enormous power M, of the order of the number of molecules in the heat bath.[13] Hence, if $\mathscr{E}$ is the energy of the system plus bath we have

$$s_\alpha = cE_\alpha{}^M = c(\mathscr{E}-\epsilon_i)^M \cong c\mathscr{E}^M[1-(M\epsilon_i/\mathscr{E})]$$

$$\cong c\mathscr{E}^M \exp(-M\epsilon_i/\mathscr{E}), \quad \text{(A-10)}$$

[13] See reference 9, p. 490, and E. Schrödinger, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1952), pp. 38 and 89.

where $\mathscr{E}=\epsilon_i+E_\alpha$. Identifying $\mathscr{E}/M$ with kT we have

$$s_\alpha = c\mathscr{E}^M e^{-\epsilon_i/kT}, \quad s_\beta = c\mathscr{E}^M e^{-\epsilon_j/kT}, \quad \text{(A-11)}$$

since $\mathscr{E}$, the total energy, is also equal to ϵ_j+E_β.

Using Eq. (A-2) with Eq. (A-9) and (A-11), we obtain finally

$$a_{ij}e^{-\epsilon_i/kT} = a_{ji}e^{-\epsilon_j/kT},$$

which is Eq. (A-5).

Flow of Electrons and Holes through the Surface Barrier Region in Point Contact Rectification*

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Equations are derived for the flow of electrons and holes through a surface barrier region by using the emission theory. The solution allows for nonequilibrium concentration of carriers on the semiconductor side of the barrier. It also allows for the possibility that part of the applied potential is between the metal surface and the semiconductor surface, as would occur if the surface states do not remain in equilibrium with the metal. The solution for the rectification characteristic is completed for the special case of small currents by combining the barrier region equations with the solution for current flow beyond the barrier region. The resulting equations are compared with those for *p-n* junctions, and the implications are discussed with regard to the relative roles of diffusion and emission in the flow of electrons and holes. Finally, the small current equations are compared with experiment, with a discussion of the evidence for the existence of an intersurface potential.

1. INTRODUCTION

THE early "diode" theory for point contact rectification was based on the flow of a single type of carrier, and did not consider the effects of minority carrier injection.[1,2] After the discovery of the latter phenomenon, the small current theory for *p-n* junctions was advanced by Shockley.[3] The application of this theory to point contacts was also discussed.[4]

The present theory of point contact rectifiers does not agree with experiment in the current voltage characteristic. The discrepancies have been discussed extensively.[5,6] particularly with reference to the reverse characteristic.[7] In view of this disagreement, it seems desirable to develop the theory in a more systematic and rigorous fashion. In such a manner, one may be able to investigate more carefully the validity of the accepted model for surface rectification.

The behavior of a rectifier may be obtained from the combination of the solutions of two separate problems: The flow of electrons and holes in the barrier region, which is "emission" controlled; and the flow beyond the barrier region, which is diffusion controlled.[8] A solution of the latter kind, which is one dimensional and applicable to *p-n* junctions or large area surface contacts has been derived by Van Roosbroeck.[9] The purpose of this paper is to present a self-contained solution to the former problem; that is, for the emission of electrons and holes through the barrier region of a semiconductor. In addition the solution will be completed for small currents in point contacts, for which case the diffusion problem has been solved; the results are compared with *p-n* junction theory. A general solution for the diffusion problem with radial flow, in combination with the emission equations, would permit the discussion of the forward (large current) characteristic of point contact rectifiers. This will be done in a later paper.

The emission equations to be derived are more general than the original diode equations in two ways.

* This work was first presented at the Cambridge American Physical Society Meeting in February, 1953 [Phys. Rev. **90**, 337 (1954)].

[1] R. C. Torrey and C. A. Whitmer, *Crystal Rectifiers* (McGraw-Hill Book Company, Inc., New York, 1948), Chap. 4.

[2] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), Chap. 5.

[3] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), Chap. 12.

[4] See reference 3, pp. 95–101.

[5] S. Benzer, J. Appl. Phys. **20**, 804 (1949).

