Measurement of Germanium Surface States by Pulsed Channel Effect*

G. RUPPRECHT†
University of Illinois, Urbana, Illinois
(Received February 11, 1958)

Densities, cross sections, and activation energies of several fast germanium surface states are inferred from low-temperature conductivity relaxations in a thin diffused surface layer. Relaxations are induced by application of a sudden reverse biasing pulse. The observed rate of change of channel conductance as a function of temperature is analyzed in terms of a model wherein the equilibrium surface Fermi level is presumed to remain in close proximity to a trap level. The results indicate the existence of an electron trap 0.24 ev from the conduction band and two hole traps 0.17 ev and 0.22 ev from the valence band.

INTRODUCTION

THE hypothesis of surface states was proposed by Bardeen[1] to explain the abnormally low-experimental values of field-effect mobility in germanium and the virtual independence of metal-semiconductor contact potentials of the work function of the metal. This has given rise to a series of investigations aimed at the determination of the properties of such states. These have been experimentally classified into two groups: "fast" states and "slow" states. The slow states, characterized by room temperature relaxation times in germanium of the order of 0.1 sec or more, presumably consist of localized states residing on the outer surface of the oxide layer. The fast states, characterized in germanium by room temperature relaxation times extending from 10^{-2} sec to beyond the microsecond range, are presumed to be localized states within the forbidden range of the energy gap and to be located at or near the oxide-semiconductor interface.[2]

The action of the fast states as screening centers in field-effect experiments has been studied by various investigators.[3–5] From analysis of field-effect mobility as a function of surface potential it is in principle possible to determine fast state densities and the positions of the traps in the energy gap.

An alternative method for determining these parameters employs the "channel effect,"[6,7] wherein the conductance of thin inversion layers is studied as a function of reverse bias between the layer and the bulk.

The proposed action of fast states as recombination centers has led to a series of experiments by various investigators.[8–10] A detailed analysis of surface recombination velocity as a function of surface potential and temperature yields, in principle, the energies of the traps which dominate the recombination process, as well as the ratios of their capture cross sections for holes and electrons. In this type of experiment, surface recombination velocity can be measured by photoconductance or by transient lifetimes of injected carrier disturbances; surface potential variations are effected by means of gas ambients or strong electric fields applied normal to the crystal surface.

The present method is an attempt to determine simultaneously trap energies, densities, and cross sections by studying the temperature variation of channel carrier relaxations induced by a sudden change in quasi-Fermi level at the surface. Experimentally this is achieved by measuring the time variation of resistance of a diffused inversion layer on germanium under the influence of an abrupt change in reverse bias. These relaxation effects, which at room temperature occur in times less than a microsecond, can be slowed down to easily observable rates by sufficient reduction of the sample temperature.

EXPERIMENTAL METHOD

The sample geometry is shown in Fig. 1(a). A rectangular block of 20 ohm-cm p-type germanium ($3\times6\times2$ mm) was prepared with a diffused n-type layer on the top surface. Leads were soldered to the sample as shown, the two leads on the surface making an ohmic contact to the n-type layer. The base of the block was soldered to a Kovar plate to insure good thermal contact to the cold finger to which the plate was attached. An accurate temperature determination was secured by means of a thermocouple in thermal contact with the block. Prior to mounting the sample on the plate, the upper leads were masked with wax and the n layer was then etched in $CP4$ until the room temperature channel resistance between the leads was reduced to 360 ohms. The resulting channel had a ratio of length to width of 1:6. The effective density of donors per unit square for such a geometry can then be

* This research was made possible by a fellowship from the International Cooperation Administration of the U. S. Government and by the U. S. Air Force through the Office of Scientific Research of the Air Research and Development Command.

† Now at Research Division, Raytheon Manufacturing Company, Waltham, Massachusetts.

[1] J. Bardeen, Phys. Rev. **71**, 727 (1947).
[2] W. H. Brattain and J. Bardeen, Bell System Tech. J. **32** (1953).
[3] W. Shockley and G. L. Pearson, Phys. Rev. **74**, 232 (1948).
[4] Bardeen, Coovert, Morrison, Schrieffer, and Sun, Phys. Rev. **104**, 47 (1956).
[5] H. C. Montgomery and W. L. Brown, Phys. Rev. **103**, 865 (1956).
[6] W. L. Brown, Phys. Rev. **91**, 518 (1953).
[7] Statz, Davis, and deMars, Phys. Rev. **98**, 540 (1955).
[8] D. T. Stevenson and R. F. Keyes, Physics **20**, 1051 (1954).
[9] A. Many and D. Gerlich, Phys. Rev. **107**, 404 (1957).
[10] S. Wang and G. Wallis, Phys. Rev. **107**, 947 (1957).

