

Analytic Expressions Relating Surface Charge and Potential Profiles in the Space-Charge Region in Semiconductors*

VIN-JANG LEE AND DONALD R. MASON

Department of Chemical and Metallurgical Engineering, University of Michigan, Ann Arbor, Michigan

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The potential on the surface of a semiconductor is formulated analytically as a function of surface charge concentration by a double integration of Poisson's equation in one-dimensional form. All combinations of the types of semiconductors and surface charge have been considered, as they produce accumulation, depletion, or inversion layers. The variation of diffusion potential as a function of distance from the surface towards the interior of the semiconductor is also discussed.

INTRODUCTION

MANY authors have formulated relationships between the ion concentration on semiconductor surfaces and surface potential or the variation of diffusion potential with distance for some special cases, but the completely general double integration using boundary conditions appropriate for an electric charge layer on a semiconductor surface has been performed only with the aid of numerical methods. In this paper, the potential change at the boundary between a semiconductor or an insulator and a gas or vacuum phase is formulated analytically as a function of the concentration of ionized donor or acceptor centers on a solid surface of semiinfinite extent, for all combinations of the types of semiconductors and the ions on the surface, and the limitations of the analytical integration are defined.

Aigrain and Dugas,¹ Hauffe and Engell,² and Weisz,³ all have derived relationships between surface ion concentration and surface potential. Mott,⁴ Schottky,⁵ and Garrett and Brattain,⁶ have discussed relationships between accumulation, depletion or inversion layers on semiconductor surfaces and surface potentials. Kingston and Neustadter,⁷ Dousmanis and Duncan,⁸ Mowery,⁹ Young,¹⁰ Macdonald,¹¹ Seiwatz and Green,¹² have used numerical integration to calculate the space charge and diffusion potential relationships. Bohnenkamp and Engell¹³ have derived an analytic expression relating

the surface ion concentration to the surface potential for accumulation layers on semiconductors. These last authors have tacitly assumed that the semiconductor has a semiinfinite extension, and applied Gauss' law to calculate the space charge. In this paper all these derivations are placed in context as being representative of certain special cases, and are mentioned in the appropriate sections.

Many persons believe that the above literature represents an exhaustive analysis of this problem. However, careful reading of these papers shows that they deal only with simplified special cases, or consider only surface potential or only diffusion potential, or present their results in graphical form for only selected values of the variables. By having analytic equations relating diffusion potential to surface ion concentration by way of the surface potential, the graphical representations are not required. Furthermore the analytic expressions can be used as a basis for additional theoretical derivations relating surface and bulk properties, which could not be carried out readily using the graphical correlations.

In this paper the variation of surface potential as functions of bulk carrier concentration and surface ion concentration for accumulation layers on intrinsic and extrinsic semiconductors is presented. The variation of diffusion potential as functions of surface potential and bulk carrier concentration is also presented for similar conditions.

The analytic representation of the surface potential as functions of surface ion concentration and bulk carrier concentration is also given for the situations wherein depletion and inversion layers on extrinsic semiconductors are formed. However, the resulting equation is rather complex and can be simplified only for certain values of surface potential relative to the bulk diffusion potential.

Exact expressions for the variation of the diffusion potential beneath the surface as a function of distance can be obtained only if the surface potential is very small ($u_s \leq 0.9$), or if x is very small ($x \rightarrow 0$) over certain values of surface potential relative to the bulk diffusion potential. A general solution to this problem can be obtained only by numerical integration methods.

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MODEL

Since Poisson's equation represents the macroscopic variations of the average potential inside a charged crystalline solid over distances which are large in comparison to atomic dimensions, this model is valid only for those situations in which the total potential variation extends over many atomic distances. The thickness of the space-charge region has been characterized by a screening length, which is also known as the Debye length for an intrinsic semiconductor. Typically, this screening length may vary from 10^{-7} to 10^{-5} cm. By assuming that the dimensions parallel to the surface are much larger than the thickness of the space-charge region, the one-dimensional form of Poisson's equation can be used. This covers the majority of cases wherein the minimum dimension of the solid particle is equal to or greater than 10^{-4} cm. When the surface charge is mobile the potential beneath the surface may fluctuate in response to the motion of the charges. If this surface motion is two-dimensionally random then Poisson's equation describes the time-average potential beneath the surface. When the surface charge is immobile, then the average distance between the individual surface charges should be no greater than the screening length in order to use the one-dimensional form of Poisson's equation.