[6] J. Bardeen and W. H. Brattain, Phys. Rev. **75**, 1208 (1949).

[7] J. H. Simpson and H. L. Armstrong, J. Appl. Phys. **24**, 25 (1953).

[8] This approach is discussed in a paper which has appeared recently. See P. C. Banbury, Proc. Phys. Soc. (London) **B66**, 833 (1953).

[9] W. Van Roosbroeck, Bell System Tech. J. **29**, 560 (1950).

They allow for nonequilibrium concentrations of electrons and holes near the barrier, and for the possibility that part of the voltage drop in the surface region may occur between the metal and semiconductor surfaces, rather than entirely in the barrier. The former phenomenon, due to injection or depletion of minority carriers, is well established experimentally. The extent to which it takes place will be determined by the associated solution for the diffusion region. The latter phenomenon is hypothetical and is included here mainly to permit its discussion as a possible explanation for the discrepancy between theory and experiment in diode behavior. For the purpose of the derivation, both effects enter in terms of arbitrary parameters, so that the latter hypothesis will not limit the generality of the equations. In order to fix our ideas, we shall consider the particular case of the surface in n-type germanium, which has a barrier for electrons; the extension to other types of barriers will be obvious.

The equations to be obtained are almost self-evident, and the derivation in terms of a kinetic theory would be quite simple. We shall base the solution on the consideration of transitions of electrons between energy levels in the metal and the semiconductor. This has some advantages over considering the flow of particles. One obtains a more rigorous solution, in which the nature of the approximations which are used is made clear. Also, the nature of the flow of holes between metal and semiconductor is clarified. The derivation shows that the unoccupied energy levels of the metal below the Fermi level act as holes as far as electronic transitions with the semiconductor is concerned. In view of the simplicity of the final results, the derivation will be in a condensed form. The reader is referred to a recent paper,[10] in which the theoretical analysis has a similar form.
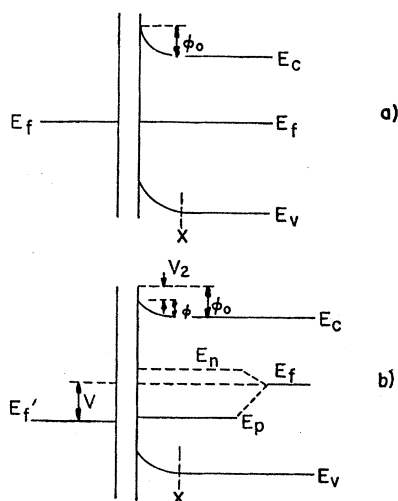

FIG. 1. Energy level diagram for the surface.
1a. Equilibrium, and 1b. forward bias V.

[10] W. Shockley and W. T. Read, Jr., Phys. Rev. 87, 836 (1952).

2. EMISSION CURRENT THROUGH THE SURFACE BARRIER

a. Model for the Theory

The energy level diagram for the surface region is shown in Fig. 1. At equilibrium, the surface barrier is ϕ_0. On the application of a forward bias V in the surface region, a part of it, V_1, is assumed to lie between the metal surface and the semiconductor surface; the remainder V_2 is in the barrier region between the semiconductor surface and a hypothetical point X, where X is the boundary between the barrier region and the bulk. If E_f' is the Fermi level in the metal when the bias is applied, and E_f the equilibrium Fermi level, then

$$E_f' - E_f = qV. \tag{1}$$

Also, the new barrier height ϕ is lower by the amount qV_2:

$$\phi_0 - \phi = qV_2. \tag{2}$$

The holes and electrons at X may not be in equilibrium when a bias exists. They may be regarded as being in quasi-equilibrium, each in their own band, and characterized by quasi-Fermi levels E_p and E_n:[3]

$$p = p_0 \exp[(E_f - E_p)/kT], \tag{3}$$

$$n = n_0 \exp[(E_n - E_f)/kT], \tag{4}$$

where p and n are hole and electron concentrations, respectively, and the zero subscript denotes equilibrium values. For purposes of the derivation, both E_p and E_n will be referrred to as E_f'', with the understanding that the latter parameter will have different values depending on whether the carriers are in the valence band or in the conduction band.

