

For the case of several particles, analogous considerations would lead to our Eqs. (4) and (3) respectively.

Therefore Dirac's derivation is in accord with the one of Infeld and Wallace outlined previously. However, we noted that Dirac himself calls his theory fundamentally symmetrical between retarded and advanced potentials. The contradiction seems to come from the fact that Dirac considers his theory symmetrical due to the apparent symmetry of the use of retarded and advanced fields in definitions (D 8) and (D 9) (and the analogous definitions (D 38) and (D 39) for the many-body problem).

However, it should be noted that in the derivation by Dirac outlined above, he is only using (D 8) (respectively D 38). The definition (D 9) never enters into any of his calculations which lead to his equations of motion. It is only used in a purely formal manner to introduce the notion of  ${}_{\text{rad}}F$  (see (D 10)) into some of the equations;<sup>17</sup> but the results themselves are independent of it.

<sup>17</sup> The purely formal character of any definition of the radiation field can be seen also from the fact that in WF the term "radiation field" is used for just  $1/2 {}_{\text{rad}}F$  of D, without in any way leading to contradictions, as the only physically significant equations are the equations of motion of the point charges.

## The Photo-Voltaic Effect

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(Received March 19, 1948)

The *Schottky-Mott* theory of the barrier layer rectification is extended with respect to the action of light absorbed in the barrier layer. The essential physical assumptions to be used are as follows: (a) The barrier layer is a boundary layer of a semiconductor with a reduced density of mobile charges (either electrons or "holes"); (b) both positive *and* negative mobile charges are released by light; (c) the recombination within the barrier layer is negligible; and, (d) the electrons and "holes" have the same properties whether released by light or by thermal agitation. Thus an "equation of state" connecting photo-voltage, photo-current, light intensity, wave-length, external resistance, etc., is derived. Among others the regularities of short circuit current, open circuit voltage, photo-characteristic, dark characteristic (barrier layer rectification), power output, and spectral distribution of the quantum yield are involved.

### I. INTRODUCTION

THE most successful theory in the explanation of the barrier rectification is the theory of W. Schottky<sup>1</sup> and N. F. Mott.<sup>2</sup> In his discussion of the action of light in a barrier layer of the nature described by the above theory, N. F. Mott has already succeeded in explaining the sign of the photo-voltage.<sup>3</sup> In this paper we generalize the fundamental assumptions of W. Schottky and N. F. Mott and derive a comprehensive formula for the barrier layer photo-effect.<sup>4</sup> The establishment of one formula

for the manifold of barrier layer photo-cells varying in peculiarities is possible since the peculiarities of minor importance enter only into the parameters of the formula, which remain open to a further discussion in special cases.

We shall treat explicitly the photo-effect in semiconductors only for the case where the mobile carriers of charge are electrons (*n*-type semiconductors) and shall state the corresponding results for semiconductors with "hole" conductance (*p*-type semiconductors).<sup>5</sup>

### II. BASIC CONCEPTS ABOUT THE BARRIER LAYER

In principle both barrier layer rectifiers and barrier layer photo-cells consists of a semicon-

<sup>1</sup> W. Schottky, *Zeits. f. Physik* **113**, 367 (1939); *Zeits. f. Physik* **118**, 539 (1942), and other publications.

<sup>2</sup> N. F. Mott, *Proc. Roy. Soc. London* **A171**, 27 (1939).

<sup>3</sup> N. F. Mott, *Proc. Roy. Soc. London* **A171**, 281 (1939).

<sup>4</sup> This formula has been communicated in a previous note by the author in *Optik* **1**, issue 3 (1946).

<sup>5</sup> K. Lehovc, *Zeits. f. Naturforsch.* **2**, 398 (1947).

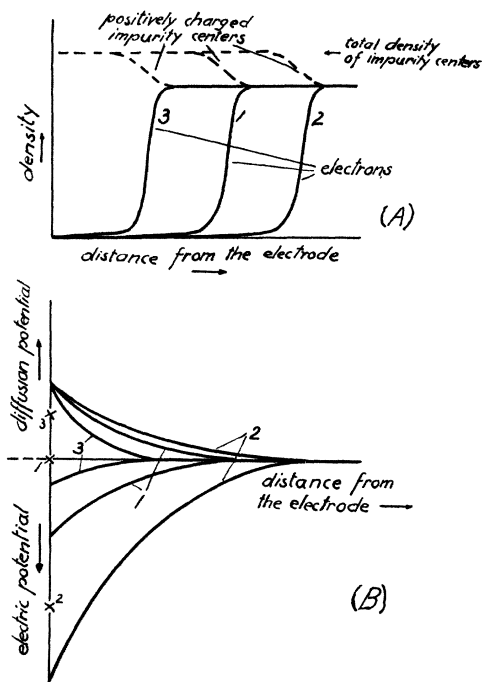


FIG. 1. A. Distribution of the densities of free electrons and of charged impurity centers in the barrier layer. B. Distribution of the diffusion potential and of the electric potential in the barrier layer.  $\times$  is the potential appearing outside. Curve 1: balance; curve 2: current flowing in the high resistance direction; curve 3: current flowing in the low resistance direction.

