2. Irradiation of *n*- and *p*-type specimens leads to an increase in surface potential which causes the observed changes in surface conductance and quenches the photoconductivity in the shoulder region. With increasing electron energy, the irradiation becomes less effective in producing a change in surface potential.

3. Irradiation with 4.5-Mev electrons introduces volume defects which, however, do not contribute to the photoconductivity beyond the absorption edge. In *n*-type specimens, the resulting decrease in surface potential now allows transitions to empty states in a second group of slow surface states lying between 0.2 ev and 0.4 ev above the valence band.

4. It is shown experimentally that a considerable concentration of fast surface states exists within 0.05 ev of the conduction band.

ACKNOWLEDGMENTS

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Semiconductor Surface Potential and Surface States from Field-Induced Changes in Surface Recombination

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Experiments are reported on the effects of ac electric fields and ambients on the surface recombination velocity in germanium and silicon. The variations in surface recombination are detected by changes in the reverse current of large area "back surface" diodes. The experimental method is an improved version of that of Thomas and Rediker and is a convenient means of exploring surface type, stability, time effects at the surface, and effects induced by high ac fields and ambients on the slow surface states. Observation of a maximum of surface recombination in terms of applied field provides a reference point from which the zero-field value of the surface potential can be evaluated, and the dependence of the surface recombination velocity (s) on the surface potential (ϕ_s) can be established. Values of ϕ_s are in the range of ± 0.25 v in Ge and ± 0.5 v in Si. The energies of the main recombination states are at 6 kT to 9 kT from mid-gap in Ge and at $+16$ kT or -16 kT in Si. Information on the surface potential and the surface states obtained by the present technique is in reasonable agreement with that derived from other types of measurements. The present results are independent of uncertainties due to surface mobility. Experimental patterns show directly that the "charge" surface states are also the ones that give rise to surface recombination. The width of the observed curves of s *vs* induced charge (and ϕ_s) depends on bulk resistivity and is smaller for the higher resistivity samples. Such behavior could arise from contributions to s from recombination states distributed in the surface space-charge region.

1. INTRODUCTION

FIELD-INDUCED effects in semiconductor surfaces yield substantial information on the physics of the surface and on its electrical behavior. These effects include changes induced in surface conductivity upon application of an external electric field[1-5] (usually called the field-effect), as well as changes in surface recombination velocity.[6-8] The present work is concerned with the effects of ambients and ac electric fields, in the frequency range of 0.01 to 1000 cps, on the semiconductor surface potential and the corresponding changes in surface recombination velocity.

The electric field is applied normally to the "back" surface of alloy-type germanium and silicon diodes and the effects on the surface recombination velocity are detected by the changes in the diode current.[7,9] This technique is shown to be a very effective one in determining the type of surface (p, n, or intrinsic) that one obtains with a given chemical treatment and ambient atmosphere as well as the extent of stability of the surface potential with time. A new method of approximately determining the zero-field value of the surface potential (ϕ_s) is provided by the observation of a maximum of surface recombination (s) in terms of an applied field E. The experimental curves of s *vs* E and those of s *vs* ϕ_s are discussed and interpreted in terms of the energy levels, distribution, and carrier capture cross sections of the surface states that give rise to recom-

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[2] J. Bardeen and S. R. Morrison, Physica **20**, 873 (1954).
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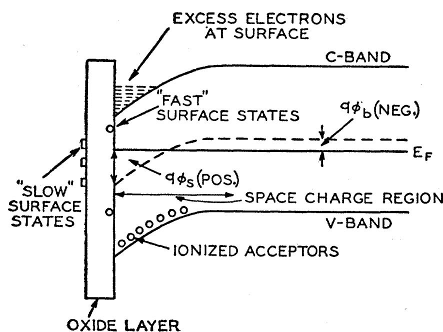

FIG. 1. Energy bands at semiconductor surface for the case of p-type material with n-type surface.

bination. The frequency dependence of the effect of the field on s yields information on the distribution of time constants of the slow surface states.

The experimental curves of s *vs* induced charge show distortions that are attributed to charge change in fast surface states. Variations are observed in the width of the s *vs* ϕ_s curves with impurity concentration that may well indicate contributions to the surface recombination velocity from states distributed in the surface space-charge region.

2. SEMICONDUCTOR SURFACE, FIELD-INDUCED CHANGES IN SURFACE POTENTIAL, AND RECOMBINATION VELOCITY

The currently accepted model for the energy band structure at a semiconductor surface is shown in Fig. 1. Surface treatments and ambients introduce allowed energy levels in the forbidden band at the surface and these surface states have been the subject of considerable work.[1,3–5,10–17] The net charge bound at the surface states necessitates a bending of the bands near the surface. The amount of bending is measured by ϕ_s. The electron and hole densities are given everywhere by

$$n=n_ie^{q\phi/kT},\quad p=n_ie^{-q\phi/kT}, \tag{1}$$

where n_i refers to the carrier concentration in intrinsic material and q is the absolute value of the electron charge. ϕ varies between ϕ_b in the bulk (determined exclusively by impurity concentration[18]) and ϕ_s at the surface. The integrated total charge in the space-charge region, including in addition to the carriers given by (1) the ionized donors and acceptors, is equal and opposite to the charge bound per unit area at the surface states.

The dependence of the surface recombination velocity s on ϕ_s has been studied[6–9,11,19–22] and is, at least qualitatively, understood. Depending on the density, energy levels, distribution and carrier capture cross sections of the recombination states, one calculates curves of the type shown in Fig. 2. These curves will be discussed in Sec. 4 below. Here we note that there is a maximum of s near a middle region of ϕ_s, with very small values of s at high (absolute) values of ϕ_s (strongly n or p-type surface). The equilibrium value of ϕ_s is determined primarily by surface treatment and by ambients. A change in ambient atmosphere, for example, from wet O_2 to dry O_2, changes germanium surfaces from n to p type.[5]

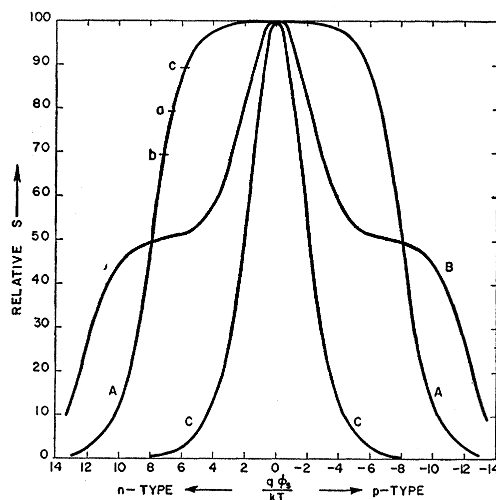

FIG. 2. Curves of s *vs* $q\phi_s/kT$ for various types of distributions of the surface recombination states. A: curve for a single surface state level. B: two energy levels equally effective for recombination. C: continuous distribution of levels.

Application of an ac electric field, normal to the semiconductor surface, introduces changes in ϕ_s about its equilibrium value. If frequencies of 60 to 1000 cps are used, the "slow" states with effective time constants larger than 0.03 sec do not have time to change their charge during the ac cycle. The fast states, on the other hand, with time constants of the order of microseconds, have ample time to follow the field variations and are in equilibrium with the bulk at each point of the ac

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cycle. As far as these states and the space-charge region are concerned, the effect of the field is equivalent to changes in the charge of the slow states and the bending of the energy bands at the surface. Use of strong fields (up to 5×10^5 volts/cm) allows variations in bending between the extremes of upwards and downward types (ϕ_s varying between strongly n and p type).

The surface recombination velocity, through its dependence on ϕ_s, is effectively "modulated" by the applied field about its zero-field value. In Fig. 2, the changes of ϕ_s and s would be represented by excursions, over a portion of the curve, about an equilibrium point determined by surface treatment and ambient. Changes of ambient, and also dc fields, result in shifts of this "operating" point along the curve.

