roosbroeck<sup>12</sup> obtained the following condition for maximum power delivered to the load:

$$G = z \ln z + z - 1, \quad (7)$$

where

$$z = e^{eV/kT}, \quad (8)$$

$V$  is the voltage, and  $G$  is a dimensionless reduced current proportional to  $I_g$ . It is assumed that  $I_f$  obeys an ideal junction characteristic<sup>26,27</sup>

$$I_f = eAJ_0(e^{eV/kT} - 1), \quad (9)$$

where  $A$  is the junction area and  $J_0$  is a characteristic particle current density. The reduced current  $G$  is then defined by the relation

$$G = I_g/eAJ_0 = (N/J_0)Q. \quad (10)$$

The over-all efficiency can be written<sup>12</sup>

$$\epsilon = \frac{kT}{W} Qz \frac{(\ln z)^2}{G}, \quad (11)$$

where  $z$  is the solution of (7), and

$$W = N^{-1} \int_0^\infty N(\lambda) (hc/\lambda) d\lambda. \quad (12)$$

Clearly  $W$  is the radiant energy absorbed on the average to produce one hole-electron pair. For large  $G$ , (7) becomes

$$G \approx z \ln z \quad G \gg 1, \quad (13)$$

and (11) becomes

$$\epsilon \approx (eV/W)Q. \quad (14)$$

Here  $eV$  is the work done on the load and  $W/Q_1$  is the energy absorbed per carrier flowing in the load. The approximation of large  $G$  is fully justified, since in full sunlight  $G$  will be of the order  $10^7$ . The efficiency for large  $G$  can also be written

$$\epsilon_1 \approx (kT/W)Q_1 \ln G, \quad (15)$$

which exhibits the logarithmic dependence of the efficiency on the light intensity. It will be noted that the over-all efficiency  $\epsilon_1$  depends upon the collection efficiency  $Q_1$  through the factor  $Q_1$  and also through  $G$ .

### III. THE PHOTODENSITY METHOD

The collection problem consists in solving (1) subject to (3) and (4). We begin by observing that the function

$$\int_0^{\lambda G} N(\lambda) \tau \frac{\alpha(\lambda)}{1 - \alpha^2 L^2} e^{-\alpha x} d\lambda, \quad (16)$$

where  $L = (D\tau)^{1/2}$  is the diffusion length, is a particular solution of (1). It satisfies the boundary condition at infinity but none of the other boundary conditions. If ambiguity arises due to the pole  $\alpha L = 1$  occurring in the range of integration, the integral can be taken as a prin-

cial value. The pole is removed if we combine (16) with an appropriate solution of the homogeneous equation (5), and write

$$n(x)_p = \int_0^{\lambda_g} N(\lambda) \tau \frac{\alpha(\lambda)}{1 - \alpha^2 L^2} (e^{-\alpha x} - e^{-x/L}) d\lambda. \quad (17)$$

This function is a solution of (1) and satisfies

$$n(\infty) = n(0) = 0, \quad (18)$$

which is the form taken by (3) when the recombination velocity  $s$  is very large. Therefore,  $n(x)_p$  represents the density of excess minority carriers in a semiconductor without junctions illuminated on a surface with fast recombination. The derivative of  $n(x)_p$  at the surface is

$$n'(0)_p = \int_0^{\lambda_g} N(\lambda) \frac{\alpha(\lambda)}{1 + \alpha L} d\lambda. \quad (19)$$

We call  $n(x)_p$  the *photodensity*. It can be readily evaluated by numerical integration (see Appendix), since the integrand is a simple expression with no poles.

It is convenient now to introduce dimensionless quantities

$$\begin{aligned} \zeta &= x/L, & \beta &= \alpha L, & \gamma &= a/L, \\ \nu(\lambda) &= N(\lambda)/N, & \omega &= D/sL, \end{aligned} \quad (20)$$

and define the function

$$\varphi(z) = (e^z - 1)/z. \quad (21)$$

Then the photodensity can be written

$$n(x)_p = (N\tau/L)F(\zeta, L),$$

where  $F(\zeta, L)$  is the *photodensity function*

$$F(\zeta, L) = \zeta e^{-\zeta} \int_0^{\lambda_g} \nu(\lambda) \frac{\beta}{1 + \beta} \varphi[\zeta(1 - \beta)] d\lambda. \quad (22)$$

This function is shown in Fig. 1 as a continuous function of  $\zeta$  for three values of  $L$  ( $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$  cm) based on the solar spectrum and the absorption curve for silicon.<sup>32†</sup> The calculation of  $F(\zeta, L)$  is discussed in the Appendix. For small  $\zeta$  the photodensity function has the expansion

$$F(\zeta, L) = \zeta \int_0^{\lambda_g} \nu(\lambda) \frac{\beta(\lambda)}{1 + \beta} d\lambda - \frac{1}{2} \zeta^2 \int_0^{\lambda_g} \nu(\lambda) \beta(\lambda) d\lambda + \dots \quad (23)$$

† Values of  $\alpha > 10^5 \text{ cm}^{-1}$  required as discussed in the Appendix for the calculation of Fig. 5 are from Pfestorf.<sup>33</sup>

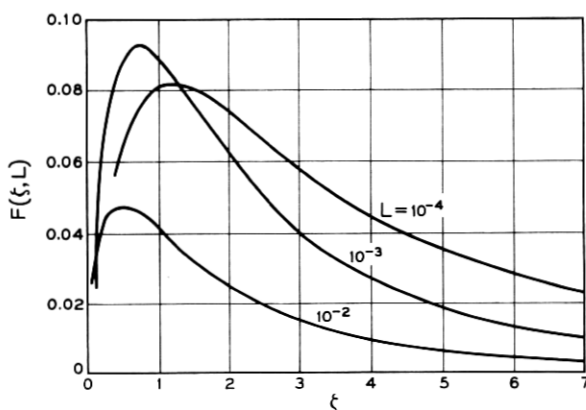


Fig. 1 — The photodensity function (22) for silicon as a function of  $\xi$  for  $L = 10^{-4}$ ,  $10^{-3}$  and  $10^{-2}$  cm.

Once  $F(\xi, L)$  has been obtained, the solution  $n(x)$  satisfying (1), (3) and (4) is readily constructed from  $F(\xi, L)$  and the functions  $e^{\pm \xi}$ , which satisfy the homogeneous equation (5). The solution may be written

$$n(x) = (N\tau/L)[Ae^{\xi} + Be^{-\xi} + F(\xi, L)], \quad (24)$$

where for  $0 \leq x \leq a$

$$\begin{aligned} A &= -\frac{1}{2} \frac{F(\lambda)(1 + \omega) + \omega e^{-\gamma} F'(\gamma)}{\sinh \gamma + \omega \cosh \gamma}, \\ B &= \frac{1}{2} \frac{F(\gamma)(1 - \omega) + \omega e^{\gamma} F'(\gamma)}{\sinh \gamma + \omega \cosh \gamma}, \end{aligned} \quad (25)$$

and for  $a \leq x < \infty$

$$\begin{aligned} A &= 0, \\ B &= -e^{\gamma} F(\gamma), \end{aligned} \quad (26)$$

where  $F' = dF/d\xi$  and for brevity  $L$  has been omitted as an argument of  $F$ . The solution in the region  $a \leq x < \infty$  is, of course, independent of  $\omega$ . In the region  $0 \leq x \leq a$  the solutions in the limiting cases  $\omega \rightarrow 0$  and  $\omega \rightarrow \infty$  are

$$n(x) \xrightarrow{\omega \rightarrow 0} \frac{N\tau}{L} \left[ F(\xi) - \frac{\sinh \xi}{\sinh \gamma} F(\gamma) \right], \quad (27)$$

$$n(x) \xrightarrow{\omega \rightarrow \infty} \frac{N\tau}{L} \left[ F(\xi) - F(\gamma) + \frac{\sinh(\gamma - \xi)}{\cosh \gamma} F'(\gamma) \right]. \quad (28)$$

The boundary conditions satisfied by these solutions at  $x = 0$  are  $n(0) = 0$  and  $n'(0) = 0$  respectively.