ductor sandwiched between two metal electrodes. The d.c. resistance of a suitable combination depends on the amount and the direction of the current. The rectification is located at one of the contacts between the electrode and semiconductor,<sup>6</sup> the other contact having a low and negligible resistance. Therefore, it will be sufficient to deal with the system semiconductor-barrier layer-electrode, and "electrode" refers hereafter to the "electrode at the barrier layer." The rectifying contact has a considerable capacity as shown by a.c. measurements.<sup>7</sup> Using the formula for a plate condenser (with a dielectric constant of about 10), we get a thickness of the order of  $10^{-5}$  cm corresponding to the capacity. A layer of this thickness with a lattice structure different from both metal and semiconductor could not generally be detected by

<sup>6</sup> Schottky, Waibel, and Stoermer, *Zeits. f. Hochfrequenztechnik* **37**, 162 (1931).

<sup>7</sup> W. Schottky and W. Deutschmann, *Physik. Zeits.* **30**, 839 (1929); L. A. Wood, *Rev. Sci. Inst.* **4**, 434 (1933) and others.

chemical methods or x-ray diffraction. Moreover, the change of capacity with the applied voltage points to a physical effect. Considering the numerical values of capacity and resistance of this so called "barrier layer" or "blocking layer," it is found that the conductance of the semiconductor decreases by many orders of magnitude in approaching the electrode. Since a change of electronic mobility of that order seems out of question, we have to assume that the density of free electrons in the semiconductor decreases considerably in approaching the electrode.

There is still some question about the cause of this decrease in electron density. It has been explained by the differences in the work functions of metal and semiconductor<sup>8</sup> and by surface states.<sup>9</sup> The influence of tunnel effect, image force, and discontinuous distribution of space charge have been treated as secondary effects.<sup>1,10</sup> However, for our general theory of the photovoltaic effect we may leave this question open noticing that the parameter "density of free electrons at the border of the electrode" may well depend on several influences.

Except for intrinsic semiconductors, the free electrons come from disturbance or impurity centers in the semiconductor lattice. The dissociation equilibrium is determined by the mass action law

$$(N^+n/N^0) = \text{const}; \quad (N^+ + N^0 = N_{\text{total}}). \quad (1)$$

$n$  is the density of the free electrons,  $N^+$  and  $N^0$  is the density of the positively charged and of the undissociated impurity centers, respectively.<sup>11</sup> In the bulk of the semiconductor we have no space charge and, therefore,  $n = N^+$ . In the barrier layer  $n$  decreases and therefore  $N^+$  increases, effecting a positive space charge and a negative potential relative to the bulk semiconductor. Thus an electric field already existing without any external voltage drives the electrons in the barrier layer from the metal toward the semiconductor. On the other hand, the density gradient drives the electrons toward the elec-

<sup>8</sup> W. Schottky, *Physik. Zeits.* **41**, 570 (1940).

<sup>9</sup> J. Bardeen, *Phys. Rev.* **71**, 717 (1947).

<sup>10</sup> E. Courant, *Phys. Rev.* **69**, 684 (1946).

<sup>11</sup> To avoid cumbersome formulations, the total density of impurity centers,  $N_{\text{total}}$ , may be considered as approximately constant though this is not a necessary assumption for our calculations.

trode. Both currents compensate each other, if no external voltage is applied. Then the electric potential is just compensated by the diffusion potential (see Fig. 1B, curve 1).

