

Slow Capture of Holes and Electrons by Surface States on Germanium and Silicon at Low Temperatures

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Field-effect decay curves at temperatures the order of liquid nitrogen are presented for *n*- and *p*-type germanium and for *p*-type silicon. A strongly asymmetric decay is observed, depending upon whether the induced charge is positive or negative. The decay is strongly influenced by illumination, temperature, and magnitude and sign of the field. Injected minority carriers also affect the decay rate. It is suggested that the trapping centers involved are the fast states, or recombination centers at the surface. After a disturbance of the charge in these states the approach to steady state is slow due to the limited supply of minority carriers arriving at the surface. The results observed are compared with a model which takes surface barrier effects into consideration and are found in reasonably quantitative agreement.

INTRODUCTION

IT has been found that a very slow decay phenomenon is associated with the surface states of germanium and silicon at temperatures the order of liquid nitrogen. If the charge in these states is disturbed from its steady-state value, as in a field effect measurement, the rate of the return to steady state may be very low. The rate depends upon several parameters, including the temperature, the illumination intensity, and the amount and sign of the disturbance.

It will be suggested below that the surface states under observation in these experiments are the surface recombination centers. If this hypothesis is correct, the decay effects observed should thus be related to surface recombination rates. This phenomenon may thus be analogous to the slow recombination at bulk recombination centers which has been observed by many investigators on germanium¹ and silicon.^{2,3} In the case of the bulk, slow recombination models have been proposed by Haynes and Hornbeck^{2,3} and Morrison⁴ to explain the behavior. With the latter model, one might expect an analogous occurrence at the surface, for the model is based upon barrier effects, and the barrier around dislocations in the bulk material has many characteristics in common with the surface barrier.

EXPERIMENTAL RESULTS

Field-effect measurements using the potentiometer probe method were made on slabs of material the order of 0.2 mm thick. The contacts were on the opposite face from the metal plate used for the application of the electric field. The qualitative behavior did not appear to depend critically on the surface etch treatment, similar results being obtained using varying mixtures of HF-HNO₃ etchant, and antimony etch (4HF:2HNO₃:4H₂O + 0.2 mg/cc SbCl₃). Some attempts were made, particularly when measuring the *n*-type germanium for comparison with theory, to reduce the heterogeneity of the

surface barrier. These attempts involved procedures such as a thorough desiccation of the sample, and a thermal treatment at about 250°K (to establish slow state equilibrium at this temperature, before cooling in helium to liquid nitrogen temperature). Also, care was taken to provide uniform illumination over the surface of the sample, to reduce this form of heterogeneity. It was found that consideration of such details considerably altered the decay characteristics in quantitative examination (causing the slow decay, defined below, to become more linear with time at high disturbances and the lifetime for fast and slow decay to become more nearly equal for low disturbance, as predicted by the theory to follow).

The decay curves were observed by feeding the output of the potentiometer into a dc amplifier and thence to a recorder. The sample was illuminated on the side opposite to that used for field-effect measurements by light which had passed through a filter to remove infrared.

The measurements to be described below all involve the observation of the changes in conductance following the application of an electric field normal to the surface. Figure 1 shows the type of behavior almost always observed in the measurements on *n*-type germanium. When the field is applied, the conductance abruptly changes due to the added charge induced by the field. If the field is negative (the metal plate negative, the germanium positive), the conductance, following the abrupt decrease, slowly rises during the period the field is applied, to a new steady-state value (times t_1 to t_2 in Fig. 1). When the negative field is removed, at t_2 , the conductance very quickly returns to the zero field steady state value. If a positive field is applied, as at t_3 , the conductance rapidly attains its new steady-state value. However, when the positive field is removed, the conductance overshoots the value for zero field, as at t_4 in Fig. 1, then slowly decays back.

In the following discussions the decay observed after making the field more negative (with *n*-type germanium) will be referred to as the "slow decay." The approach to steady state after making the field more positive will be termed the "fast decay." The fast-decay portions of

¹ Fan, Navon, and Gebbie, *Physica* **20**, 855 (1954).

² J. R. Haynes and J. A. Hornbeck, *Phys. Rev.* **90**, 152 (1953).

³ J. A. Hornbeck and J. R. Haynes, *Phys. Rev.* **97**, 311 (1955).

⁴ S. R. Morrison, *Phys. Rev.* **104**, 619 (1956).

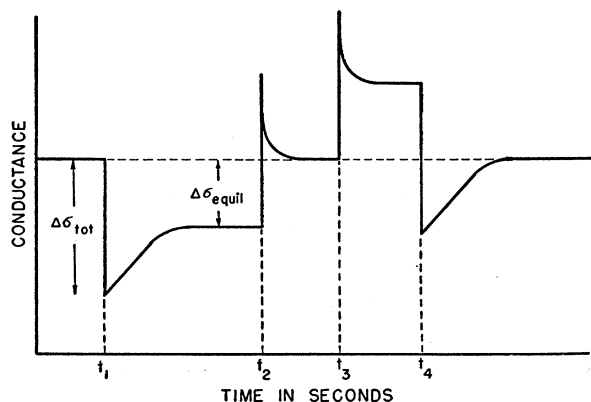


FIG. 1. A typical field-effect decay on *n*-germanium. A negative field is applied at t_1 , and removed at t_2 . A positive field is applied at t_3 , and removed at t_4 .