In one-dimensional form the equation is

$$(1/kT)[d^2E(x)/dx^2] = [4\pi q^2\rho(x)/\epsilon kT] = 2L_m\rho(x), \quad (1)$$

where $q\rho(x)$ = bulk charge density, positive charges/cm³; $[\rho(x)]$ is at least a sectionally continuous function of x . Note that this includes the case wherein there is a surface charge.] $E(x)$ = electron energy, eV; $-(1/q)E(x)$ = electrostatic potential at x , volts; ϵ = dielectric constant, dimensionless; q = unit positive charge, 4.802×10^{-10} esu; x = distance into the bulk region of the semiconductor; from the surface, cm; $V(x)$ = electrostatic potential, statvolts; and

$$L_m = 2\pi q^2/\epsilon kT \quad (\text{in cm}), \quad (2)$$

which is a length, independent of charge concentration and dependent only on the dielectric constant of the material and the absolute temperature. The variable of integration can be changed by defining

$$Y(x) = [E_{cB} - E_c(x)] = [E_{vB} - E_v(x)] = [E_{iB} - E_i(x)], \quad (3)$$

$$u = Y(x)/kT = \text{normalized diffusion potential,} \\ (kT) \text{ units.} \quad (4)$$

The sign of $Y(x)$ and u are then taken as positive when the surface becomes more n type. Boundary conditions for the integration can be defined as

$$u = u_s \quad \text{at } x = 0, \quad (5)$$

$$u = 0 \quad du/dx = 0 \quad \text{at } x = \infty, \quad (6)$$

and electroneutrality across the surface requires that

$$-\int_0^\infty \rho(x)dx = \sum_{\square} = (\sum \nu D^{\nu+} - \sum \delta A^{\delta-}), \quad (7)$$

where $q\sum$ = net positive surface charge, esu/cm²; $D^{\nu+}$ = ionized donors with valence state ν , donors/cm²; $A^{\delta-}$ = ionized acceptors of valence state δ , acceptors/cm².

The summation is carried out for all possible ν and δ and includes both fast and slow surface states¹⁴ and both components of any dipole layer which may exist on the surface. Substitution of Eqs. (3) and (4) into (1) and integration gives

$$0 - \left(\frac{du}{dx}\right)_0 = -2L_m \int_0^\infty \rho(x)dx = 2L_m \sum_{\square}, \quad (8)$$

where the result from Eq. (7) has been introduced. This relationship must be combined with other equations yet to be derived to relate surface potential to surface charge concentration.

The bulk charge density can be defined as

$$\rho(x) = (N_a^+) - (N_a^-) + p(x) - n(x), \quad (9)$$

where (N_a^-) = concentration of acceptor centers in the bulk, acceptors/cm³; (N_a^+) = concentration of donor centers in the bulk, donors/cm³; $p(x)$ = hole concentration at x , holes/cm³; and $n(x)$ = electron concentration at x , electrons/cm³. If it is assumed that the semiconductor is in a nondegenerate condition, the Boltzmann statistics are applicable and all donors or acceptors are ionized, then the hole and electron concentrations in the space-charge region can be written as:

$$p(x) = p_B \exp[-Y(x)/kT] = p_B \exp(-u) \\ = p_i \exp(-u_B) \exp(-u), \quad (10a)$$

$$n(x) = n_B \exp[Y(x)/kT] = n_B \exp u \\ = n_i \exp(u_B) \exp(u). \quad (10b)$$

When $n_i = p_i$ then

$$\rho(x) = \rho(u) = (N_a^+) - (N_a^-) - 2n_i \sinh(u_B + u), \quad (11)$$

where $u_B = \frac{1}{2} \ln(n_B/p_B)$ = bulk diffusion potential, displacement of the Fermi level from midband position. The variable in Eq. (1) can be changed from x to u , and Eq. (11) introduced to give

$$d^2u/dx^2 = d/dx(du/dx) = du/dx(d/du)(du/dx) \\ = \frac{1}{2} d/du[(du/dx)^2] = -2L_m\rho(u) \\ = -2L_m[(N_a^+) - (N_a^-) - 2n_i \sinh(u_B + u)]. \quad (12)$$

In order to investigate all possible interrelationships between the charge on the surface and the electrical nature of the semiconductor, it is necessary to consider three groups of cases which increase in mathematical complexity. The first group of cases can be defined for surface donors or acceptors on an intrinsic semiconductor. The second group of cases can be defined for surface donors on an n -type semiconductor, and for surface acceptors on a p -type semiconductor. In these two groups of cases accumulation layers are formed underneath the semiconductor surfaces. For brevity

¹⁴ J. Bardeen, R. E. Coover, S. R. Morrison, J. R. Schrieffer, and R. Sun, Phys. Rev. **104**, 47 (1956).

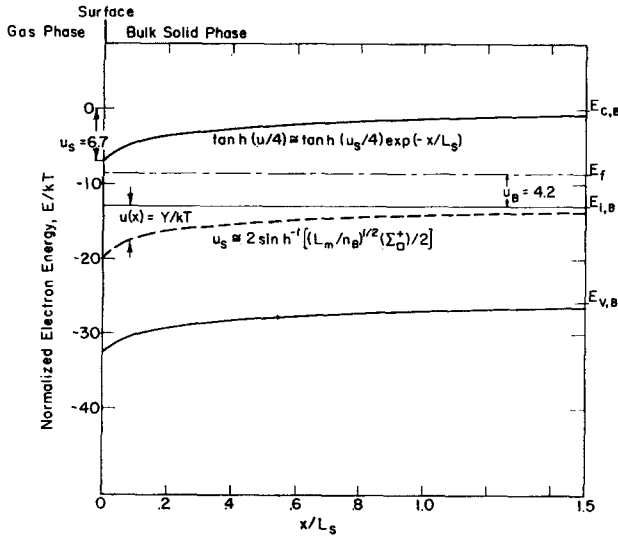


FIG. 1. Electron potential energy diagram for surface donors on 1- Ω cm n -type germanium. $T=300^\circ\text{K}$; $E_g=0.66$ eV $=25.6kT$; $u_B=4.2$; $n_B=1.58 \times 10^{16}$ electrons/cm 3 ; $L_s = \frac{1}{2}(L_m n_B)^{1/2} = 8.55 \times 10^{-6}$ cm.

only the second group is considered in detail since the first group can be obtained as a simplified special case of the second.