The volume charge in the barrier layer is compensated by a "surface charge" which extends over a few angstroms at both sides of the interface metal/semiconductor. In this zone the density of the free electrons decreases from the high value in the metal to the small value in the barrier layer.<sup>12</sup> This is shown in Fig. 2, and for the purpose of comparison a graph of the electron density at metal-vacuum boundary is also sketched. The striped areas mark, respectively, the positive and negative resulting charges. In the region of the semiconductor between the metal surface and the minimum of electron density in the barrier layer the electrons are still in close interaction with the metal and the "effective metal border" might, therefore, be considered as being at the position of the minimum of the density of free electrons in the barrier layer. Even before the semiconductor is placed in contact with a metal, the surface states may already have caused the formation of a barrier layer.<sup>9</sup>

From this point of view the rectification can be understood.<sup>13</sup> If an external voltage is applied at the barrier layer the positive space charge is increased, or respectively, decreased depending on whether the applied electric field has the same or opposite direction as the existing inner electric field. Since the space-charge density is limited by the density of the disturbance centers, a change in the space charge will result essentially in a change of the thickness of the space-charge layer. If the metal is the negative terminal the space charge is increased, the barrier layer gets thicker, and the resistance increases (high resistance direction); the field current is larger than the diffusion current and the electric potential is larger than the diffusion potential (Fig. 1, curves 2). If the metal is the positive terminal, the space charge is decreased, the barrier layer gets thinner, and the resistance decreases (low resistance direction); the diffusion

current is larger than the field current and the diffusion potential is larger than the electric potential (Fig. 1, curves 3). The external voltage at the barrier layer in the low resistance direction is limited by the diffusion potential. At this value the thickness of the barrier layer approaches zero and the current infinity. However, the other resistances of the circuit limit the current and, therefore, this condition will never be reached practically.

For *p*-type semiconductors the signs of low resistance direction and high resistance direction change in full agreement with the experiments. In intrinsic semiconductors a barrier layer with very high resistance cannot exist since the total density of mobile charges would always be higher in layers with space charge than in layers without space charge. In intrinsic semiconductors at thermal equilibrium the product of the densities of free electrons and holes is constant; consequently the sum of the densities is a minimum if both densities are equal.

### III. BASIC CONCEPTS ABOUT THE PHOTO-EFFECT IN THE BARRIER LAYER

After having considered the fundamental properties of the barrier layer, the behavior of additional free carriers of charge released by light has to be discussed.<sup>14</sup> For every kind of carriers of charge the following balance exists in each volume unit and for each time interval (formulated for electrons): Total change = number of electrons released by light, minus the number of electrons carried away by (necessarily space dependent) electron currents, minus the number of electrons recombining. We will con-

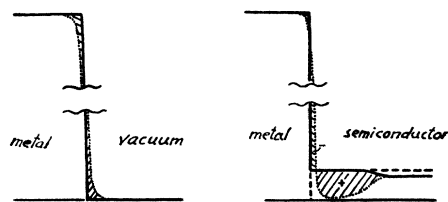


FIG. 2. Distribution of the densities of positive ions (—) and of free electrons (····) in the boundary metal/vacuum and metal/semiconductor. The ordinate is interrupted, since the density of free electrons in the metal is very much higher than in the bulk semiconductor. The area of the negative charge in the right figure would just compensate the positive area.

<sup>12</sup> For a more complete treatment see H. Y. Fan, *Phys. Rev.* **62**, 388 (1942).

<sup>13</sup> A comprehensive mathematical treatment is given by W. Schottky and E. Spence, *Wiss. Veroff. Siemenswerke* **18**, 225 (1939).

<sup>14</sup> K. Lehovc, *Zeits. f. Naturforsch.* **1**, 258 (1946).

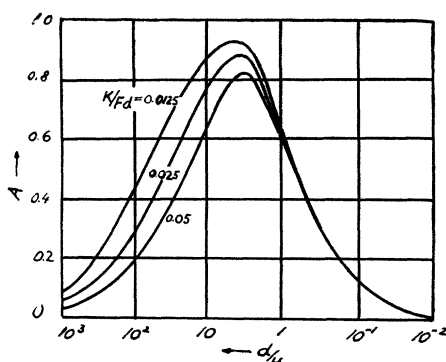


FIG. 3. Spectral distribution of the front wall photo-effect referring to the same amount of light quanta. Abscissa: thickness of the barrier layer/absorption length (the values of  $d/\mu$  are drawn decreasing from left toward right, because small  $d/\mu$  corresponds with long wavelengths, generally).

sider only the stationary state where the total change is zero.

(a) *The release of electrons by light.* Let us first assume that the light releases free electrons and immobile ions only. For constant density of positive ions, as postulated in the stationary state, an equal number of electrons has to recombine in the same unit volume as are released by light and no additions to a spontaneous photocurrent could result. For the same reason the thermal dissociation and recombination of electrons from immobile impurity centers have not been mentioned in our balance, since these two terms always compensate each other. In the following we shall neglect such "ineffective absorptions" and shall only deal with the "effective absorptions" where each absorbed light quantum releases an equal number, say  $\alpha$ , of free electrons and *mobile* positive charges.