Fig. 1 have an initial amplitude about equal to the slow decay, but the initial portion of the decay is not generally observed on our chart recorder, as this initial portion generally lasts only a fraction of a second. All that is observed on the recorder is the tail of the fast decay. The characteristics of both the slow and the fast decays of Fig. 1 are found to be dependent on the field strength, the illumination of the sample, and on the temperature. The effect of these parameters will be discussed under separate subheadings below.

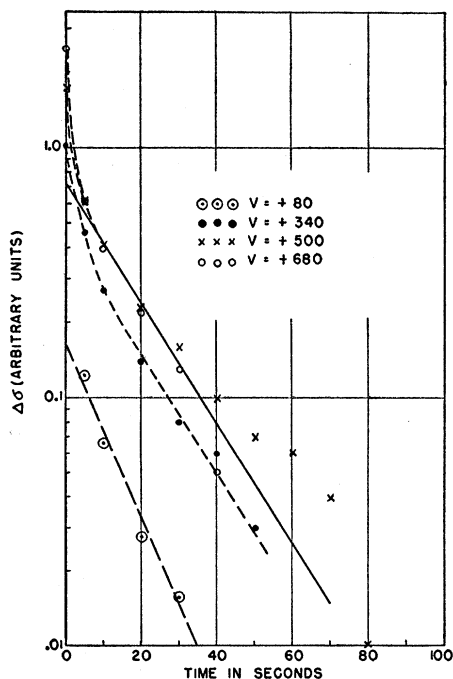


FIG. 2. Fast decay on *n*-type germanium. A positive field is applied. The decay curve approaches the solid line for fields with $V > 350$ volts and $t > 10$ seconds.

Effect on the Decay Characteristics of an Electric Field Variation

In Fig. 2 is shown a typical plot of the conductance change as a function of time for the fast decay with 15 ohm-cm *n*-germanium as observed on the recorder. The field is applied at time zero; $\Delta\sigma = |\sigma - \sigma_\infty|$, where σ_∞ is steady-state conductance with the field applied. Here the applied field effect voltage is recorded as a parameter, as the absolute field strength could not be accurately determined with the experimental arrangement used. The temperature is the order of liquid nitrogen, the illumination intensity a convenient arbitrary value. It is observed that for fields greater than that produced by about 350 volts, the portion of the decay

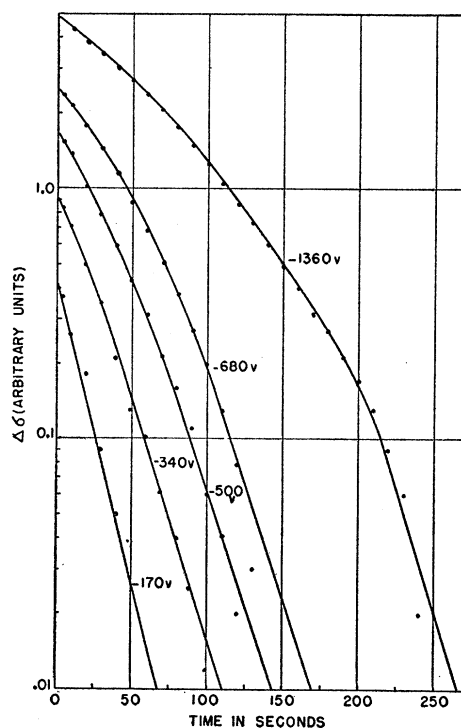


FIG. 3. Slow decay on *n*-type germanium. A negative field (metal plate negative, germanium positive) is applied.

characteristic illustrated becomes independent of voltage. Also shown in Fig. 2 is the value of the conductance change at time zero to illustrate that the apparent lifetime is very low near time zero. The method of obtaining this value will be discussed below. The unit of conductance change used in this figure and to Fig. 6 corresponds to the change due to the addition of 1.6×10^9 electrons per cm^2 in the conduction band.

Figure 3 is a plot of the conductance change with time for the corresponding slow decay, when a negative field is applied. It is observed that the effective "lifetime" is very high near time zero, the conductance varying almost linearly with time. However, at large time, or, more specifically, when the conductance change is small,

the "lifetime" decreases and the decay becomes more exponential.

Thus, comparing Figs. 2 and 3, when $\Delta\sigma$ is small, the apparent lifetime is about the same for both the fast and slow decays. Only for large $\Delta\sigma$ does the asymmetry arise, in which condition the "lifetime" is small for the fast decay, large for the slow decay.