The third group of cases can be defined for surface donors on a p -type semiconductor or for surface acceptors on an n -type semiconductor, and is subdivided into several cases depending on whether the surface layers are depletion layers, intrinsic, or inversion layers.

Accumulation Space-Charge Regions on Extrinsic Semiconductors

Either an n -type semiconductor with donor centers on the surface or a p -type semiconductor with acceptor centers on the surface can be considered. The first situation is presented in detail so that the results for the other case need only be summarized.

Case 1. Accumulation Layers from Surface Donors

In the case of an n -type semiconductor it can be assumed that the acceptor concentration in the bulk region is negligible in comparison with the donor concentration. An energy band diagram for this situation is shown in Fig. 1. Integration of Eq. (12) gives

$$(du/dx)^2 = 4L_m \{ 2n_i \cosh(u_B + u) - 2n_i \cosh u_B - (N_d^+)u \} \quad (13a)$$

and the hyperbolic functions in this equation can be resolved through identities to give

$$(du/dx)^2 = 4L_m \{ 4n_i \exp(u_B) [\sinh(u/2)]^2 + 2n_i [1 - \exp(-u)] \sinh u_B - (N_d^+)u \}. \quad (13b)$$

This equation now can be used as a basis for deriving

the surface potential and the diffusion potential relationships.

(a) *The surface potential u_s .* Equation (13b) can be evaluated at $u=u_s$ and $x=0$, and the significance of the second term on the right relative to the first term can be investigated. Differentiation shows that the second term has its maximum influence as the surface potential approaches zero. However, when u_s is small, then $[1 - \exp(-u_s)] \approx u_s$ and the second and third terms cancel. When u_s is large then the exponentials in the \sinh^2 term dominate the expression. Therefore, by neglecting the second and third terms and taking the square root with the negative sign, (since u must decrease from a positive value to zero as x increases) the result is

$$(du/dx)_0 = -4(L_m n_B)^{1/2} \sinh(u_s/2). \quad (14)$$

By combining Eq. (14) with Eq. (8) the result is

$$\sinh(u_s/2) = (L_m/u_B)^{1/2} (\Sigma_{\square}^+)/2. \quad (15)$$

For an intrinsic semiconductor n_B is replaced with n_i , and this result has been derived by Bohnenkamp and Engell.¹³

Whenever the *surface ion concentration is low* so that $(u_s/2) \leq 0.9$, and $\sinh(u_s/2) \approx (u_s/2)$ then it can be shown from Eq. (15) that

$$u_s \approx (L_m/n_B)^{1/2} (\Sigma_{\square}^+) \quad (16)$$

and the surface potential varies linearly with the surface ion concentration. If $(u_s/2)$ is so *large* that the hyperbolic sine can be approximated by an exponential, then

$$u_s = \ln \{ (L_m/n_B) (\Sigma_{\square}^+)^2 \} = -u_B + \ln \{ (L_m/n_i) (\Sigma_{\square}^+)^2 \}. \quad (17)$$

These expressions for surface potential are very similar to those which would be derived for the intrinsic semiconductor, except that the surface potential on the n -type semiconductor is reduced by an amount equal to the Fermi diffusion potential in the bulk of the semiconductor u_B .

(b) *The diffusion potential $u(x)$.* To investigate the diffusion potential $u(x)$ the second term in Eq. (13b) can be neglected as before. After taking the square root with the negative sign, the variables can be separated in this equation and the following transformation can be used.

$$2d\xi/\sinh 2\xi = d\xi/\sinh \xi \cosh \xi = d\{\ln[\tanh(\xi)]\}. \quad (18)$$

Integration using the boundary condition at $x=0$ gives

$$\tanh(u/4) \approx \tanh(u_s/4) \exp[-2x(L_m n_B)^{1/2}], \quad (19)$$

where $\frac{1}{2}(L_m n_B)^{1/2}$ = screening length, and is equal to the Debye length for an intrinsic semiconductor. This equation is plotted in Fig. 1 for 1- Ω cm Ge at 300 $^\circ$ K. For intrinsic Ge the Fermi level would be at the midband position. Now if u is large then the \sinh^2

term is dominant in Eq. (13b), which again leads to Eq. (19). Therefore, Eq. (19) is a fair approximation throughout the space-charge region since $\sinh(u/2)$ is a monotonically increasing function. If $u_s \gg 4$, so that $\tanh(u_s/4) \approx 1$, then

$$\tanh(u/4) \approx \exp[-2x(L_m n_B)^{1/2}] \quad (20)$$

and the variation of the diffusion potential with distance is obtained.