3. EXPERIMENTAL METHOD AND RESULTS

One is provided with a convenient method of detecting changes in s, induced by fields applied to the surface of a semiconductor diode, by changes in the diode current if the reverse saturation current is proportional to s. In a thin wafer having a p-n junction alloyed to one side and the opposite side exposed to fields and ambients, the diode reverse saturation current will be proportional to s if the thickness of the sample is comparable to or smaller than the diffusion length of minority carriers.[23] This specifies that minority carrier lifetime is to be limited by surface rather than volume recombination. In the samples used in this work (width $\sim$0.017 cm) this condition is satisfied. The reverse biased p-n junction collects the minority carriers thermally generated at the free or "back" surface of the base wafer.

Field-induced effects on the reverse saturation current of n-type germanium diodes have been reported by Thomas and Rediker.[7] In the present work, effects on both forward and reverse currents of n- and p-type germanium samples are observed. Similar effects are observed in silicon. The effects on the two currents are interpreted in terms of modulation, by virtue of its dependence on s, of the parameter I_0 in the conventional rectification formula

$$I=I_0(e^{qv/kT}-1). \tag{2}$$

The reverse saturation current I_0, being to a good approximation simply proportional to s, is easier to interpret. Hence we are concerned in this paper with field-induced effects on this, rather than on the forward current.

Effects on the diode current due to changes of surface conductivity, that may complicate interpretation of the results, are negligible by comparison to those of surface recombination.

The experimental arrangement is an improved version of that of Thomas and Rediker[7] and is shown in Fig. 3. I_0 is applied on the vertical of the oscilloscope (terminal A) while the horizontal sweep is driven by the same field that is applied normally to the diode "back" surface. One therefore directly observes I_0 *vs* the field intensity E or, qualitatively, portions of the s *vs* ϕ_s curve (Fig. 2) since s is proportional to I_0 and the change in ϕ_s is a monotonic (although not a linear) function of E.

[23] W. M. Webster, Proc. Inst. Radio Engrs. 43, 277 (1955).

A difficulty in previous arrangements[7] is the voltage drop across the semiconductor specimen due to the displacement current through the dielectric (mica spacer, Fig. 3) between the semiconductor and the field electrode. This appears on the oscilloscope and can obscure the real effect of E on s. With the additional RC circuit of Fig. 3, a balancing signal is applied to the differential input of the oscilloscope (terminal B), and the spurious effect is removed. The range of applicability of the surface measuring technique, in frequency as well as in sample resistivity, is now considerably increased.

The diodes are of the alloy-type and the base material is cut from large diameter ($\frac{1}{2}$ to 1 in.) crystals. A large junction area (0.3 cm^2) provides better sensitivity through the increased portion of the back surface that is exposed to field and ambient. Ohmic contact is made to a supporting piece of metal along the periphery of the semiconductor wafers (Fig. 3). The specimens are dried and all parts, excepting the surface opposite the p-n junction, are covered with a polystyrene coating. This protects the junction and the electrical connections from etches to which the back surface is subsequently subjected. Provision is made for exposing the back surface to various gases at nearly atmospheric pressures. Because of the use of the mica spacer, some caution is to be exercised in applying the present conclusions to entirely free surfaces.

Upon application of small ac fields ($<10^4$ volts/cm), the observed pattern of I_0 *vs* E is a straight line that corresponds to small amplitude modulation of ϕ_s and s, such as the portion bc of the curve in Fig. 2, about the equilibrium point a. From the slope of the observed pattern and the polarities of I_0 and E, it can be immediately deduced whether the surface is p or n type, or close to intrinsic (if a maximum is observed). Changes

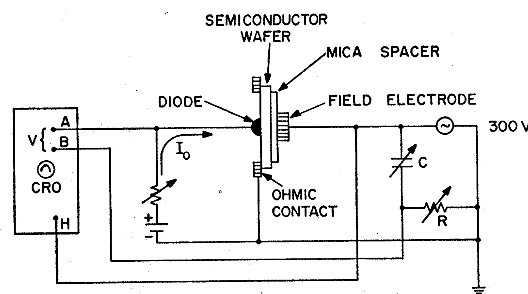

FIG. 3. Circuit for measurement of the effect of electric fields on surface recombination velocity.

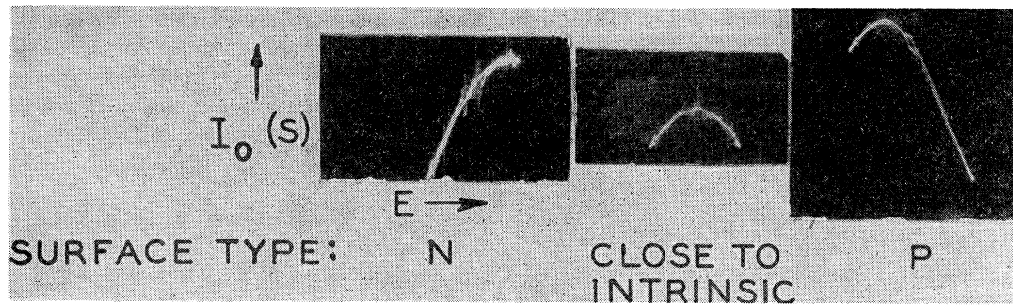

FIG. 4. Patterns of I_0 (or surface recombination velocity) *vs* applied field or induced charge in 0.3-ohm-cm n-type germanium and relation to surface type. The horizontal and vertical gains are different in each case. The frequency is 60 cps.

of the pattern with time are indicative of the extent of surface stability after a given chemical or other treatment.

The effects of the field on silicon are, by comparison to germanium, more difficult to observe. Since the diffusion length of minority carriers is smaller in silicon, the p-n junction for a given wafer thickness, is, by comparison to germanium, less influenced by the changes on the opposite face of the wafer. Differences between the two cases can also be understood in terms of the difference in width of the s *vs* ϕ_s curves. In addition, the effect of the field on ϕ_s is substantially different in the two cases. These points are discussed in Secs. 4 and 5 below.

Exposure of the surface to light reverses the slope of the I_0 *vs* E patterns, as already reported by Thomas and Rediker.[7] This has been attributed to the fact that for large light-injected densities of minority carriers I_0 is not proportional to s. The two quantities are proportional to each other only as long as the minority carrier density p in the bulk is less than p_0. For large injected densities, because of the larger minority carrier loss by recombination for larger s, I_0 decreases as s increases. To this, however, one must add the effect of light on ϕ_s and hence on s and I_0. Light-injected carriers tend to flatten the bands at the surface, hence move ϕ_s from either side, p or n, towards the point where $\phi_s=\phi_b$. Accordingly, s will move towards the maximum plateau region of the s *vs* ϕ_s curve when the sample is illuminated. Such a behavior of s has been observed when the samples have been exposed to gradually increasing light intensities.

If strong fields (10^5 to 10^6 volts/cm) are used, one observes curvature in the oscilloscope patterns indicating modulation of ϕ_s over a wide range of the curves of Fig. 2. Photographs of patterns of this type are shown in Fig. 4. In the first, taken with a 0.3-ohm-cm germanium sample after treatment in CP_4, ϕ_s is clearly on the n side and the field swings it towards the $n+$ side on the left, and towards the top of the curve to the p side on the right. The second pattern was obtained with the same diode when the surface was at some point in the plateau of the s *vs* ϕ_s curve. The field here introduces wide changes in ϕ_s. The third pattern shows a p-type surface. The peak value of the applied field is 5.6×10^5 volts/cm in all three patterns but the gain is different in each case.