A plot of the fast decay where $\Delta\sigma$ is plotted as a function of the logarithm of time, is shown in Fig. 4. A display of the results in this form enables a more detailed examination of the decay characteristics at very short times. The method used to obtain the values for times less than 1 second in this plot is as follows. We shall use Fig. 1 in the discussion. If we shorten the time $t_4 - t_3$ sufficiently (using positive pulses), the overshoot at t_4 is decreased. This is interpreted as indicating that during the pulse time steady state is not reached, and the surface levels have only captured a charge corresponding to the overshoot. Thus by varying the pulse length the

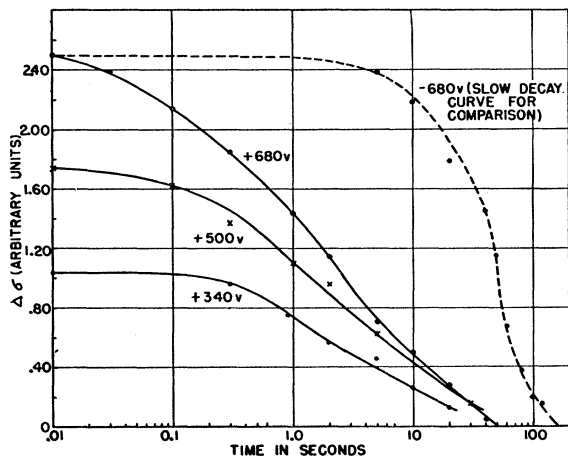


FIG. 4. Fast decay on *n*-type germanium. The method by which data for $t < 1$ are obtained is explained in the text.

amount of charge capture during the fast decay can be plotted as a function of time, as in Fig. 4.

Effect on the Decay Characteristics of a Variation in Light Intensity

The variation of the slow-decay characteristics of *n*-germanium with illumination intensity is shown in Fig. 5. Here no absolute value was determined for the illumination intensity, and the intensity is expressed in terms of the photoconductance, that is the fractional change in conductance due to the illumination. The field used was that corresponding to 1000 volts on the field-effect plate. It is observed that the decay is very sensitive to illumination, and the rate increases rapidly with a very small intensity applied. The corresponding variation of the fast decay with illumination intensity is shown in Fig. 6.

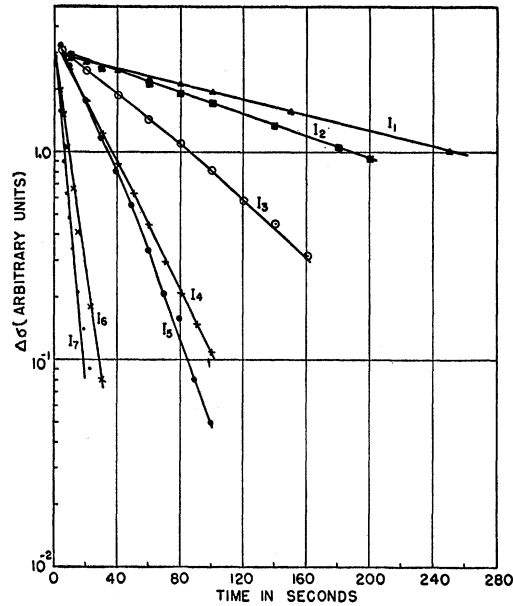


FIG. 5. Slow decay on *n*-type germanium vs illumination intensity. For illuminations I_1 to I_7 , the corresponding values of the photoconductance $\Delta\sigma/\sigma_0$ are 3.3×10^{-4} , 4.5×10^{-4} , 6.8×10^{-4} , 1.0×10^{-3} , 1.1×10^{-3} , 1.5×10^{-3} , and 1.7×10^{-3} , respectively.

Effect on the Decay Characteristics of a Temperature Variation

It is observed in Fig. 3 that, although the slow-decay curves are nonexponential, they are close enough to exponential to be approximated by a time constant τ ,

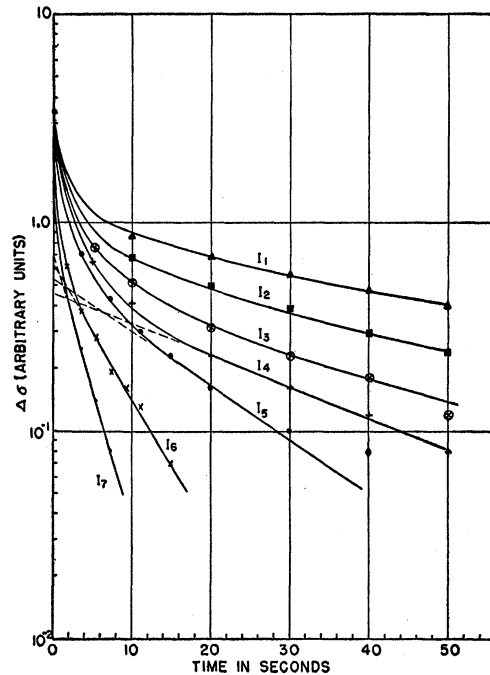


FIG. 6. Fast decay on *n*-type germanium vs illumination intensity. The illumination intensities are recorded with Fig. 5.