The collection efficiency for single junction cells can now be obtained from (6) in the following form:

$$Q_1 = \frac{F(\gamma)(1 + \omega) e^\gamma + \omega F'(0)}{\sinh \gamma + \omega \cosh \gamma}. \quad (29)$$

In the limits  $\omega \rightarrow 0$  and  $\omega \rightarrow \infty$  this reduces to

$$\begin{aligned} Q_1 &\xrightarrow{\omega \rightarrow 0} F(\gamma)(1 + \coth \gamma), \\ Q_1 &\xrightarrow{\omega \rightarrow \infty} F(\gamma)(1 + \tanh \gamma) + F'(0) \operatorname{sech} \gamma, \end{aligned} \quad (30)$$

which refer to fast and slow surface recombination respectively.

Much of the simplicity of (29) and (30) results from the assumption of "effective" values for  $D$  and  $\tau$  which apply to both sides of the junction. The difficulty of measuring these parameters in an actual cell, especially as a function of depth, justifies this simplification for most considerations. The most conspicuous case where this assumption may lead to serious error is in some of the compound semiconductors where the mobility and diffusion constant may be an order of magnitude less for holes than for electrons.<sup>†</sup> When different  $L$  obtain on the two sides of the junction (24), (25) and (26) are still formally valid but (29) is no longer valid. The collection efficiency can then be written  $Q_1 = Q_- + Q_+$ , where

$$\begin{aligned} Q_- &= \frac{F(\gamma)(\cosh \gamma + \omega \sinh \gamma) + \omega F'(0)}{\sinh \gamma + \omega \cosh \gamma} - F'(\gamma), \\ Q_+ &= F(\gamma) + F'(\gamma) \end{aligned} \quad (31)$$

are the contributions from  $0 \leq x \leq a$  and  $a \leq x < \infty$  respectively. If the same  $L$  is used for both sides of the junction  $Q_- + Q_+$  reduces to (29).

The fast surface recombination limit  $\omega = 0$  is valid if  $\omega$  satisfies the two conditions  $\omega \ll 1$ ,  $\omega \ll \gamma$ . In silicon solar cells the junction depth is considerably less than the diffusion length ( $\gamma \ll 1$ ) so that the second condition implies the first. Therefore the criterion for high surface recombination velocity is

$$s \gg D/a. \quad (32)$$

The diffusion constant  $D$  can be obtained from measured mobilities  $\mu$  by

<sup>†</sup> Ref. 24, p. 12.



means of the Einstein relation,<sup>34</sup> which in conventional laboratory units is

$$D \text{ (in cm}^2\text{/second)} = 0.026 \left( \frac{T}{300^\circ\text{K}} \right) \mu \text{ (in cm}^2\text{/volt-second)}, \quad (33)$$

with  $T$  the absolute temperature in  $^\circ\text{K}$ . The mobility in highly doped silicon has been studied by Backenstoss,<sup>35</sup> who finds that for impurity concentrations greater than  $10^{19} \text{ cm}^{-3}$  the mobilities of electrons and holes approach the limiting values of 80 and 40  $\text{cm}^2\text{/volt-second}$  respectively. Since  $a \sim 10^{-4} \text{ cm}$ , the criterion (32) gives  $s > 10^5 \text{ cm/second}$  in silicon. Although surface treatments are known<sup>21</sup> which can reduce  $s$  in pure silicon to below  $10^2 \text{ cm/second}$ , Prince and Wolf<sup>6</sup> point out that these treatments tend to increase significantly the reflectivity of the surface. If this occurred the treatment might well reduce rather than increase the over-all efficiency of the cell. On the other hand, Malovetskaya, et al.<sup>16</sup> have reported antireflection films that greatly reduce reflection losses without increasing the surface recombination. The effect of surface recombination on  $Q_1$  is shown in Fig. 2 for a silicon solar cell having the typical parameters

$$\begin{aligned} D &= 5 \text{ cm}^2\text{/second,} \\ \tau &= 2 \times 10^{-5} \text{ second,} \\ L &= 10^{-2} \text{ cm,} \\ a &= 10^{-4} \text{ cm.} \end{aligned} \quad (34)$$

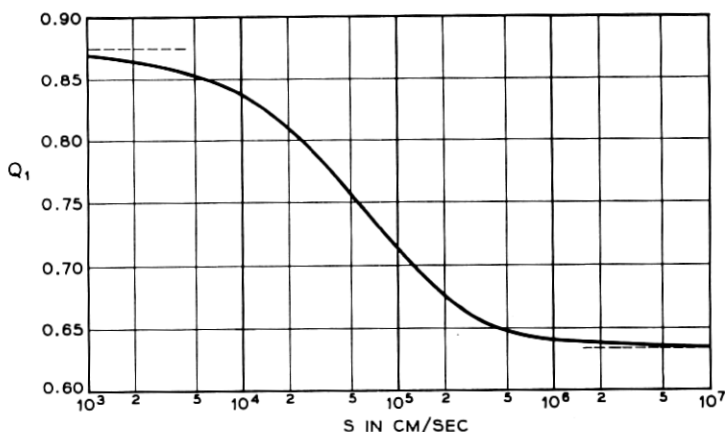


Fig. 2 — The collection efficiency as a function of surface recombination velocity for a silicon cell having the parameters (34).

For this cell  $Q_1$  increases from 63 to 87 per cent as  $s$  decreases from  $10^7$  to  $10^3$  cm/second. This example shows that considerable improvement in  $Q_1$  would result from the elimination ( $s < 10^3$  cm/second) of surface recombination. The presence of surface recombination in commercial silicon cells is indicated by the rapid fall-off in the spectral response<sup>10,18</sup> at short wavelength  $\lambda < 6 \mu$ . Little is known about surface recombination in the compound semiconductors. The fact that body lifetimes tend to be short<sup>24</sup> ( $\tau \sim 10^{-8}$  second) suggests that surface recombination is probably very fast ( $s \sim 10^7$  cm/second). On the basis of these considerations, the most reliable guess is to set  $\omega = 0$  except where specific information to the contrary is available.

The dependence of  $Q_1$  upon the junction depth is shown in Fig. 3 for a silicon cell with  $D$ ,  $\tau$  and  $L$  as given in (34). The curves shown for  $\omega = 0$  and  $\omega \rightarrow \infty$  are envelopes for the entire family  $Q_1(\gamma, \omega)$ . Although the limiting curves have quite different forms they approach the same form for small and large depths:

$$Q_1 \xrightarrow[\gamma \rightarrow 0]{} F'(0) = \int_0^{\lambda_g} \nu(\lambda) \beta(\lambda) (1 + \beta)^{-1} d\lambda, \quad (35)$$

$$Q_1 \xrightarrow[\gamma \rightarrow \infty]{} 2F(\gamma).$$

The monotonic decrease of  $Q_1(\gamma, 0)$  with increasing  $\gamma$  is typical of silicon cells. In semiconductors of considerably higher energy gap the condition  $F'(0) + \frac{1}{2}F''(0) > 0$  may be satisfied, in which case  $Q_1(\gamma, 0)$  will at first

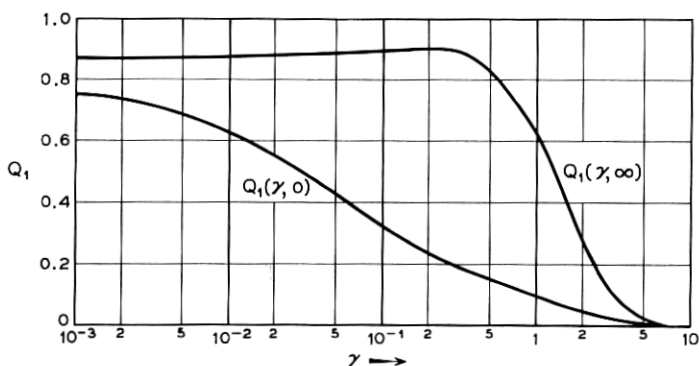


Fig. 3 — The collection efficiency as a function of junction depth for a silicon cell with parameters  $D, \tau, L$  given by (34). The abscissa is  $\gamma = a/L$ , where  $a$  is the junction depth and  $L$  the diffusion length. The curve  $Q_1(\gamma, \infty)$  refers to zero and  $Q_1(\gamma, 0)$  to infinite surface recombination velocity.

