Ambipolar Carrier Transport and Surface Recombination Velocity in Semiconductor Surface Layers*

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In discussing charge-carrier recombination at a semiconductor surface it is natural to characterize the recombination properties of the surface itself by a true surface-reflection coefficient which expresses the nonrecombination probability for an excess carrier in a single collision with the surface. It is also possible to arrive at an effective surface-reflection coefficient from experimental data by ignoring any effects which might be associated with the presence of a surface space-charge layer. The latter quantity is simply an effective value which involves effects contributed not only by the actual surface, but also by the space-charge layer which is present in the neighborhood of the surface. For a sample with a given photoconductive response, by equating expressions involving the reflectance calculated for a sample having the actual space-charge layer and for one in which space-charge effects are ignored, one may arrive at a relation between the true and effective surface-reflection coefficients. By this procedure one can define in an operational way an effective surface recombination velocity. The combined effects of a space-charge layer and an actual physical surface can then be studied as a function of the space-charge parameters and sample thickness. Results relating true and effective recombination velocities are presented, using an ambipolar-transport formulation, for both depletion-inversion and accumulation layers. Previously developed methods for relating true and effective surface recombination velocities are reviewed and compared to the operational method used herein. Certain advantages connected with the definition adopted here are pointed out. The calculations are based upon known diffusion and mobility parameters for p-type silicon.

I. INTRODUCTION

IN the study of the surface properties of semiconductors, the effect of surface recombination may be described phenomenologically by solving the transport equations for excess carriers and introducing a surface-boundary condition containing a parameter known as the surface recombination velocity.[1] For a given sample and a given set of surface conditions this parameter is ordinarily regarded as a constant. If one defines the surface recombination velocity s as the ratio of the flux of excess carriers into the surface to the excess carrier concentration at the surface, then the surface recombination velocity may be related to the true reflection coefficient of the surface R_s which expresses the probability that excess carriers escape recombination in each of their encounters with the actual surface of the sample, by

$$s=\tfrac{1}{2}\bar{c}(1-R_s)/(1+R_s)\,, \qquad (1)$$

where $\bar{c}=(8kT/\pi m^*)^{1/2}$ is the mean thermal velocity.[2,3] This definition of s is independent of the existence of any space-charge layer at the surface.

The behavior of excess carrier distributions in semiconductor crystals is most easily studied by observing the photoconductivity which arises when they are present. The magnitude of the observed photoconductive response will be affected both by the bulk excess-carrier recombination rate and by excess-carrier recombination which takes place at the surface. Surface recombination is associated with the trapping of electrons and holes in surface states, and in a given sample is essentially independent of the bulk-recombination rate.

In discussing the results of actual dc photoconductivity measurements, a reflection coefficient may be calculated very simply by ignoring altogether any effects associated with the presence of a surface space-charge layer and simply assuming the conduction and valence-band edges are constant and undistorted up to the physical surface of the sample. It is clear that such a reflection coefficient is not the true surface reflectance R_s, but only an effective value which we may conveniently designate as R_s^*. The value of R_s^* will obviously depend not only upon the actual reflectance of the physical surface, but also upon the properties of the space-charge layer intervening between the actual surface and the field-free interior of the crystal. In order to determine the relationship between R_s and the effective value R_s^*, which after all, is what is ordinarily derived from experimental data, it is necessary to undertake a detailed analysis of how the presence of the space-charge layer hinders or facilitates the recombination of excess charge carriers at the surface. It is the purpose of this article, in part, to undertake such an analysis. It will become apparent in the course of these investigations that R_s and R_s^* may in some cases differ by many orders of magnitude.

In cases where it is necessary to determine R_s rather than R_s^*, it is essential to know when the effect of the space-charge layer will be significant. If the photoconductance is known, it is possible to solve for both R_s and R_s^* and compare the two values for given values

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[1] W. Shockley, *Electrons and Holes in Semiconductors* (D. van Nostrand and Company, Inc., Princeton, New Jersey, 1950), p. 321.
[2] J. P. McKelvey and R. L. Longini, J. Appl. Phys. **25**, 634 (1954).
[3] W. Shockley, Phys. Rev. **125**, 1570 (1962).

of the surface parameters and the parameters of the space-charge region. Since the flux-transport equations which arise are in general linear differential equations with nonconstant coefficients, it is usually necessary to resort to approximate or numerical methods of solution.

In this article the calculational methods for solving the flux equations[3–5] in the presence of an accumulation or depletion-inversion layer are outlined. Specific calculations are presented for an inversion layer in p-type silicon. These results may be obtained by numerical integration, which is best performed with the aid of an electronic computer. The development of the general methods used herein for obtaining solutions to the flux-transport equations in specific situations is discussed elsewhere.[6]

II. DISCUSSION OF SURFACE PARAMETERS

Several authors have examined the problem of relating the surface recombination velocity to the true bulk lifetime and the observed photoconductive "filament lifetime" of a given sample.[1,2,7] In these investigations, the surface recombination velocity can be determined by the numerical solution of a transcendental equation. The effect of the surface space-charge layer is neglected throughout in these calculations; when a space-charge is present these methods yield an *effective* value s^* for the surface recombination velocity, which is related to the effective surface reflectivity R_s^* by an equation having precisely the form of (1).