When u becomes small such that $\tanh(u/4) \approx u/4$, then

$$u(x) \approx 4 \exp[-2x(L_m n_B)^{1/2}]. \quad (21)$$

Mott and Gurney¹⁵ have derived this equation to explain the potential barrier which exists at the interface between two solids.

Alternatively, when u is large, then the \sinh in Eq. (13b) can be expressed as an exponential, and integration using the boundary condition at $x=0$ gives

$$u(x) \approx 2 \ln[\exp(-u_s/2) + x(L_m n_B)^{1/2}]^{-1}. \quad (22)$$

Equations (19) through (22) then represent the variation of the diffusion potential with distance using first-order approximations.

Case 2. Accumulation Layers from Surface Acceptors

In this case the energy band diagram is shown in Fig. 2 for 2.1-Ω cm Ge at 300°K. Since acceptors on the surface tend to make the space-charge region become p type, then the surface potential must be inherently negative in this situation. Therefore, in order to deal with positive values of the surface potential and the diffusion potential in the equations, primed values are defined such that

$$u' = -u; \quad u_s' = -u_s; \quad u_B' = -u_B. \quad (23)$$

When these substitutions are made and \sum_{\square}^- is substituted for \sum_{\square}^+ , the above equations represent the situation adequately.

Depletion-Inversion Space-Charge Regions on Extrinsic Semiconductors

In this group the combinations of a p -type semiconductor with donor centers on the surface, and an n -type semiconductor with acceptor centers on the surface are included. Since the mathematical treatments are similar for the two situations, a complete analysis will be given only for the p -type semiconductor, and the equations for the other combination can be obtained as indicated previously.

Case 3. Depletion-Inversion Layers from Surface Donors

The surface donor centers introduce mobile electrons into the space-charge region. On a p -type semiconductor

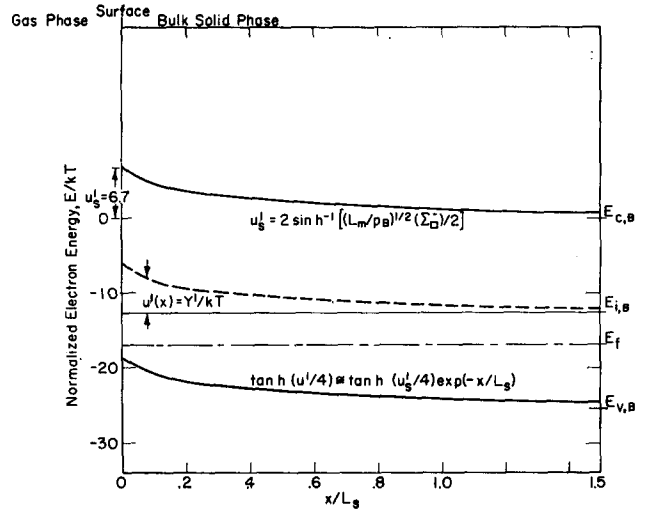


Fig. 2. Electron potential energy diagram for surface acceptors on 2.1-Ω cm p -type germanium. $T = 300^\circ\text{K}$; $E_g = 0.66 \text{ eV} = 25.6kT$; $u_B' = 4.2$; $p_B = 1.58 \times 10^{16} \text{ holes/cm}^3$; $L_s = \frac{1}{2}(L_m p_B)^{1/2} = 8.55 \times 10^{-6} \text{ cm}$.

then the space-charge region at the surface must become less p type. However, the hole neutralization can proceed to the point where the surface becomes intrinsic, or even n type. These changes, of course, depend on the bulk carrier concentration and the ionized surface donor concentration.

A criterion for these changes can be obtained by the fact that at the intrinsic plane, $p(x) = n(x) = n_i$. At the intrinsic plane, the sum of the mobile charge must be equal to zero and the particular value of diffusion potential u_i is defined, so that $u_B' = u_i = \ln(p_B/n_B)^{1/2}$. When the surface potential is equal to the intrinsic diffusion potential, then the outermost surface is just intrinsic. Whether there is an inversion in the space-charge region or just a depletion of majority carriers depends on the relationship between the bulk hole concentration of the p -type semiconductor and the ionized surface donor (in this case) concentration.

A generalized expression for the surface potential as a function of surface ion concentration can be obtained as before. Integration with respect to u gives

$$\begin{aligned} (du/dx)^2 = 4L_m \{ & (N_a^-)u \\ & + 2n_s[\cosh(u - u_B') - \cosh u_B'] \}. \end{aligned} \quad (24a)$$

By using hyperbolic identities this equation can also be written as

$$\begin{aligned} (du/dx)^2 = 4L_m \{ & p_B[\exp(-u) + u - 1] \\ & + n_B[\exp(u) - u - 1] \}. \end{aligned} \quad (24b)$$

When Eqs. (24) are evaluated using the boundary condition at the surface and combined with Eq. (8) the result is

$$\begin{aligned} L_m(\sum_{\square}^+)^2 = & p_B[\exp(-u_s) + u_s - 1] \\ & + n_B[\exp(u_s) - u_s - 1], \end{aligned} \quad (25a)$$

¹⁵ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), 2nd ed., p. 176.