In Fig. 5 a pattern of 0.3-ohm-cm n-type Ge is compared with one taken with 3-ohm-cm material. The horizontal scale is linear in induced charge Q (or field E). Note that a considerably larger induced charge is required to sweep out the curve of the low-resistivity

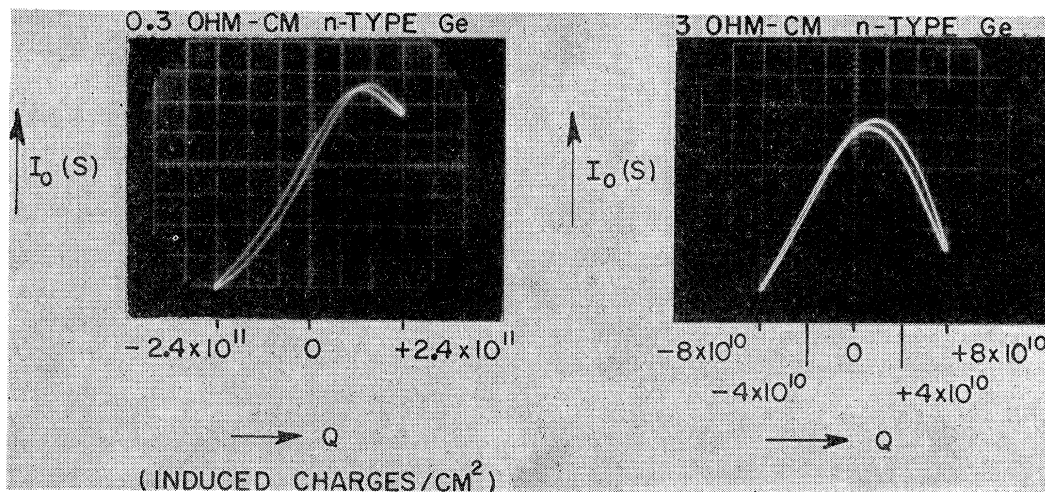

FIG. 5. Patterns of I_0 (or surface recombination) *vs* induced charge Q in 0.3- and 3-ohm-cm n-type germanium.

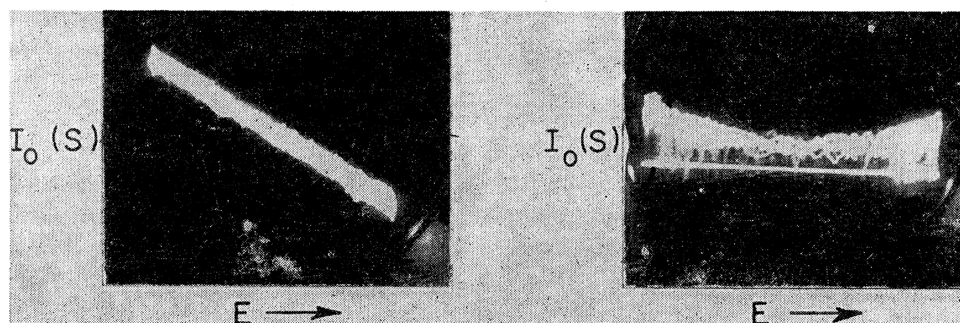

FIG. 6. Patterns of I_0 (or s) vs applied field E in 0.1-ohm-cm p-type Si. The maximum of s is here shown as a minimum because of the reversed polarity of I_0 with respect to that of the other figures. For comparison an horizontal line is shown on the oscilloscope.

material. This trend continues in material of 12-ohm-cm resistivity. The significance of this will be discussed in Sec. 6 below.

The patterns in Figs. 4 and 5 show predominance of a single energy level for the fast surface states. That the experimental curve is not as flat as Curve A, Fig. 2 is due to the fact that the experimental result is strictly s vs E (or induced charge Q) rather than s vs ϕ_s. When the abscissa is changed from E to ϕ_s, one obtains a curve that closely fits the one expected from single-level theory.

Patterns similar to Fig. 4 are obtained with 0.1-ohm-cm p-type silicon. The maximum here (Fig. 6) is broader, but aside from this, a single level again is indicated for the surface recombination states.

In some cases more complicated patterns have been observed. For example in some samples of 12-ohm-cm n-type Ge, one observes the pattern of Fig. 7 with the ambient intermediate between wet and dry O_2. The conspicuous asymmetry suggests the presence of more than one energy level, which is confirmed by further exploration of the left (n type) side, yielding the additional structure seen in Fig. 8. The ambient here is wet air and the vertical gain by comparison to that of Fig. 7 is ten times larger. Figure 8 can be fitted on the left of Fig. 7 to form a single pattern that is in reasonable agreement with that expected from two discrete levels of different densities and energies.

The frequency of the applied field in Figs. 4–8 is 60 cps.

Careful study of the curves of s vs induced charge reveals small distortions corresponding to the inflection point of the s vs ϕ_s curves and on the n-type side (positive ϕ_s). Such a distortion is shown in the pattern of Fig. 9 and can be attributed to charge change in fast surface states of discrete energy. The charge states change their charge most rapidly when $q\phi_s = E_t - E_i$. But this value of ϕ_s is also the one that corresponds to the inflection point of the s vs ϕ_s curve arising from the main recombination states (see Sec. 4). The fact that the distortion in the patterns occurs at the inflection point of the curves shows directly that these charge states are the same as the recombination states. That they are observed on the positive side of ϕ_s shows that the levels are above rather than below mid-gap, a fact that cannot be determined from the width of the curves alone.

The amount of charge change due to the surface state can be approximately determined from the horizontal extent of the distortion in Fig. 9. This is $\frac{1}{3}$ of the total charge induced in $\frac{1}{2}$ cycle or about 5×10^{10} charges/cm^2. This value is in fairly good agreement with those derived from field-effect conductivity measurements.

The prominent hysteresis loop in Fig. 7 is partly due to voltage drop across the specimen. Even if the direct voltage drop is completely balanced by the RC circuit (Fig. 3), hysteresis effects are persistently observed and become more prominent at high frequencies. From their frequency dependence, as also observed in field-effect conductivity measurements,[3] one may conclude that at higher frequencies they are associated with minority

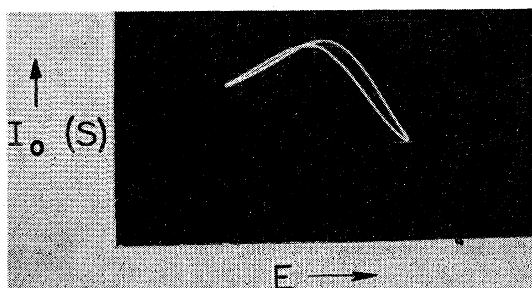

FIG. 7. An asymmetric pattern of I_0 (or s) vs E obtained in some cases with 12-ohm-cm n-type germanium.

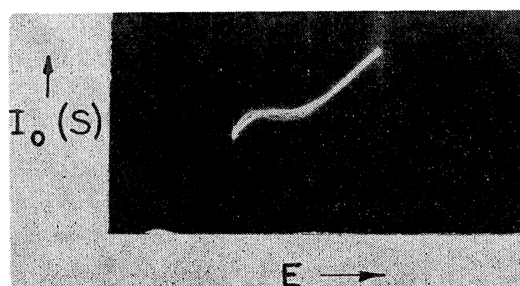

FIG. 8. I_0 (or s) vs E obtained with the sample of Fig. 7 in a wet air atmosphere. This pattern is a continuation far to the left (or n type) side of Fig. 7. The vertical gain is ten times that of Fig. 7. The additional structure here, and the asymmetry of Fig. 7, show presence of a second energy level for the surface recombination states.

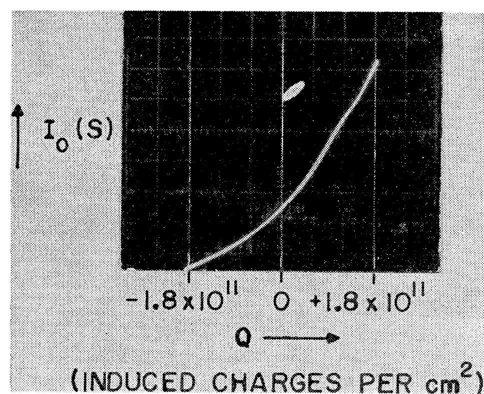

FIG. 9. A distortion in the pattern of s *vs* applied field attributed to charge change in fast states of discrete energy. That it occurs at the inflection point of the curve shows that the states are the same with the ones responsible for surface recombination. Since it occurs on the n-type (positive ϕ_s) side of the curve it indicates that the levels are above rather than below mid-gap. From the horizontal extent of the distortion one concludes that the charge change involved is about $5q\times 10^{10}/cm^2$.

carrier lifetimes in that the recombination-generation process is not fast enough to supply the carriers necessary to balance the applied field. Some of the hysteresis effects are ambient-dependent, being more prominent in a wet air than a dry O_2 atmosphere.