b. Flow between Single Energy Levels

The rate of flow of electrons j' from states in the metal at an energy level E_1 to states in the semiconductor at an energy level E_2 is

$$j'(E_1, E_2) = g'(E_1) f'(E_1) g''(E_2)$$
$$\times [1 - f''(E_2)] k'(E_1, E_2), \tag{5}$$

where $g'(E_1)$ is the density of energy states in the metal at energy E_1, and $f'(E_1)$ is the Fermi factor

$$\{1 + \exp[(E_1 - E_f')/kT]\}^{-1}.$$

g'' and f'' are similar functions for the semiconductor; f'' contains E_f'' in place of E_f', and $k'(E_1, E_2)$ is the transfer coefficient from the metal at energy E_1 to the semiconductor at energy E_2. It is noted that $g''(E_2)$ is zero for values of E_2 between the upper valence band edge E_v and the lower conduction band edge E_c.

A similar expression describes the rate of flow of electrons $j''(E_2, E_1)$ in the reverse direction. The net flow of electrons from E_2 and E_1 is the difference

between j'' and j':

$$j(E_2,E_1) = g'(E_1)g''(E_2)\{k''(E_2,E_1)f''(E_2)$$
$$\times [1-f'(E_1)] - k'(E_1,E_2)f'(E_1)[1-f''(E_2)]\}. \quad (6)$$

The principle of detailed balancing, which requires that $j(E_2,E_1)=0$ at equilibrium (when $E_f'=E_f''=E_f$), leads to the relation:

$$k''(E_2,E_1) = k'(E_1,E_2)\exp[(E_2-E_1)/kT]. \quad (7)$$

On substituting this back into Eq. (6), and simplifying, one obtains

$$j(E_2,E_1) = g'(E_1)g''(E_2)k'(E_1,E_2)f'(E_1)$$
$$\times [1-f''(E_2)]\{\exp[(E_f''-E_f')/kT]-1\}. \quad (8)$$

c. The Total Current

The total current is obtained from Eq. (8) by integrating over all values of E_1 and E_2. The integration over the semiconductor energy levels E_2 is broken into two parts: the integral from $-\infty$ to E_v gives the net hole current j_p; the integral from E_c to ∞ is the net electron current j_n.

With the assumption that the quasi-Fermi levels are always far from the band edge energies compared to kT, the integrals are simplified by the following considerations: One can expect that $k'(E_1,E_2)$ will be extremely small if $|E_2-E_1|$ is large compared to kT. For all values of E_1 and E_2, then, for which $k'(E_1,E_2)$ is not zero, the Fermi factors can be approximated by the corresponding Boltzmann factors. At this point, E_f'' is replaced by E_p and E_n in the two bands, and the flow equations become:

$$j_p = j_{p0}\{\exp[(E_p-E_f')/kT]-1\}$$
$$\times \exp[(E_f-E_p)/kT], \quad (9)$$

$$j_n = j_{n0}'\{\exp[(E_n-E_f')/kT]-1\}$$
$$\times \exp[(E_f'-E_f)/kT], \quad (10)$$

where

$$j_{p0} = \int_{-\infty}^{\infty}dE_1\int_{-\infty}^{E_v}dE_2 g'(E_1)g''(E_2)k'(E_1,E_2)$$
$$\times \exp[(E_2-E_f)/kT], \quad (11)$$

$$j_{n0}' = \int_{-\infty}^{\infty}dE_1\int_{E_c}^{\infty}dE_2 g'(E_1)g''(E_2)k'(E_1,E_2)$$
$$\times \exp[(E_f-E_1)/kT], \quad (12)$$

and j_{p0} is a constant. However, j_{n0}' is not a constant, since $k'(E_1,E_2)$ must be zero for values of E_2 between the conduction band edge E_c and the top of the barrier $(E_c+\phi)$, and ϕ varies with the bias according to Eq. (2). (We are neglecting here the effects of barrier penetration.) A good approximation for Eq. (12) is

$$j_{n0}' = j_{n0}\exp[(\phi_0-\phi)/kT], \quad (13)$$

where j_{n0} is a constant:

$$j_{n0} = \int_{-\infty}^{\infty}dE_1\int_{E_c+\phi_0}^{\infty}dE g'(E_1)g''(E)k''(E,E_1)$$
$$\times \exp[(E_f-E)/kT]. \quad (14)$$

This is obtained by making the transformation $E_2=E+\phi-\phi_0$, substituting Eq. (7), noting that the integral is zero for $E<E_c+\phi$, and using the assumption that all the other factors in the integral vary slowly compared to the exponential factor.

