Distribution and Cross-Sections of Fast States on Germanium Surfaces

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A theoretical treatment of the field effect, surface photo-voltage and surface recombination phenomena has been carried out, starting with the Hall-Shockley-Read model and generalizing to the case of a continuous trap distribution. The theory is applied to the experimental results given in the previous paper. One concludes that the distribution of fast surface states is such that the density is lowest near the centre of the gap, increasing sharply as the accessible limits of surface potential are approached. From the surface photo-voltage measurements one obtains an estimate of 150 for the ratio (σ_p/σ_n) *of the cross-sections for transitions into a state from the valence and conduction bands, showing that the fast states are largely acceptor-type. On the assumption that surface recombination takes place through the fast states, the cross-sections are found to be:* $\sigma_p \sim 6 \times 10^{-15}$ *cm²* *and* $\sigma_n \sim 4 \times 10^{-17}$ *cm².*

I. INTRODUCTION

The existence of traps, or "fast" states, on a semiconductor surface, becomes apparent from three physical experiments: measurements of field effect,[1] of surface photovoltage,[2] and of surface recombination velocity s. Results of combined measurements of these three quantities on etched surfaces of p- and n-type germanium have been presented in the preceding paper.[3] The present paper is concerned with the conclusions which may be drawn from these experiments as to the distribution in energy of these surface traps, and the distribution of cross-sections for transitions between the traps and the conduction and valence bands.

The statistics of trapping at a surface level has been developed by Brattain and Bardeen[2] and by Stevenson and Keyes,[4] following the work on body trapping centers of Hall[5] and of Shockley and Read.[6]

It is known that surface traps are numerous on a mechanically damaged surface[7] or on a surface that has been bombarded but not annealed;[8]

and that on an etched surface their density is comparatively low. It is also known that the available results cannot be accounted for by a single level, or even two levels, so that one is evidently dealing either with a large number of discrete states or a continuous spectrum. A given trapping centre is completely described by specifying: (i) whether it is donor-like (either neutral or positive) or acceptor-like (neutral or negative); (ii) its position in energy; and (iii) the values for the constants C_p and C_n (related to cross-sections) occurring in the Shockley-Read theory. In this paper we shall deduce what we can about these quantities, using the experimental results previously presented.

At the outset it must be admitted that it is by no means certain that the same set of surface states appear in the field-effect experiment and give rise to surface recombination. However, (i) it is found that such surface treatments as increase s also reduce the effective mobility in the field-effect experiment; (ii) any surface trap must be able to act as a recombination centre, unless one of the quantities C_p and C_n is zero;[9] and (iii) the capture cross-sections obtained by assuming that the field-effect traps are in fact recombination centres are, as we shall see below, eminently reasonable.

As to the nature of the surface traps, not too much can be said at the moment. The lack of sensitivity to the cycle of chemical environment used argues against their being associated with easily desorbable surface atoms; the intrinsically short time constants (Section 5) suggest that they are on or very close to the germanium surface. The possibility that the surface traps are Tamm levels[10] remains; or they could be corners or dislocations. However, the reproducibility with which a given value of s may be obtained by a given chemical treatment of a given sample, followed by exposure to a given ambient, suggests that there is nothing accidental about their occurrence.

II. STATISTICS OF A DISTRIBUTION OF SURFACE TRAPS

We start by quoting results from the work of Shockley and Read[6] and Stevenson and Keyes[4] on the occupancy factor f_t and the flow U of minority carriers (per unit area) into a set of traps having a single energy level and statistical weight unity:

$$f_t = (C_n n_s + C_p p_1)/[C_n(n_s + n_1) + C_p(p_s + p_1)] \tag{1}$$

$$U = C_n C_p(p_s n_s - n_i^2)/[C_n(n_s + n_1) + C_p(p_s + p_1)] \tag{2}$$

where the symbols have the following meanings:

n_s , p_s — densities of electrons and holes present at the surface

n_1, p_1 — values which the equilibrium electron and hole densities at the surface would have if the Fermi level coincided with the trapping level

$C_n = N_t v_{Tn} \sigma_n$; $C_p = N_t v_{Tp} \sigma_p$, where N_t stands for density of traps per unit area, v_{Tn} is the thermal speed for electrons and v_{Tp} that for holes, and σ_n and σ_p are the cross-sections for transitions between the traps and the conduction and valence bands respectively.

If we introduce the surface potential Y and the quantity δ, defined as $(\Delta p/n_i)$, where Δp is the added carrier density in the body of the semiconductor, we may write:

$$\begin{aligned} n_s &= \lambda^{-1} n_i e^{Y}(1 + \lambda\delta) \\ p_s &= \lambda n_i e^{-Y}(1 + \lambda^{-1}\delta) \end{aligned} \tag{3}$$

where $\lambda = p_0/n_i$, p_0 being the equilibrium hole concentration in the body of the semiconductor. We further introduce the notation:

$$\begin{gathered} n_1 = n_i e^{-\nu} \qquad p_1 = n_i e^{\nu} \\ (C_p/C_n)^{\frac{1}{2}} = \chi \end{gathered} \tag{4}$$

The quantity ν thus represents the energy difference, measured in units of (kT/e), between the trapping level and the centre of the gap;* and is positive for states below, negative for those above, this level. The parameter χ will be most directly associated with whether the state is donor-like or acceptor-like. If it is donor-like (neutral or positive), a transition involving an electron in the conduction band will be aided by Coulomb attraction whereas one involving a hole will not; so one would expect $\chi \ll 1$. For an acceptor-like trap, (neutral or negative) the contrary holds, and one expects $\chi \gg 1$.