Information on the slow-state time constants can be obtained from the frequency dependence[22] of the amplitude of the effects of the field on s. The results of measurements of the frequency dependence of the effect of the field on s are shown in Fig. 10. The measurements cover the frequency range of 0.01 to 1000 cps. Response here means simply the magnitude of the vertical signal that corresponds to a change in s induced by a small ac field. The response is normalized to unity at 1000 cps. The curves are qualitatively similar to those obtained from measurements on surface conductivity.[17] Analysis of the present results by the method used by Kingston and McWhorter[17] yields the wide spread of time constants of the slow states indicated by the conductivity measurements. The distribution of the time constants τ however does not vary as $1/\tau$, but is intermediate between one that is independent of τ and one that varies as $1/\tau$. It is interesting to note that this intermediate distribution suggests a low-frequency noise spectrum that varies approximately as $1/f^{1.5}$ instead of the $1/f$ dependence derived from the $1/\tau$ distribution.

Besides influencing ϕ_s and s, ambients, electric fields or dc bias can affect the diode current through changes in channels, if such channels are formed. No appreciable channel effects were observed in this work, possibly because of the large distance between the p-n junction and the ohmic contacts at the wafer periphery (Fig. 3). In view of their importance, the effects of ambients on ϕ_s and s must be considered in work dealing with ambient-induced changes in reverse p-n junction characteristics, which have been hitherto attributed exclusively to channel formation.[24]

At extremely strong fields (about 10^6 volts/cm) one observes that the maximum of s is shifted (in terms of E) and the shape of the pattern changes appreciably, whereas, before this critical field is reached, an increase in field strength simply increases by smooth extension the part of the s *vs* ϕ_s curve that is being "modulated." In view of the particular significance of the maximum, whose position in terms of E is determined by the carrier capture cross sections and the charge in slow states (Secs. 4 and 5 below), one concludes that the ac field induces a net charge in the slow states thereby shifting the "operating point" on the s *vs* ϕ_s curve. The

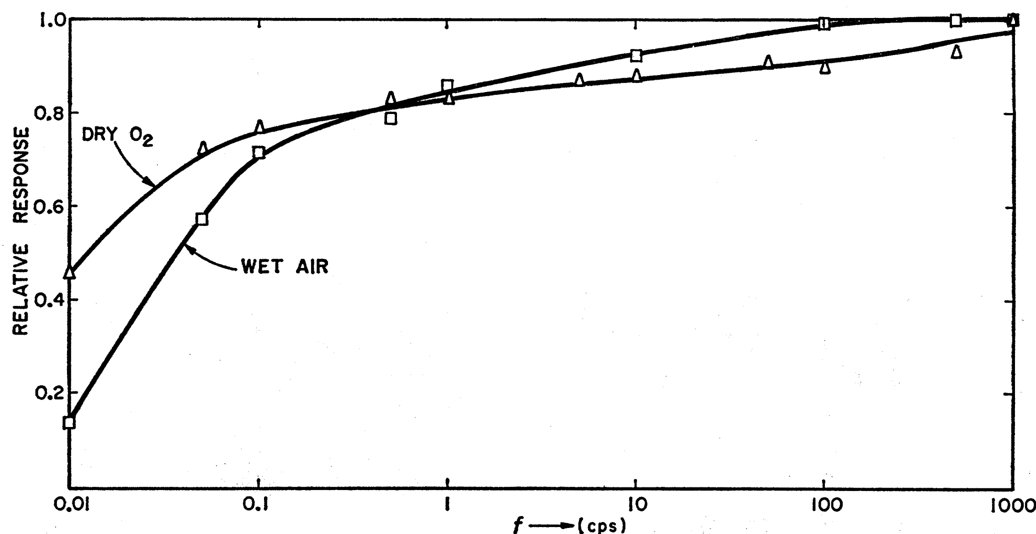

FIG. 10. The response of surface recombination to an applied field as a function of frequency. The vertical signal for given field is taken as unity at 1000 cps.

[24] J. J. Carasso and I. Stelzer, J. Chem. Soc., 3726 (1956).

charging up of the slow states by the ac field can be understood in view of the nonlinearity of the relation between E_s and ϕ_s (see Sec. 4 and also Fig. 11). The high fields must shorten the lifetimes of the states, as indicated from similar observations in conductivity measurements,[3] since the effects are not observed at all (instead of being smoothly reduced) at smaller fields and at the same frequency.

4. SURFACE RECOMBINATION, SURFACE POTENTIAL, AND EFFECTS OF FAST STATES

The surface parameters involved in the present work are the surface potential and the energy levels, distribution, and cross sections of the surface states that give rise to recombination. It is because of the direct involvement of the properties of these states in the experimental patterns that the present technique seems to be very promising for their investigation. These are called here "fast" states because of their small time-constants but are not to be *a priori* identified with the states involved in field effect[3,4] and channel measurements.[13,25]

From the Hall[26] and Shockley-Read[27] process, assuming a discrete level for the surface states, the surface recombination velocity is derived as[19–21]

$$s=\frac{(C_pC_n)^{\frac{1}{2}}N_t(n_0+p_0)}{2n_i}\left\{\cosh\left[\frac{q\phi_s}{kT}-\frac{1}{2}\ln\left(\frac{C_p}{C_n}\right)\right]+\cosh\left[\frac{E_t-E_i}{kT}-\frac{1}{2}\ln\left(\frac{C_p}{C_n}\right)\right]\right\}^{-1}, \quad (3)$$

where the symbols are defined as follows: C_p=probability, per state per unit time, for hole capture at the recombination centers (=cross section×thermal velocity); C_n=probability for electron capture; N_t=density of states (per unit surface area) that give rise to surface recombination; n_0, p_0=bulk carrier densities; and n_i=free carrier density for intrinsic material.

Curve A of Fig. 2 is a single-level curve as given by (3) with $(E_t-E_i)/kT=8$, $C_p/C_n=1$. We note briefly that the curves are symmetric about the maximum of s, which occurs at

$$q\phi_s/kT=\tfrac{1}{2}\ln(C_p/C_n), \quad (4)$$

and the values of ϕ_s at the $\frac{1}{2}$ maximum points of s are given by

$$\begin{aligned} q\phi_s&=E_t-E_i,\\ q\phi_s&=-(E_t-E_i)+kT\ln(C_p/C_n), \end{aligned} \quad (5)$$

in the approximation

$$\cosh[(E_t-E_i)/kT-\tfrac{1}{2}\ln(C_p/C_n)]\geqslant 2.$$

The total width of the curve at $\frac{1}{2}$ maximum s is, in this approximation,

$$\Delta(q\phi_s)=2(E_t-E_i)-kT\ln(C_p/C_n). \quad (6)$$

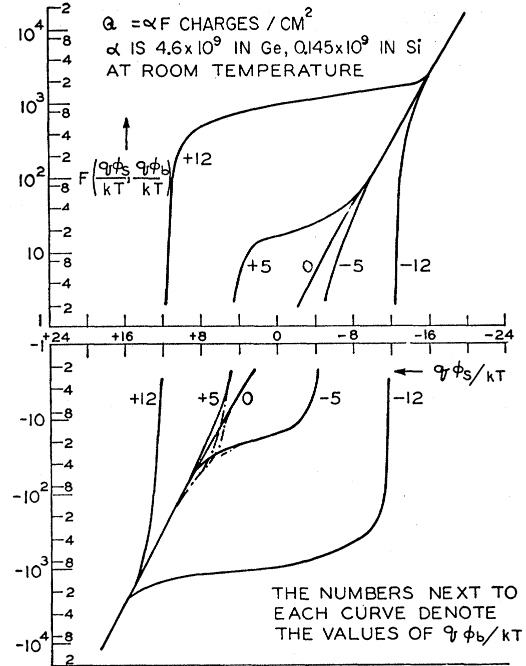

FIG. 11. Surface charge (or electric field) *vs* surface potential for various values of bulk potential. The full curves show the charge in the space-charge region alone. The dotted curves are obtained by addition to Q_{sc} of charge in fast states of density $5\times10^{10}/\mathrm{cm}^2$ located at $8kT$ above mid-gap. The distortions due to fast states are in this case small because of the low state density and large distance from mid-gap.

If more than one energy level for the recombination states is present, s will be given by a superposition of curves of the type (5). Curve B of Fig. 2 results from two levels with $(E_{t1}-E_i)/kT=2$, $C_{p1}/C_{n1}=1$, $(E_{t2}-E_i)/kT=12$, $C_{p2}/C_{n2}=1$, and s is given by the sum of two terms of the type (5), assuming that the two states act independently in the recombination process. The two levels are assumed to be equally effective for surface recombination. The presence of multiple levels tends to make the s curves vary less sharply with ϕ_s.