It is generally believed that the Shockely-Read trapping theory[8] is valid for surface recombination phenomena in covalent and III-V semiconductors.[7,9] Moreover, instead of attempting directly to solve the continuity equations for holes and electrons along with Poisson's equations, it has been customary to use the quasiequilibrium approximation.[10] In this approximation the added carriers at the surface are assumed to be in equilibrium with those in the bulk interior of the crystal, and bulk recombination within the space-charge layer is neglected, so that the carrier fluxes in this region can be taken to be constant. In this way a relation between an effective surface recombination velocity and the height of the surface potential barrier is obtained. This relation has been studied experimentally by combined field effect and filament lifetime measurements, and is found under certain conditions to be in good agreement with experiment.[11] The effective surface recombination velocity s_{eff} derived from these considerations is related to s by

$$s_{\text{eff}} = s e^{(\varphi_B - \varphi_s)/kT}, \tag{2}$$

where φ_B and φ_s represent the values of the electrostatic potential in the bulk and at the surface, respectively.[12] Several recent investigations have considered the range of application of the quasi-equilibrium approximation[13] and the general question of the validity of s_{eff}, as defined above, as a meaningful surface parameter.[14–16] The conclusion is that a relatively simple calculation, using either flux methods[3–5] or continuity equations,[17] and again neglecting bulk recombination within the surface space-charge layer, suffices to show that a correction factor to s_{eff} as given by (2) is necessary. In this calculation the ratio of reflected to incident flux from the surface and a space-charge layer of extent δ is calculated, where δ is a cutoff length which must be defined in some arbitrary way. For this purpose it is assumed that at a distance greater than δ from the surface the effect of the space-charge field can be neglected in the transport equations.

The effective surface recombination velocity obtained in this way, *without* the quasiequilibrium assumption, will be denoted here by $s\dagger$. At this point one should be careful to note the distinction between $s\dagger$ and the previously defined quantity s^*, and certain shortcomings arising in connection with the effective recombination velocity $s\dagger$ should be pointed out. The quantity s^* is defined in an operational way, as arising from an experimental determination of photoconductance, and can therefore be calculated *directly* from experimental measurements, while $s\dagger$ is a mathematical construct restricted in application to samples wherein the extent of the space-charge layer is negligible compared to the total sample thickness. The parameter $s\dagger$ has another disadvantage, arising from the fact that the extent of the space-charge layer must be defined in terms of an arbitrary cutoff distance. Since the thickness of the space-charge layer can be expressed only through this arbitrarily chosen cutoff length, the definition of $s\dagger$ is likewise ambiguous and imprecise. For these reasons the quantity s^* is to be preferred as a representation of the effective surface recombination velocity, and it is therefore used herein as a reference parameter in developing the results to be discussed below. It should be noted that s^*, as well as $s\dagger$, is defined without resorting to the quasiequilibrium approximation.

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III. AMBIPOLAR FLUX-TRANSPORT THEORY FOR NONEXTRINSIC SURFACE REGIONS

The flux-transport equations for holes and electrons in a one-dimensional steady-state situation can be written[3] in the form

$$(dr_h/dx) = -k_h(r_h - l_n) - w_h r_h + hE(r_h + l_h) + \tfrac{1}{2}g, \quad (3)$$

$$(dl_h/dx) = -k_h(r_h - l_h) + w_h l_h + hE(r_h + l_h) - \tfrac{1}{2}g, \quad (4)$$

$$(dr_e/dx) = -k_e(r_e - l_e) - w_e r_e - hE(r_e + l_e) + \tfrac{1}{2}g, \quad (5)$$

$$(dl_e/dx) = -k_e(r_e - l_e) + w_e l_e - hE(r_e + l_e) - \tfrac{1}{2}g, \quad (6)$$

where r and l represent the fluxes to the right and left, k and w represent the backscattering and recombination probabilities per unit distance along the x direction, g is the bulk generation rate for electron-hole pairs, and $h = e/(2kT)$. The subscripts h and e refer to holes and electrons, respectively. In the thermal-equilibrium state

$$r_{h0} - l_{h0} = r_{e0} - l_{e0} = 0, \quad (7)$$

while, as a consequence of Maxwell-Boltzmann statistics,

$$\begin{aligned} \tfrac{1}{2}p_0\bar{c}_h &= r_{h0} + l_{h0}, \\ \tfrac{1}{2}n_0\bar{c}_e &= r_{e0} + l_{e0}, \end{aligned} \quad (8)$$

where the zero subscript refers to the thermal-equilibrium condition, p_0 and n_0 are the equilibrium hole and electron concentrations, respectively, and where $\bar{c}_{h,e} = (8kT/\pi m_{h,e}^*)^{1/2}$ is the mean thermal speed. In addition it may be shown[4] that

$$k_e = 3/4\lambda_e, \qquad k_h = 3/4\lambda_h, \quad (9)$$

$$w_e = 2/\bar{c}_e\tau_e, \qquad w_h = 2/\bar{c}_h\tau_h, \quad (10)$$

where λ_e, λ_h are the scattering mean free paths for electrons and holes, respectively, and where τ_e, τ_h are the mean electron and hole lifetimes, respectively.

Under nonequilibrium conditions it is convenient to represent the fluxes and the electric field by

$$\begin{aligned} r &= r_0 + \Delta r, \\ l &= l_0 + \Delta l, \\ E &= E_0 + \Delta E, \end{aligned} \quad (11)$$

where r_0, l_0, and E_0 are the thermal equilibrium values of the respective quantities. It is also useful, in this situation, to write the bulk generation rate as

$$g(x) = g_0 + g'(x), \quad (12)$$

where g_0 is the bulk generation rate at thermal equilibrium and $g'(x)$ is the generation rate due to illumination or to any other exciting influence. Upon substituting Eqs. (7), (8), and (11) into Eqs. (3)–(6), neglecting second-order terms, one may obtain for the *net* electron and hole fluxes

$$\Delta r_h - \Delta l_h = -\frac{1}{2k_h + w_h}\frac{d(\Delta r_h + \Delta l_h)}{dx} + \frac{2hE_0}{2k_h + w_h}(\Delta r_h + \Delta l_h) + \frac{h\Delta E\bar{c}_h p_0}{2k_h + w_h}, \quad (13)$$

$$\Delta r_e - \Delta l_e = -\frac{1}{2k_e + w_e}\frac{d(\Delta r_e + \Delta l_e)}{dx} - \frac{2hE_0}{2k_e + w_e}(\Delta r_e + \Delta l_e) - \frac{h\Delta E\bar{c}_e n_0}{2k_e + w_e}. \quad (14)$$