increase with  $\gamma$  to reach a maximum and then fall to zero as  $\gamma$  is increased further. A very broad maximum in  $Q_1(\gamma, \infty)$  is seen in Fig. 3 near  $\gamma = 0.2$ . The shape of the curve shows that relatively deep junctions ( $\gamma \sim 0.5$ ) could be used if surface recombination were absent, which would permit the internal resistance of the cell to be greatly reduced. On the other hand, deep junctions cannot be used if the surface recombination is important. This calculation also shows that in a cell with surface recombination reducing  $a$  from  $10^{-4}$  ( $\gamma = 0.01$ ) to  $5 \times 10^{-5}$  cm ( $\gamma = 0.005$ ) would improve the collection efficiency only slightly. Therefore, one may regard  $a = 10^{-4}$  cm as close to the optimum junction depth for silicon solar cells.

The dependence of  $Q_1$  on diffusion length is shown in Fig. 4 for a silicon cell with a junction depth  $a = 10^{-4}$  cm. The curves  $Q_1(L, \infty)$  and  $Q_1(L, 0)$  are envelopes for the family  $Q_1(L, \omega)$  considered as continuous functions of  $L$ . These calculations show that  $L > 0.1$  cm may be considered essentially infinite. The limiting values as  $L \rightarrow \infty$  are

$$\begin{aligned} Q_1(L, \infty) &\rightarrow 1, \\ Q_1(L, 0) &\rightarrow \int_0^{\lambda a} \nu(\lambda) \frac{1 - e^{-\alpha a}}{\alpha a} d\lambda, \end{aligned} \quad (36)$$

which are indicated in the figure. It will be observed that  $Q_1$  increases relatively little as  $L$  increases beyond  $10^{-2}$  cm. On the other hand considerable improvement results from increasing  $L$  from  $10^{-3}$  to  $10^{-2}$  cm.

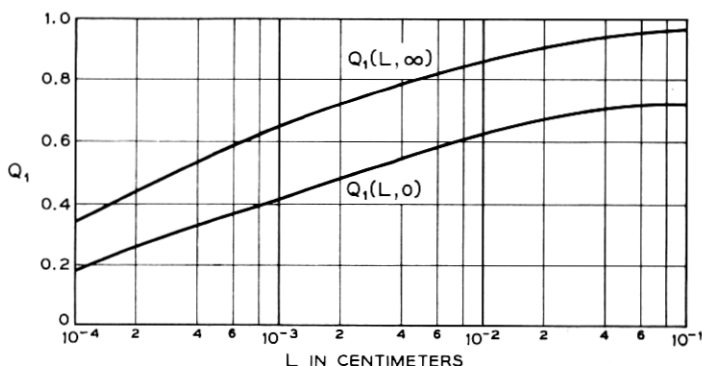


Fig. 4 — The collection efficiency as a function of diffusion length for a silicon cell with the junction depth  $10^{-4}$  cm. The curve  $Q_1(L, \infty)$  refers to zero and  $Q_1(L, 0)$  to infinite surface recombination velocity.

## IV. THE EFFECT OF AN ELECTRIC FIELD

In his review, Rappaport<sup>30</sup> has suggested that a "built-in" electric field may exist near the surface of solar cells causing minority carriers to drift toward the junction. If sufficiently strong this electric field would in effect eliminate surface recombination. One would expect that to reduce surface recombination significantly the field would have to be of the order  $E \sim s/\mu \sim 10^3$  volts/cm, assuming the typical values  $s \sim 2 \times 10^5$  cm/second,  $\mu \sim 200$  cm<sup>2</sup>/volt-second. The built-in electric field could arise in two ways, from a gradient in the impurity concentration, and from a gradient in the energy gap. In the first case the field is given by<sup>36</sup>

$$E \sim (0.026/a) \ln (N_0/N_a) \quad \text{volts/cm}, \quad (37)$$

where  $N_0, N_a$  are the carrier concentrations at  $x = 0$  and  $x = a$  respectively, and  $0.026 = kT/e$  at room temperature. This is just the field required to cancel the diffusion current in equilibrium according to the Einstein relation (33). Actually (37) is an approximation giving an average effective field over the region  $0 \leq x \leq a$ . Consider as an example a cell made by the diffusion of boron from the vapor phase into  $n$ -type silicon.<sup>6,10,11</sup> The surface concentration of boron is about<sup>11</sup>  $N_0 \sim 18^{18}$  cm<sup>-3</sup> and  $N_a \sim 10^{17}$  cm<sup>-3</sup>. If  $a \sim 10^{-4}$  cm, the built-in field is  $E \sim 500$  volts/cm, which is probably much less than  $s/\mu$  and therefore not large enough to cause much reduction in surface recombination. We may conclude that in commercial solar cells the built-in field can be neglected, as in the treatment of the last section and in the previous literature. On the other hand, the possibility remains that much larger built-in fields could be obtained, since  $N_0$  might be made to approach the solid solubility,<sup>37</sup> which for boron exceeds  $10^{20}$  cm<sup>-3</sup>. The built-in field would then be about  $E \sim 1800$  volts/cm, which might cause a significant improvement in collection efficiency.

It appears that really large fields  $E \gg s/\mu$  might be obtained from gradients in the energy gap. Such a gradient could be obtained in GaAs by diffusing in phosphorous from the surface. Mixed crystals<sup>38</sup> † GaAs-GaP can exist in all proportions, and the energy gap varies as a function of composition from 1.4 (GaAs) to 2.4 (GaP). If the impurity concentration is approximately constant, the band edge corresponding to the majority carriers must also be approximately constant. The gradient of the energy gap therefore appears almost entirely in the band edge for the minority carriers, and is equivalent to a built-in electric field acting

† See also Ref. 24, p. 52.

on the minority carriers. It seems quite feasible that the field may be of order  $E \sim 10^4$  volts/cm in GaAs-P. In addition to producing the field, the gradient in energy gap causes the absorption coefficient to become a function of position  $\alpha(\lambda, x)$ . To make the analysis more tractable we may regard  $\alpha(\lambda)$  as an "effective" absorption coefficient independent of position.

To take into account a constant electric field it is only necessary to add to the left side of (1) the term  $-\mu E(dn/dx)$ , giving

$$D \frac{d^2 n}{dx^2} - \frac{n}{\tau} - \mu E \frac{dn}{dx} + \int_0^{\lambda_g} N(\lambda) \alpha(\lambda) e^{-\alpha x} d\lambda = 0. \quad (38)$$

This is conveniently written in the reduced form

$$\frac{d^2 y}{d\zeta^2} - y - 2\varepsilon \frac{dy}{d\zeta} + \int_0^{\lambda_g} \nu \beta e^{-\beta \zeta} d\lambda = 0, \quad (39)$$

where

$$\begin{aligned} \varepsilon &= \frac{E}{2D/\mu L}, \\ y &= \frac{n}{N\tau/L}, \end{aligned} \quad (40)$$

and  $\beta, \nu, \zeta$  are defined in (20). The boundary conditions on  $y(\zeta)$  are

$$y'(0) = Sy(0), \quad y(\gamma) = 0, \quad y(\infty) = 0, \quad (41)$$

where

$$S = 2\varepsilon + \omega^{-1} \quad (42)$$

depends on the electric field as well as the surface recombination velocity. If the last term in (39) is dropped the resulting homogeneous equation has the solution  $e^{-\rho\zeta}$ ,  $e^{\sigma\zeta}$ , where

$$\begin{aligned} \rho &= (1 + \varepsilon^2)^{\frac{1}{2}} - \varepsilon \leq 1, \\ \sigma &= (1 + \varepsilon^2)^{\frac{1}{2}} + \varepsilon \geq 1, \\ \rho\sigma &= 1. \end{aligned} \quad (43)$$