We note further that if the surface has a nonuniform ϕ_s ("patchy surface") or if the recombination states are not localized in a plane of given ϕ_s but distributed in distance from the surface, then again a rounding effect on s would result. The similarity of the effects of surface nonuniformity and a spread in the energy levels is apparent from the more or less equivalent way in which ϕ_s and surface state energies enter expression (3).

At the extreme where there is a continuous set of energy levels, distributed over the forbidden band, s can be obtained by integration of the product of (3) and the desired distribution function over this energy interval. The meaning of N_t given above has to be changed

[25] R. H. Kingston, Phys. Rev. **98**, 1766 (1955).
[26] R. N. Hall, Phys. Rev. **83**, 228 (1951); **87**, 387 (1952).
[27] W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952).

from number of states per unit surface area to number of states per unit area per unit energy. For a continuous distribution with constant density of surface states one has

$$s=\frac{(C_pC_n)^{\frac{1}{2}}N_t(n_0+p_0)}{2n_i}\int_{E_c}^{E_v}\left\{\cosh\left[\frac{q\phi_s}{kT}-\frac{1}{2}\ln\left(\frac{C_p}{C_n}\right)\right]+\cosh\left\{\frac{E_t-E_i}{kT}-\frac{1}{2}\ln\left(\frac{C_p}{C_n}\right)\right\}\right\}^{-1}dE_t. \quad (7)$$

It is assumed that the cross sections are constant throughout the forbidden band. One of course can add terms like (7), each with its own density, cross sections, and distribution. More general forms of surface integrals have been discussed by Garrett and Brattain.[21]

The integral of (7) can be approximately evaluated (see Appendix) to give, for $2|q\phi_s/kT-\frac{1}{2}\ln(C_p/C_n)| < (E_c-E_v)/kT$,

$$s=\frac{(C_pC_n)^{\frac{1}{2}}N_t(n_0+p_0)}{n_i}\times\ln\left\{2\cosh\left[\frac{q\phi_s}{kT}-\frac{1}{2}\ln\left(\frac{C_p}{C_n}\right)\right]+1\right\}\times\left\{\cosh\left[\frac{q\phi_s}{kT}-\frac{1}{2}\ln\left(\frac{C_p}{C_n}\right)\right]\right\}^{-1}. \quad (8)$$

The quantity s, as given by (8) for $C_p=C_n$, is plotted in Fig. 2 (curve C). One notes that the position of the maximum in a continuous distribution is identical with that of a single level. The curve, however, is now much narrower and the plateau region, characteristic of a single level, is absent.

The additional relationships required for the interpretation of the results are those connecting the surface potential with the electric charge at the surface. This charge is due either to the bending of the bands or is externally induced. In our case, the combined effects of both have to be considered. Solution of the Poisson equation in the space-charge region yields,[28] in the case of no external field,

$$Q_{sc}^{(0)}=\pm\left(\frac{\epsilon}{\pi}n_ikT\right)^{\frac{1}{2}}\left[\left(\frac{q\phi_b-q\phi_s}{kT}\right)\sinh\frac{q\phi_b}{kT}+\cosh\frac{q\phi_s}{kT}-\cosh\frac{q\phi_b}{kT}\right]^{\frac{1}{2}}, \quad (9)$$

where $Q_{sc}^{(0)}$ is the charge per unit area in the space-charge region and ϵ the dielectric constant of the semiconductor. Q_{sc} is negative for n-type surfaces (positive ϕ_s). Note that $Q_{sc}=0$, if $\phi_b=\phi_s$, as expected when the bands are flat up to the surface. The bracketed part of (9) is designated as $F(q\phi_s/kT, q\phi_b/kT)$. This function is plotted in Fig. 11. Q_{sc} per cm^2 for germanium and silicon can be obtained by multiplying F by $4.6q\times10^9$ and $0.145q\times10^9$. These numerical factors apply at room temperature. The values appropriate at other temperatures can be derived from the T dependence of the term that multiplies the bracket in (9). The field E_s at the surface edge of the space-charge region is given by $4\pi Q_{sc}/\epsilon$.

When an external field is applied, the total charge is

$$Q_{tot}=Q_{sc}^{(0)}+Q_{ind}, \quad (10)$$

where Q_{ind} is the externally induced charge as determined by the measured condenser capacity and the applied voltage. The new value of ϕ_s is given by (9) with Q_{sc} replaced by Q_{tot} from (10). In (10) it is assumed that the charge in slow states does not have time to change during the ac cycle.

In transforming the abscissa of the experimental patterns from Q_{ind} to ϕ_s, expressions (9) and (10) are the appropriate ones to be used, along with the relations developed below for determining the equilibrium value of the surface potential. In (9) and (10) the effects of slow states, applied fields, and the space-charge region are taken into account. The fast states, whose charge changes when ϕ_s is close to their level, have been so far neglected. The effect of fast states can be explicitly introduced in the theory by using for their charge an expression of the form

$$Q_{fs}=-qN_t\left[1+\exp\left(-\frac{q\phi_s}{kT}+\frac{E_t-E_i}{kT}\right)\right]^{-1}. \quad (11)$$

Their influence would result in some distortion of the relations of Q_{sc} to ϕ_s when $q\phi_s$ becomes comparable to (E_t-E_i). The modifications of the curves introduced by fast states with $N_t=5\times10^{10}$/cm^2 and $(E_t-E_i)/kT=8$ are shown by the dotted parts of the curves in Fig. 11. One notes that the distortions are similar to those introduced to the intrinsic curve by doping, but smaller in magnitude. The charge given by (11) is to be added to (9) and (10) above to yield the expression for Q_{tot}. A considerable amount of information on fast states has been reported in the literature[3,4,13,15] from conductivity type measurements. There is no detailed agreement among the various sources as to the energy, distribution, and density of the states. The charge change in fast states observed here is within the range of those reported earlier, but on the lower magnitude side.

5. A NEW METHOD FOR DETERMINING THE SURFACE POTENTIAL

The surface potential is a rather elusive quantity for direct experimental determination. Its values have been inferred from several types of measurements including

[28] R. H. Kingston and S. F. Neustadter, J. Appl. Phys. 26, 718 (1955).

(1) contact potential differences,[11] (2) surface conductance in ambient cycles,[21,29] (3) surface conductivity in field-effect,[1,3–5] and channel measurements[13,25] and (4) changes in surface barrier height by low-[21] and high-intensity light signals.[30] The agreement between these sources has been so far only qualitative, which is not surprising in view of the diversity in experimental approach, and also of the several assumptions that are necessarily involved, not to mention the ever-present question of whether the surface treatments, handling, etc. are identical in the different laboratories.

A new method will be outlined here for approximately determining ϕ_s from measurements of surface recombination velocity in terms of an applied field. One utilizes the fact that the maximum of s, occurring at $q\phi_s=\frac{1}{2}kT\ln(C_p/C_n)$ [see (3) above], provides an absolute reference point from which the equilibrium value of ϕ_s can be evaluated. The total effect of the applied field and the equilibrium surface field at s maximum is such that the surface potential has the above value [which is close to zero if $\frac{1}{2}\ln(C_p/C_n)$ is small]. The equilibrium E_s (from which the zero-field value of ϕ_s can be evaluated) can be obtained from the value of the applied field at that point. For small values of $\frac{1}{2}\ln(C_p/C_n)$, E_s is closely equal and opposite to the applied field at s maximum in the case of high-resistivity samples if the dielectric constant of the outside medium is equal to that of the semiconductor.

$$Q_s^{(0)}+Q_{\text{induc. at } s\max}=\pm\left(\frac{\epsilon}{\pi}n_ikT\right)^{\frac{1}{2}}\times\left[\left(\frac{2q\phi_b-kT\ln(C_p/C_n)}{2kT}\right)\sinh(q\phi_b/kT)+\cosh[\tfrac{1}{2}\ln(C_p/C_n)]-\cosh(q\phi_b/kT)\right]^{\frac{1}{2}}. \quad (12)$$

The equivalent field relations can be used if one measures the field. In (12) the unknown quantities are $Q_s^{(0)}$ (or $E_s^{(0)}$) and $\frac{1}{2}\ln(C_p/C_n)$. Information on this last can be obtained from the width and other features (half-maximum points, etc.) of the experimental patterns (see Sec. 6 below) but even if this term in the bracketed part of (12) is completely neglected, only negligible error will result since $\frac{1}{2}\ln(C_p/C_n)$ will be quite small despite the possibility of a large value for the ratio C_p/C_n.