Now since there can be no net current normal to the surface, which is assumed to be normal to the x direction, we must have

$$\Delta r_h - \Delta l_h = \Delta r_e - \Delta l_e. \quad (15)$$

In addition, in the general nonequilibrium situation, provided that the distribution function is not vastly disturbed from what it is in the equilibrium state, it is easily shown[18] that the fluxes r_h and l_h can be written as

$$r_h = \tfrac{1}{4}\bar{c}_h p(x - \tfrac{2}{3}\lambda_h) + \tfrac{1}{2}\mu_h E p(x) \quad (16)$$

and

$$l_h = \tfrac{1}{4}\bar{c}_h p(x + \tfrac{2}{3}\lambda_h) - \tfrac{1}{2}\mu_h E p(x).$$

The first term on the right-hand side of these expressions can be understood as the usual Maxwellian gross flux $p\bar{c}_h/4$ resulting from the integration of the flux contribution from individual particles over all positive (or negative) velocities, with the added proviso that since the fluxes reaching the point x originated in collisions which took place, on the average, a distance of the order of the mean free path to the left or to the right of that point, the concentrations which are relevent in the Maxwellian flux formula are associated with points approximately a mean free path ($\frac{2}{3}\lambda_h$, to be exact) away. Under these circumstances, expanding these terms in Taylor's expansions about the point x and neglecting all but the first two terms (an approximation which is justified provided that the fractional variation of concentration over a mean free path is small), and adding the two resulting equations, one may obtain

$$r_h + l_h = \tfrac{1}{2}p\bar{c}_h. \quad (17)$$

Using (11) and (8) to eliminate the equilibrium concentrations and fluxes, it is then obvious that

$$\Delta r_h + \Delta l_h = \tfrac{1}{2}\bar{c}_h\Delta p. \quad (18)$$

Similar considerations lead to the expression

$$\Delta r_e + \Delta l_e = \tfrac{1}{2}\bar{c}_e\Delta n \quad (19)$$

[18] J. P. McKelvey and R. L. Longini, Phys. Rev. 99, 1227 (1955).

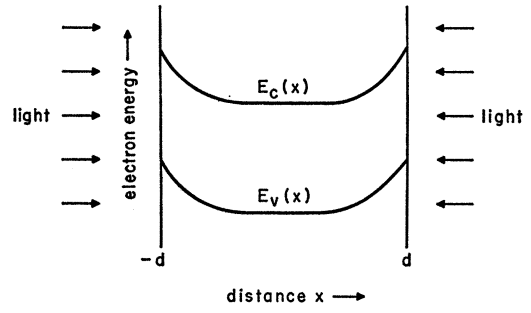

FIG. 1. Cross-sectional diagram of a one-dimensional plane-parallel sample, showing variation of energy-band edges near surfaces, and illustrating assumed conditions of illumination.

for electrons.[19] If one now makes the assumption that the quasineutrality condition[17] $\Delta n=\Delta p$ is satisfied, Eqs. (18) and (19) yield the expression

$$\bar{c}_e(\Delta r_h+\Delta l_h)=\bar{c}_h(\Delta r_e+\Delta l_e), \tag{20}$$

which relates the gross electron and hole fluxes.

One may now eliminate ΔE between Eqs. (13) and (14) whereby

$$\frac{d(\Delta r_h+\Delta l_h)}{dx}=-(2k_h+w_h)\left(\frac{n_0+p_0b^*}{n_0+p_0}\right)(\Delta r_h-\Delta l_h)+2hE_0\frac{n_0-p_0}{n_0+p_0}(\Delta r_h+\Delta l_h), \tag{21}$$

where [recalling (10)]

$$b^*=\frac{\bar{c}_h}{\bar{c}_e}\left(\frac{2k_e+w_e}{2k_h+w_h}\right), \tag{22}$$

while from (3) and (4) one may easily show with the aid of (11) that

$$\frac{d(\Delta r_h-\Delta l_h)}{dx}=g'-w_h'(\Delta r_h+\Delta l_h), \tag{23}$$

where w_e' and w_h' are *excess* carrier-recombination probabilities defined by

$$\begin{aligned} &w_h'(\Delta r_h+\Delta l_h)=w_h(r_h+l_h)-w_{h0}(r_{h0}+l_{h0}) \\ \text{and} \quad &w_e'(\Delta r_e+\Delta l_e)=w_e(r_e+l_e)-w_{e0}(r_{e0}+l_{e0}). \end{aligned} \tag{24}$$

In these equations w_{h0} and w_{e0} refer to the values of w_h and w_e in the equilibrium state of the system, when $\Delta p=\Delta n=0$. In a situation where w_e and w_h may be functions of Δp, these expressions define excess carrier-recombination probabilities in much the same way in which the equation

$$\frac{\Delta p}{\tau}=\frac{p}{\tau_h}-\frac{p_0}{\tau_{h0}}=\frac{n}{\tau_e}-\frac{n_0}{\tau_{e0}}$$

defines an *excess* carrier lifetime τ in the conventional continuity equation formulation. It may easily be shown, using (10) and (17), that the relation

$$w_h(r_h+l_h)=w_e(r_e+l_e)$$

follows from the requirement that the total electron and hole recombination rates n/τ_e and p/τ_h be equal. Also, using the above relation and (20) to express electron fluxes in terms of hole fluxes in the second equation of the set (24), it is easy to show that

$$\bar{c}_e w_e'=\bar{c}_h w_h'.$$

In general we shall confine ourselves to the discussion of systems wherein w_e' and w_h' are independent of Δp, corresponding to the low-level injection case wherein the excess carrier lifetime is independent of Δp. The equilibrium electric field E_0 is obtained from Poisson's equation, which may be written in the form

$$\frac{dE_0}{dx}=\frac{4\pi e}{\kappa}(N_d-N_a+n_0-p_0), \tag{25}$$

where N_d and N_a are the concentrations of donor and acceptor impurities (assumed herein to be completely ionized), and where κ is the dielectric constant.