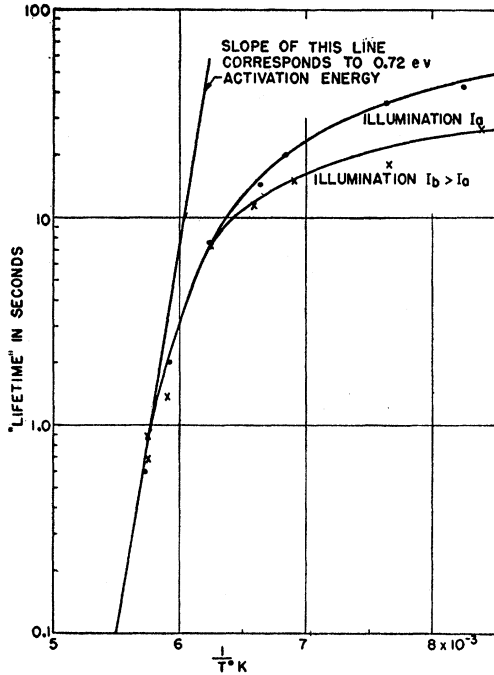


FIG. 7. Temperature dependence of the decay constant; n -type germanium, $V = 380$ volts.

particularly for low $\Delta\sigma$. The variation of this time constant τ with temperature is shown for two illumination intensities I_a and I_b , where $I_b > I_a$, in Fig. 7. The applied voltage was 380 volts. It is found that as the temperature increases, the time constant decreases, and at relatively high temperature, the illustrated variation in illumination intensity has no observable effect. It is also found that the activation energy corresponding to the slope of the $\log\tau$ vs $1/T$ curve appears to approach a value at high temperature close to the value of the energy gap in germanium.

It is observed that the decay constant is insensitive to temperature at low temperatures. Because of this observation, the exact temperature was not monitored in most of the experiments discussed. The temperature was close to that of liquid nitrogen, but in some instances may have varied as much as five or ten degrees.

Other Observations with n -Germanium.—A study of the wavelength response of the slow decay has been made. It is found that the decay rate varies with wavelength of illumination in a manner characteristic of absorption of light in germanium.

An investigation has also been made to determine the effect of injected holes on the decay times. A sample of n -germanium was prepared with indium fused into one side of the slab, the field-effect voltage being applied on the other. It is found that hole injection increases the decay rate.

Observations with p -type Silicon and Germanium.—Effects similar to those described above also appear in studies of 20 ohm-cm p -silicon and 12 ohm-cm p -type

germanium. In these cases, the sign of the effect is reversed, the slower decay occurs upon making the field more positive (metal plate more positive). The ratio $\Delta\sigma_{\text{equil}}/\Delta\sigma_{\text{tot}}$ (Fig. 1) is different also. Using the surface treatment described earlier, with p -germanium, the ratio is the order of 0.5; with n -germanium the ratio is the order of 0.1 to 0.2, and the p -silicon the ratio is nearly zero.

The slow decay characteristics for p -silicon at liquid air temperature with applied field and illumination as parameters are shown in Figs. 8 and 9. Here the photo-conductance $\Delta\sigma_i$ is in arbitrary units. The fast decay was not measurable with the present methods, as it was virtually complete in 10^{-4} second, the limit of our apparatus, with applied fields down to 80 volts. At this

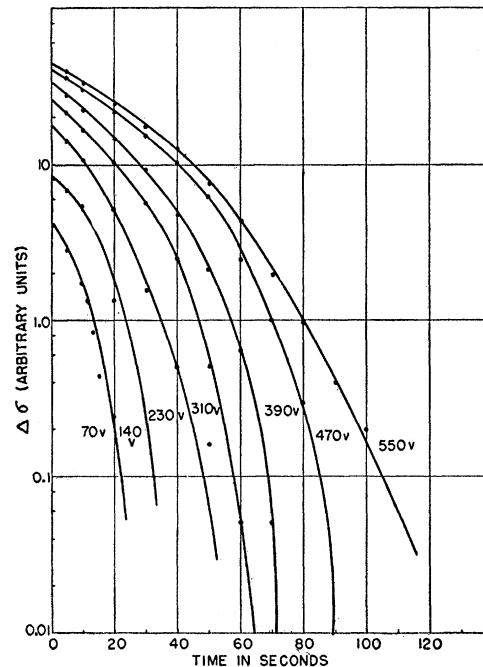


FIG. 8. Slow decay on p -type silicon (liquid nitrogen temperature) with varying applied field.

voltage and below, the latter part of the fast decay was in principle measurable, but the experimental error with such low fields was too great to attach much significance to the results.

Consistent with the minority carrier theory of the following section, the asymmetric decay on p -silicon was measurable at the temperature of dry ice. The results are shown in Fig. 10. As was shown earlier, the same curve is obtained whether a negative field is removed or a positive field applied. In this p -silicon case, the application of a dc positive field was not practical as slow symmetric decay, involving effects not of interest here, occurred, masking the asymmetric decay effects of interest. However it was found that if a positive field were applied, then quickly removed (a pulse field), the

unwanted symmetric decay, with time constant the order of 10 sec, could not follow it, and only the asymmetric decay (corresponding to the removal of the field) was observed. Thus, in Fig. 11 the slow decay corresponds to the removal of a field which has been applied the order of 0.5 sec. The curves shown for the fast part of the asymmetric decay were obtained, as usual, by shortening the pulse length until even the fast decay could not follow it.