Usually it will be an absorption in the semiconductor lattice where for each absorbed light quantum one electron and one "hole" are released. However, for very short wavelengths (x-rays) for each absorbed quantum many electrons and "holes" can be released in the semiconductor.<sup>15</sup>

(b) *The behavior of electrons released by light.* Unlike most of the former theories<sup>16</sup> about the

<sup>15</sup> K. Scharf and O. Weinbaum, *Zeits. f. Physik* **80**, 465 (1933).

<sup>16</sup> For instance, E. Perucca and R. Deaglio, *Zeits. f. Physik* **72**, 102 (1931); G. Liandrat, *Ann. de physique* **6**, 419 (1936); V. Körösy and P. Selenyi, *Physik. Zeits.* **32**, 847 (1931).

photo-voltaic effect which are based on a surplus of energy of the electrons released by light (according to Einstein's relation), we assume the other limiting case: the surplus energy is soon dissipated by collisions with the lattice, and there is no difference from the other free electrons.<sup>17</sup> Moreover, we assume that the energy distribution of the free electrons is not changed essentially either by the light or by the strong fields in the barrier layer so that Ohm's law (field current proportional to the density of free electrons times field intensity) and the ordinary diffusion law (diffusion current proportional to the gradient of electron density) may be applied.

Because of the high field intensity in the barrier layer (thickness about  $0.1\mu$ ; voltage about 0.5 volt; field intensity about 50,000-volt/cm) the average gain of electron energy between two collisions with the lattice is already of the order of the energy equivalent to the lattice temperature. Therefore, deviations from Ohm's law may well take place which will increase with increasing external voltage in the high resistance direction and also with decreasing temperature. Fortunately the photo-voltage corresponds to a voltage in the low resistance direction, as we shall see, where the mentioned effect does not seem to be very significant though already present.

(c) Recombination of free carriers of charge. Since a quantum yield as high as almost 100 percent has been reached,<sup>18</sup> the recombination within the barrier layer must be very small (assuming that each light quantum has released one electron). This can be understood since the barrier layer is a layer with small concentration of free electrons. Therefore, the assumption that the recombination within the barrier layer is negligible seems reasonable for a first approximation of the problem.

(d) An additional assumption for distinguishing between photo-effect of the barrier layer and that of the bulk semiconductor. A comprehensive calculation would require not only the treatment of the barrier layer region but also the treatment of the bulk semiconductor region nearby, where a negative space charge may be built up and the recombination has to be considered. However, it seems reasonable for many purposes to neglect the action of light in the bulk semiconductor.<sup>3</sup>

<sup>17</sup> Cf. N. F. Mott and R. W. Gurney, *Electronic processes in ionic crystals* (Oxford University Press, London, 1940), p. 190.

<sup>18</sup> H. Schröppel, Sitzber, Phys. Med. Sozietät Erlangen **70**, 87 (1938).

Moreover, this photo-effect has a considerable time lag, which allows its experimental separation from the barrier layer photo-effect.<sup>19</sup> For our calculations we separate the barrier layer photo-effect from the bulk photo-effect by the somewhat deliberate assumption that there will be an "effective thickness"  $d$  of the barrier layer with the following properties: (a) the recombination within this layer is negligible; (b) the additions to photo-current and voltage by the semiconductor outside this thickness may be neglected; (c) the boundary conditions valid for the bulk semiconductor a large distance from the electrode may already be applied to the border of the barrier layer  $x=d$ .

It will be noticed that this "effective thickness" is an idealized mathematical concept and may not coincide with the layer with diminished density of free electrons (or with positive space charge) or with the "capacity length," though these might be good first approximations.

**IV. DERIVATION OF THE "EQUATION OF STATE" OF THE PHOTO-VOLTAIC EFFECT**

Compilation of the symbols to be used:

- $x$  space coordinate perpendicular to the surface, increasing toward the semiconductor;  $x=0$  ("effective") metal semiconductor interface
- $d$  "effective thickness" of the barrier layer
- $n$  density of free electrons;  $n_0$  and  $n_d$  density for  $x=0$  and  $x=d$  respectively
- $V$  electric potential;  $V_0$  electric potential at  $x=0$ ;  $V=d$  electric potential at  $x=d$
- $F$  absolute value of the field intensity at  $x=0$
- $E$  photo-voltage or external voltage at the barrier layer
- $I$  photo-current or current through the barrier layer
- $e$  electron charge
- $v$  mobility of electrons
- $D$  diffusion constant for electrons
- $K$  voltage equivalent of temperature ( $=kT/e$ )
- $J$  intensity of light when entering the semiconductor
- $h\nu$  energy of one light quantum
- $\alpha$  number of electrons released by one light quantum
- $\mu$  absorption length (distance in the semiconductor in which the intensity of light is decreased to the 2.73th part)
- $\rho$  reflection coefficient of light coming from semiconductor to electrode
- $\Lambda$  thickness of the semiconductor
- $R$  resistance in the external circuit

In the following the front wall effect in excess semiconductors (electron conduction) is con-

<sup>19</sup> H. Kerschbaum, Naturwiss. 18, 39 (1930).