The general solution can be written

$$y(\zeta) = Be^{-\rho\zeta} + Ae^{\sigma\zeta} + F(\zeta, L, \varepsilon), \quad (44)$$

where

$$F(\zeta, L, \varepsilon) = \int_0^{\lambda g} \nu \frac{\beta}{1 + \rho\beta} \frac{e^{-\beta\zeta} - e^{-\rho\zeta}}{1 - \sigma\beta} d\lambda. \quad (45)$$

For the region  $0 \leq \zeta \leq \gamma$ ,

$$\begin{aligned} B &= \frac{F'(0) + (S - \sigma)F(\gamma)e^{-\sigma\gamma}}{\rho + \sigma e^{-(\rho+\sigma)\gamma} + S(1 - e^{-(\rho+\sigma)\gamma})} \\ A &= -\frac{F'(0)e^{-(\rho+\sigma)\gamma} + (S + \rho)F(\gamma)e^{-\sigma\gamma}}{\rho + \sigma e^{-(\rho+\sigma)\gamma} + S(1 - e^{-(\rho+\sigma)\gamma})}. \end{aligned} \quad (46)$$

As  $\varepsilon$  approaches zero,  $F(\zeta, L, \varepsilon)$  approaches  $F(\zeta, L)$  defined by (22) and  $A, B$  of (46) go over into  $A, B$  of (25). It will be assumed that the electric field exists only in the region  $0 \leq \zeta \leq \gamma$ . Thus the solution in the region  $\zeta \geq \gamma$  is

$$y(\zeta) = F(\zeta, L) - F(\gamma, L)e^{\gamma-\zeta}. \quad (47)$$

Since  $y$  vanishes at the junction, the current is just the diffusion current and the collection efficiency is  $Q_1 = Q_- + Q_+$ , where

$$\begin{aligned} Q_+ &= y'(\gamma_+), \\ Q_- &= -y'(\gamma_-). \end{aligned} \quad (48)$$

From (47),

$$Q_+ = F(\gamma_+) + F'(\gamma_+) \quad (49)$$

as in (31). From (44) and (46),

$$\begin{aligned} Q_- &= \frac{F(\gamma)[1 - e^{-(\rho+\sigma)\gamma} + S(\sigma + \rho e^{-(\rho+\sigma)\gamma})] + F'(0)e^{-\rho\gamma}(\rho + \sigma)}{\rho + \sigma e^{-(\rho+\sigma)\gamma} + S(1 - e^{-(\rho+\sigma)\gamma})} \\ &\quad - F'(\gamma_-), \end{aligned} \quad (50)$$

where  $F'(\zeta) = (d/d\zeta)F(\zeta, L, \varepsilon)$ . In the limit  $\varepsilon \rightarrow 0$  this goes over into  $Q_-$  given in (31). If  $2\varepsilon \gg \beta$ ,  $2\varepsilon \gg 1/\beta$  and  $2\varepsilon \gg \gamma$ , (50) becomes

$$Q_1 \xrightarrow{\varepsilon \rightarrow \infty} \int_0^{\lambda g} \nu(1 - e^{-\beta\gamma}) d\lambda - \frac{1}{2\varepsilon} \int_0^{\lambda g} \nu\beta e^{-\beta\gamma} d\lambda. \quad (51)$$

Since the first term of (51) is the probability of absorbing a photon in the layer  $0 \leq \zeta \leq \gamma$ , the limit  $\varepsilon \rightarrow \infty$  corresponds to complete collection of minority carriers produced in this layer.

A plot of  $Q_-$  as a function of  $\varepsilon$  is shown in Fig. 5 for a silicon cell with the parameters

$$\begin{aligned}
 D &= 5 \text{ cm}^2/\text{second}, \\
 \mu &= 190 \text{ cm}^2/\text{volt-second}, \\
 \tau &= 2 \times 10^{-5} \text{ second}, \\
 L &= 10^{-2} \text{ cm}, \\
 a &= 10^{-4} \text{ cm}, \\
 s &= 2 \times 10^5 \text{ cm/second}, \\
 2D/\mu L &= 5.3 \text{ volts/cm}, \\
 s/\mu &= 1050 \text{ volts/cm}.
 \end{aligned} \tag{52}$$

The electric field is therefore  $E = 5.3\varepsilon$  volts/cm. The value of  $Q_+$  corresponding to these parameters is 0.52, so that the collection efficiency  $Q_1 = Q_- + Q_+$  varies from 0.67 at zero field to 0.87 at infinite field. It will be observed that these values correspond in Fig. 2 to  $s = 2 \times 10^5$  cm/second and  $s \rightarrow 0$  respectively, as one would expect. The critical field  $s/\mu$  indicated in the figure is the field at which about half the surface

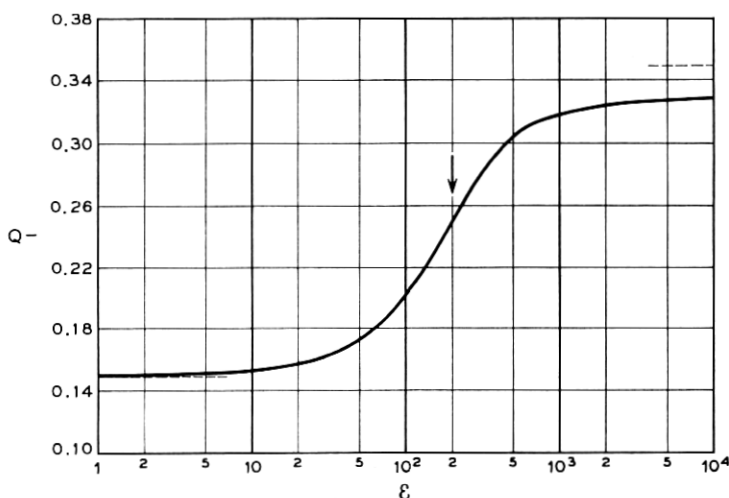


Fig. 5 — The collection efficiency as a function of built-in electric field for a silicon cell with parameters (52). The abscissa is  $\varepsilon = E\mu L/2D$  and  $2D/\mu L = 5.3$  volts/cm. The critical field  $s/\mu$  and the asymptotic limits of  $Q_1$  are indicated by dotted lines.

recombination has been eliminated. Although it would be difficult to obtain built-in fields much larger than this in silicon, the high-field portion of the curve shows qualitatively the results to be expected from a gradient in the energy gap in a solar cell made of a compound semiconductor such as GaAs-P. The asymptotic formula (51) holds only for much higher fields than  $\mathcal{E} = 10^4$  because of the extremely high values<sup>33</sup> of  $\alpha$  near  $\lambda \sim 0.3 \mu$ . The asymptotic limits at low and high fields are indicated by dotted lines. For estimating the effects of a given field it is convenient to regard the field as effectively lowering the surface recombination velocity. For estimating the effective velocity  $s^*$  one may use the recipe

$$s^* = s[1 + (E\mu/s)(1 + sa/D)]^{-1}. \quad (53)$$

The collection efficiency can then be estimated from (29) by using an effective surface parameter  $\omega^* = D/Ls^*$  with considerably less labor than by evaluating (50) exactly.

#### V. THE EFFECT OF THE ABSORPTION CURVE

The absorption curve is the curve obtained by plotting the absorption coefficient  $\alpha(\lambda)$  as a function of wavelength  $\lambda$ . Different semiconductors have quite different absorption curves as well as different energy gaps. In the several studies that have been made on the effect of the energy gap no consideration has been given to the absorption curve.<sup>8,11,13,14,15,30</sup> All of these studies have been concerned with spectrum and junction losses rather than collection losses. From the standpoint of collection efficiency, however, the absorption curve is of essential importance if there is any considerable surface recombination in the cell. Although the elimination of surface recombination may be in prospect, it is still of interest to consider the effect of the absorption curve in a cell with essentially infinite surface recombination velocity. This provides another standpoint from which to discuss the advantages of different semiconductors.