Equations (21) and (23) may be used to discuss the transport of excess carriers by the flux method where ambipolar diffusion and drift effects are important, in much the same way in which the ambipolar transport equations of van Roosbroeck,[17] derived with reference to continuity equations for electron and hole density, are used. They form the basis for the calculations which are outlined in the next section. In this connection, it should be noted that although only hole fluxes are discussed explicitly, the electron fluxes $\Delta r_e+\Delta l_e$ and $\Delta r_e-\Delta l_e$ can be obtained by use of (15) and (20); indeed these relations can easily be utilized to convert (21) and (23) to differential equations for electron fluxes. Also, it is clear that the excess carrier concentrations Δp and Δn can be obtained from the fluxes by (18) and (19), provided that the excess carrier distribution is approximately Maxwellian.

IV. CALCULATIONS RELATING s AND s^* IN THE PRESENCE OF A SURFACE SPACE-CHARGE LAYER

If a semiconductor sample having the form of a parallel-sided slab which is infinite in the y and z directions is illuminated as shown in Fig. 1, the change in steady-state conductivity $\Delta\sigma$ due to illumination

[19] If the two equations resulting from Taylor's expansion of (16) are subtracted rather than added, then the usual expression for the *net* flux r_h-l_h as a sum of a diffusion contribution proportional to $\partial p/\partial x$ and a drift contribution $\mu_h Ep$ is obtained. The diffusion coefficient is clearly seen to be $\lambda_h\bar{c}_h/3$, a result which can be derived independently from the Boltzmann transport equation. This observation may be regarded as a proof of the correctness of the choice $2\lambda_h/3$ as the average source distance for fluxes arriving at point x.

will be

$$\Delta\sigma=\frac{e}{2d}\left[\mu_h\int_{-d}^{d}\Delta p\,dx+\mu_e\int_{-d}^{d}\Delta n\,dx\right], \tag{26}$$

where $2d$ is the sample thickness, μ_e and μ_h are electron and hole drift mobilities, and where Δp and Δn are the steady-state excess hole and electron densities arising from photoexcitation. Assuming complete symmetry of the sample about the central plane, and assuming that the quasineutrality condition is satisfied, whereby $\Delta p=\Delta n$, Eq. (26) may be written in the form

$$\Delta\sigma=\frac{e}{d}(\mu_e+\mu_h)\int_0^d\Delta p\,dx. \tag{27}$$

Expressing the boundary condition for excess holes at the surface as

$$(\Delta l_h)_d=R_{\rm sh}(\Delta r_h)_d, \tag{28}$$

where $R_{\rm sh}$ is the surface reflection coefficient for excess holes, and where the d subscript refers to quantities evaluated at $x=d$, one may write the net excess hole flux at the surface

$$(\Delta r_h-\Delta l_h)_d=(\Delta r_h)_d-R_{\rm sh}(\Delta r_h)_d=(1-R_{\rm sh})(\Delta r_h)_d. \tag{29}$$

On the other hand, from (18) and (28), it is clear that

$$(\Delta p)_d=\frac{2}{\bar c_h}(\Delta r_h+\Delta l_h)_d=\frac{2}{\bar c_h}(1+R_{\rm sh})(\Delta r_h)_d. \tag{30}$$

Solving for $(\Delta r_h)_d$ in (30) and substituting into (29), one may obtain finally

$$(\Delta r_h-\Delta l_h)_d=\frac{(\Delta p)_d\bar c_h}{2}\frac{1-R_{\rm sh}}{1+R_{\rm sh}}=s_h(\Delta p)_d \tag{31}$$

with

$$s_h=\frac{\bar c_h}{2}\frac{1-R_{\rm sh}}{1+R_{\rm sh}}. \tag{32}$$

A similar calculation for excess electrons will yield an analogous set of equations, wherein the subscript h is replaced by e. Comparing the two results, noting that $(\Delta p)_d=(\Delta n)_d$, and recalling (15), one may obtain the (rather obvious) result

$$s_h=s_e\equiv s. \tag{33}$$

It is not quite so obvious, but nevertheless a necessary consequence of these results, that the excess electron and hole reflection coefficients are not equal, but are instead related by

$$\frac{1-R_{\rm se}}{1+R_{\rm se}}=\frac{\bar c_h}{\bar c_e}\frac{1-R_{\rm sh}}{1+R_{\rm sh}}=\left(\frac{m_e^*}{m_h^*}\right)^{1/2}\frac{1-R_{\rm sh}}{1+R_{\rm sh}}. \tag{34}$$

In the sample geometry shown in Fig. 1, the symmetry of the sample requires that

$$(\Delta r_h-\Delta l_h)_{x=0}=0. \tag{35}$$

Under these circumstances, with the aid of (18) and (10), Eq. (23) may be integrated from $x=0$ to $x=d$, the result being

$$\int_0^d\Delta p\,dx=\tau G-\tau(\Delta r_h-\Delta l_h)_d, \tag{36}$$

where

$$G=\int_0^d g'(x)dx.$$

Assuming that G is independent of the surface model, and that τ is constant throughout the sample, it is evident from this equation and from (27) that equating the net surface flux obtained by solving the flux equations for a model in which the energy bands are constant throughout the sample to the net surface flux obtained from a similar calculation in which the effect of a surface space-charge layer is explicitly taken into account is equivalent to equating the change in dc photoconductance obtained from both models. This enables one to relate the effective surface recombination velocity s^* to the true surface recombination velocity s, and, in effect, to relate the true surface reflection coefficients $R_{\rm sh}$ and $R_{\rm se}$ to the effective values $R_{\rm sh}^*$ and $R_{\rm se}^*$ which would be calculated from a dc photoconductivity experiment.