The value of E_s given by (12) can then be used to evaluate the zero-field value of ϕ_s using (10) above. Once this value of E_s has been determined, the abscissa of patterns such as those in Figs. 4–5 can be changed from E to ϕ_s. The values of ϕ_s, for all other values of the applied field, can then be determined from Q_{ind} and $Q_s^{(0)}$. The above procedure can be understood most conveniently by use of Fig. 11. One reads the value of the ordinate that corresponds to the value $\frac{1}{2}\ln(C_p/C_n)$ for the abscissa. Subtracting from this value of the ordinate the value of Q applied at $s_{\max}$, one obtains $Q_s^{(0)}$ (and $E_s^{(0)}$). The value of ϕ_s corresponding to $E_s^{(0)}$ or $Q_s^{(0)}$ is the zero-field value of the surface potential. To each value of Q of the s vs Q curves one adds $Q_s^{(0)}$ and obtains Q_{tot}. The corresponding value of ϕ_s is the proper one that corresponds to the value of Q.

The effects of fast states are taken into account in this scheme as follows: One adds to the ordinate in Fig. 11 the charge given by (11). [The information required in (11) is either approximated from the extent (in terms of Q) of the distortion on s and consistency considerations, as in the present work, or in general has to be supplied more accurately by an independent experiment.] One then obtains a modified curve of Q_{tot} (or E_{tot}) vs ϕ_s which is used in the transformation of Q to ϕ_s and determination of ϕ_s at zero-field in the manner indicated above.

The requirement for application of this method is that the maximum of s be observed. In semiconductor surfaces this is always possible, at least in principle, by use of strong fields. As indicated above for germanium and silicon surfaces, this has been achieved with fields of about 10^5 volts/cm.

6. INTERPRETATION OF RESULTS AND DISCUSSION

The experimental patterns of s vs Q (or E) can be transformed to those of s vs ϕ_s by use of (9), (10), and (12) above modified by the addition of Q_{fs} to Q_{sc} to form Q_{tot}. Figure 12 shows the results obtained from data on n-type germanium. One procedure that can be followed in deriving the curves of s vs ϕ_s from the observed patterns of s vs Q_{ind} will be briefly outlined here: A value is assumed for the ratio C_p/C_n. In the curves of Fig. 11 (using the dotted-line portions to take into account charge change in fast states) the value of Q at $q\phi_s/kT=\frac{1}{2}\ln(C_p/C_n)$ is that of Q_{tot} at $s_{\max}$. Subtraction of the induced Q at $s_{\max}$ yields the equilibrium $Q_s^{(0)}$ and the corresponding $\phi_s^{(0)}$. Addition of $Q_s^{(0)}$ to Q_{ind} at each point of the s vs Q_{ind} curves yields Q_{tot} at each point and the corresponding ϕ_s is obtained from Fig. 11. If the resulting curve is identical or close to a theoretical one of s vs ϕ_s whose value of C_p/C_n is that assumed above, then the energy level associated with this last curve must be that of the recombination states. If a different value for C_p/C_n is indicated, the procedure is repeated until the theoretical curve and that derived experimentally are in agreement.

The conspicuous difference in shape between the curves of s vs Q and those of s vs ϕ_s (Fig. 12) stems from the pronounced nonlinearity of the relation between ϕ_s and the surface fields as can be seen from (9) above and also Fig. 11. The curve compares well with those expected from theory involving single levels for the fast states. From Fig. 12 one concludes that (E_t-E_i)

[29] S. R. Morrison, J. Phys. Chem. 57, 860 (1953).
[30] E. O. Johnson, Bull. Am. Phys. Soc. Ser. II, 2, 66 (1957); Phys. Rev. 111, 153 (1958).

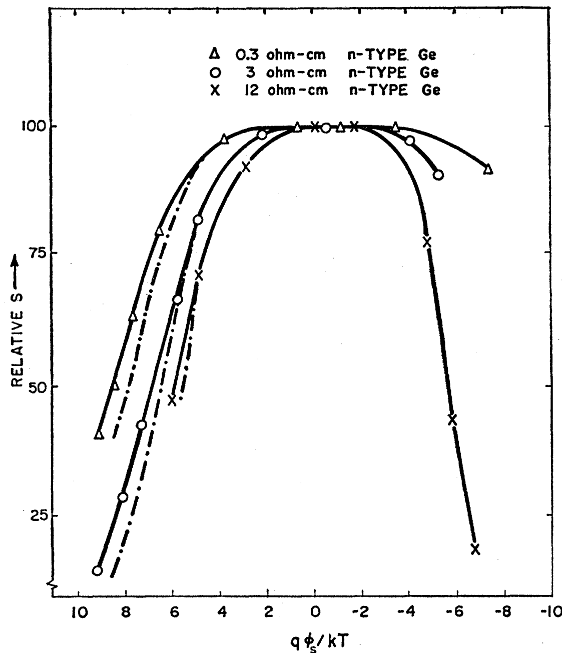

FIG. 12. Curves of s *vs* ϕ_s obtained from single patterns of s *vs* applied field. The full curves are obtained by taking into account, in the transformation of Q (or E) to ϕ_s, the space charge alone. The dotted parts are obtained by taking in addition into account the charge change in fast states observed in the present work.

equals $\pm(6\ kT$ to $9\ kT)$, and $\ln(C_p/C_n)\sim 0$. The uncertainty in the sign is removed by the observation of small distortions of the type of Fig. 9 due to charge change in fast states. Their occurrence at the inflection point of the curves identifies them with the recombination states, as discussed in Sec. 3, and the fact that they occur on the positive side of ϕ_s indicates that (E_t-E_i) is positive. Both the sign and magnitude of the energies is in good agreement with the results of Many *et al.*[8] Likewise the width of the 12-ohm-cm curve is close to that reported, for corresponding resistivity, by Brattain and Garrett.[21]

Similar results with low-resistivity (0.1 ohm-cm) p-type silicon yield levels at $+0.4$ or -0.4 ev from the middle of the forbidden band. Because of smaller sensitivity, the results in Si are not as accurate as those in Ge. A level at -0.46 ev had been earlier indicated from channel measurements[13] in n-type silicon.

In Fig. 12 the full curves are the ones one derives by taking into account only space charge. One notes that the difference with the dotted ones, where the charge change in fast states is taken into account, is not large. This is a result of the low density of the states (5×10^{10}) and their relatively large distance from mid-gap (6-9 kT units).

The values of ϕ_s observed in Ge treated in CP_4 and similar etches lie between the extremes of ± 0.25 v. In Si larger values in the range of ± 0.5 v are observed. Variations of ϕ_s over the Bardeen-Brattain cycle of ambients are within the above limits. These results are in agreement with surface photovoltage measurements made by Johnson in this laboratory.[30]

That no other distortions are presently observed than those due to the recombination states does not entirely remove the possibility of other charge changes in fast states. Such changes would escape observation if the states were continuously distributed or if the surfaces were inhomogeneous. This last is illustrated by the fact that the distortions of the type of Fig. 9 are not observed in all our patterns. The distortion is not large so that it could be obscured by surface or field inhomogeneity. This may well be the reason that no such discrete level distortions have been observed in the comparable oscilloscope patterns of field-effect conductivity modulation.[3]

The assignment of patterns of the type of Fig. 8 to two-level recombination curves rather than charge change in fast states is based on the extreme flatness of the distortion. Such a pattern can be produced by the superposition of two Shockley-Read type curves with their broad maxima. Calculations show that the second level in Fig. 8 must be located more than 11 kT units from mid-gap.

That the curves in Fig. 12 are approximately centered about $\phi_s=0$ indicates that $C_p\sim C_n$. Values of C_p/C_n reported from other sources[8,15,21] are in the range of 9 to 150. The accuracy of the present work is such that cross-section ratios at the order of 10 are not excluded.