In Fig. 6 are shown the absorption curves for silicon,<sup>32</sup> GaAs† and InP,<sup>39</sup> in the range  $10^2 \leq \alpha < 10^5 \text{ cm}^{-1}$ . It will be observed that the curve for silicon differs from the other two in its gradual drop off with increasing wavelength. For  $\alpha < 10^2 \text{ cm}^{-1}$  it falls off more steeply, although not as steeply as GaAs or InP. The reciprocal  $\alpha(\lambda)^{-1}$  of the absorption coefficient

† The solid curve for GaAs is based on unpublished transmission measurements by W. G. Spitzer. The dashed part of the curve is an extrapolation based on a single additional reflection measurement by R. J. Archer giving  $\alpha \sim (1 \pm 0.3) \times 10^5 \text{ cm}^{-1}$  at  $0.546 \mu$ .



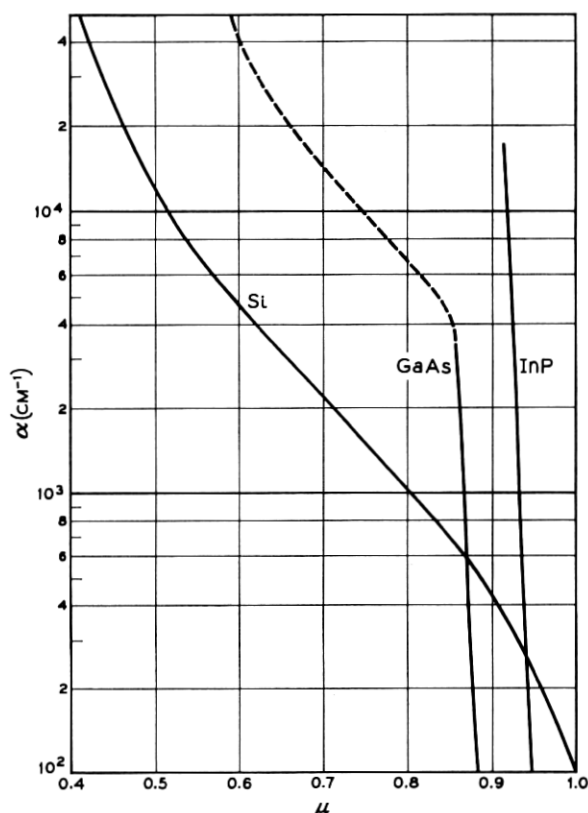


Fig. 6 — The absorption curves for silicon, GaAs and InP.

cient is a measure of the penetration distance of light of wavelength  $\lambda$ . There is some wavelength  $\lambda_1$ , for which

$$\alpha(\lambda_1)^{-1} \sim a, \quad (54)$$

which is the shortest wavelength of light useful in the cell. Light of shorter wavelength than  $\lambda_1$  is absorbed too close to the surface to be collected at the junction. Similarly, there is a wavelength  $\lambda_2$ , for which

$$\alpha(\lambda_2)^{-1} \sim L, \quad (55)$$

which is the longest wavelength of useful light. If  $L = 10^{-2}$  cm or larger  $\lambda_2$  is nearly equal to the intrinsic absorption edge  $\lambda_g$  corresponding to the energy gap. Light of longer wavelength than  $\lambda_2$  is absorbed too far from the junction to be collected, or else is not absorbed at all. Since

the effective light lies in the range  $\lambda_1 \leq \lambda \leq \lambda_2$  an effective photon flux can be defined:

$$N_{\text{eff}} = \int_{\lambda_1}^{\lambda_2} N(\lambda) d\lambda. \quad (56)$$

The collection efficiency may be written

$$Q_1 = N_{\text{eff}}/N, \quad (57)$$

where the flux  $N$  is defined by (2). The limits  $\lambda_1$ ,  $\lambda_2$ , and hence  $Q$ , evidently depend in an essential way on the absorption curve.

The first equation (30) gives  $Q_1$  for the present case in terms of the photodensity function  $F(\xi, L)$  defined by (22). Therefore, the qualitative considerations given above enter into determining the value of  $F(\gamma, L)$ . According to (22),  $F(\gamma, L)$  contains an integral over  $\lambda$  of the product of two functions  $\beta/(1 + \beta)$  and  $\varphi[\gamma(1 - \beta)]$ . The weighting function  $\nu(\lambda)$  representing the solar spectrum is slowly varying and not relevant to the present discussion. Fig. 7 shows plots of the two functions for a silicon cell with the parameters (34). It is clear from this figure that  $\lambda_1$  and  $\lambda_2$  correspond to cutoffs in  $\varphi$  and  $\beta/(1 + \beta)$  respectively. The integrand in (22) is evidently small except in the region between the vertical lines in the figure corresponding to  $\alpha a = 1$  and  $\alpha L = 1$ .

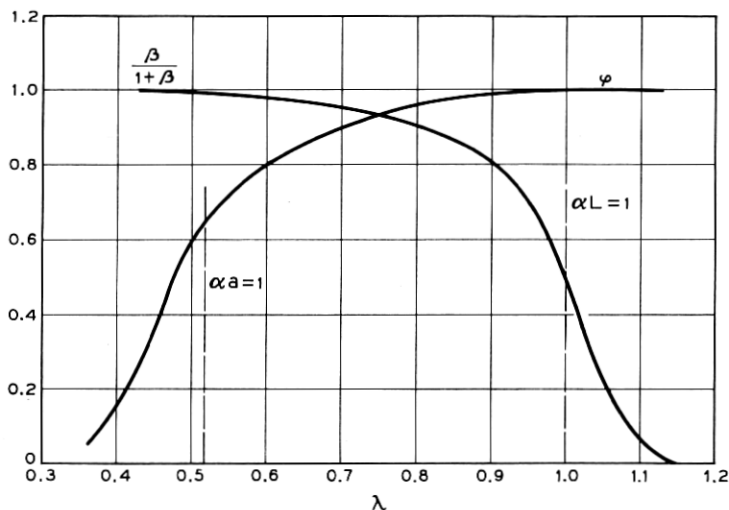


Fig. 7 — The functions  $\beta/(1 + \beta)$  and  $\varphi$  entering into the integrand of (22) defining the photodensity function. Calculation refers to a silicon cell with  $a = 10^{-4}$ ,  $L = 10^{-2}$  cm. Dashed lines show cutoffs  $\lambda_1$ ,  $\lambda_2$  corresponding to (54) and (55).

It is now clear that when  $\lambda_1$  lies very close to  $\lambda_2$  the collection efficiency will be relatively low. This is the case with very steep absorption curves like that of InP. On the other hand, a gradual absorption curve like that of silicon leads to relatively high collection efficiency. If  $\lambda_1, \lambda_2$  are defined by  $\alpha(\lambda_1) = 10^4$  and  $\alpha(\lambda_2) = 10^2 \text{ cm}^{-1}$ , (57) predicts the collection efficiencies 0.70, 0.21 and 0.045 for silicon, GaAs and InP respectively. The value for GaAs is subject to considerable uncertainty because it is based on a little-known part of the absorption curve. In any case, all of these numbers are qualitative, and mainly of interest to show that if surface recombination is high silicon is much superior to GaAs or InP. It is important to notice that this should be true in spite of the higher energy gap of the other two materials, because the differences in efficiency predicted for these materials on the basis of their energy gaps are much smaller than the differences in collection efficiency obtained here. For example, Loferski<sup>15</sup> finds that silicon and GaAs have relative efficiencies of 0.21 and 0.24 respectively, whereas silicon may have three times the collection efficiency of GaAs and 15 times that of InP.