Using (4), the occupancy factor (1) becomes

$$\begin{aligned} f_t &= \frac{\chi^{-1}\lambda^{-1}e^{Y}(1 + \lambda\delta) + \chi e^{\nu}}{\chi^{-1}\lambda^{-1}e^{Y}(1 + \lambda\delta) + \chi^{-1}e^{-\nu} + \chi\lambda e^{-Y}(1 + \lambda^{-1}\delta) + \chi e^{\nu}} \\ &= \tfrac{1}{2}\lambda^{-\frac{1}{2}} e^{-\frac{1}{2}Y} e^{\frac{1}{2}\nu} \operatorname{sech}\left[\tfrac{1}{2}(Y + \nu) - \tfrac{1}{2}\ln\lambda\right] \qquad \text{for } \delta = 0 \end{aligned} \tag{5}$$

Note that, in thermodynamic equilibrium, the occupancy factor does not depend in any way on the cross-sections, whereas for $\delta \neq 0$ it does, through the ratio χ.

* Strictly speaking, one should say "position of the Fermi level for intrinsic semiconductor" instead of "centre of the gap." These will fail to coincide if the effective masses of holes and electrons are unequal, as they certainly are in germanium.

Similarly, the flow of carrier-pairs to the surface (2) becomes:

$$U = N_t(v_{Tn}v_{Tp})^{1/2}(\sigma_n\sigma_p)^{1/2}n_i \frac{(\lambda + \lambda^{-1})\delta + \delta^2}{\chi^{-1}\lambda^{-1}e^Y(1 + \lambda\delta)\,\chi^{-1}e^{-\nu} + \chi\lambda e^{-Y}(1 + \lambda^{-1}\delta)\,\chi e^{\nu}} \tag{6}$$

which, for $\delta \rightarrow 0$, tends to the linear law $U = sn_i\delta$, where s, the surface recombination velocity, is given by:

$$s/(v_{Tn}v_{Tp})^{1/2} = N_tS_t$$

where

$$S_t = (\lambda + \lambda^{-1})(\sigma_n\sigma_p)^{1/2}/2[ch(\nu + \ell n\,\chi) + ch(Y - \ell n\,\lambda - \ell n\,\chi)] \tag{7}$$

The surface density Σ_s of trapped charge is given by:

$$\Sigma_s = N_tf_t \tag{8}$$

where f_t is the occupancy factor, given by (5).

Now let us turn to the question of a distribution of surface traps through the energy ν. Suppose that the density of states having ν lying between ν and $\nu + d\nu$ is $\bar{N}(\nu)\,d\nu$, expressed in units $(n_i\mathcal{L})$. Then the total surface recombination velocity arising from all traps, and the total trapped surface charge density, are given by:

$$s/(v_{Tn}v_{Tp})^{1/2} = n_i\mathcal{L}\int S_t(\nu)\bar{N}(\nu)\,d\nu \tag{9}$$

$$\bar{\Sigma}_s = \int f_t(\nu)\bar{N}(\nu)\,d\nu \tag{10}$$

where $S_t(\nu)$ and $f_t(\nu)$ are explicit functions of ν, given by (5) and (7). The limits of the integrals in (9) and (10) are the values of ν corresponding to the conduction and valence band edges; however, as we shall see, it is often possible to replace these limits by $\pm\infty$.

In summing up the contributions in the way represented by (9), we have implicitly ignored the possibility of inter-trap transitions, supposing that the population of each trap depends only on the rates of exchange of charge with the conduction and valence bands, and is independent of the population of any other trap of differing energy.

What kind of function do we expect $N(\nu)$ to be? Brattain and Bardeen[2] postulated that $N(\nu)$ was of the form of two delta-functions, corresponding to discrete trapping levels high and low in the band. This assumption is not consistent with the observed facts in regard to field effect, surface photo-voltage, or surface recombination velocity. The general difficulty is that the observed quantities usually vary less rapidly with surface potential than one would expect. It is possible to fit the field-effect observations of Brown and Montgomery[11] with a larger number of discrete levels, but this would call for a "sharpening up" of the trapped charge distribution as the temperature is lowered, and this appears to be contrary to what is observed.* It is always possible that the surface is patchy, in which case almost *any* variation with mean surface potential could be explained. The simplest assumption, however, seems to be that $N(\nu)$ is a rather smoothly-varying function. All we need assume for the moment is that it is everywhere finite, continuous and differentiable. We may then differentiate equation (10) with respect to Y and δ under the integral sign, and get $(\partial\bar{\Sigma}_s/\partial Y)_\delta$ and $(\partial\bar{\Sigma}_s/\partial\delta)_Y$, the quantities for which experimental measurements were reported in the previous paper:[3]

$$\left(\frac{\partial\bar{\Sigma}_s}{\partial Y}\right)_\delta = \int \frac{\bar{N}(\nu)\, d\nu}{4\, ch^2[\frac{1}{2}(\nu + Y) - \frac{1}{2}\ell\text{n}\,\lambda]} \tag{11}$$

$$\left(\frac{\partial\bar{\Sigma}_s}{\partial \delta}\right)_Y = -\int \frac{\bar{N}(\nu)(\frac{1}{2}(\lambda^{-1} + \lambda)th[\frac{1}{2}(\nu - Y) + \frac{1}{2}\,\ell\text{n}\,\lambda + \ell\text{n}\,\chi] + \frac{1}{2}(\lambda^{-1} - \lambda))\, d\nu}{4ch^2[\frac{1}{2}(\nu + Y) - \frac{1}{2}\,\ell\text{n}\,\lambda]} \tag{12}$$

Notice that the expression in brackets in the numerator of (12) generally has the value λ^{-1} or $-\lambda$, except near the point $\nu = Y - \ell n\,\lambda - 2\ell n\,\chi$. This is indicative of the fact that, whatever the exact form of $\bar{N}(\nu)$, the ratio of $-(\partial\Sigma_s/\partial\delta)_Y/(\partial\Sigma_s/\partial Y)_\delta$ tends to these limiting values (λ^{-1} and $-\lambda$) for sufficiently large negative and positive Y respectively.