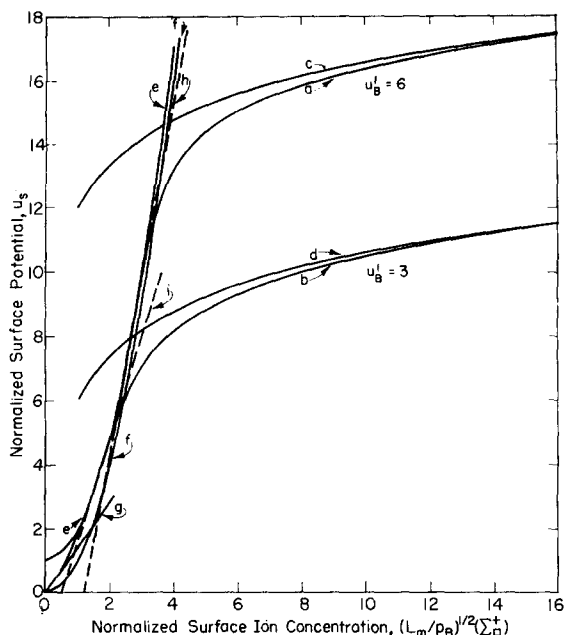


FIG. 3. Variation of surface potential as function of normalized surface donor ion concentration on *p*-type semiconductors. Curves (a) and (b) are from Eq. (25) with $u_B' = 6$ and 3. Curves (c) and (d) are from Eq. (42) with $u_B' = 6$ and 3. Curve (e) is from Eq. (29). Curve (f) is from Eq. (37). Curve (g) is from Eq. (26). Curve (h) is the tangent to Curve (a) at its point of inflection ($u_s^* = 9.3$) for $u_B' = 6$. Curve (i) is the tangent to curve (b) at its point of inflection ($u_s^* = 4.3$) for $u_B' = 3$.

or

$$(L_m/p_B)(\sum_{\square}^+)^2 = 2 \exp(-u_B') [(u_s - 1) \sinh u_B' + \cosh(u_s - u_B') - \exp(-u_B')], \quad (25b)$$

or

$$(L_m/p_B)(\sum_{\square}^+)^2 = 2 \exp(-u_B') [u_s \sinh(u_B') + \cosh(u_s - u_B') - \cosh(u_B')]. \quad (25c)$$

The Eqs. (24) and (25) are exact expressions relating surface potential and surface ion concentration as functions of the bulk diffusion potential. Equation (25) is plotted in Fig. 3 as curves (a) and (b) for values of u_B' equal to 6 and 3, respectively. However, these equations are too complex to be analyzed in this form, and it is necessary to make various approximations and simplify the situation by defining a series of six special cases. The six cases are case 3(a): slight depletion layer, $u_s \leq 0.9$; case 3(b): moderate depletion layer, $0.9 \leq u_s \leq 2$; case 3(c): depletion-inversion layer, $2 < u_s < 2u_B' - 1$; case 3(d): slight inversion layer, $u_s = 2u_B'$; case 3(e): moderate inversion layer, $(2u_B' - 1) < u_s < u_c$, where a critical value of surface potential u_c must be defined; and case 3(f): strong inversion layer, $u_c \leq u_s$. In the first three special cases above, case 3(a), case 3(b), and case 3(c), the surface either remains *p* type or just becomes intrinsic or *n* type.

Case 3(a). Slight Depletion Layer, $u_s \leq 0.9$

When the surface potential is less than 0.9 ($u_s \leq 0.9$), then the exponentials in Eq. (25a) can be expanded in series form. The result is

$$u_s \approx [2L_m / (p_B + n_B)]^{1/2} (\sum_{\square}^+) \leq 0.9. \quad (26)$$

The surface potential then varies linearly with surface charge concentration. This is plotted in Fig. 3 as curve (g). In most practical cases the surface potential can be small only when the denominator in Eq. (26) is large, so that the minority carrier concentration u_B can be neglected, and the bulk diffusion potential u_B' is at least greater than 2.0 ($u_B' \geq 2.0$).

In order to evaluate the diffusion potential Eq. (24a) must be simplified by expanding the exponentials and integrating by using the boundary conditions at the surface. The result is

$$u = u_s \exp\{-x[2L_m(p_B + n_B)]^{1/2}\}. \quad (27)$$

Case 3(b). Moderate Depletion Layer, $0.9 \leq u_s \leq 2$

In this case, Eqs. (25) cannot be simplified readily and a graphical solution is required in order to find the exact relationships between surface ion concentration, surface potential, and diffusion potential.

A good approximation can be obtained from Eq. (25a) if $u_B' \geq 2$, so then the n_B term can be neglected. The result can be written in series form as

$$\sum_{n=2}^{\infty} (-1)^n (1/n!) u_s^n = (L_m/p_B) (\sum_{\square}^+)^2. \quad (28)$$

This is implicit in u_s , but could be solved by trial and error. In this region of u_s , the denominator increases more rapidly than the numerator and each pair of terms is always positive.