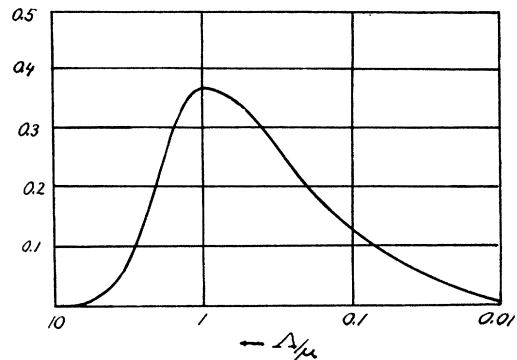


FIG. 4. Spectral distribution of the rear wall photo-effect referring to the same amount of light quanta. Abscissa is the ratio: thickness of the semiconductor/absorption length.

sidered explicitly. The thermodynamical potential at the barrier layer which gives the voltage appearing outside is the sum of an electric potential and a diffusion potential:

$$E = V_0 + K \ln(n_d/n_0). \tag{2}$$

The corresponding current will be calculated by means of the following relation:

$$\frac{J}{h\nu} \cdot \alpha \cdot \frac{1}{\mu} \cdot \exp\left(-\frac{x}{\mu}\right) = -\frac{1}{e} \frac{\partial}{\partial x} \left[ -nev \frac{\partial V}{\partial x} + eD \frac{\partial n}{\partial x} \right]. \tag{3}$$

The left side represents the amount of free electrons released by the absorbed light quanta in a unit volume at the distance  $x$  from the electrode. In the brackets on the right side there is the total current carried by electrons (positive sign means an electron current from the semiconductor toward the electrode); the first term is the current by the field (directed toward the semiconductor) and the second term is the current by diffusion (directed toward the electrode). In other words, Eq. (3) expresses the fact that each absorbed light quantum adds  $\alpha$ -free electrons to the current. Therefore, the electron current is dependent on space. The independence on space of the total current is guaranteed by an additional current of positive charges released by the light. For these positive charges an equation very similar to (3) may be written. However, for our purposes the treatment of (3) is sufficient. The boundary conditions for (3) are the densities of

electrons for  $x=0$  and  $x=d$  and the electron current at  $x=d$  which is equal to the total current through the bulk semiconductor. The mathematical treatment given in the appendix leads to the following equation:

$$(Je/h\nu) \cdot \alpha \cdot A + I = n_0 e v F \cdot [\exp(E/K) - 1], \quad (4)$$

with

$$A = [1 + (K/F\mu)]^{-1} - \exp(-d/\mu). \quad (5)$$

The factor  $A$  is closely connected to the quantum yield. The value  $A=1$  would be reached if (a) all light quanta were absorbed within the barrier layer, and (b) all released electrons were carried by the electric field toward the semiconductor. The second term of (5) which is especially significant for weak absorption of light gives the amount of light quanta which are not absorbed within the barrier layer. The difference between the first term and unity is especially significant for strongly absorbed light and refers to the electrons carried by diffusion toward the electrode.  $A$  is given in Fig. 3 as a function of  $d/\mu$ ; parameter is  $K/(Fd)$ .

In rear wall photo-cells only the light of wavelengths which are weakly absorbed reaches the barrier layer and (5) reduces to  $d/\mu$ . Considering further the absorption of light in the semiconductor located before the barrier layer and the reflection of light at the rear electrode, we have

$$A_{\text{rear wall}} = \exp(-\Lambda/\mu) \cdot d/\mu \cdot (1 + \rho). \quad (6)$$

The expression  $A_{\text{rear wall}} \cdot (\Lambda/d) \cdot (1/1 + \rho)$  is given in Fig. 4. Notice that the factor  $A_{\text{rear wall}}$  will reach only values of a few percent since  $d/\Lambda$  is generally very small compared with 1.