Equations (9) and (10) are converted into current equations by multiplying by the area A of the contact and by the electron charge magnitude q. On substituting Eqs. (1), (2), (3), (4), and (13), the current equations assume the following form:

$$I_p = I_{pe}[\exp(qV/kT)-p/p_0], \quad (15)$$

where $I_{pe}=j_{p0}Aq$, and

$$I_n = I_{ne}\exp(-qV_1/kT)[(n/n_0)\exp(qV/kT)-1], \quad (16)$$

where $I_{ne}=j_{n0}Aq$. I_p and I_n are the total hole and electron currents, respectively. It is convenient to express the constants I_{pe} and I_{ne} in an alternative form which is in the language of kinetic theory:

$$I_{pe} = qvAp_0t_p, \quad (17)$$

$$I_{ne} = qvAn_0t_n\exp(-\phi_0/kT), \quad (18)$$

where v is the average normal component of thermal velocity of holes and electrons crossing the surface from the semiconductor to the metal. The transmission coefficients for holes and electrons are, respectively, t_p and t_n. They are defined on comparison of the above equations with Eqs. (11), (14), (15), and (16). It is a matter of choice whether the effective masses for holes and electrons are used in determining v, or whether one uses the free electron mass for both and lumps the corrections, which are poorly known, into t_p and t_n; we have chosen the latter course. For most purposes, t_p and t_n may be assumed to be unity; it is expected that such an assumption will generally be correct in order of magnitude.

3. DISCUSSION

a. Comparison of Emission Equations

On comparing Eqs. (15) and (16) with the conventional emission equation,

$$I = I_0[\exp(qV/kT)-1], \quad (19)$$

the effects of the added factors considered here become apparent. The fact that the hole and electron concentrations near the surface barrier are not equilibrium ones leads to the factor p/p_0 in the current equation and n/n_0 in the electron current equation.[11] The exis-

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[11] This correction for the electron current equation was used by Swanson in a recent paper, although he did not use the accurate equation for the flow of holes. See J. A. Swanson, J. Appl. Phys. **25**, 314 (1954).

tence of an intersurface potential V_1 leads to an additional factor $\exp(-qV_1/kT)$ in the electron current equation. This factor can be combined with I_{ne} and denoted I_{ne}':

$$I_{ne}' = qAvn_0t_n \exp[-(\phi_0+V_1q)/kT]. \qquad (20)$$

We see that V_1 is added to the original barrier potential ϕ_0/q, so that it effectively increases the barrier height in the forward direction over what it would be otherwise, and decreases it in the reverse direction.

In order to provide a comparison with p-n junction theory it is desirable to complete the solution for the case of small currents. This will not only illustrate the method of combining the emission and diffusion solutions, but will also provide some further insight into the way in which the emission mechanism can become the determining factor for the point contact saturation current.[4] The total current is assumed to be small compared to the parameter I_{nd}, where

$$I_{nd} = qAn_0D_n/a. \qquad (21)$$

D_n is the diffusion constant for electrons and a is the contact radius. The solution of the spreading equations is then[12]

$$p/p_0 = 1 + I_p/I_{pd}, \qquad (22)$$

where

$$I_{pd} = qAp_0D_p/a \qquad (23)$$

and D_p is the diffusion constant for holes. Equations (22) and (23) imply that $p \ll n_0$ as long as $I \ll I_{nd}$, so that the assumption of electrical neutrality gives $n = n_0$. In addition, the spreading potential is negligibly small, so that the applied voltage can be assumed to equal the barrier voltage V. On combining these results of the diffusion problem with Eqs. (15) and (16), one has