Case 3(c). Depletion-Inversion Layer, $2 < u_s \leq (2u_B' - 1)$

When the surface potential u_s is greater than 2, ($u_s \geq 2$), and u_B' is correspondingly larger then Eq. (25b) can be evaluated to give

$$u_s = [L_m / (N_a^-)] (\sum_{\square}^+)^2 + 1. \quad (29)$$

This relationship is valid even if the surface becomes intrinsic or inverted, as long as $u_s \leq (2u_B' - 1)$, and is plotted as curve (e) in Fig. 3.

In order to find the diffusion potential in the neighborhood of $x=0$, when $u_B' \geq 2.0$, then the square root with the negative sign of Eq. (24a) reduces to

$$du/dx = -2[L_m(N_a^-)]^{1/2} (u - 1)^{1/2}. \quad (30)$$

Since Eq. (30) is applicable for the neighborhood of $x=0$, it can be integrated for small values of x extending from the surface. Therefore,

$$(u - 1)^{1/2} = (u_s - 1)^{1/2} - [L_m(N_a^-)]^{1/2} x. \quad (31)$$

Substitution of Eq. (29) into Eq. (31) with rearrangement gives

$$u = 1 + [L_m p_B] \{ (\Sigma_{\square^+}) / p_B - x \}^2. \quad (32)$$

This equation indicates that the diffusion potential is not exactly a simply parabolic function of distance as predicted previously by Mott⁴ and Schottky,⁵ and this formulation represents a better approximation near the surface.

For $u(x)$ in the neighborhood of unity, as x extends into the interior of the solid, Eq. (24) must be re-evaluated and simplified again before performing the integration. The significant term then is $p_B \exp(-u)$, and taking the square root with the negative sign gives

$$du/dx = -2(L_m p_B)^{1/2} \exp(-u/2). \quad (33)$$

The variables in Eq. (33) can be separated, and integration gives

$$\exp(u/2) = (\text{const}) - x(L_m p_B)^{1/2} \quad (34)$$

but the integration constant cannot be readily evaluated. However, an approximation could be made by matching slopes, i.e., equating Eqs. (30) and (33) solving for a particular value of u^* and, therefore, x^* from Eq. (31), and using this as a boot strap technique.

For values of x approaching infinity, such that $u(x)$ is very small and approaching zero, then the exponentials in Eq. (24b) can be expanded in series form. Therefore, taking the square root of the resulting equation with the negative sign, as before, gives

$$du/dx = -[2L_m(p_B + n_B)]^{1/2} u \simeq -[2L_m p_B]^{1/2} u. \quad (35)$$

The variables can be separated and integration gives

$$u = (\text{const}) \exp[-x(2L_m p_B)^{1/2}] \quad (36)$$

but again the integration constant cannot be evaluated readily, although the slope matching technique could be used with Eqs. (33) and (35). This equation has the same general form as Eq. (27), which was obtained for the diffusion potential under conditions of a slight depletion layer. Therefore, it seems that the addition of surface charge adds to the curvature of the diffusion potential curve rather than changes its form substantially.

It can be seen that the dependency of u goes from a complex parabolic relationship through a logarithmic relationship to an exponential relationship.

Case 3(d). Slight Inversion Layer, $u_s = 2u_B'$

This is a special case which normally would not be of significant interest, except that the results obtained in this case have been previously derived by previous authors. In this case the adsorbed ion concentration must be such that $u_s = 2u_B'$, so that the surface is inverted and the magnitude of the inversion is equal to the bulk diffusion potential. When this substitution is made into Eq. (25c) it reduces immediately to

$$u_s = [L_m / (N_a^-)] [\Sigma_{\square^+}]^2. \quad (37)$$

This equation has been derived previously by Aigrain and Dugas,¹ by Hauffe and Engell,² and by Weisz³ using a different model and different boundary conditions. It is plotted as curve (f) in Fig. 3, where it can be seen that the true parabolic relationship between u_s and (Σ_{\square^+}) is strictly valid only at one point since the exact curve crosses the simple parabolic curve with a different slope. On the other hand the parabolic relationship between surface ion concentration and $(u_s - 1)$ in Eq. (29) (curve e) is valid over a considerable range of u_s .

To find the diffusion potential the following regions can be distinctly defined. In the neighborhood of $x=0$, where $u \geq 2u_B'$, then Eq. (24) can be reduced to

$$du/dx = -2(L_m M_a^-)^{1/2} u^{1/2}. \quad (38)$$

Integration of Eq. (38) using the boundary conditions at the surface gives

$$u^{1/2} = u_s^{1/2} - x(L_m N_a^-)^{1/2} \\ = (L_m N_a^-)^{1/2} [(\Sigma_{\square^+}) / (N_a^-) - x]. \quad (39)$$

This is the well known Mott⁴-Schottky⁵ region. Garrett and Brattain⁶ have discussed Eq. (39), but mistakenly state that there is not yet an inversion in the space-charge region.