Fast and slow decay curves for *p*-germanium at liquid nitrogen temperature are shown in Fig. 11, for two illumination intensities.

PHYSICAL MODEL⁵

It has been demonstrated by several workers⁶ that there are two classes of surface states on the germanium

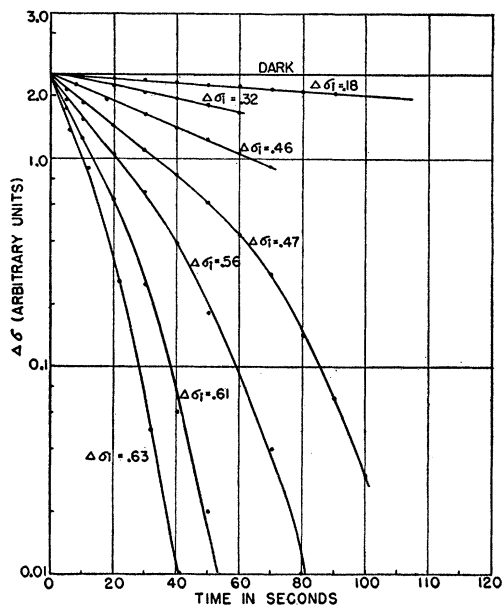


FIG. 9. Slow decay on *p*-type silicon (liquid nitrogen temperature) as a function of illumination intensity. $\Delta\sigma_1$ = photoconductance (arbitrary units). $V = 550$ volts.

surface, the "slow" states, and the "fast", or "recombination" states. It is of major importance to discriminate in this work between the two possibilities. However, evidence is available from the results of Morrison⁷ and Statz and his co-workers,⁸ who found a strong temperature dependence in the decay associated with the "slow" states. It was found⁷ that the "lifetimes" associated

⁵ Subsequent to the preparation of this paper, Banbury, Cajdovski, and Nixon have reported ac field effect measurements on germanium at low temperatures [Bull. Am. Phys. Soc. Ser. II, 3, 376 (1958)]. From anomalous results observed, they have independently developed a similar physical model to describe the behavior of the germanium surface at these low temperatures. It is of importance that their observed effective mobility was almost equal to the bulk mobility, as predicted by the model.

⁶ Reviewed by R. H. Kingston, J. Appl. Phys. 27, 101 (1956).

⁷ S. R. Morrison, Phys. Rev. 102, 1297 (1956).

⁸ Statz, deMars, Davis, and Adams, Phys. Rev. 101, 1272 (1956).

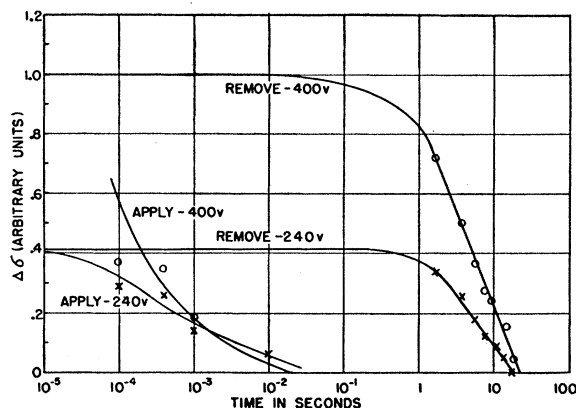


FIG. 10. Asymmetric field effect on *p*-type silicon at dry ice temperature. The curves are extrapolated to their initial value ($t=0$).

with the slow states became very long as the temperature decreased, varying from seconds at room temperature to almost infinity at about 200°K. However, it is seen in Fig. 7 that the relaxation under study here involves "lifetimes" the order of seconds at 160°K, and an extrapolation to 200°K indicates times the order of milliseconds for that temperature. Further evidence arises from the strong effect of illumination and minority carrier injection on the results observed here. No corresponding effect has been observed connected with the slow states. Thus it seems reasonable to conclude that the phenomenon observed here is not associated with the slow states, and we will assume the trapping observed involves the recombination centers.

The model which seems best to explain all the observed characteristics is with the band structure of Fig. 12, and physical arguments as follows: When a positive field is applied to *n*-germanium (Fig. 1), the recombination states trap extra electrons. Thus after

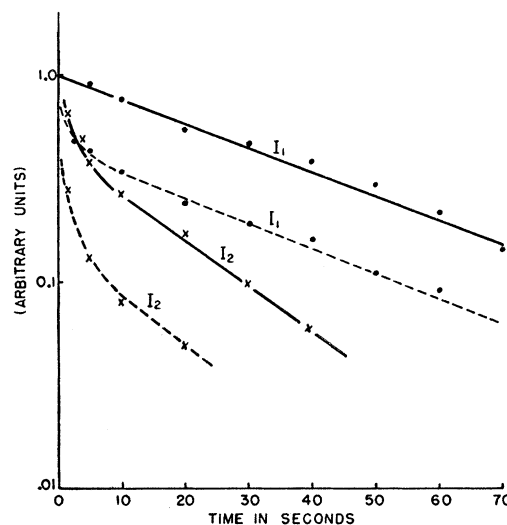


FIG. 11. Decay on *p*-type germanium at liquid nitrogen temperature. Illumination $I_2 > I_1$. Solid curves represent application of +320 volts, dotted curves removal of the voltage.