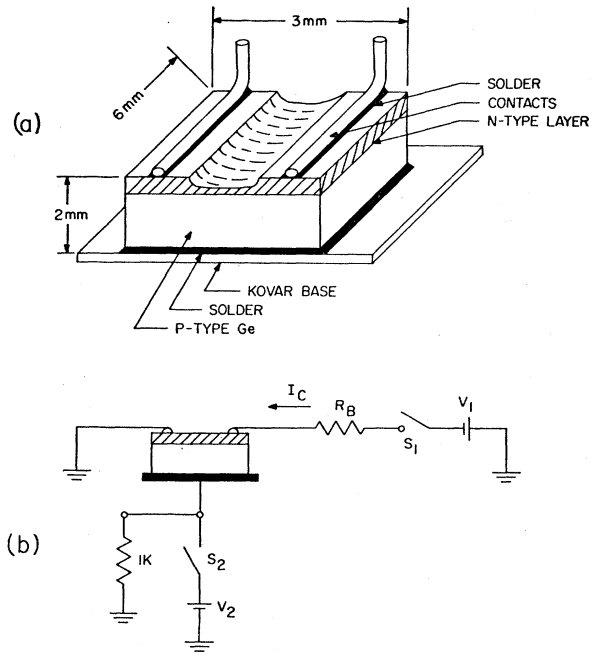

FIG. 1. Sample geometry and pulse circuit for measurement of pulsed channel effect.

calculated from the following equation:

$$N=l/\omega Re\mu, \tag{1}$$

where N=density of donors/cm^2, l=length of the channel, ω=width of the channel, e=electronic charge in coulombs, μ=bulk mobility in cm^2/volt sec, and R=resistance of the channel in ohms. Thus we have a donor density of 7.6×10^{11} cm^{-2}.

To observe the transient variation of free carrier density in the channel, a constant current I_c is passed between the two channel contacts; the resulting voltage drop in the channel is observed directly in the oscilloscope. The circuit is shown in Fig. 1(b). The quasi-Fermi level at the surface is periodically abruptly shifted by applying a square reverse bias pulse to the base contact by means of a multivibrator driven mercury relay S_2.

To minimize heating effects in the channel, the channel current is applied in the form of square current pulses of low duty cycle by means of another mercury relay S_1. The two relays are so synchronized that the channel current is applied shortly before the base pulse and remains constant until all transient effects have died out. The current pulse is then turned off shortly before the base signal is removed. The condition of constant current while S_1 is closed is fulfilled by setting the ballast resistor R_B at a value greatly in excess of the observed channel resistance.

The two general types of wave forms obtained by this arrangement are shown in Fig. 2 and are arbitrarily classified as pertaining to "Process I" and "Process II" respectively. With respect to either process, the voltage V_0 is simply the voltage drop across the unperturbed channel, and is given by

$$V_0=I_cR_0, \tag{2}$$

where R_0 is the channel resistance in the absence of bias. The voltage V_i is observed immediately upon application of the base pulse, and is a measure of the initial channel resistance R_i at this time. The resulting relaxation process leads to an equilibrium value V_F corresponding to the final channel resistance R_F after all transient effects have subsided. The subsequent removal of the current pulse leaves a small residual voltage V_R which is linearly related to the junction reverse current. All voltages are measured with respect to the reverse voltage in order to eliminate this additive error. To insure immediate relaxation of the charge stored in the junction capacitance, a one-thousand-ohm resistor is permanently connected from base to ground. Experimentally, it is sometimes observed in certain temperature ranges that a competition occurs between process I and process II; however, the relaxation times involved are usually sufficiently different that the two processes can be readily distinguished from one another.

The experimental procedure which is employed in this experiment is to measure the time constant τ of the relaxation process, and the voltages V_0, V_i, V_F, V_B as a function of temperature. For those cases wherein the relaxation is not a simple exponential function, the initial slope of the relaxation curve is measured also.