Several investigators have studied GaAs photocells. Gremmelmaier<sup>40</sup> obtained an over-all efficiency of about 4 per cent and a collection efficiency of about 0.2, in agreement with the estimates given above. An over-all efficiency of 6.5 per cent for a cell of very small area ( $0.007 \text{ cm}^2$ ) has been reported by Jenny, Loferski and Rappaport.<sup>41</sup> These authors give current and voltage information for a somewhat larger cell ( $0.059 \text{ cm}^2$ ) having an over-all efficiency of 3.2 per cent, from which it can be deduced that the collection efficiency was about 0.26. It may be significant that the efficiency of 6.5 per cent was apparently obtained using a very low level of illumination ( $0.0057 \text{ watt/cm}^2$ ). Also, very low collection efficiencies have been reported for InP cells by Rappaport,<sup>30</sup> although he attributes this to poor ohmic contacts to the cell. According to the present argument GaAs and InP will always give low collection efficiencies unless surface recombination can be eliminated, either by reducing the surface recombination velocity to below  $10^4 \text{ cm/second}$ , or by means of a built-in electric field of order  $10^4 \text{ volts/cm}$ .

It should be mentioned that the spectral response for a GaAs cell reported by Jenny et al.<sup>41</sup> is not at all in agreement with the assumption of fast surface recombination. These authors observe an almost constant quantum efficiency from 5 to  $9 \mu$ . This differs radically from an earlier measurement by Seraphin,<sup>†</sup> which showed a pronounced fall-off at short wavelengths characteristic of surface recombination. No explanation has been advanced for this result nor can any be offered here. It may mean

<sup>†</sup> Ref. 24, p. 65.

that surface recombination can be effectively eliminated in GaAs cells by treatments not yet defined, understood or controlled.

## VI. THE TWO-JUNCTION CELL

In the typical silicon solar cell having the parameters (52), about 20 per cent of the minority carriers produced are lost to surface recombination and 13 per cent to body recombination. Therefore large reductions in surface recombination will be more rewarding in terms of over-all efficiency improvement than will proportionate reductions in body recombination. The two preceding sections have been concerned primarily with surface recombination. It is also worthwhile to consider body recombination in some detail, particularly since high-temperature applications may be in prospect which will require high energy gap material.<sup>42</sup> As discussed in the introduction, body lifetimes tend to be short in these materials. From Fig. 4 one may estimate that  $Q_1$  is likely to be no larger than 0.2 in a cell with short lifetime. How this low collection efficiency may be improved by means of a second junction is discussed in this section.

The collection efficiency for a two-junction cell will be denoted  $Q_2$ . If the second junction is located at depth  $b$  below the surface, and  $\eta = b/L$ , the solution  $n(x)$  in the region  $a \leq x \leq b$  is

$$n(x) = \frac{N\tau}{L} \left[ F(\xi) - \frac{\sinh(\eta - \xi)}{\sinh(\eta - \gamma)} F(\gamma) - \frac{\sinh(\xi - \gamma)}{\sinh(\eta - \gamma)} F(\eta) \right], \quad (58)$$

which satisfies (1) and the boundary conditions  $n(a) = n(b) = 0$ . In the region  $x \geq b$  the solution is

$$n(x) = \frac{N\tau}{L} [F(\xi) - e^{\eta - \xi} F(\eta)]. \quad (59)$$

The solution in the region  $0 \leq x \leq a$  is the same as that obtained in Section III and given by (24) and (25). For the case of fast surface recombination  $\omega = 0$ , this is

$$n(x) = \frac{N\tau}{L} \left[ F(\xi) - \frac{\sinh \xi}{\sinh \lambda} F(\gamma) \right], \quad (60)$$

satisfying  $n(0) = n(a) = 0$ . From (6), the total collection efficiency is

$$Q_2 = F(\gamma) [\coth \gamma + \tanh \frac{1}{2}(\eta - \gamma)] + F(\eta) [1 + \tanh \frac{1}{2}(\eta - \gamma)]. \quad (61)$$

As  $\eta \rightarrow \gamma$ ,  $Q_2 \rightarrow Q_1$  for the case  $\omega = 0$  given by (30). The effectiveness of the second junction may be measured by the quantity

$$\delta = (Q_2 - Q_1)/Q_1, \quad (62)$$

where  $Q_1$  is the collection efficiency for a cell with a single junction at depth  $a$ . From (61),

$$\delta(\eta, \gamma, L) = \frac{F(\eta)}{F(\gamma)} \frac{1 + \tanh \frac{1}{2}(\eta - \gamma)}{1 + \coth \gamma} - \frac{1 - \tanh \frac{1}{2}(\eta - \gamma)}{1 + \coth \gamma}. \quad (63)$$

Fig. 8 shows  $\delta(\eta, \gamma, L)$  plotted as a function of  $\eta$  for a silicon cell with  $a = 10^{-4}$  cm and  $L = 10^{-4}$ ,  $10^{-3}$  and  $10^{-2}$  cm. These calculations show that  $\delta(\eta)$  has a well-defined maximum which defines the optimum depth for the second junction for given  $a, L$ .

Due to the loading effect of the second junction the relative improvement in over-all efficiency will be somewhat less than  $\delta$ . This effect may be taken into account by use of the Pfann-Van Roosbroeck<sup>12</sup> efficiency expression (15). For the two-junction cell the reduced current may be written

$$G_2 = \frac{1}{2}(Q_2/Q_1)G_1, \quad (64)$$

where  $G_1 = I_g/eAJ_0 = (N/J_0)Q_1$  is the reduced current for the single-junction cell. Thus the efficiency expression for the two-junction cell is

$$\epsilon_2 \approx \frac{kT}{W} Q_2 \ln G_2. \quad (65)$$

The relative improvement in over-all efficiency can be measured by

$$\delta' = (\epsilon_2 - \epsilon_1)/\epsilon_1, \quad (66)$$

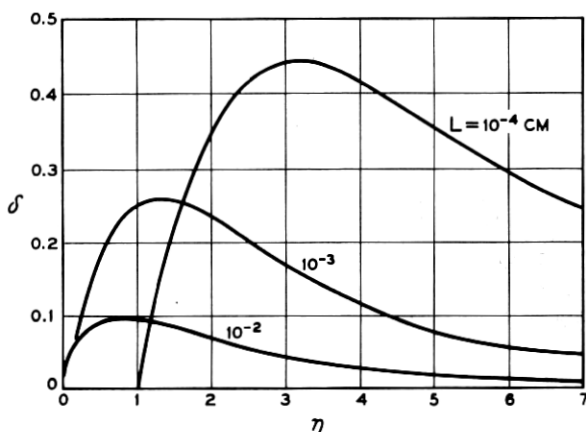


Fig. 8 — The improvement of collection efficiency (defined by (62)) as a function of the depth of the second junction for a silicon cell with first junction at depth  $10^{-4}$  and  $L = 10^{-4}$ ,  $10^{-3}$  and  $10^{-2}$  cm.

where  $\epsilon_1$  given by (15) is the efficiency of the single-junction cell with the junction at depth  $a$ . Finally, the over-all improvement  $\delta'$  can be written as a function of the collection improvement  $\delta$ :

$$\delta' = \delta + (1 + \delta) \frac{\ln \frac{1}{2}(1 + \delta)}{\ln G}. \quad (67)$$

For practical purposes one may set  $\ln G = 18$  in (67). The second term gives the effect of the loading due to the second junction. Two extreme cases may be noted: if  $\delta > 1$ , the second junction is a more effective collector than the first function and  $\delta' > \delta$ ; if  $\delta < \ln \frac{1}{2}/\ln G \sim 0.04$ , the second junction acts mainly as a load on the first junction and  $\delta' < 0$ . A summary of calculations for silicon two-junction cells is presented in Table I. In each case it is assumed that the first junction is at  $a = 10^{-4}$  cm and the second junction at the optimum depth given in the third column. The collection improvement  $\delta$  and over-all improvement  $\delta'$  are given in the fourth and fifth columns. In the second column is given the single junction collection efficiency in agreement with  $Q_1(L, 0)$  of Fig. 4. The last row with  $L = 10^{-2}$  cm is the most typical of good silicon solar cells. For this case the improvement in collection efficiency is only  $\delta = 0.092$ . On the other hand, for  $L = 10^{-4}$  cm,  $\delta = 0.44$  and  $\delta' = 0.42$ . This case applies qualitatively to any short-lifetime cell, and shows that the two-junction structure may be useful for improving the efficiency of high energy gap cells.