For  $p$ -type photo-cells ("hole" conduction)  $E$  and  $I$  change only their signs. Denoting with  $|E|$  and  $|I|$  the absolute values of photo-voltage and photo-current, the formula

$$(Je/h\nu) \cdot \alpha \cdot A - |I| = n_0 e v F [\exp(|E|/K) - 1] \quad (7)$$

may be written for both  $n$ -type and  $p$ -type photo-cells; of course  $n_0$  and  $v$  refer to electrons or "holes," respectively.

Equation (4) has been derived with considerable generality. The result would not be influenced if  $n_0$  were dependent on the field or on the light; there has been no need for assumptions about the distribution of the disturbance centers or about their balance with the electrons. Even

a small mobility of the charged impurity centers would not change the general form of (4) but only influence the parameters, especially  $F$  and  $d$ , and make them dependent on time.

Of course the parameters  $E$ ,  $F$ , and  $d$  are not independent, but they are connected by Poisson's equation and this connection is influenced by the distribution of the disturbance centers and their dissociation. Formulae for simplified cases might be of some value. In general,  $E$ ,  $F$ , and  $d$  can be derived from experimental data and the distribution of the disturbance centers can then be calculated.

## V. GENERAL DISCUSSION

In this chapter we discuss only some of the basic connections among  $E$ ,  $I$ , and  $J$ , as they are involved explicitly in (4). We shall not mention minor deviations which might be effected by changes in the dielectric constant, in the dissociation equilibrium of the disturbance centers, or in the electron density at the border of the metal, though these deviations may well have a certain significance in special cases. References to the experiment will be made only where disagreements seem to exist.

(a) *Sign of photo-voltage and photo-current.* Combining (4) with  $-E=RI$  (the negative sign refers to the fact that the total voltage drop in a closed circuit is zero), it is found in every case that  $E \geq 0$  and  $I \leq 0$  for semiconductors with electron conduction. For semiconductors with "holes" in every case  $E \leq 0$  and  $I \geq 0$ . Therefore, the electrode at the barrier layer becomes the positive (negative) terminal by illumination if the semiconductor is of the  $n$ -type ( $p$ -type), and this corresponds in every case to a voltage in the low resistance direction. The photo-current corresponds to a current of electrons ("holes") from the electrode at the barrier layer to the semiconductor for  $n$ -type ( $p$ -type) semiconductors and this corresponds in every case to a current through the photocell in the high resistance direction.

(b) For vanishing illumination ( $J=0$ ) Eq. (4) gives the *d.c. characteristic of the unilluminated barrier layer*. The formula is practically equivalent to an equation given by W. Schottky,<sup>20</sup>

<sup>20</sup> W. Schottky, Zeits. f. Physik 118, 539 (1942), (Eq. (12)).

where a more comprehensive discussion may be found.

For our purposes the low resistance direction is of particular value because this part of the characteristic is closely related to the photo-characteristic (see h). The theory requires an increase of  $I$  approximately proportional to  $\exp(E/K)$ , but the experiments show mostly somewhat slower increases. This might be due to the effect of an increase of the average electron energy in the strong electric fields of the barrier layer.

(c) *The short circuit current* ( $R=0$ ,  $E=0$ ) is proportional to the intensity of light.

(d) *The open circuit voltage* ( $R=\infty$ ,  $I=0$ ) is approximately proportional to the light intensity or to the logarithm of the light intensity according to whether the photo-voltage is small or large in comparison with the voltage equivalent of temperature.

(e) *The spectral distribution* is determined by the factor  $A$  (see Figs. 3 and 4), if the incident light is referred to the same amount of light quanta. From Eqs. (5) and (6) it will be noted that  $A$  decreases slightly with increasing voltage  $E$ , since the field intensity  $F$  and the thickness  $d$  decrease. Therefore, only the spectral distribution of the short circuit current where  $E=0$  is independent from the light intensity. It will be noted that the spectral distribution of a barrier layer photo-effect can be calculated, if the absorption curve of the semiconductor is known (with some not critical assumptions about the thickness of the barrier layer, etc.).

(f) *The dependence of photo-current and photo-voltage on the external resistance* (at constant light intensity) may be calculated by combining (4) with  $-E=RI$ . This curve has approximately the shape of a step function according to the exponential function on the right side of (4). Starting from small external resistances, the photo-current remains at first practically equal to the short circuit current, and the voltage increases proportional to the external resistance. Then, after a narrow transition region, the photo-voltage becomes practically equal to the open circuit voltage and the photo-current decreases inversely proportional to the external resistance.