The variation of the width of the curves of Fig. 12 with resistivity is not expected from levels with energies independent of resistivity and located at a definite plane (presumably the semiconductor-oxide interface). The question arises as to the extent of contributions from recombination centers in the space charge region to what one measures as surface recombination velocity. These contributions will vary with ρ because of the appreciable dependence of the extent of the space-charge region on resistivity. In a surface modulation experiment, of course, one changes not simply ϕ_s but the entire surface space-charge region.

Figure 13 shows the exact shape and extent of the space-charge regions for $\phi_b=0$, 3, and 5 corresponding in Ge to intrinsic material, $\rho=3$ ohm-cm and $\rho=0.5$ ohm-cm, respectively. These curves are obtained by numerical integration of the Poisson equation in the space-charge region.[31] From the appreciable difference of the curves, contributions to s from recombination states in the space-charge region would be more significant in intrinsic than heavily doped material. From Sec. 4 above the results of such contributions would be a narrowing of the curves, since a distribution of levels in distance within the semiconductor is more or less equivalent to a spread of the levels across the band-gap.

The curves of s in Fig. 12 are in agreement with this picture in that the purer samples exhibit a narrower

[31] G. C. Dousmanis and R. C. Duncan, Jr., J. Appl. Phys. (to be published).

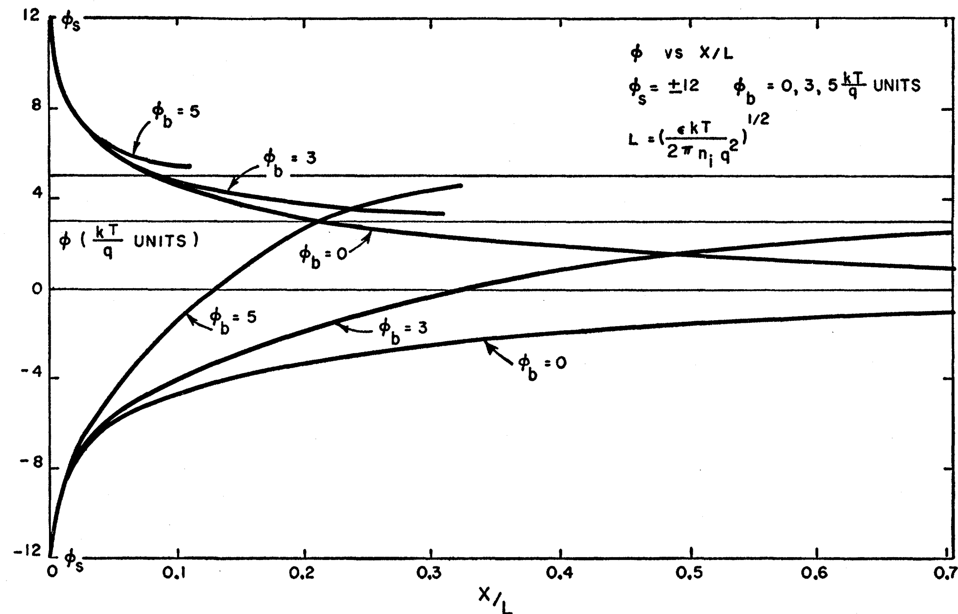

FIG. 13. Shape and extent of the surface space-charge region. The electrostatic potential is shown as a function of distance inside the semiconductor. The distance is measured from the surface edge of the space-charge region.

curve than the more heavily doped ones. If the difference in the three curves is to be solely attributed to this cause, the contributions to s from the space-charge region must be appreciable. In such a case the more correct value of (E_t-E_i) for the interface states would be that given by the width of the curve taken with the more heavily doped samples. Additional work will be required to establish the exact contribution to s from traps in the space-charge region, as well as differences in the curves arising from undetected charge changes in any continuously distributed fast states, etc.

Besides the shape of the s *vs* ϕ_s curves, the energies of the recombination states influence the absolute value of s, and even more drastically because of the hyperbolic relationship in (3) above. With $(E_t-E_i) = 7\ kT$ and $s_{\max}\sim 500$ in 3-ohm-cm Ge, one derives a value of 6×10^{-15} cm² for the effective cross section $(\sigma_p\sigma_n)^{\frac{1}{2}}$. This is close to the value 2×10^{-15} derived recently from high-frequency field-effect conductivity measurements.[16]

The reasonable agreement of the experiment with theory (Fig. 12 and curve A, Fig. 2), as far as the shape of the curves is concerned, confirms the Hall and Shockley-Read mechanism for the recombination process as applied in this case to the surface. No attempt will be made here to identify the recombination centers as foreign or impurity atoms, or as structural imperfections at the semiconductor-oxide interface.

7. CONCLUSION

The effects of electric fields on surface recombination provide a convenient means of examining the type of semiconductor surface one obtains with a given chemical or other treatment. The effects of ambients and the extent of stability of surface potential and recombination velocity can also be examined. The behavior of s with field and ambient yields direct quantitative information on the energy levels and carrier capture cross sections of the surface states that give rise to surface recombination. Observation of a maximum of s in terms of an applied field yields a reference point from which the zero-field value of the surface potential is determined.

The results so far indicate that information on aspects of the surface such as surface recombination states as well as charge change in fast states, the slow states and their time-constants, the potential barrier height and the behavior of the space-charge region, can be obtained from studies of surface recombination. This surface parameter is here used in place of surface conductivity that was earlier the main tool for semiconductor surface studies. A disadvantage of the surface recombination method is its inability to detect some charge changes in fast states such as those of continuous distributions, for example, hence it is apt to overestimate ϕ_s. The surface conductivity technique, because of some reduction in mobility near the surface is likely to underestimate ϕ_s. It is gratifying to see that despite these differences the conclusions from the two approaches are in fair agreement.

The observation of variation of the surface recombination curves with resistivity raises the question of contributions to what is measured as surface recombination velocity from recombination states in the surface space-charge region or, less likely, a direct dependence of the interface state energies on impurity concentration. In addition to these the problem of surface inhomogeneity seems to require further examination.

8. ACKNOWLEDGMENTS

The author takes pleasure in acknowledging substantial contributions from E. O. Johnson of this laboratory to both the experimental and conceptual aspects of this work. The experiments have also benefited from the technical aid of F. H. Corregan, Jr.

APPENDIX. SURFACE RECOMBINATION INTEGRAL FOR A UNIFORM DISTRIBUTION OF LEVELS

An approximate treatment is needed for the evaluation of integral (7). By use of the contracted notation

$$A=[(C_pC_n)^{\frac{1}{2}}N_t(n_0+p_0)kT]/2n_i,$$
$$u=(E_t-E_i)/kT-\tfrac{1}{2}\ln(C_p/C_n),$$
$$v=q\phi_s/kT-\tfrac{1}{2}\ln(C_p/C_n),$$

the integral takes the form

$$s=A\int_{(E_v-E_i)/kT-\frac{1}{2}\ln(C_p/C_n)}^{(E_c-E_i)/kT-\frac{1}{2}\ln(C_p/C_n)}[\cosh u+\cosh v]^{-1}du. \quad \text{(A-1)}$$

The interval is divided into the regions of $u<0$ and $u>0$ and $\cosh u$ is replaced by $(e^u+e^{-u})/2$. The smaller of the two exponential terms is neglected in the appropriate region of u. The resulting forms of the type

$$\int[e^x+\text{const}]^{-1}dx$$

can be integrated directly. Thus one obtains

$$s=\frac{A}{\cosh v}\ln\left[\frac{(2\cosh v+1)^2e^{(E_c-E_v)/kT}}{4\cosh^2v+e^{(E_c-E_v)/kT}+\cosh v\cosh[(E_c-E_v)/kT-\frac{1}{2}\ln(C_p/C_n)]}\right]. \quad \text{(A-2)}$$

The terms in $\cosh v$ in the denominator can be neglected by comparison with $e^{(E_c-E_v)/kT}$. Thus

$$s=\frac{2A}{\cosh v}\ln(2\cosh v+1), \quad \text{(A-3)}$$

which is formula (8) in the text. (A-2) and (A-3) are most accurate at large values of v. For $v=0$, one obtains from the approximate expression (A-3)

$$s=2A\ln 3. \quad \text{(A-4)}$$

To estimate the accuracy of the result, (A-4) will be compared with a more exact answer that can be obtained in this case. For $v=0$, (A-1) can be immediately integrated to give

$$s=A\left[\tanh^{-1}\left(\frac{u}{2}\right)\right]_{(E_v-E_i)/kT-\frac{1}{2}\ln(C_p/C_n)}^{(E_c-E_i)/kT-\frac{1}{2}\ln(C_p/C_n)}.$$

Since E_c-E_i is much larger than kT, for reasonable values of C_p/C_n, the limits of integration can be replaced by $\pm\infty$. Hence

$$s=2A \quad \text{at} \quad v=0. \quad \text{(A-5)}$$

Comparison of (A-5) with (A-4) shows that the approximate formula at $v=0$ differs from the more exact answer by the factor ln3, or is accurate to within 10%. This is the maximum error in (A-2), and (A-3), since the approximation improves very rapidly as v increases. As expected from the type of approximation involved in their derivation, (A-2) and (A-3) overestimate the values of s.