It may be verified from (7), (11) and (12) that $(\partial\bar{\Sigma}_s/\partial Y)_\delta$, found from the field effect experiment, depends only on $N(\nu)$; $(\partial\bar{\Sigma}_s/\partial\delta)_Y$, found from the surface photo-voltage, depends on $\bar{N}(\nu)$ and χ; while s, the surface recombination velocity, depends in addition on the geometric mean cross-section $(\sigma_n\sigma_p)^{1/2}$. Both χ and $(\sigma_n\sigma_p)^{1/2}$ might themselves, of course, be functions of ν. Thus relations (7), (11) and (12) are integral equations, from which the three unknown functions of ν may in principle be deduced from the experimental results. (Equation 11, in fact, may be solved explicitly. P. A. Wolff[17] has shown, however, that, to determine $N(\nu)$ unambiguously, it is necessary to know $(\partial\bar{\Sigma}_s/\partial Y)_\delta$ for all values of Y in the range $\pm\infty$.)

The foregoing considerations apply to "small-signal" measurements.

* There are some changes with temperature, but not what one would expect if there were only discrete surface states.

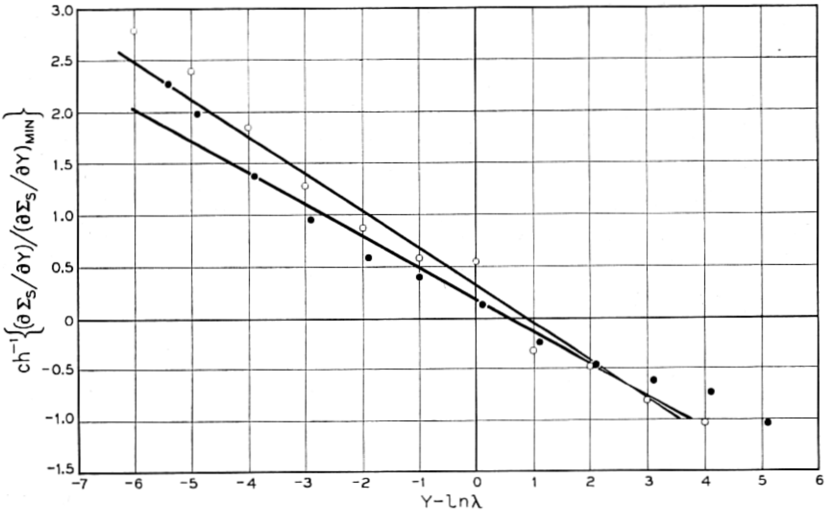

Fig. 1 — The fit between Equations (13) and (14) and the experimental data. The circles and dots give the experimental data for the n and p-type samples respectively and the solid straight lines represent Equations (13) and (14).

But it is also possible, once $N(\nu)$, χ and $(\sigma_n\sigma_p)^{1/2}$ are known, to calculate the expected behavior of the surface photo-voltage and surface recombination rate at high light intensities, and compare the answer with the experimental findings. We hope to discuss this matter in a later paper.

III. ANALYSIS OF THE EXPERIMENTAL DATA BY USE OF THE DELTA-FUNCTION APPROXIMATION

Let us first consider the interpretation of our field effect measurements by means of (11). We start by finding empirical expressions that describe the observed dependence of $(\partial\bar{\Sigma}_s/\partial Y)$ on Y (Fig. 6 of the preceding paper[3]). Except at values of $(Y - \ell n\ \lambda)$ close to the extremes reached one may fit quite well by a hyperbolic cosine function. Fig. 1 shows the function whose hyperbolic cosine is $(\partial\Sigma_s/\partial Y)/(\partial\Sigma_s/\partial Y)_{\min}$ plotted against $Y - \ell n\ \lambda$. From this figure we find:

22.6 ohm-cm n-type:

$$\left(\frac{\partial\bar{\Sigma}_s}{\partial Y}\right)_\delta = 4.5ch[0.36(Y - \ell n\ \lambda) - 0.8] \qquad (13)$$

(for $(Y - \ell n\ \lambda) > -4$

8.1 ohm-cm p-type:

$$\left(\frac{\partial \bar{\Sigma}_s}{\partial Y}\right)_\delta = 9.7ch[0.31(Y - \ell n\, \lambda) - 0.5] \tag{14}$$

$$\text{for } 2 > (Y - \ell n\, \lambda) > -4$$

For values of $(Y - \ell n\, \lambda)$ less than -4, it appears that Σ_s is changing more rapidly with Y than is indicated by (13) and (14). We shall comment on this point later. Excluding this region, we note that in both cases the variation with Y is everywhere slow in comparison with e^Y, and proceed on the assumption that $\bar{N}(\nu)$ is a function of ν that varies everywhere slowly in comparison with e^ν. Then (11) indicates that there is one fairly sharp maximum in the integrand in the range $\pm\infty$, occurring at that value of ν which coincides with the Fermi level:

$$\nu = -Y + \ell n\, \lambda \tag{15}$$

The integral in (11) could be evaluated in series about this point (method of steepest descents). The zero-order approximation is got by replacing

$$\tfrac{1}{4}\operatorname{sech}^2\left[\tfrac{1}{2}(\nu + Y) - \tfrac{1}{2}\ell n\, \lambda\right] \qquad \text{by} \qquad \boldsymbol{\delta}(\nu + Y - \ell n\, \lambda).$$