Solving Eqs. (21) and (23) for the constant-energy-band case with uniform generation within the bulk (wherein $E_0=0$, and n_0, p_0, and g' are constant) one may obtain[20] for the surface flux of holes

$$(\Delta r_h-\Delta l_h)_d=\frac{(g's^*/w_h')\sinh q^*d}{(q^*s^*/w_h')\cosh q^*d+\frac{1}{2}\bar c_h\sinh q^*d}, \tag{37}$$

where

$$q^*=\left[w_h'(2k_h+w_h)\left(\frac{n_0+p_0b^*}{n_0+p_0}\right)\right]^{1/2}. \tag{38}$$

It should be observed here that q^* plays the role of an *ambipolar* inverse diffusion length. When $n_0\gg p_0$ (extrinsic n-type material) q^* approaches the value $2k_hw_h+w_h^2$, which is expected in the absence of ambipolar diffusive and drift effects.[4] When $p_0\gg n_0$ (extrinsic p-type material) the value of this parameter approaches [by virtue of (22) and (10)] $2k_ew_e+w_e^2$, the corresponding previously obtained value for electrons in a nonambipolar environment. In the case of perfectly intrinsic material ($n_0=p_0=n_i$), q^* is given by

$$q_i^*=(1/\sqrt{2})(w_h'(2k_h+w_h)+w_e'(2k_e+w_e))^{1/2}. \tag{39}$$

In the usual scattering-dominated diffusion situation, where $k_h\gg w_h$, $k_e\gg w_e$, which is the situation discussed by van Roosbroeck,[17] it is easily demonstrated that

[20] The calculation is much simpler if one observes from the outset that on account of sample symmetry, $\Delta r_h+\Delta l_h(=2\Delta p/\bar c_h)$ must be an even function of x. This allows one to eliminate terms containing $\sinh q^*x$ from the solution at the beginning.

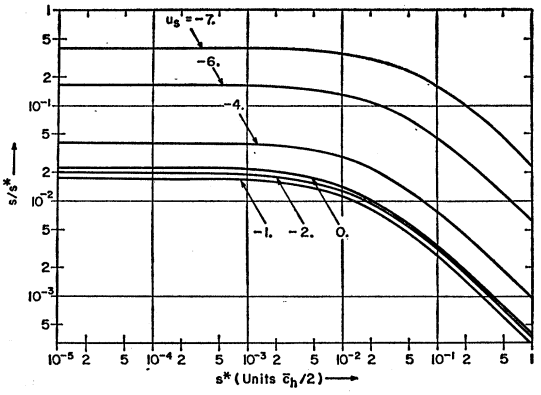

FIG. 2. The ratio s/s^* plotted as a function of s^* for surface depletion layers in a sample of p-type silicon with typical material parameters at room temperature.

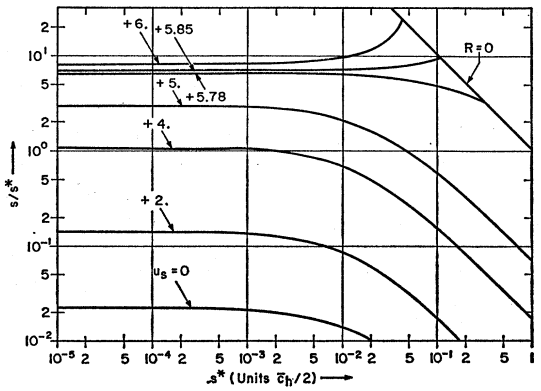

FIG. 3. The ratio s/s^* plotted as a function of s^* for surface inversion layers in a sample of p-type silicon with typical material parameters at room temperature.

(38) reduces to the expected value $(D^*\tau)^{-1/2}$, where D^* is van Roosbroeck's ambipolar diffusion coefficient.[20a]

In order to obtain the surface flux in the presence of a surface space-charge layer, Eqs. (21), (23), and (25) must be solved simultaneously. If the excess carrier density is everywhere small compared to the equilibrium majority carrier density, then (25) can be solved for E_0 and the value so obtained may be used in (21) and (23) to calculate the required fluxes and thus the required concentrations. With the aid of Eqs. (37) and (31) one may then obtain a relation between s and s^*. A first integral of Eq. (25) for a finite symmetric sample is discussed in the Appendix.