(g) Based on the above, the *maximum power*

*output* might be set equal approximately to the product of the short circuit current and the open circuit voltage. The deviation of this approximation from the correct value might well be as high as a factor 4, but the right order of magnitude is given by it. Considering (c) and (d), we find that the maximum power output will increase approximately with the square of the light intensity or with the product of the light intensity and the log of light intensity, respectively. The corresponding external resistance is approximately constant, or decreases proportionally with the ratio of the log of the light intensity to the light intensity, respectively. The transition from the one approximation to the other takes place in a range of the light intensity, for which the corresponding open circuit voltage is of the order of the voltage equivalent of temperature.

(h) *The relation between the open circuit voltage and the short circuit current for different light intensities* (photo-characteristic) can be derived by eliminating the light intensity from the formulae for open circuit voltage ((4) with  $I=0$ ) and short circuit current ((4) with  $E=0$ ); namely,

$$|I|[A(E)/A(0)] = n_0 e v F \cdot [\exp(|E|/K) - 1]. \quad (8)$$

Equation (8) differs from the d.c. characteristic of the unilluminated barrier layer in the low resistance direction ((4) with  $J=0$ ) only by the deviation of the ration  $A(E)/A(0)$  from 1. Since  $A(E)$  decreases with increasing  $E$ , the open circuit voltage at an illumination  $J$  will always be a little lower than the voltage required to send through the unilluminated cell a current equal to the short circuit current at the said illumination. The deviations between the photo-characteristic and dark characteristic are hence a function of the wave-length.

Some authors<sup>21</sup> are opposed to any connection between rectifier effect and photo-voltaic effect, since a photo-voltaic effect has sometimes been observed in photo-cells which did not show any rectifying action. However, it is necessary to consider that the rectifying qualities of the photo-cell need not to be the same as the recti-

<sup>21</sup> Foster C. Nix and Arnold W. Treptow, J. Opt. Soc. Am. 29, 457 (1939); M. Borisow, C. Sinelnikow, and A. Walther, Phys. Zeits. Sowjetunion 3, 146 (1933); L. A. Wood, Rev. Sci. Inst. 6, 196 (1935); Mme. Roy-Pochon, Comptes Rendus 198, 2083 (1934).

fying qualities of the barrier layer. For instance, a sufficiently high resistance (bulk semiconductor resistance) in series with the barrier layer will diminish the rectifying action of the photo-cell by any desired amount without changing the open circuit voltage. On the other hand, some spots within the barrier layer of resistance low compared with the average resistance may diminish the rectifying action too. However, the short circuit current will not be diminished considerably as long as the resistances of these "shorts" are still large compared with the resistance of the bulk semiconductor.

(i) If the light is not monochromatic then the factor  $J/h\nu \cdot \alpha \cdot A$  has to be replaced by

$$\int J(\nu)/h\nu \cdot \alpha(\nu) \cdot A(\nu) d\nu.$$

As it might be seen from Eq. (4), only the short circuit current is a linear superposition of the currents resulting from each individual wavelength interval; the photo-voltage effected by an illumination with different wave-lengths at the same time is always smaller than the sum of the single wave effects.

(j) If the light intensity varies along the surface of the cell an Eq. (4) might be written for each element of area of the surface. If the photo-cell is homogeneous and if the voltage drop along the surface of the electrode and of the bulk semiconductor can be neglected, the voltage at the right side of each equation will be the same. Summing up all these equations, it is found that the effect will be the same as if the whole light intensity were distributed homogeneously over the whole surface.

(k) At small light intensities where the zero current voltage is small compared with the voltage equivalent of temperature, Eq. (7) yields:

$$|E| = \rho_0 (Je/h\nu) \cdot \alpha \cdot A - \rho_0 |I|, \quad (9)$$

where  $\rho_0 = (K/n_0 e v F)$  is the zero current resistance of the unilluminated barrier layer. Equation (9) corresponds to an e.m.f. of  $\rho_0 (Je/h\nu) \alpha \cdot A$  and of an internal resistance  $\rho_0$ .

(l) Generally, Eq. (7) may be interpreted simply in the following way (formulated for an  $n$ -type semiconductor):  $(Je/h\nu) \cdot \alpha \cdot A$  is the current due to the holes released by the light in

the barrier layer and following the electric field toward the electrode. An increasing accumulation of positive charge is avoided by an equal electron current to the electrode partially through the barrier layer (the term on the right side of Eq. (7) is equal to the current through the unilluminated barrier layer at the voltage  $E$ ) and partially through the external resistance ( $|I|$ ). Thus Eq. (7) is merely an extension of Eq. (38), page 195 of Mott and Gurney.<sup>17</sup> However, the theory presented goes much farther in that it gives a concrete expression for the factor  $A$  describing the spectral distribution, etc.