Later we shall proceed to an exact solution, and we shall find that this delta-function approximation is not too bad. From (11) we now find:

$$\left(\frac{\partial \bar{\Sigma}_s}{\partial Y}\right)_\delta \sim \int \bar{N}(\nu)\boldsymbol{\delta}(\nu + Y - \ell n\, \lambda)\, d\nu = \dot{\bar{N}}(-Y + \ell n\, \lambda) \qquad (15)$$

This mathematical procedure will be seen to be equivalent to identifying $(\partial\bar{\Sigma}_s/\partial Y)_\delta$ with the density of states at the point in the gap which coincides with the Fermi-level at the surface. Using (13) and (14), one gets:

22.6 ohm-cm n-type:

$$\bar{N}(\nu) = 4.5\, ch(0.36\nu + 0.8) \tag{16}$$

8.1 ohm-cm p-type:

$$\bar{N}(\nu) = 9.7\, ch(0.31\nu + 0.5) \tag{17}$$

As we shall see in the next section, the exact solutions differ from (16) and (17) only in the coefficients preceding the hyperbolic cosines.

Turning to the surface photo-voltage measurements, we take (12) and again replace

$$\tfrac{1}{4}\operatorname{sech}^2\left[\tfrac{1}{2}(\nu + Y) - \tfrac{1}{2}\ell n\, \lambda\right] \qquad \text{by} \qquad \boldsymbol{\delta}(\nu + Y - \ell n\, \lambda)$$

Using (15), one gets:

$$-\frac{(\partial\bar{\Sigma}_s/\partial\delta)_Y}{(\partial\bar{\Sigma}_s/\partial Y)_\delta} \tag{18}$$

$$= \tfrac{1}{2}(\lambda^{-1} + \lambda)\, th(-Y + \ln\lambda + \ln\chi) + \tfrac{1}{2}(\lambda^{-1} - \lambda)$$

This procedure, inaccurate as it is, has the advantage that no particular assumption need be made concerning the functional dependence of χ on ν, it being understood that χ in (18) has the value holding for $\nu = -Y + \ln\lambda$. In particular, if Y_0 is that value of Y at which the ratio $-(\partial\bar{\Sigma}_s/\partial\delta)_Y/(\partial\bar{\Sigma}_s/\partial Y)_\delta$ changes sign,

$$\ln\chi_0 = Y_0 - \ln\lambda + th^{-1}[(\lambda - \lambda^{-1})/(\lambda + \lambda^{-1})] \tag{19}$$

From the experimental data, one finds, for the n-type sample, $\ln\chi_0 \sim 2.4$ (at $\nu = -3.5$); for the p-type sample, $\ln\chi_0 \sim 1.0$ (at $\nu = 1.9$).

In view of the approximations made, these estimates would not be expected to be more precise than ± 1 to 2 units. Notice that both values are positive, and that the difference between them is small in comparison with the difference in ν. This suggests that we start afresh with the assumption that χ is independent of ν, and work out the surface photovoltage integral exactly. This is done in the next section.

IV. EXACT TREATMENT FOR THE CASE $\bar{N}(\nu) = A\, ch\,(q\nu + B)$, WITH CONSTANT CROSS-SECTIONS

The results of the previous section suggest the procedure of assuming that $N(\nu)$ is of the functional form given by (16) and (17), and evaluating the integrals (9), (11) and (12) exactly. The integral for $(\partial\bar{\Sigma}_s/\partial Y)$, (11), depends only on the form of $N(\nu)$ and may be evaluated at once. To get $(\partial\bar{\Sigma}_s/\partial\delta)$, (12), one must know how χ depends on ν. On the basis of the work of the previous section, we shall suppose that χ is independent of ν. (Properly, we need only assume that χ varies with ν more slowly than e^ν. Since the function $th[\frac{1}{2}(\nu - Y) + \frac{1}{2}\ln\lambda + \ln\chi]$ has one of the values ± 1 everywhere except close to $\nu = Y - \ln\lambda - 2\ln\chi$, and since the denominator of (12) has a sharp minimum at $\nu = -Y + \ln\lambda$, it follows that the region in which $(\partial\bar{\Sigma}_s/\partial\delta)_Y$ changes sign will be governed mainly by the value of χ at $\nu = -\ln\chi$.) To get s [(9), using (7)], one must also assume something about the geometric mean cross-section, $(\sigma_n\sigma_p)^{1/2}$. In the absence of any information on this score, we shall assume that $(\sigma_n\sigma_p)^{1/2}$ also is independent of ν, and see how the computed variation of s with Y compares with the experimental results.