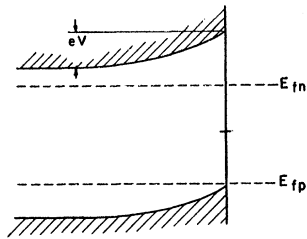


FIG. 12. Surface energy level diagram.

the immediate rise of the conductance upon application of the field, the induced electrons quickly decay into the surface levels and the conductance decays to its new equilibrium value. When the field is removed, the surface is left with too many electrons in the surface levels. The steady state condition is restored through recombination of the trapped electrons with holes in the valence band. As the supply of holes is limited, the rate at which the surface is restored to its steady state value may be slow.

It is considered that hole capture from the valence band rather than direct electron ejection back into the conduction band controls the slow decay. This is based on the observation that the parameters affecting the rate of slow decay are those expected to affect the density of bulk holes. If holes are injected by using a junction, the rate of decay increases. Only that wavelength illumination which gives rise to electron-hole production influences the rate. The temperature dependence of the rate is as expected for the temperature dependence of the bulk hole density (Fig. 7); at low temperatures the holes are produced mainly by illumination and the density is temperature insensitive, but as the temperature is raised, the thermally induced holes become dominant and the density becomes insensitive to illumination but sensitive to temperature with an activation energy the order of 0.72 eV. Thus the evidence appears quite strongly indicative of hole capture as being the dominant method of removing excess negative charge from the surface states in these experiments.

In order to develop an expression to represent the recombination process outlined above, it is convenient to estimate the rate of hole capture at the surface levels. It is possible that the rate of hole capture is close to the rate at which holes strike the surface, due to the influence of the potential well in the valence band, shown in Fig. 12. For a hole approaching the surface is expected to become trapped in the well where it will remain until captured, at the low temperatures under consideration. There is no way to directly test this possibility, as the system is not defined well enough to accurately calculate or measure the rate at which holes approach the surface. However, an order of magnitude check can be made, assuming that in the high-temperature region of Fig. 7 the density of holes is in thermal equilibrium. With the rough approximation that the rate at which holes approach the surface is that corresponding to their thermal velocity with $0.3m_e$ for the effective mass, we find that

at 175°K, holes approach the surface at a rate of the order of $5 \times 10^9 \text{ cm}^{-2} \text{ sec}^{-1}$. Experimentally, the initial disturbance of the surface states from equilibrium can be calculated to be the order of 10^{10} cm^{-2} charges, with a measured "lifetime" of 0.7 sec. This agreement with the theoretical value is adequate considering the experimental error and the gross theoretical approximations used, and is thus at least indicative that a large fraction of the holes approaching the surface are captured.

In the analysis to follow, the simplifying assumption will be made that the rate of hole capture is insensitive to n_s , the surface charge density. This assumption is indicated by the experimental observation that the rate of slow decay (hole capture) is close to a constant, almost independent of n_s , for large variations in n_s (Fig. 3, etc.). The suggestion of the preceding paragraph is a sufficient, but not a necessary, condition for this assumption to be valid.

With the conclusion that the rate of electron excitation from the surface levels into the conduction band is negligible, the expression for the rate of change of charge density n_s on the surface levels can be written in a form such as

$$\frac{dn_s}{dt} = A_1 n_0 (N_s - n_s) e^{-eV/kT} + A_2 (N_s - n_s) e^{-eV/kT} - \alpha p_0, \quad (1)$$

where n_0 and p_0 are the electron and hole density in the bulk material, N_s is the density of recombination states, V is the height of the surface barrier, and A_1 and A_2 are constants. The quantity αp_0 represents the rate of hole capture, the first term represents the rate of electron capture from the conduction band, and the second represents the rate of hole ejection into the valence band. It is easily seen from an examination of Fig. 12, an energy level diagram illustrating the accepted band structure, that the first two terms must be dependent upon the height of the surface barrier. Such a dependence is included in Eq. (1).

There are several points to emphasize in the expression (1). As discussed above, the last term is assumed independent of surface properties, except for a slow dependence which may arise through the "constant" α . Thus in steady state the first terms settle at a value independent of the surface condition. An increase in the density of trapped electrons n_s must be compensated by a decrease in V , the barrier height, for steady state.

The relative magnitude of the first two terms is not of great importance in the first analysis, since the variables are in the same form allowing addition of the terms. However, if the assumption is valid that most holes arriving at the surface are captured, it seems unlikely that the second term, representing hole ejection from the surface states, is important.

The barrier height V depends on two parameters, n_s and in our experiments, the applied electric field. For small changes in n_s , the barrier height will change proportionally. As expression (1) is zero for steady state, and as the change in conductance is proportional to the

change in n_s , we find that after a field is applied or removed, the excess conductance should decay according to a relation of the form

$$d\Delta\sigma/dt = B[\exp(-\beta\Delta\sigma) - 1]. \quad (2)$$

Here $B = \alpha p_0$; $e\Delta V/kT = \beta\Delta\sigma$.