$$I_p = I_{p0}[\exp(qV/kT)-1], \qquad (24)$$

$$I_n = I_{ne}'[\exp(qV/kT)-1], \qquad (25)$$

where

$$I_{p0}^{-1} = I_{pe}^{-1} + I_{pd}^{-1}. \qquad (26)$$

At this point, it is noted that the various I parameters (those with two subscripts) with dimensions of current function as admittances in the sense that the current is proportional to their values for any given voltage.[3] Continuing this analogy, we shall also refer to their reciprocals as impedances. Moreover, they can be described in terms of their origin; thus I_{pe} and I_{ne} are emission admittances, and I_{pd} is a diffusion admittance for holes.

In terms of these concepts, Eqs. (24), (25), and (26) show clearly the difference between surface rectification and p-n junction rectification. The diffusion controlled electron saturation current of p-n junction theory is replaced by an electron emission admittance parameter

I_{ne}'. The difference is the result of the fact that the effective diffusion distance of electrons in the surface p region is so small that emission, and not diffusion is the controlling factor. This was implicit in our derivation of the emission equations.

The last point becomes clearer on consideration of the change in the hole current equation. According to Eqs. (25) and (26), the impedance I_{p0}^{-1} for hole flow is the sum of the diffusion impedance I_{pd}^{-1} and emission impedance I_{pe}^{-1}. Thus the hole admittance corresponds to two admittance I_{pd} and I_{pe} in series, and is determined by the smaller one. If, as is usually the case, I_{pd} is small compared to I_{pe}, the diffusion impedance is dominant and determines I_{p0}. But in the opposite situation, the hole current would be emission controlled, as is the electron current. One additional difference is that the saturation hole current $I_{p0}(\cong I_{pd})$ is inversely proportional to the contact radius, rather than the diffusion distance of p-n junction theory.

An interesting result, closely connected with the above discussion, is the fact that the derivation of the rectification equation by the separate consideration of the emission and diffusion provides a quantitative measure of the change in the quasi-Fermi level in the barrier region. Shockley's derivation of the p-n junction equations made use of the approximation that there is no change in the quasi-Fermi level for holes on passing through the barrier. This is equivalent to assuming, in our equations, that $p/p_0 = \exp(qV/kT)$. Equations (22), (24), and (26) provide an exact relationship between the two quantities:

$$(p/p_0-1)/[\exp(qV/kT)-1] = I_{pe}/(I_{pe}+I_{pd}). \qquad (27)$$

Therefore, Shockley's approximation is correct if the diffusion admittance is small compared to the emission admittance $(I_{pd}/I_{pe} \ll 1)$. This requirement is amply fulfilled in large area barriers; it may not be quite true in small area point contacts, which may have values for this ratio of the order of 0.1. Also, as will be shown in a later paper, the approximation is not always valid for large currents.

The introduction of the hypothetical intersurface potential V_1 presents a possible alternative explanation for the deviation of experimental point contact characteristics from the behavior predicted by theory.[13] If one plots $I[\exp(qV/kT)-1]^{-1}$ as a function of V in the range of small V (say, from -100 mv to $+100$ mv), one should obtain a horizontal straight line with an ordinate equal to $I_{p0}+I_{ne}'$, according to Eqs. (24) and (25), if the value of I_{ne}' is constant. In practice, such a plot yields a curve whose ordinate decreases with increasing V. The existence of an intersurface potential, which causes I_{ne}' to be variable, is consistent with this behavior.

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[12] This equation is derived by Bardeen, Bell System Tech. J. **29**, 469 (1950). In addition, a number of points discussed here are contained either explicitly or implicitly in that paper, or in reference 6.

[13] The hypothesis most commonly accepted involves the multicontact theory; see, for instance, H. J. Yearian, J. Appl. Phys. **21**, 214 (1950); Johnson, Smith, and Yearian, J. Appl. Phys. **21**, 283 (1950), and reference 4.