We assume:

$$\bar{N}(\nu) = A\ ch\ (q\nu + B) \tag{20}$$

and substitute in (11), (12) and (7). In view of the sharp maximum in the integrands of these expressions, it is permissible to set the limits which should correspond to the edges of the gap or of the state distribution equal to $\pm\infty$. The integrals are conveniently evaluated by the contour method (see Appendix 1) and yield the following results:

$$\left(\frac{\partial \bar{\Sigma}_s}{\partial Y}\right)_\delta = A\pi q \text{ cosec } \pi q\ ch\,[B - q(Y - \ell n\, \lambda)] \tag{21}$$

$$\left(\frac{\partial \bar{\Sigma}_s}{\partial \delta}\right)_Y = -A\pi q \text{ cosec } \pi q\ ch\,[B - q(Y - \ell n\, \lambda)] \times$$

$$\left[\tfrac{1}{2}(\lambda^{-1} + \lambda)\left(-\coth \mathcal{Y} + \frac{sh\, q\mathcal{Y}\, ch\, \mathcal{B}}{q\, sh^2 \mathcal{Y}\, ch\,(q\mathcal{Y} - \mathcal{B})}\right) + \tfrac{1}{2}\,(\lambda^{-1} - \lambda)\right] \tag{22}$$

where

$$\left.\begin{aligned} \mathcal{Y} &= Y - \ell n\, \lambda - \ell n\, \chi \\ \mathcal{B} &= B - q\, \ell n\, \chi \end{aligned}\right\} \tag{23}$$

$$\frac{s}{(v_{Tn}v_{Tp})^{1/2}} \tag{24}$$

$$= \tfrac{1}{2}\,(\lambda + \lambda^{-1})(\sigma_n\sigma_p)^{1/2} n_i \mathfrak{L}\, 2\pi\, A\, sh\, q\mathcal{Y}\, ch\, \mathcal{B} \text{ cosec } \pi q \text{ cosech } \mathcal{Y}$$

Comparing (21) with (15), we see that the delta-function approximation is in error to the extent that it replaces πq cosec πq by 1. With the value of q found experimentally, this is not too bad; we can now, however, by fitting the right-hand side of (21) to the experimental facts, (13) and (14), obtain exact solutions for $N(\nu)$:

22.6 ohm-cm n-type

$$N(\nu) = 3.6\ ch(0.36\nu + 0.8) \qquad (\text{for } \nu < 4)$$

8.1 ohm-cm p-type (25)

$$N(\nu) = 8.3\ ch(0.31\nu + 0.5) \qquad (\text{for } \nu < 4)$$

The question arises as to whether this solution for the distribution is unique. We have already pointed out that the mathematical methods fail if the distribution is discontinuous. It seems that (25) represents the only solution that is slowly-varying, in the sense used in the previous section; its correctness could presumably be checked by carrying out experiments at different temperatures. For $\nu > 4$, the above expressions do not fit the observed facts, because, for $Y - \ell n\, \lambda < -4$, the charge in fast states is found to change more rapidly than is given by the empirical expressions in (13) and (14). The behaviour in this region is perhaps indicative of the existence of a discrete trapping level just beyond the range of ν which can be explored by our techniques. The observations (see Fig. 6 of preceding paper[3]) can be described by postulating, in addition to the continuous distribution of states given above, a level of density about 10^{11} cm^{-2}, situated at $\nu = 6$, or a higher density still further from the center of the gap. Statz et al,[13] using the "channel" techniques, which are valuable for exploring the more remote parts of the gap, have proposed a level of density $\sim 10^{11}$ cm^{-2}, situated at about 0.14 volts below the center of the gap ($\nu = 5.5$): this is not in disagreement with the foregoing.

In order to compare (22) with the experimental data derived from the surface photo-voltage, it is necessary to choose a value for χ. Fig. 2 shows the comparison with the results presented in the preceding paper. On the vertical axis, the values of $(\partial\Sigma_s/\partial\delta)/(\partial\Sigma_s/\partial Y)$ plotted have been divided by $(\lambda + \lambda^{-1})$, in order to show the n and p-type results on the same scale. (Note that the limiting values of this quantity should be $\lambda/(\lambda + \lambda^{-1})$ and $-\lambda^{-1}/(\lambda + \lambda^{-1})$, so that the vertical distance between the limiting values should be 1, independent of λ). The theoretical curves have been drawn with the value $\ell n\, \chi = 2.5$, in order to give best fit between theory and experiment at the points at which the ordinate changes sign. (It may be seen from the form of (22) that, with the actual value of the other parameters, the main effect of adopting a different value of $\ell n\, \chi$ would be to shift the theoretical curve horizontally, while a change of λ shifts it *vertically* without in either case greatly modifying its shape). The fit between theory and experiment is not quite as good as could be expected, even taking into account the rather low accuracy of the measurements. The variation of $(\partial\Sigma_s/\partial\delta)/(\partial\Sigma_s/\partial Y)$ with Y found experimentally seems to be rather slower than the theory would lead one to expect. The main points to make are: (i) the difference in Y between the zeros for the two samples (5.4 ± 1) is about what it should be (4.8) on the assumption that $\ell n\, \chi$ is the same for both samples and of the order of unity; and (ii) paying attention mainly to the zeros, the estimate $\ell n\, \chi = 2.5$ is likely to be good to ± 1.

Now let us consider the surface recombination velocity. Here we are on somewhat shakier ground, in that, in deriving (24), we have had to assume not only that χ is independent of ν, but $(\sigma_n \sigma_p)^{1/2}$ also. First we note from (24) that the maximum value of s should occur at $Y - \ell n\, \lambda = \ell n\, \chi$. Comparing with the experimental results given in the preceding paper,