## VII. SUMMARY

In this paper the present status of solar cell theory has been reviewed, with emphasis on clearly defining the various mechanisms causing losses of efficiency. This review leads to the conclusion that the problem of the collection of minority carriers has not received attention in the literature commensurate with its importance.

The collection problem is formulated and then solved by a new method in which all the effects of the solar spectrum and absorption curve are contained in a single function, the photodensity function. The method is convenient for most solar cell collection problems and especially so when a single diffusion length can be used.

TABLE I

$L$ (in cm)	$Q_1$	$b$ (in cm)	$\delta$ (max)	$\delta'$
$10^{-4}$	0.186	0.032	0.443	0.417
$10^{-3}$	0.420	0.013	0.258	0.226
$10^{-2}$	0.634	0.008	0.092	0.055

The familiar single-junction silicon cell is considered first and calculations are presented to show how the collection efficiency varies with surface recombination velocity, junction depth and diffusion length. It is found that the elimination of surface recombination would not only improve collection efficiency but also permit the internal resistance to be greatly reduced. Little or no improvement in silicon cells is to be expected from making the junction depth less than  $10^{-4}$  cm or the diffusion length longer than  $10^{-2}$  cm.

The theory is extended to include a constant built-in electric field, and calculations are presented for silicon. It is concluded that commercial silicon cells do not have large enough built-in fields to affect the collection efficiency significantly. Sufficiently large fields should be obtainable in some compound semiconductors from gradients in the energy gap. An approximate relation is given for an effective surface recombination velocity less than the true velocity, which takes into account the effect of the built-in field in reducing surface recombination.

A discussion is given of the dependence of the collection efficiency on the absorption curve of the semiconductor. This discussion provides another basis beside the energy gap on which to compare different semiconductors for solar battery use. It is shown that silicon has a very favorable absorption curve in comparison with GaAs and InP. It is suggested that this accounts to a large extent for the continuing superiority of silicon over other materials with larger energy gaps. The theoretical superiority of GaAs and several other higher gap materials over silicon can only be realized if surface recombination can be drastically reduced; specifically, it is necessary that the effective surface recombination velocity be reduced to  $10^4$  cm/second or lower.

Finally, a two-junction cell is considered in connection with the problem of reducing body recombination. Although body recombination is considerably less important than surface recombination in good silicon cells, it will be probably much more important in high energy gap cells. The illustrative calculations presented for silicon also have qualitative significance for other cells. It is shown that an improvement of about 42 per cent in over-all efficiency may be expected from the two junction structure in material with a diffusion length of  $10^{-4}$  cm. The improvement in a good silicon cell with a diffusion length of  $10^{-2}$  cm would only be 6 per cent.

#### VIII. ACKNOWLEDGMENT

It is a pleasure for the author to acknowledge the helpful cooperation of W. G. Spitzer, G. L. Pearson, F. M. Smits and G. C. Dacey of Bell Telephone Laboratories.

*Note.* Since the completion of this work a review paper by Wolf<sup>43</sup> has appeared which discusses some of the topics taken up here.

#### APPENDIX

In this section some comments are given which may be helpful for the evaluation of the photodensity function (22). A very accurate and convenient method is the Gauss quadrature,<sup>44</sup> which approximates the integral by a summation over the values of the integrand at certain specific (not equidistant) points. The limits  $0, \lambda_g$  in (22) can be replaced by  $\lambda_1, \lambda_2$  so chosen that the contributions from the regions  $0 < \lambda < \lambda_1$  and  $\lambda_2 < \lambda < \lambda_g$  are negligible. The approximation is to represent the integral

$$\begin{aligned} F(\xi, L) &= \int_0^{\lambda_g} g(\lambda) d\lambda \\ &\cong \int_{\lambda_1}^{\lambda_2} g(\lambda) d\lambda \\ &= \frac{1}{2}(\lambda_2 - \lambda_1) \sum_{j=1}^{10} R_j g(\lambda_j). \end{aligned} \quad (68)$$

The choice of a 10-point Gauss quadrature here is arbitrary, but has proved to be a satisfactory compromise between convenience and accuracy. For *silicon* one can choose  $\lambda_1 = 0.42 \mu$ ,  $\lambda_2 = 1.08 \mu$ , and (68) becomes

$$\int g(\lambda) d\lambda = \sum (0.33R_j)g(\lambda_j). \quad (69)$$

The wavelengths  $\lambda_j$  and corresponding absorption coefficients<sup>32</sup>  $\alpha(\lambda_j)$  and solar spectrum<sup>31</sup> weights  $\nu(\lambda_j)$  for this case are given in Table II, along with the quadrature weights  $0.33R_j$ . The integrand  $g(\lambda)$  can be readily evaluated with a slide rule for each  $\lambda_j$ .

TABLE II

$\lambda(\mu)$	$0.33R$	$\alpha$ (in $\text{cm}^{-1}$ )	$\nu(\mu^{-1})$
0.429	0.0220	$3.7 \times 10^4$	1.22
0.465	0.0492	2.0(4)	1.50
0.526	0.0723	9.0(3)	1.57
0.607	0.0888	4.3(3)	1.62
0.701	0.0977	2.2(3)	1.51
0.799	0.0977	1.03(3)	1.36
0.893	0.0888	4.5(2)	1.26
0.974	0.0723	1.56(2)	1.12
1.035	0.0492	42.	1.05
1.071	0.0220	17.	1.02



The accuracy of (69) may be tested with an elementary integral having a qualitative behavior similar to  $g(\lambda)$  in the range of integration. Such an integral is

$$\int_{0.42}^{1.08} (1.08 - \lambda)^{\frac{1}{2}} (\lambda - 0.42)^{\frac{1}{2}} d\lambda = 0.17106.$$

The quadrature (69) with  $\lambda_j$  and  $0.33R_j$  from Table II gives 0.17111.

The derivative  $F'(\zeta, L)$  is defined by the integral

$$\begin{aligned} F'(\zeta, L) &= e^{-\zeta} \int_0^{\lambda_g} \nu(\lambda) \frac{\beta}{1 + \beta} \frac{1 - \beta e^{\zeta(1-\beta)}}{1 - \beta} d\lambda \\ &= e^{-\zeta} \int_0^{\lambda_g} \nu(\lambda) \frac{\beta}{1 + \beta} \{1 - \beta \zeta \varphi[\zeta(1 - \beta)]\} d\lambda. \end{aligned} \quad (70)$$

This integral may be accurately evaluated by (69), providing  $\beta(\lambda_1)\zeta \gg 1$  to insure that the truncation error at  $\lambda_1$  is small. The photodensity function for a constant electric field defined by (45) can be written

$$F(\zeta, L, \mathcal{E}) = \rho \zeta e^{-\rho \zeta} \int_0^{\lambda_g} \nu \frac{\beta}{1 + \rho \beta} \varphi[\rho \zeta(1 - \sigma \beta)] d\lambda, \quad (71)$$

and its derivative is defined by

$$F'(\zeta, L, \mathcal{E}) = \rho e^{-\rho \zeta} \int_0^{\lambda_g} \nu \frac{\beta}{1 + \rho \beta} \{1 - \beta \zeta \varphi[\rho \zeta(1 - \sigma \beta)]\} d\lambda. \quad (72)$$

These expressions are in the form of (22) and (70) respectively, and can be evaluated by (69) in most cases.