The variation of the diffusion potential farther beneath the surface is defined in form by the relationships previously derived, with appropriate changes in the distance parameter, which cannot be precisely defined.

Case 3(e). Moderate Inversion Layer, $(2u_B' - 1) < u_s < u_c$

In this case the surface potential u_s is greater than $2u_B'$ but less than some critical value u_c . Equation (25a) can be evaluated at the surface using the restriction that $\exp(u_s) \gg u_s$, and, therefore, $\exp(-u_s) \ll 1$. It follows directly that

$$(L_m / p_B) (\Sigma_{\square^+})^2 = (u_s - 1) + \exp(-2u_B' + u_s). \quad (40)$$

When u_s becomes sufficiently greater than $2u_B'$ the exponential dominates the right hand side of Eq. (40) and a critical value of surface potential, u_c , can be defined from the relationship

$$n_B \exp(u_c) = \zeta p_B (u_c - 1). \quad (41)$$

When $\zeta = 20$, the linear term accounts for less than 5% of the total value. In this situation, when $u_B' = 1$, then $u_c = 6.75$; when $u_B' = 2$, then $u_c = 9.08$; and when $u_B' = 3$, then $u_c = 11.35$. Therefore, when u_s is less than u_c , Eq. (40) must be solved graphically or by a trial and error.

Case 3(f). Strong Inversion Layer, $u_s \geq u_c$

When the surface potential exceeds the critical value u_c defined above, then Eq. (40) becomes

$$u_s = \ln \{ (L_m / n_B) (\Sigma_{\square^+})^2 \} \\ = 2u_B' + \ln \{ (L_m / p_B) (\Sigma_{\square^+})^2 \}. \quad (42)$$

This equation is plotted in Fig. 3 as curves (c) and (d) for u_B' equal to 6 and 3, respectively.

To find the *diffusion potential* under these conditions, the square root of Eq. (24a) with the negative sign gives

$$\begin{aligned} du/dx &= -2(L_m n_B)^{\frac{1}{2}} \exp(u/2) \\ &= -2(L_m p_B)^{\frac{1}{2}} \exp(-u_B) \exp(u/2). \end{aligned} \quad (43)$$

Integration from the surface of the semiconductor into the interior gives

$$u = -2 \ln\{\exp(-u_s/2) + x(L_m n_B)^{\frac{1}{2}}\}. \quad (22)$$

This is equal to Eq. (22) which was derived for case 1, an accumulation layer on an *n*-type semiconductor. When it is realized that now the substrate is a *p*-type semiconductor, then this equation can be rearranged to the form

$$u = -2 \ln\{\exp(-u_s/2) + x(L_m p_B)^{\frac{1}{2}} \exp(-u_B')\}. \quad (44)$$

These relationships are valid as long as $u_s > u_c$, and indicate a similarity in surface behavior between an accumulation layer and a strong inversion layer.

Case 4. Depletion-Inversion Layers from Surface Acceptors

As has already been observed in cases 1 and 2, there is a symmetrical relationship between the results which are obtained when a *p*-type semiconductor is replaced with an *n*-type semiconductor, and surface donors are replaced with surface acceptors. The surface potential and bulk diffusion potential can be expressed with the equations already derived by changing from an electron energy reference to a hole energy reference, and making the appropriate changes in the majority carrier and surface ion designations.

DISCUSSION

The variation of surface potential as functions of bulk carrier concentration and surface ion concentration have been represented by analytic functions for accumulation layers on intrinsic and extrinsic semiconductors. The variations of diffusion potential as functions of surface potential and bulk carrier concentration have also been represented by analytic functions under similar conditions.

Furthermore the analytic representation of the surface potential as a function of surface ion concentration and bulk carrier concentration for the situations wherein depletion and inversion layers on extrinsic semiconductors are formed has also been given. However, the resulting equation is rather complex and can be simplified only for certain values of u_s relative to u_B' . This was done by defining a series of special cases which provided considerable insight into the functional relationships, and some of the relationships have already been plotted in Fig. 3.

Figure 3 also shows that u_s can be approximated by a

linear function from $u_s = (u_B' - 1)$ to $u_s = (2u_B' + 1)$ of the form

$$u_s = (\text{slope})[(L_m/p_B)^{\frac{1}{2}}(\Sigma_{\square}^+)] - (\text{intercept}). \quad (45)$$

This linear function is found by constructing the tangent to the curve defined by Eq. (25c) at its point of inflection. By taking the first and second derivatives of this function, with respect to the surface ion parameter, the point of inflection u_s^* for a fixed value of u_B' can be found by trial and error solution of the relationship

$$\begin{aligned} [\sinh u_B' + \sinh(u_s^* - u_B')]^2 &= 2 \cosh(u_s^* - u_B') \\ &\times \{u_s^* \sinh(u_B') + \cosh(u_s^* - u_B') - \cosh(u_B')\}. \end{aligned} \quad (46)$$

The corresponding value of $[(L_m/p_B)^{\frac{1}{2}}(\Sigma_{\square}^+)]^*$ can be computed from any form of Eq. (25) and the slope through the inflection point then is given by

$$(\text{slope}) = \frac{[(L_m/p_B)^{\frac{1}{2}}(\Sigma_{\square}^+)]^* \exp u_B'}{\sinh(u_B') + \sinh(u_s^* - u_B')}. \quad (47)$$

These results are plotted as curves (h) and (i) in Fig. 3 for u_B' equal to 6 and 3, respectively.