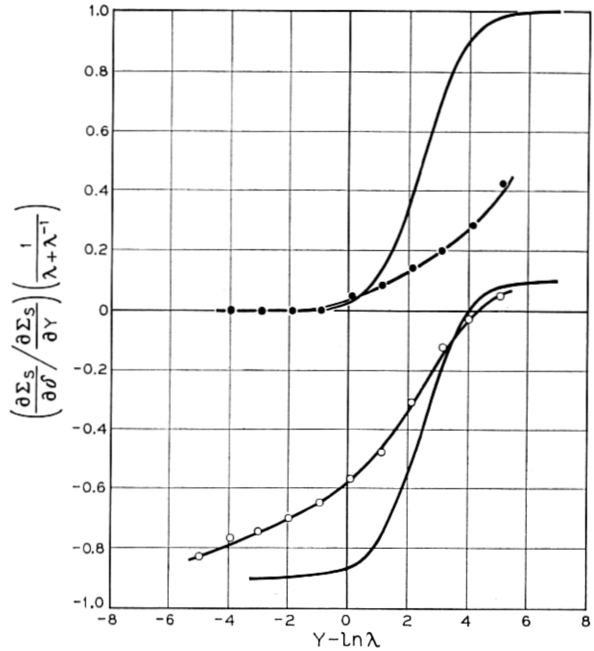

Fig. 2 — Experiment and theory for

$$\left[\left(\frac{\partial\Sigma_s}{\partial\delta}\right)\Big/\left(\frac{\partial\Sigma_s}{\partial Y}\right)\right]\Big/\frac{1}{\lambda+\lambda^{-1}}$$

Solid lines theory; circles and dots, with smooth curves through the points, represent experimental results for n and p-type samples, respectively.

we see maxima at $Y - \ell n\ \lambda = 2.0$ for the p-type sample, and 3.5 for the n-type sample. Both these values are within the limits to $\ell n\ \chi$ given in the previous paragraph, thus confirming the estimate made there. Fig. 3 shows a comparison between the experimental results and (24). The graph has been fitted horizontally, by setting $\ell n\ \chi = 2.5$, as found above; vertically, to agree with the mean value at that point. The agreement with experiment is reasonable, although again, just as in Fig. 2, the experimental variation of s with $(Y - \ell n\ \lambda)$ is rather slower than one would expect.

The fact that the experimental values, both of surface photo-voltage and of surface recombination velocity, vary more slowly than expected, is susceptible of a number of interpretations: (i) The deduced distribution of fast states might be wrong. However, the most likely alternative distributions — isolated levels, or a completely uniform distribution —

give (in at least some ranges of Y) a more rapid instead of a smoother variation of these quantities so long as the surface is homogeneous. (ii) The estimates of the changes in Y might be too large. It is unlikely that our calibration is sufficiently in error, and other workers have obtained results comparable to ours. The only possibility would be that the mobility of carriers near the surface is larger (instead of smaller, as found by Schrieffer) than inside — which seems quite out of the question. (iii) The ratio of capture cross-sections varies with ν. This, however, would only be in the right direction if one were to assume that the ratio χ *increases* with the height of the level in the gap — i.e., that the high states behave like acceptors, and the low ones like donors. While not quite impossible, this is an unlikely result. (iv) The surface is patchy. It is probable that a range of variation of two to four times (kT/e) in surface potential would be sufficient to account for the observed slow variation of surface photo-voltage and recombination velocity with mean surface potential. We have refrained from detailed calculations of patch effects, on the grounds that, without detailed knowledge of the magnitude and distribution of the patches, it would be possible to construct a model that could indeed fit the facts, but one would have little confidence in the result. The possibility of patches warns us to view with caution the exact distribution function deduced for the fast states. It would still be conceivable, for example, that one has but two discrete states, as originally proposed by Brattain and Bardeen,[2] and that the apparent existence of a band of states in the middle of the gap arises from the fact that there are always some parts of the surface at which the Fermi level is close to one or other of these states. Fortunately the conclusions as to the cross-sections are not too sensitive to the exact distribution function assumed.

Using the mean of the two coefficients in (25), substituting $n_i = 2.5 \times 10^{13}$ cm^{-3}, $\mathfrak{L} = 1.4 \times 10^{-4}$ cm, $(v_{Tn}v_{Tp})^{1/2} = 1.0 \times 10^7$ cm/sec, in (24), and using the experimental result (see Fig. 3) that $s_{\max}/(\lambda + \lambda^{-1}) = 1.2 \times 10^2$ cm/sec, one obtains $(\sigma_p\sigma_n)^{1/2} = 5 \times 10^{-16}$ cm^2. Now setting $(\sigma_p/\sigma_n) = \chi^2 \sim e^5 \sim 150$, one gets for the separate cross-sections:

$$\sigma_p = 6 \times 10^{-15} \text{ cm}^2$$

$$\sigma_n = 4 \times 10^{-17} \text{ cm}^2$$

There values appear to be eminently reasonable. Burton et al,[12] who studied recombination through body centres associated with nickel and copper in germanium, found $\sigma_p > 4 \times 10^{-15}$ cm^2, $\sigma_n = 8 \times 10^{-17}$ cm^2 for nickel, and $\sigma_p = 1 \times 10^{-16}$, $\sigma_n = 1 \times 10^{-17}$ for copper. The fact that