The assumption has been made that the variation of $N_s - n_s$ is slow compared to $\exp(-eV/kT)$ with a variation in n_s , or that $N_s \gg n_s$. This assumption must be tested for each set of readings, as the value of n_s is variable, depending on the slow state charge which has been frozen in. There are two indications of the validity of the assumption, first the linearity with time of the high voltage slow decay, which arises with the dominance of the barrier, and second, the ratio of $\Delta\sigma_{\text{equil}}/\Delta\sigma_{\text{tot}}$ (Fig. 1). If the barrier dominates, $\Delta\sigma_{\text{equil}}$ should be very small, as the barrier must return to its initial value to restore steady state [Eq. (1)], and the restoration of the barrier infers the capture of all the induced charge. If the coefficient dominates, from (1) n_s must be about the same with or without the field, so there is little trapping of the induced charge, and $\Delta\sigma_{\text{equil}}$ is close to $\Delta\sigma_{\text{tot}}$.

For the n -type germanium discussed above, $\Delta\sigma_{\text{equil}}/\Delta\sigma_{\text{tot}}$ is the order of 0.15, indicating a reasonably strong barrier effect. With p -silicon at liquid air temperature, this observation is even more marked. The steady state conductance with the field on is, within experimental error, equal to that with the field off. In this case the slow decay is very close to linear with time. With p -germanium the opposite holds. In the investigations made the value of $\Delta\sigma_{\text{equil}}$ (Fig. 1) was about 50% of $\Delta\sigma_{\text{tot}}$. In this case the slow decay is close to exponential or more rapidly varying than a simple exponential and the decay curves are not amenable to the approximations made in the analysis being undertaken for n -germanium. In this n -germanium analysis it would appear likely that one of the major sources of disagreement between the theory and experiment will arise in the neglect of the variation of the coefficients in Eq. (1). The case of p -silicon would be expected to provide much closer agreement, but the extremely strong asymmetry makes experimental measurements considerably more difficult.

Experiments have been initiated to study the transition between the dominance of the barrier and its coefficient, with satisfying preliminary observations. It is felt that an analysis of this transition region may provide more useful information about the surface states themselves.

In the following section the experimental curves for n -germanium will be compared with the form suggested by Eq. (2). This form has been proposed in recent publications to describe many cases where barrier effects are dominant. It has been applied to effects occurring with the slow states on the germanium surface,⁷ to recombination characteristics at dislocations,⁴ and has

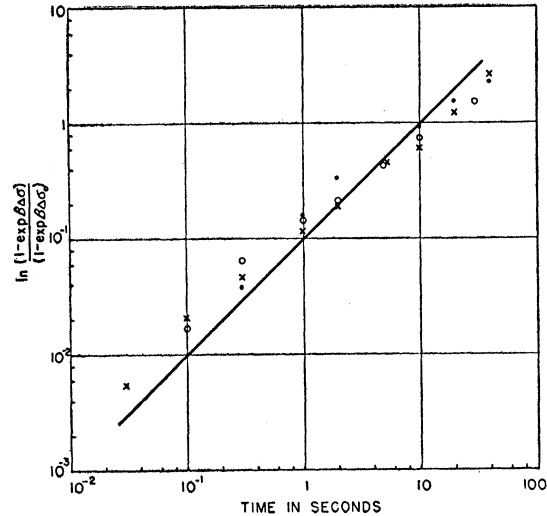


Fig. 13. Fast decay on n -type germanium plotted according to $1 - \exp(\beta\Delta\sigma) = A_0 \exp(-\gamma t)$, with $\beta = -1.4$. The 680-volt readings are denoted by \times , the 500-volt readings by \circ , and the 340-volt readings by dots.

been analyzed as a possible source of excess noise.⁹ It will be observed below that the present study appears to exhibit the characteristic behavior expected in a far more lucid fashion than the earlier studies.

MATHEMATICAL ANALYSIS

It is clear that an equation of the form of (2) is reasonable to fit the experimental data qualitatively. The strong asymmetry between positive and negative disturbances which is seen in Figs. 2, 3, and 4, is also apparent in Eq. (2). If $\beta\Delta\sigma$ is large and positive in Eq. (2), the rate of change of $\Delta\sigma$ is $(-B)$. If $\beta\Delta\sigma$ is large and negative, the rate of change is $B \exp(-\beta\Delta\sigma)$, a much higher rate. Another qualitative observation is that for the "slow decay" $d\Delta\sigma/dt = -B$, and $\Delta\sigma$ should be linear in time. This is observed in Fig. 3, where $d\Delta\sigma/dt$ is observed to be approximately independent of $\Delta\sigma$ for large $\Delta\sigma$.

For a more quantitative comparison, Eq. (2) can be integrated to yield

$$1 - \exp(\beta\Delta\sigma) = A_0 \exp(-\gamma t), \quad (3)$$

where A_0 is the constant of integration, $\gamma = \beta B$. It is difficult to plot the experimental data in this form unless the value of the constant β is known. This constant can be determined by trial and error, as has been done in an earlier publication,⁷ but with the more complete data here, an easier method is available.