One might expect such a potential to occur as the result of a thin oxide layer between the surfaces of the metal and the semiconductor. One could reasonably expect V_1, in such a case, to be a monotonic function of V. The actual relationship would of course depend on the electronic processes which occur in the oxide. It should be noted, however, that extensive scattering of electrons in the oxide might limit the validity of the derivation, in particular the assumption about $k'(E_1,E_2)$ used in obtaining Eqs. (9) and (10). In such a case, our equations would be merely an indication of what to expect.

Finally, we would like to discuss briefly some formal implications of the generalized emission equations for a barrier. In the general case, the equations would have the following form:

$$I_p = qvA\{p_1 \exp[-q(V_2-V_1)/kT] - p_2\}, \qquad (28)$$

where the subscripts refer to the two sides of the barrier. (The situation for electrons is exactly analogous, and will not be discussed.) It is assumed, without loss of generality, the region 1 is more p type than region 2.

On substituting Eqs. (4) and (5), one obtains

$$I_p = qvA\,p_{20} \exp(E_{f2}/kT)$$
$$\times [\exp(-E_{p2}/kT) - \exp(-E_{p1}/kT)], \qquad (29)$$

where p_{20} is the equilibrium hole concentration in region two. The interesting aspect of this result is that the flow is proportional to the difference in the Boltzmann factors for the quasi-Fermi levels. This is analogous to the expression for the diffusion flow:[3]

$$I_p = qD_pA\,p\nabla(E_f-E_p)/kT. \qquad (30)$$

Indeed, one can derive Eq. (30) in a crude way from Eq. (29) by considering the diffusion process to be the result of emission between successive regions separated by a distance equal to the mean free path for carriers λ. One obtains the above result on assuming that $(E_{p2}-E_{p1})/kT \ll 1$, and identifying the product $v\lambda$ with D_p.

Effect of Oxygen on the Electrical Properties of Lead Telluride Films*

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The effect of oxygen on the electrical properties of PbTe films has been investigated. Oxygen, which presumably is adsorbed on the surface of the film, causes an increase in film resistance, followed by a decrease in resistance with increasing exposure to oxygen. The film which is originally "n" type changes to "p" type in the vicinity of the resistance maximum. The magnitude of the photoresistive and photovoltaic effect varies with the amount of oxygen adsorbed by the film. A model has been presented whereby oxygen removes electrons first from the conduction band, then from trapping states, and finally from the valence band, thereby producing the observed effects.

I. INTRODUCTION

IN the study of the electrical properties of thin films adsorbed oxygen is generally undesirable since it obscures the true properties of the film. Sometimes, however, films must be exposed to oxygen to bring out properties which cannot be observed otherwise. PbS, PbSe, and PbTe films exhibit photoconductivity after the films have been treated with oxygen. Sensitization techniques require certain recipes whereby maximum sensitivity is obtained if well-tested empirical rules are followed. Lead telluride cells, as described in the literature,[1-3] have been used in recent

years as detectors of infrared radiation. They have a rapid response time (time constants of the order of 10 microseconds), high sensitivity, and a long wavelength threshold at about 5.5 microns with peak sensitivity at about 4.5 microns. PbTe cells show this sensitivity only if they are cooled below 100°K. Figure 1 shows a conventional PbTe cell. The Dewar construction is necessary to permit cooling of the sensitive layer. A sapphire window whose transmission remains satisfactory to 6 microns is sealed to the Pyrex by means of a graded seal.

The cell is prepared by placing powdered PbTe, formed by the fusion of stoichiometric amounts of Pb and Te, into a cell blank and subliming it in a high vacuum. The PbTe vapor is condensed onto the region between previously ruled conducting electrodes by cooling this region with an air jet. Sensitization consists of oxygen treatments until optimum sensitivity is

[1] O. Simpson, Trans. Roy. Soc. (London) A243, 547–584 (1951).
[2] R. A. Smith, Advances in Physics 2, 321–369 (1953).
[3] R. A. Smith, *Semiconducting Materials* edited by H. K. Henisch (Butterworth Publications Ltd., London, 1951), p. 205.