V. CALCULATED RESULTS FOR p-TYPE SILICON

In this section we shall present the results of numerical calculations[21] relating the real and effective values of surface recombination velocity, calculated as described previously, with parameters chosen to represent accumulation, depletion, and inversion layers in p-type silicon. The fixed parameters were assigned the values: $k_h=4.50\times10^5$ cm^{-1}, $k_e=1.60\times10^5$ cm^{-1}, $\tau=123\times10^{-6}$ sec, $b^*=0.2734$, $L_D=3.54\times10^{-3}$ cm, $u_B=e\varphi_B/kT=-8.0$, $m_h^*=0.44m_0$, $m_e^*=0.26m_0$, $T=300$°K. Here φ_B refers to the electrostatic potential far from the surface, and L_D refers to the Debye length, defined as

$$L_D=(\kappa kT/8\pi e^2 n_i)^{1/2}. \tag{40}$$

The calculated values for the ratio s/s^* are shown in Fig. 2 for a depletion layer and in Fig. 3 for an inversion layer, plotted as a function of s^* for several different values of the surface-potential parameter $u_s=e\varphi_s/kT$, wherein φ_s represents the electrostatic potential at the surface. Under these circumstances, the effective reflection coefficients are less than the true reflection coefficients for depletion and weak inversion conditions, since the minority carriers (electrons) are trapped in the surface layer because of the reduction in surface potential energy relative to the bulk value, and hence fewer are reflected back to the bulk than in the absence of a space-charge layer. For strong inversion layers, the minority carriers in the surface region are holes which are *repelled* from the surface by the potential barrier, and under these conditions the effective reflection coefficient increases, eventually becoming greater than the true reflection coefficient in strong inversion layers, as shown by Fig. 3. As shown by Fig. 4, the

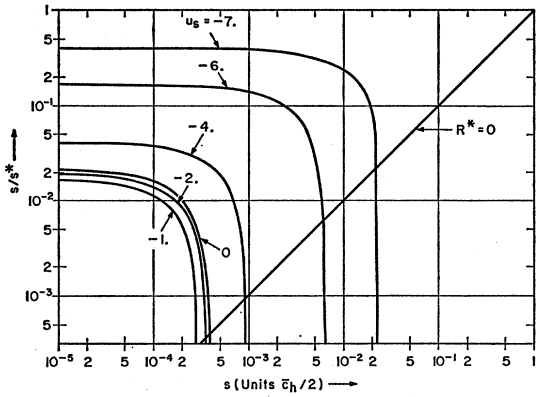

FIG. 4. The ratio of s/s^* plotted as a function of s for surface depletion layers in a sample of p-type silicon with typical material parameters at room temperatures.

[20a] *Note added in proof.* If, on the other hand, the situation is *not* necessarily scattering-dominated, it can be shown, by setting the right-hand side of (38) equal to $(D^*\tau)^{-1/2}$, substituting then the value of b^* from (22) and using the relations $\bar{c}_e w_e=\bar{c}_h w_h$, $w_e'=2/\bar{c}_e\tau$, and $w_h'=2/\bar{c}_h\tau$ to simplify the resulting expression, that

$$D^*=\frac{(n_0+p_0)D_e^{\dagger}D_h^{\dagger}}{n_0D_e^{\dagger}+p_0D_h^{\dagger}},$$

where $D_h=\frac{1}{2}\bar{c}_h/(2k_h+w_h)$ and $D_e^{\dagger}=\frac{1}{2}\bar{c}_e/(2k_e+w_e)$. This is a *generalized* expression for the ambipolar diffusion coefficient, which is applicable to situations where k_e and k_h may not necessarily be much larger than w_e and w_h. The expression has the same form as that derived previously by van Roosbroeck[17] except that the conventional diffusion coefficients D_e and D_h are replaced by the generalized diffusion coefficients D_e and D_h obtained by Shockley[3] which are applicable in situations other than the usual scattering-dominated state of affairs.

[21] These calculations were performed with the aid of the IBM model 7074 digital computer at the Pennsylvania State Computation Center.

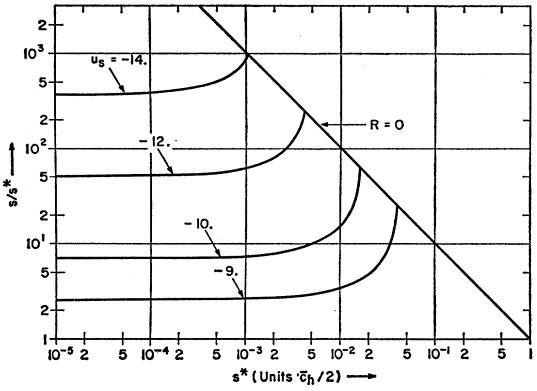

FIG. 5. The ratio s/s^* plotted as a function of s^* for surface accumulation layers in a sample of p-type silicon with typical material parameters at room temperature.

effective reflection coefficient approaches zero in this instance for a finite positive value of the true reflection coefficient. For values of the true reflection coefficient less than this, it is clear that s^* exceeds one-half the thermal velocity which, according to (32) or its analog for electrons, implies a negative value for the effective reflection coefficient. This situation arises as a result of the way in which s^* is defined; under these circumstances excess carriers are being removed from the bulk in the actual sample faster than they could ever be removed from a sample in which no surface potential existed, even if s^* were assigned the maximum possible value of half the thermal velocity. The only physical requirement is that the true reflection coefficient lie between zero and unity, and this is clearly not violated.

For an accumulation layer, one would expect the effect to be just the opposite, since under these conditions there exists a potential barrier which, depending upon its height, is more or less effective in preventing the minority carriers from reaching the surface. That this is indeed the case is illustrated by Figs. 5 and 6, in which the dependence of s/s^* upon s and s^* is plotted for several values of the surface-potential parameter u_s

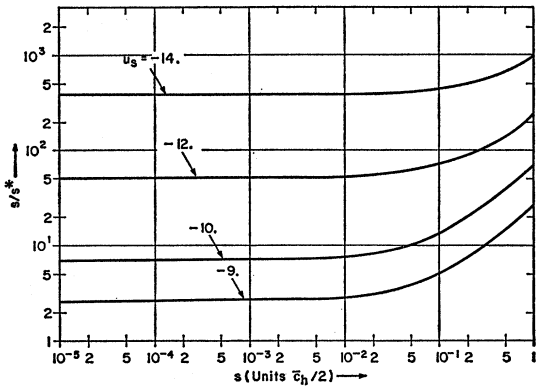

FIG. 6. The ratio s/s^* plotted as a function of s for surface accumulation layers in a sample of p-type silicon with typical material parameters at room temperature.

which correspond to accumulation layer conditions. It is clear in this case that s/s^* is always greater than unity, whereby the effective reflection coefficient is always greater than the actual one. In this instance, even if the actual reflection coefficient is zero, the effective reflection coefficient has a finite positive value which reflects the degree to which the surface potential barrier is effective in preventing minority carriers incident upon it from ever reaching the true surface.