The variation of the diffusion potential beneath the surface for depletion-inversion layers can be expressed as a function of distance only if u_s is very small ($u_s \leq 0.9$) or if x is very small ($x \rightarrow 0$) over certain values of u_s relative to u_B' . A general solution to this problem can be obtained only by numerical integration methods. Approximations could be made by extending the analytic functions through the transition regions and evaluating integration constants by matching the slopes.

In order to illustrate the minimum surface ion concentration for which these derivations should be expected to be valid, consider 1- Ω cm *p*-type germanium at room temperature. The screening length is equal to $1/[2(L_m p_B)^{\frac{1}{2}}]$, as obtained from Eqs. (19) or (27) and is about 5×10^{-6} cm. Therefore, since the average distance between the individual fixed surface charges should be no greater than the screening length, the surface ion concentration of localized ions must be greater than 10^{10} ions/cm². If the ions are mobile, then the equations presented here are valid even for much lower surface ion concentrations.

A direct experimental evaluation of the validity of these relationships is extremely difficult if not impossible, and the authors know of no such definitive direct experimental measurements. A direct substantiation of these equations then is possible at the present time only by comparing graphical results obtained by using the equations derived herein with graphical results published from numerical evaluation of the integrals. Equation (19) relating the diffusion potential to distance and surface potential for an accumulation layer on a *p*-type semiconductor has been checked against Figs. 4-8 published in the paper by Young,¹⁰ and the results agree within the precision of the published curves. A check of Eqs. (19), (26), (29), and

(42) relating surface ion concentration, surface potential, and bulk conductivity for accumulation, depletion and inversion layers have been checked against Fig. 1 of Mowery's paper,⁹ again giving results within the ability to read the published curves.

An indirect experimental check of these curves is considerably easier to obtain.

By integrating the diffusion potential relationships from u_s to zero over an accumulation layer, the surface conductivity can be computed. By carrying out such

an integration and comparing results with published experimental work, satisfactory agreement is obtained, and this work will be reported soon.¹⁶

The work function and electron affinity of a semiconductor are functions of the surface ion concentration, and these effects also will be discussed soon in a separate publication.¹⁷

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Photoelectric and Thermionic Schottky Deviations for Tungsten Single Crystals

D. F. STAFFORD*† AND A. H. WEBER

Saint Louis University, Saint Louis 3, Missouri

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The periodic Schottky deviations have been obtained for photoelectric and thermionic emission in the [111] direction from a tungsten single crystal in a dual experiment. The thermionic deviations, compared with well-established experimental results and theory, serve as a check on the photoelectric work. The photoelectric deviations, not previously established experimentally in detail, are compared with theory. A composite theory, using Cutler-Gibbons thermionic parameters in Juenker's photoelectric analysis, is in best agreement with the experimental photoelectric results.

The photoelectric deviations are in fair agreement in period and phase with the thermionic deviations, the agreement being better at the larger applied electric fields (corresponding to the earlier time of a run) than at the smaller field values. The photoelectric deviation amplitude is 1.7% at $E^{\frac{1}{2}}=350$ (V/cm)[‡].

1. INTRODUCTION

PERIODIC deviations from the photoelectric Schottky curve¹⁻³ similar to the well-known thermionic Schottky deviations⁴⁻⁷ have been predicted but have not been established experimentally in detail for pure metals because of difficulties peculiar to the photoelectric experiment. Photoemitting surfaces at room temperature are difficult to maintain free of adsorbed gas, and available photocurrents are several orders-of-magnitude smaller than thermionic currents, as ordinarily obtained, so that their delineation from unavoidable background currents is difficult. Juenker *et al.*^{8,9} recently reported inability to detect periodic

photoelectric deviations for single-crystal molybdenum and polycrystalline tantalum.

The difficulties were especially considered in the design of the experimental research tube and periodic Schottky deviations, both photoelectric and thermionic, were obtained with a single-crystal tungsten emitter in the same experimental tube under conditions as identical as possible. Thus an experimental correlation between photoelectric and thermionic Schottky deviations for tungsten is obtained and compared with theory.

The theory of Schottky deviations involves the calculation of field-dependent transmission coefficients for electrons escaping over the mirror image-applied electrostatic field potential barrier at the emitting surface. Although the basic theory has not changed since the original work of Guth and Mullin⁸ the formulation in terms of period, phase, and amplitude of the deviations has been altered^{4,10,11} to achieve expressions more suitable for analysis and comparison with experiment through the use of the parameters $|\mu|$ and δ . The more recent formulations of the theory have included different potential barrier shapes (notably Cutler-Gibbons⁴), and involve computational approximations which vary somewhat in the several treatments.

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† Present address: Gonzaga University, Spokane Washington.

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