The value of A_0 is $1 - \exp(\beta\Delta\sigma_0)$. In the case of high-voltage fast decay, $\beta\Delta\sigma_0$ is large and negative, so A_0 is close to unity. Thus, when $\Delta\sigma$ approaches zero during the high-voltage fast decay, Eq. (3) reduces to

$$\beta\Delta\sigma = -\exp(-\gamma t). \quad (4)$$

Thus with these conditions the decay should be exponential and independent of the initial disturbance.

⁹ S. R. Morrison, Phys. Rev. **99**, 1904 (1955).

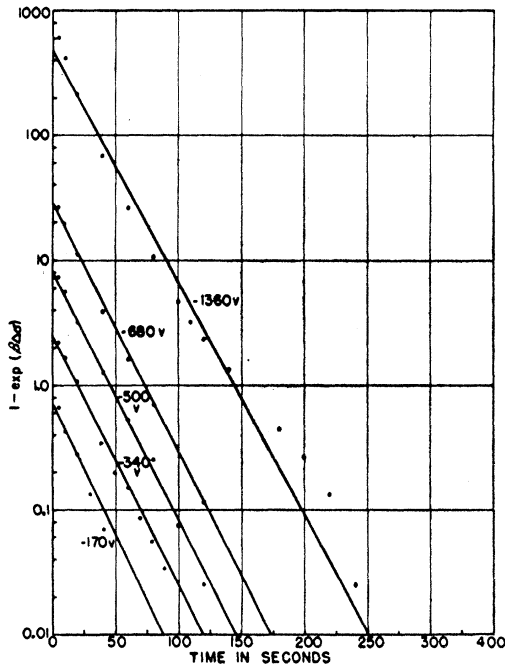


FIG. 14. Slow decay on *n*-type germanium. plotted according to $1 - \exp(\beta\Delta\sigma) = A_1 \exp(-\gamma t)$, with $\beta = -1.4$.

This effect is observed in Fig. 2, where it is seen that with disturbances greater than that corresponding to $V=340$, and for times greater than 6 sec, the decay curve is approximately exponential and independent of the initial disturbance to experimental error. Extrapolating this saturation region back to time zero yields a value for β , according to (4). This is shown by the solid line.

Using this value of β , $\beta = -1.4$, we can now express the data of Figs. 3 and 4 in the form of Eq. (3). The fast decay is shown plotted in this manner in Fig. 13, the slow decay in Fig. 14. It is observed that the curves are linearized quite well by Eq. (3). The method used in plotting the fast decay should yield a line with slope of unity, such as the solid line in Fig. 13. The agreement is thus far from perfect, although suggestive of the validity of the model.

DISCUSSION

This phenomenon under study is a very interesting effect in itself, and appears to be a clear illustration of the effect of the surface barrier in rate processes. It appears to provide a useful means of calculating the effective bulk hole density, and to provide a method of studying surface recombination. However, it does not seem to provide much direct data at this time about the actual band structure at the surface.

This failing arises principally because the effect is easily observable only under thermally nonequilibrium conditions. The density of charge in the recombination centers depends on the rate at which bulk holes reach the surface; the surface states become charged up until

the rate of electron capture is equal to this hole capture rate. Thus the energy of the surface states is not a parameter, so the energy of the surface states cannot be calculated from the data. The density of surface states N_s appears as a parameter in the form $N_s - n_s$ [Eq. (1)] but as n_s is not known, N_s cannot be calculated. The height of the surface barrier V can be calculated, but n_s cannot be found from this without a knowledge of the charge in the slow states.

The values of E_s and N_s may be determined in future experiments by an analysis of the decay in the "high-temperature" region of Fig. 7, where it is thought that the system is close to thermal equilibrium. Or the value of N_s may be determined through a study of the variation of $N_s - n_s$ with a variation in the charge on the slow states or with a large applied field. Experiments to utilize these possibilities are planned.

The model used in this paper to account for the observed phenomena shows good semiquantitative agreement with the experimental results. However, the results clearly are not in complete quantitative agreement. Assuming that the basic theory described above is correct, there are three areas in which the observed errors could arise aside from the probable errors inherent in the detecting devices. The first is, of course, approximation in the theory. By allowing severe complications, improvements could be made in this respect. The second is nonuniformity in the field, in particular edge effects or nonuniformity of illumination. As the equations are nonlinear, these effects could seriously alter the decay characteristics. With appropriate experimental care, these problems also could be minimized considerably. The third source of error is heterogeneity of the surface properties. If the surface barrier, and hence the value of β in Eq. (3), varies from area to area on the surface, the observed decay characteristics will be considerably different from the theoretical predictions. It is not clear at the present time how to improve the surface characteristics in this respect.

Little has been said regarding the interpretation of these measurements in terms of surface recombination. However, it is apparent that if the model is valid, the results are very intimately associated with surface recombination. The major difference between the field effect case discussed here and the illumination response is in the fact that with illumination the minority carrier density also varies with time upon switching the light on or off. Thus the mathematics becomes somewhat more complicated. An analysis similar to that presented earlier for dislocations⁴ should be applicable.

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