As the surface potential changes sign, an inversion layer is formed, the effect of which is illustrated in Fig. 7. The results shown there can be understood by observing that the transport of carriers in the inversion layer is governed primarily by the transport behavior of the minority carrier (holes, in this example). The minima in s/s^* in Fig. 7 occur just before the point where the surface potential changes sign. One would expect these minima to occur when the right side of Eq. (21) changes sign; actually it is clear that at the inversion point ($n_0 = p_0 = n_i$), the drift current term in (21) is zero, and the first term in this expression has a minimum value, so that the change in sign occurs not far from this value of surface potential. Again, from Eq. (21) one would expect the slope of the curves to be steeper for positive values of u_s, because then both terms on the right-hand side of the equation have the same sign, whereas in the depletion layer their signs are opposite. This feature is clearly evident in Fig. 7.

In Figs. 2–7 the sample thickness was kept constant at approximately 4.0×10^{-3} cm, while the extent of the space-charge layer (as defined by the cutoff distance $|u_B - u_s| = 1$) is of the order of 4.0×10^{-4} cm at each surface. In these examples, therefore, about 20% of

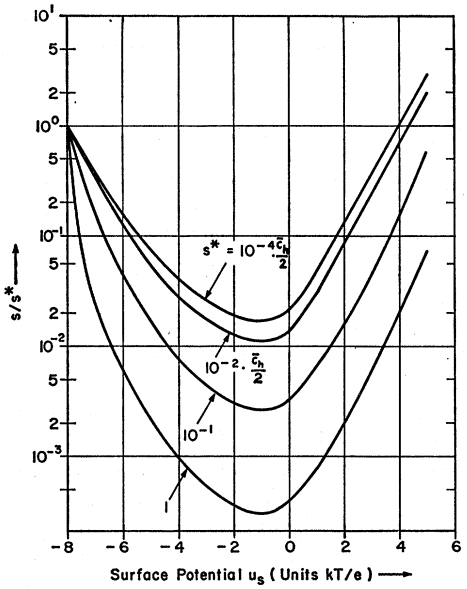

FIG. 7. The ratio s/s^* plotted as a function of surface potential for surface depletion and inversion conditions in a sample of p-type silicon with typical material parameters at room temperature.

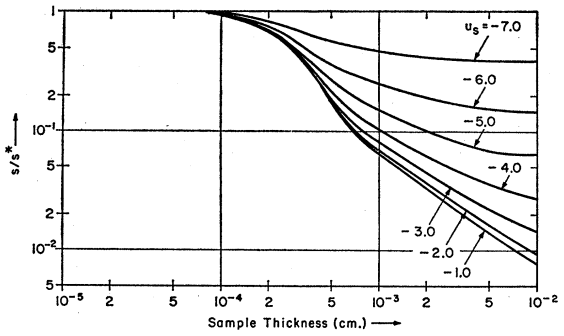

FIG. 8. The ratio s/s^* plotted as a function of sample thickness for surface depletion layer conditions in samples of p-type silicon with typical material parameters at room temperature.

the volume of the sample lies within the space-charge region. The effect of varying the sample thickness is illustrated, for the case of a depletion layer, in Fig. 8. Here the surface-recombination velocity is assumed to be sufficiently small that only the flat portion of the curves in Figs. 2 and 3 need be considered. Since the thickness of the space-charge regions is essentially constant, as the thickness of the sample is increased, the fraction of total sample volume belonging to those regions decreases. Beyond a certain point, one is merely adding bulk material to the sample and the effect of the space-charge layer becomes independent of sample thickness. This is clearly shown in Fig. 8, where for a weak depletion region ($|u_B-u_s|<5$) the curves begin to level off for sample thicknesses greater than about 5×10^{-3} cm.

For thin samples, $|u_s-u_0|$ is small for all values of u_s, and indeed $u_0\rightarrow u_s$ in the limit where the sample thickness approaches zero. Under these circumstances one must naturally expect that s/s^* approach unity for all values of u_s, as indeed, according to Fig. 8, it does.

VI. DISCUSSION AND CONCLUSIONS

Because of the large number of parameters involved, only sample calculations, based upon p-type silicon samples of typical characteristics are presented in this article. It would, of course, be desirable to extend these results to embrace a wide range of materials and sample parameters.

Results obtained by previous authors[15,16] have shown that the calculations of an effective surface recombination velocity based upon the quasi-equilibrium approximation are ordinarily valid for the case of germanium. For silicon, on the other hand, a more detailed investigation is necessary. In this instance, because of the long Debye length and higher attainable surface potentials, corrections to the effective surface recombination velocity as defined by (3) are usually required. At present only a limited amount of experimental work in which the surface recombination velocity is determined as a function of the surface potential appears to have been done for silicon.[22] Results calculated herein, relating in detail real and suitably defined effective values of surface recombination velocity, are in agreement with physical expectation based upon the previously established behavior of excess carrier distributions in ambipolar transport situations. For samples thin in comparison with the Debye length, the ratio s/s^* reduces to unity independent of the surface potential.