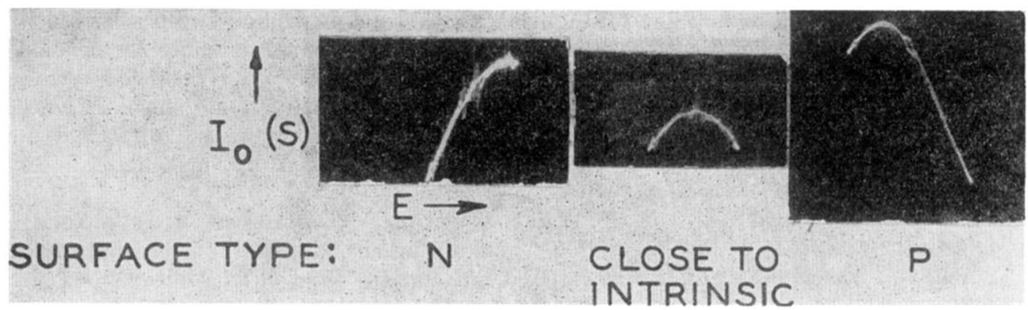

FIG. 4. Patterns of I_0 (or surface recombination velocity) *vs* applied field or induced charge in 0.3-ohm-cm *n*-type germanium and relation to surface type. The horizontal and vertical gains are different in each case. The frequency is 60 cps.

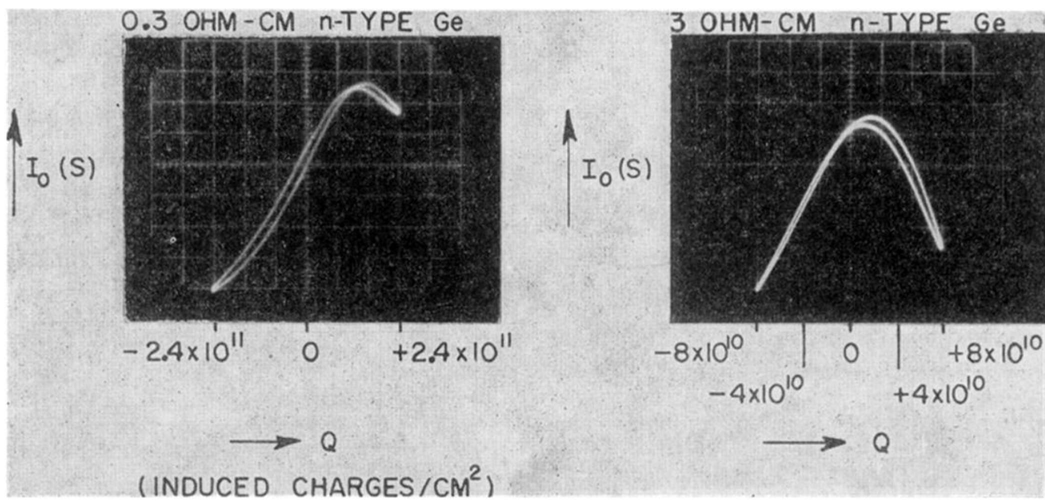

FIG. 5. Patterns of I_0 (or surface recombination) *vs* induced charge Q in 0.3- and 3-ohm-cm *n*-type germanium.

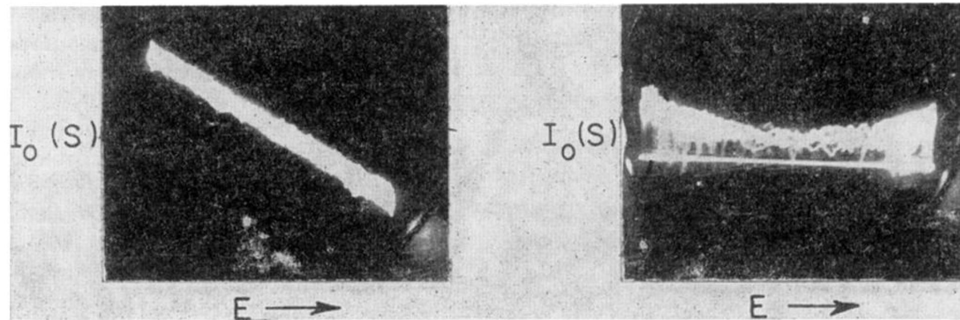

FIG. 6. Patterns of I_0 (or s) *vs* applied field E in 0.1-ohm-cm p-type Si. The maximum of s is here shown as a minimum because of the reversed polarity of I_0 with respect to that of the other figures. For comparison an horizontal line is shown on the oscilloscope.

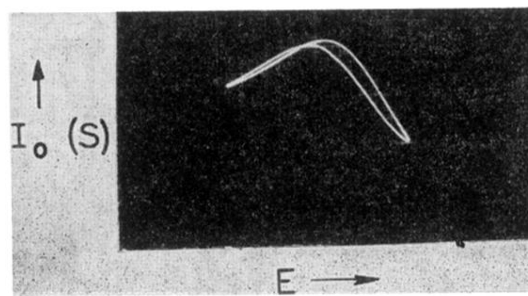

FIG. 7. An asymmetric pattern of I_0 (or s) *vs* E obtained in some cases with 12-ohm-cm n-type germanium.

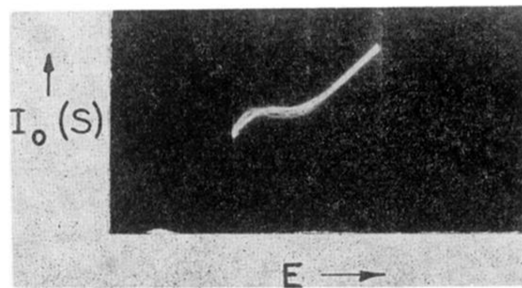

FIG. 8. I_0 (or s) *vs* E obtained with the sample of Fig. 7 in a wet air atmosphere. This pattern is a continuation far to the left (or n type) side of Fig. 7. The vertical gain is ten times that of Fig. 7. The additional structure here, and the asymmetry of Fig. 7, show presence of a second energy level for the surface recombination states.

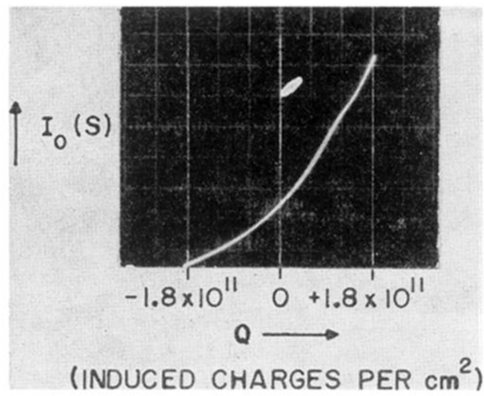

FIG. 9. A distortion in the pattern of s *vs* applied field attributed to charge change in fast states of discrete energy. That it occurs at the inflection point of the curve shows that the states are the same with the ones responsible for surface recombination. Since it occurs on the n-type (positive ϕ_s) side of the curve it indicates that the levels are above rather than below mid-gap. From the horizontal extent of the distortion one concludes that the charge change involved is about $5q \times 10^{10}/\text{cm}^2$.