These selected examples show that the theory presented here is well adapted to deal with the various problems encountered by the barrier layer photo-effect.

#### ACKNOWLEDGMENT

I wish to express my thanks to the members of the Micro-Optical Section, Components and Materials Branch of the Squier Signal Laboratory, Signal Corps Engineering Laboratories, for many helpful discussions.

#### APPENDIX

The first integral of Eq. (3) of the text is:

$$J/h\nu \cdot \alpha \cdot [\exp(-x/\mu) - \exp(-d/\mu)] \\ = -nv \partial V/\partial x + D \partial n/\partial x - I/e.$$

The integration constant has been expressed by the values at  $x=d$ . This is a linear differential equation of the first order in  $n$ ; its integral has the general form

$$n = [\text{const} + L] \exp(V/K),$$

where the relation  $K = D/v$  and the abbreviation

$$L = J/h\nu \cdot \alpha/D \cdot \int_0^x \left\{ \exp(-x/\mu) - \exp(-d/\mu) \right. \\ \left. + \frac{I \cdot h\nu}{J \cdot e \cdot \alpha} \right\} \exp(-V/K) dx$$

have been used.

According to the boundary conditions we have

$$\text{const} = n_0 \exp(-V_0/K)$$

and

$$n_d = n_0 \exp(-V_0/K) + L_{x=d}.$$



Appreciable contributions to the integrand of  $L$  are given only by the lowest values of the voltage  $V$  (which is negative); for  $V_0 \ll -K$ , we may, therefore, use the approximation

$$V \approx V_0 + Fx + \dots$$

and extend the limits of the integral from 0 to  $\infty$ . (A second approximation will be given below.) Then we get

$$L_{x=d} = \frac{J \cdot \alpha \cdot K}{h\nu \cdot D \cdot F} \cdot \exp\left(-\frac{V_0}{K}\right) \cdot \left\{ \left(1 + \frac{K}{F\mu}\right)^{-1} - \exp\left(-\frac{d}{\mu}\right) + \frac{I \cdot h\nu}{J \cdot e \cdot \alpha} \right\}$$

Using the connection between  $n_a$  and  $L_{x=d}$  mentioned above, we have with regard to Eq. (2) of the text:

$$\frac{Je}{h\nu} \cdot \alpha \cdot \left[ \left(1 + \frac{K}{F\mu}\right)^{-1} - \exp\left(-\frac{d}{\mu}\right) \right] + I = n_0 e v F \left[ \exp\left(\frac{E}{K}\right) - 1 \right]$$

which can be split up into the basic equations (4) and (5) of the text.

The second approximation

$$V \approx V_0 + Fx - Mx^2 + \dots$$

gives with

$$\exp(Mx^2/K) \approx 1 + Mx^2/K$$

and

$$\int_0^d x^2 \exp(-Fx/K) dx \approx 2K^3/F^3$$

$$L_{x=d} = \frac{J \cdot \alpha \cdot K}{h\nu \cdot D \cdot F} \cdot \exp\left(-\frac{V_0}{K}\right) \cdot \left\{ \left(1 + \frac{K}{F\mu}\right)^{-1} + 2 \frac{MK}{F^2} \left(1 + \frac{K}{F\mu}\right)^{-3} - \left[ \exp\left(-\frac{d}{\mu}\right) - \frac{I \cdot h\nu}{J \cdot e \cdot \alpha} \right] \left(1 + 2 \frac{MK}{F^2}\right) \right\}$$

Then we have

$$\frac{Je}{\nu} \cdot \alpha \cdot A + I = \frac{n_0 e v F}{1 + 2MK/F^2} \cdot \left[ \exp\left(\frac{E}{K}\right) - 1 \right]$$

with

$$A = \left(1 + \frac{K}{F\mu}\right)^{-1} + \frac{2MK/F^2 \cdot (1 + K/F\mu)^{-2}}{1 + 2MK/F^2} - \exp\left(-\frac{d}{\mu}\right)$$

For  $M=0$  obviously Eq. (4) appears. If the density of the impurity centers is approximately constant within the barrier layer, it can be shown that  $2MK/F^2$  is of the order  $-K/2V_0$  which is very small compared with 1, if  $V_0 \ll -K$ . Therefore, in the text only the first approximation is used.

The assumption  $V_0 \ll -K$  excludes only comparatively high voltages in the low resistance direction, being closer to the diffusion potential than about  $4K$  ( $4K \sim 100$  mv at room temperature). These voltages are generally not reached by measurements.