Further studies are needed to determine the effect of the variation of bulk excess carrier lifetime within the surface layer upon calculated results such as these. The Shockley-Read theory[8] predicts a complex change in bulk lifetime as a function of the position of conduction and valence-band edges with respect to the equilibrium Fermi energy and to certain trapping levels associated with dislocations and certain types of impurity centers, and therefore such a variation within the surface layer is to be expected. In this study, this variation has been neglected, the carrier lifetime being assumed constant throughout the sample. Ordinarily, in thick samples, the bulk recombination taking place within the thin surface layer is negligible, while in very thin samples s/s^* is nearly unity in any case, so that the lifetime within the surface layer is often not an extremely important factor. When it is, the present treatment may be viewed as a first approximation toward taking it into account, although the desirability of a more accurate treatment which considers in detail the variation within the surface layer is not to be denied. In addition, the variation of the ambipolar diffusion length with equilibrium carrier concentration within the space-charge layer has been neglected in the calculations presented herein. In the case of the inversion layer, for example, this quantity is assumed to have the value associated with the p-type bulk interior material up to the inversion point, and the value associated with a point at the surface throughout the surface layer beyond. In the case of germanium and silicon, where the mobility ratio is not large, this does not lead to serious errors, but for the III-V intermetallic semiconductors, this could lead to erroneous results. The correction for surface mobility discussed by Schrieffer[23,24] has been shown[25] to be small for silicon samples of the type discussed herein, and has therefore been neglected.

Since the surface recombination velocity is not a directly measurable quantity, one must be careful in stating how this quantity is defined and calculated from observable data. In this treatment, the surface boundary conditions always involve true surface-reflection coefficients, and the values of true and effective surface recombination velocity are rigorously related thereto. The effective surface recombination velocity is defined

[22] T. M. Buck and F. S. McKim, J. Electrochem. Soc. **105**, 709 (1958).
[23] J. R. Schrieffer, Phys. Rev. **97**, 641 (1955).
[24] J. R. Schrieffer, *Semiconductor Surface Physics* (The University of Pennsylvania Press, Philadelphia, 1957), p. 55.
[25] R. F. Greene, D. R. Frankl, and J. Zemel, Phys. Rev. **118**, 967 (1960).

in a unique way, and when so defined is directly derivable from experimental data in a fully operational way. These considerations avoid certain ambiguities and other difficulties which may arise in applying the usual surface-boundary conditions to the conventional continuity-diffusion equations.

A knowledge of s/s^* for a given space-charge configuration is useful because, although s^* can be calculated from experimental photoconductance data, the actual recombination velocity s remains undetermined unless some model for added carrier transport within the surface layer is adopted. In order to obtain meaningful information about the true surface-reflection coefficient from experimental data, the ratio s/s^* as defined and calculated herein (or its equivalent) must be known. This, in turn, requires a knowledge of the surface potential which, however, can be obtained from a simple independent-field-effect measurement.[26] In those cases where the s_{eff} of (3) is not approximated by s^*,[14–16] the methods of arriving at s/s^* outlined herein must then be applied in the determination of s.

APPENDIX

The electric field in the space-charge layer can be calculated from (25). These calculations have been outlined previously[12] for a semi-infinite layer, but must be recast here for the case of a sample of finite thickness $2d$. The electric field is assumed to be symmetric about the central plane ($x=0$). Under these circumstances, (25) can be written in reduced form as

$$d^2u/dx^2=(1/L_D^2)(\sinh u-\sinh u_B)\,, \tag{A1}$$

where

$$N_d-N_a=2n_i\sinh u_B\,,$$
$$n_0=n_i\exp(e\varphi/kT)\,,$$
$$p_0=n_i\exp(-e\varphi/kT)$$
$$u=e\varphi/kT\,,$$

and where φ is the electrostatic potential. The potential function is defined in such a way that the value $\varphi=0$ is assigned to an electron with electrostatic potential energy corresponding to the intrinsic Fermi energy. Integrating Eq. (A1) from the center of the sample toward the surface, and noting that $du/dx=0$ at $x=0$, one may obtain

$$\frac{du}{dx}=\frac{1}{L_D^2}\int_{u_0}^{u}(\sinh u'-\sinh u_B)du'$$
$$=\pm\frac{\sqrt{2}}{L_D}[(u_0-u)\sinh u_B-\cosh u_0+\cosh u]\,, \tag{A2}$$

where u_0 represents the value of the reduced potential at the center of the sample, corresponding to $x=0$. The electric field is, of course, given by

$$E(x)=-\frac{d\varphi}{dx}=-\frac{kT}{e}\frac{du}{dx}\,. \tag{A3}$$

If one defines a "reduced field" F as

$$F=L_D\frac{du}{dx}\,, \tag{A4}$$

one may formally express the distance x from the center of the sample to an arbitrary interior point, where the reduced potential has the value u, by integrating (A2) once more to obtain

$$x=\left|L_D\int_{u_0}^{u}\frac{du'}{F(u')}\right|\,. \tag{A5}$$

This is an implicit relationship which allows one, in principle, to determine the potential throughout the sample as a function of x.

The sign of F in (A5) is determined by the impurity type and by the type of surface layer which is formed. This determination is summarized in Table I for x positive (the opposite sign applying in all cases when x is negative).

TABLE I. Choice of algebraic sign for F in Eq. (A5).

Impurity type	Type of surface layer	Condition on u_s and u_0	Sign of F
p type	Depletion	$u_B<u_0<u_s$	+
	inversion		
($u_B<0$)			
	Accumulation	$u_s<u_0<u_B$	−
n type	Depletion	$u_s<u_0<u_B$	−
	inversion		
($u_B>0$)			
	Accumulation	$u_B<u_0<u_s$	+

[26] W. L. Brown, W. H. Brattain, C. G. B. Garrett, and H. C. Montgomery, *Semiconductor Surface Physics* (The University of Pennsylvania Press, Philadelphia, 1957), p. 111.