Some of the integrals occurring in the theory cannot be evaluated with sufficient accuracy by (69) because of large contributions from the short wavelengths  $\lambda < \lambda_1 = 0.42 \mu$ . As an example of this difficulty consider

$$\int_0^{\lambda_g} \nu(\lambda) d\lambda = 1, \quad (73)$$

which follows from the definition of  $\nu(\lambda)$  in (20) and of  $N$  in (2). The quadrature (69) gives 0.905 for this integral, which shows that

$$\int_0^{0.42} \nu d\lambda = 0.095.$$

This result can be used to correct (69) for the evaluation of

$$F'(0, L) = \int_0^{\lambda_g} \nu \frac{\beta}{1 + \beta} d\lambda \quad (74)$$

occurring in (31). If  $\beta(\lambda_1) \gg 1$  it is only necessary to add 0.095 to the right side of (69); thus for *silicon*

$$F'(0, L) = 0.095 + \sum_{j=1}^{10} (0.33 R_j) \nu_j \frac{\beta_j}{1 + \beta_j}. \quad (75)$$

The evaluation of  $F'(0, L, \varepsilon)$  occurring in (50) is more difficult and requires a numerical integration over the larger region  $0 < \lambda < \lambda_g$ . To carry out the integration the absorption curve must be known for very high absorption<sup>33</sup>  $\alpha \sim 10^6 \text{ cm}^{-1}$ . There may also be a significant correction to be added to (69) in the evaluation of  $F(\zeta, L, \varepsilon)$  for very high fields  $\varepsilon > 100$ . These corrections can be readily calculated by integrating from 0.22 to 0.42  $\mu$  by the trapezoid rule. The necessary data for silicon is listed in Table III. For large fields (72) becomes

$$F'(\zeta, L, \varepsilon) \rightarrow \frac{1}{\varepsilon \rightarrow \infty} \frac{1}{2\varepsilon} \int_0^{\lambda_g} \nu \beta e^{-\beta \zeta} d\lambda, \quad (76)$$

which can be evaluated by (69) if  $\beta(\lambda_1)\zeta \gg 1$ . For silicon with  $a = 10^{-4} \text{ cm}$  the following values were found for the integrals appearing in (23), (36), (51) and (76):

$$\begin{aligned} \int \nu \alpha d\lambda &= 3.7 \times 10^4 \text{ cm}^{-1}, \\ \int \nu \frac{1 - e^{-\alpha a}}{\alpha a} d\lambda &= 0.754, \\ \int \nu (1 - e^{-\alpha a}) d\lambda &= 0.351, \\ \int \nu \alpha e^{-\alpha a} d\lambda &= 1490 \text{ cm}^{-1}. \end{aligned} \quad (77)$$

TABLE III

$\lambda(\mu)$	$\nu(\mu^{-1})$	$\alpha \text{ (cm}^{-1}\text{)}$
0.22	0.00477	$1.2 \times 10^6$
0.24	0.0148	1.4
0.26	0.0506	1.5
0.28	0.0625	1.6
0.30	0.178	1.5
0.32	0.306	1.3
0.34	0.448	0.9
0.36	0.538	0.4
0.38	0.654	0.1
0.40	0.801	0.06
0.42	1.14	0.04

## REFERENCES

1. Daniels, A. F., *Proc. I.R.E.*, **48**, 1960, p. 636.
2. Smith, D. H., *Comm. & Elect.*, No. 45, 1959, p. 530.
3. Van Allen, J. A., *J. Geophys. Res.*, **64**, 1959, p. 1683.
4. Loferski, J. and Rappaport, P., *Phys. Rev.*, **111**, 1958, p. 432.
5. Brown, W. L. and Pearson, G. L., to be published.
6. Prince, M. B. and Wolf, M., *J. Brit. I.R.E.*, **13**, 1958, p. 583.
7. Hoefler, D. C., *Electronic News*, **5**, May 23, 1960, p. 4.
8. Carpenter, E. F., ed., *Transactions of the Conference on the Use of Solar Energy — The Scientific Basis*, Vols. I-V, Univ. of Arizona, Tucson, 1955.
9. Telkes, M., *J. Appl. Phys.*, **25**, 1954, p. 765.
10. Chapin, D. M., Fuller, C. S. and Pearson, G. L., *J. Appl. Phys.*, **25**, 1954, p. 676.
11. Prince, M. B., *J. Appl. Phys.*, **26**, 1955, p. 534.
12. Pfann, W. G. and Van Roosbroeck, W., *J. Appl. Phys.*, **25**, 1954, p. 1422.
13. Cumerow, R., *Phys. Rev.*, **95**, 1954, p. 16.
14. Rittner, E. S., *Phys. Rev.*, **96**, 1954, p. 1708.
15. Loferski, J., *J. Appl. Phys.*, **27**, 1956, p. 777.
16. Malovetskaya, V., Vavilov, V. S. and Galkin, G. N., *Soviet Physics Solid State (English trans.)*, **1**, 1960, p. 1099.
17. Hrostowski, H. in Hannay, N. B., ed., *Semiconductors*, Reinhold, New York, 1959, p. 437.
18. Hoffman Electronics Corp., *Technical Information Bulletin 32-58*, September 1, 1958.
19. Vavilov, V. S., Smirnov, L. S. and Patskevitch, V. M., *Soviet Physics Solid State (English trans.)*, **1**, 1960, p. 1344.
20. Theuerer, H. C., Whelan, J. M., Bridgers, H. E. and Buehler, E., *J. Electrochem. Soc.*, **104**, 1957, p. 721.
21. Theuerer, H. C., *J. Electrochem. Soc.*, **107**, 1960, p. 296.
22. Buck, T. M. and McKim, F. S., *J. Electrochem. Soc.*, **105**, 1958, p. 709.
23. Wertheim, G., private communication.
24. Welker, H. and Weiss, H. in Seitz, F. and Turnbull, D., eds., *Solid-State Physics*, Vol. 3, Academic Press, New York, 1956.
25. Morin, F. and Maita, J., *Phys. Rev.*, **96**, 1954, p. 28.
26. Shockley, W., *Electrons and Holes in Semiconductors*, D. Van Nostrand Co., New York, 1950, Section 12.5.
27. Shive, J., *The Properties, Physics and Design of Semiconductor Devices*, D. Van Nostrand Co., Princeton, N. J., 1959, Section 19.2.
28. Braunstein, R., Moore, A. and Herman, F., *Phys. Rev.*, **109**, 1958, p. 695.
29. Sah, C., Noyce, R. and Shockley, W., *Proc. I.R.E.*, **45**, 1957, p. 1228.
30. Rappaport, P., *RCA Rev.*, **20**, 1959, p. 373.
31. Forsythe, W. E., ed., *Smithsonian Physical Tables*, Smithsonian Institution, Washington, 1954, Tables 812, 813.
32. Dash, W. C. and Newman, R., *Phys. Rev.*, **99**, 1955, p. 1151.
33. Pfestorf, G., *Ann. Physik*, **81**, 1926, p. 906.
34. Shockley, W., *Electrons and Holes in Semiconductors*, op. cit., Section 12.3.
35. Backenstoss, G., *Phys. Rev.*, **108**, 1957, p. 1416.
36. Krömer, H., *Archiv elect. Übertragung*, **8**, 1954, p. 223.
37. Trumbore, F. A., *B.S.T.J.*, **39**, 1960, p. 205.
38. Folberth, O. G., *Z. Naturforsch.*, **10a**, 1955, p. 502.
39. Newman, R., *Phys. Rev.*, **111**, 1958, p. 1518.
40. Gremmelmaier, R., *Z. Naturforsch.*, **10a**, 1955, p. 501.
41. Jenny, D., Loferski, J. and Rappaport, P., *Phys. Rev.*, **101**, 1956, p. 1208.
42. Wysocki, J. and Rappaport, P., *J. Appl. Phys.*, **31**, 1960, p. 571.
43. Wolf, M., *Proc. I.R.E.*, **48**, 1960, p. 1246.
44. Lowan, A. N., Davids, N. and Levenson, A., *Bull. Am. Math. Soc.*, **48**, 1942, p. 739.