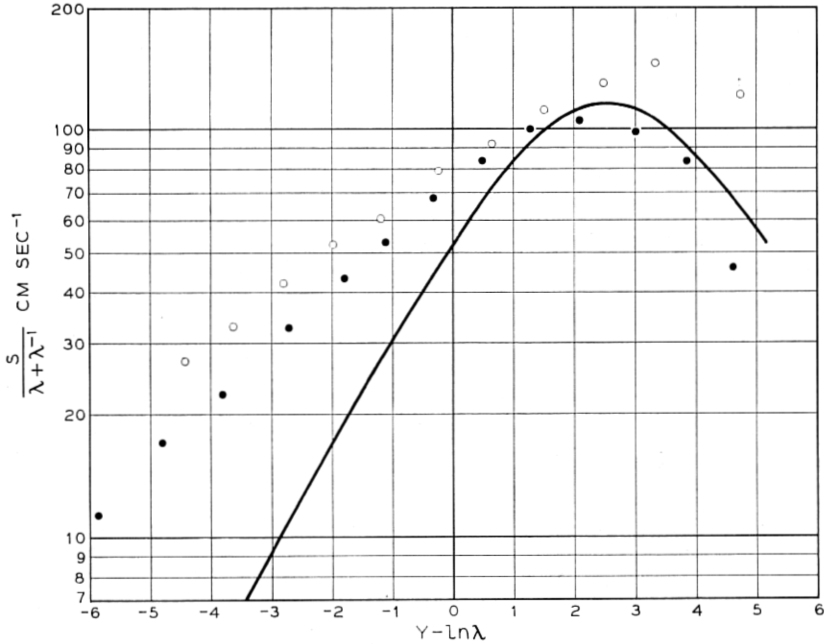

Fig. 3 — Experiment and theory for surface recombination. Solid curve theory circles and dots for n and p-type samples, respectively.

our estimates for σ_p and σ_n appear to be of the expected order of magnitudes lends strong support to the view that identifies the traps appearing in the field-effect and surface photo-voltage experiments with those responsible for surface recombination.

The result that $(\sigma_p/\sigma_n) = 150$ is good evidence that the fast states are acceptor-like. This statement must be restricted to the range $|\nu| < 4$; the states that are outside this range might be of either type. Also one might allow a rather small fraction of the states near the middle to be donor-type, without serious trouble; but the experimental results compel one to believe that most of the fast states within 0.1 volts or so of the centre of the gap are acceptor-like.

V. TRAPPING KINETICS

The foregoing considerations have concerned the steady-state solution to the surface trapping problem. If the experimental constraints are changed sufficiently rapidly, however, there may be effects arising from the finite time required for the charge in surface states to adapt itself to the new conditions.[14] This section will concern itself with the trapping time constants (which are not directly related to the rate of recombination of minority carriers).

One case of trapping kinetics has been discussed by Haynes and Hornbeck.[9] A general treatment of surface trapping kinetics is necessarily quite involved, and will be taken up in a future paper. Here we shall restrict ourselves to giving an elementary argument relating to the high-frequency field effect experiment of Montgomery.[15] To simplify the discussion, we assume that the surface in question is of the "super" type; i.e., the surface excess of the bulk majority carrier is large and positive. At time $t = 0$, a large field is suddenly applied normal to the surface; the induced charge appears initially as a change in the surface excess of the bulk majority carrier; as time elapses, charge transfer between the space-charge region and the fast states takes place, until equilibrium with the fast states has been re-established. What time constant characterizes this process?

Take electrons as the majority carrier. Then the flow of electrons into the fast states must equal the rate of decrease of the surface excess of electrons. For a single level one may write:

$$\begin{aligned} U_n &= N_t v_{Tn} \sigma_n [(1 - f_t) n_s - f_t n_1] \\ &= -\dot{\Gamma}_n \end{aligned} \tag{26}$$

For a continuous distribution of levels, one can say that only those levels within a few times (kT/e) of the Fermi level at the surface will be effective, so that one may regard the distribution as being equivalent to a single state with $n_1 = n_i \exp (Y - \ln \lambda)$, which will be about half full. We assume further that the density of fast states is sufficient for the changes in Γ_n to be large in comparison with those in f_t, as is reasonable, having regard to the relative magnitudes of the measured values of $(\partial \Sigma_s / \partial Y)_\delta$ found in the present research, and of $(\partial \Gamma_p / \partial Y)_\delta$ and $(\partial \Gamma_n / \partial Y)_\delta$. Thus f_t may be treated as a constant in equation (26). Further, we may set $n_s = 4\Gamma_n^2 / n_i \mathfrak{L}^2$, as may be proved from considerations on the space-charge region.[16] Solving (26) with these conditions, one finds, for the transient change in Γ_n between the initial and the quasi-equilibrium state:

$$\Delta \Gamma_n \propto \left(1 - th \frac{t}{\tau}\right) \tag{27}$$

where

$$\tau = \lambda e^{-Y} \mathfrak{L} / [N_t v_{Tn} \sigma_n \sqrt{2} \sqrt{f_t (1 - f_t)}]$$

To clarify the order of magnitude of time constant involved, let us substitute $\mathfrak{L} \sim 10^{-4}$ cm, $N_t \sim 10^{11}$ cm^{-2}, $v_{Tn} \sim 10^7$ cm/sec., $\sigma_n \sim 10^{-15}$ cm^2, $f_t \sim 0.5$, $\lambda e^{-Y} \sim 1$. This gives $\tau \sim 10^{-7}$ sec, which suggests that one would be unlikely to run into trapping time effects in the field-effect experiment at frequencies less than 10 Mcyc/sec. This conclusion is consonant with the findings of Montgomery.[15]

Appendix 1

EVALUATION OF THE INTEGRALS IN SECTION 4

The integrals occurring in Section 4, giving the experimentally accessible quantities $(\partial\bar{\Sigma}_s/\partial Y)$, $(\partial\bar{\Sigma}_s/\partial\delta)$ and s in terms of the surface trap distribution and cross-sections, are conveniently evaluated by contour integration. In view of the general applicability of this method in dealing with integrals of the sort that arise from such a distribution of traps, we include here a short note on the precedure used. The integrals needed are:

$$I_1 = \int_{-\infty}^{+\infty} ch(cx + g) \operatorname{sech}^2 x \, dx$$

$$I_2 = \int_{-\infty}^{+\infty} th(x + b) \, ch(cx + g) \operatorname{sech}^2 x \, dx$$

$$I_3 = \int_{-\infty}^{+\infty} \frac{ch(cx + g)}{chx + chk} \, dx$$

To evaluate I_1, we evaluate $\int ch(cz + g) \operatorname{sech}^2 z \, dz$ around the contour shown in Fig. 4. The contributions from the parts $z = \pm R$ vanish in the limit $R \rightarrow \infty$, so that the integral has the value:

$$(1 - \cos c\pi) \int_{-\infty}^{+\infty} ch(cx + g) \operatorname{sech}^2 x \, dx - i \sin c\pi \int_{-\infty}^{+\infty} sh(cx + g) \operatorname{sech}^2 x \, dx$$

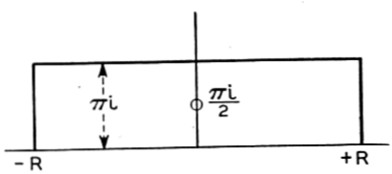

Fig. 4 — Evaluation of I_1.

The integrand has one pole within the contour, at $x = \frac{1}{2}i\pi$, at which the residue is $-c(\cos \frac{1}{2}c\pi \, sh\, g + i \sin \frac{1}{2}c\pi \, ch\, g)$. Multiplying by $2\pi i$ and equating the real part to that in the above expression, one obtains:

$$I_1 = \pi c \operatorname{cosec} \tfrac{1}{2}c\pi \, ch\, g$$

The same contour is used in evaluating I_2; there are now poles at $z = \frac{1}{2}i\pi$ and at $z = \frac{1}{2}i\pi - b$, and one obtains:

$$I_2 = \pi c \coth b \, ch\, g \operatorname{cosec} \tfrac{1}{2}c\pi - 2\pi \operatorname{cosec} \tfrac{1}{2}c\pi \operatorname{cosech}^2 b \, sh\, \tfrac{1}{2}bc \, ch(\tfrac{1}{2}bc - g)$$

To evaluate I_3, one integrates $\int [ch(cz + g)/(chz + chk)]\, dz$ around the contour shown in Fig. 5. There are poles at $i\pi \pm k$. Proceeding as before, one finds:

$$I_3 = 2\pi \, sh\, ck \, ch\, g \operatorname{cosec} \pi c \operatorname{cosech} k$$

Appendix 2

LIMITATION OF SURFACE RECOMBINATION ARISING FROM THE SPACE-CHARGE BARRIER

The question of the resistance to flow of carriers to the surface arising from the change in potential across the space-charge layer has been discussed by Brattain and Bardeen.[2] Here we shall recalculate this effect by a better method, which again shows that, within the range of surface potential studied, the effect of this resistance on the surface recombination velocity is for etched surfaces quite negligible.

Let I_p and I_n be the hole and electron (particle) currents towards the surface, and let x be the distance in a direction perpendicular to the surface, measuring x positive outwards. Then the gradient of the quasi-Fermi levels φ_p and φ_n at any point is given by:

$$\nabla\varphi_{\substack{p\\n}} = \mp (I_{\substack{p\\n}}/\mu_{\substack{p\\n}})/\binom{p}{n} \tag{1}$$

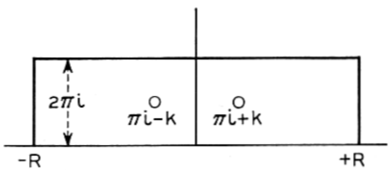

Fig. 5 — Evaluation of I_3.

Then the total *additional* change in φ_p and φ_n across the space-charge region, arising from the departure in uniformity in the carrier densities p and n, is:

$$\begin{aligned}\Delta\phi_p &= -\frac{I_p}{\mu_p}\int\left(\frac{1}{p}-\frac{1}{p_0}\right)dx\\ \Delta\varphi_n &= \frac{I_n}{\mu_n}\int\left(\frac{1}{n}-\frac{1}{n_0}\right)dx\end{aligned} \qquad (2)$$

Suppose now that the true surface recombination rate is infinite, so that the quasi-Fermi levels must coincide at the surface, and:

$$\varphi_p + \Delta\varphi_p = \varphi_n + \Delta\varphi_n \qquad (3)$$

These equations, together with the known space-charge equations,[16] complete the problem. Notice first, from (2), that $\Delta\varphi_p$ will be large only if there is a region in which p is small ($Y \gg 1$), while $\Delta\varphi_n$ is large only when, in some region, n is small ($Y \ll -1$). Introducing the quantity δ, approximating for δ small, equating I_p and I_n and setting the result equal to $sn_i\delta$, one finds:

$Y \ll -1$

$$s \rightarrow (D_n/\mathfrak{L})(\lambda^{1/2} + \lambda^{-3/2})e^{\frac{1}{2}Y}$$

$Y \gg 1$ (4)

$$s \rightarrow (D_p/\mathfrak{L})(\lambda^{-1/2} + \lambda^{3/2})e^{-\frac{1}{2}Y}$$

The coefficients $(D_n/\mathfrak{L})$ and $(D_p/\mathfrak{L})$ are of the order of 4×10^5 cm/sec. The most extreme case encountered in our work is that occurring at the ozone extreme for the n-type sample ($\lambda = 0.34$, $Y = -6$), for which the surface recombination velocity, if limited by space-charge resistance alone, would be about one-quarter of this (10^5 cm/sec). The fact that the observed surface recombination velocity is lower than that by more than two orders of magnitude shows that space-charge resistance is not a limiting factor in the present experiments. Equations 4 might well hold on a sand-blasted surface, however, where the trap density is much higher.

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