By suitable analysis of such data it is possible in principle to determine trap energies, densities, and cross sections. Variations in equilibrium surface Fermi level were achieved by introduction of ozone and wet air into the system.

THEORY

For simplicity we shall consider an n-type surface with a single electron trap level located at some point in the upper half of the energy gap. The treatment which we shall derive can be immediately extended to hole traps near the valence band with no loss of generality. The behavior of the trap population under the influence of a sudden shift in quasi-Fermi level will depend upon the position of initial Fermi level F with respect to the trap energy E_T and the direction in which the Fermi level is shifted to its new value F'. We therefore recognize six basic configurations, three of which we shall analyze in detail.

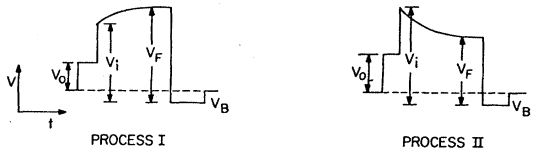

FIG. 2. Characteristic wave forms exhibited during the relaxation process.

(a) $F>E_T>F'$. This configuration is illustrated in Fig. 3, where E_T is the trap energy, E_c and E_v are, respectively, the energies of the edges of the conduction and valence bands, and F and F' denote respectively the positions of the quasi-Fermi level for conduction electrons immediately before and immediately after the bias pulse is applied. Note that in this case the quasi-Fermi level for conduction electrons passes across the trap. We assume immediate equilibrium between the bulk and the conduction band at the surface. At sufficiently low temperatures, however, it is possible that the traps may require an appreciable amount of time to reach equilibrium with the conduction band. Moreover we shall assume that the primary mechanism whereby trap equilibrium is attained is a direct transfer of electrons between the trap and the conduction band; thus the rate-determining process is the rate of this charge interchange.

Denoting F_T as the quasi-Fermi level for the trapped electrons, it is evident that for the equilibrium surface immediately before pulsing, $F_T=F$. However, the inability of the trap to establish immediate equilibrium with the conduction band implies that the trap will be overpopulated until sufficient electrons have been generated from the trap to the conduction band to allow F_T to drop down to a point where it again coincides with the quasi-Fermi level for conduction electrons.

Every electron generated from the trap to the conduction band during this relaxation process contributes directly to the channel conductance. Thus the channel resistance decreases with time, and we identify this type of relaxation with "Process II."

Read and Shockley[11] and Hall[12] have treated the steady-state kinetics of trapping in detail. For nonequilibrium conditions we note that the rate of change of trap population is equal to the net excess of recombination over generation. Thus we may write

$$(dn_T/dt)=rn_s(N_T-n_T)-gn_T(N_c-n_s), \tag{3}$$

where n_T=number of trapped electrons per cm^2, N_T =number of traps per cm^2, n_s=surface concentration of free electrons per cm^3, N_c=effective density of states in the conduction band per cm^3, r=recombination factor, and g=generation factor. From detailed balancing we have

$$g=r\exp[-(E_c-E_T)/kT]. \tag{4}$$

It therefore follows that

$$dn_T/dt=rn_sN_T-rn_T(n_s+n_1), \tag{5}$$

where we have used the approximation that $N_c\gg n_s$, and have defined n_1 as the free electron concentration at the surface for the particular case where the Fermi level for free electrons is located at the trap.

[11] W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952).
[12] R. N. Hall, Phys. Rev. **83**, 228 (1951).

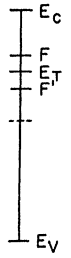

FIG. 3. Assumed behavior of surface in configuration (a).

We may therefore define a relaxation time τ for this process:

$$\tau^{-1}=r(n_s'+n_1). \tag{6}$$

For the initial rate of change immediately after pulsing, we find

$$(dn_T/dt)_0=rn_s'(N_T-n_{T0})-rn_1n_{T0}, \tag{7}$$

where n_s' is the new surface free electron concentration, governed by the new quasi-Fermi level F' and n_{T0} is the trap population before pulsing.

We shall assume for simplicity that F and F' are removed from E_T by an amount considerably in excess of kT. To this approximation we may then write

$$\tau^{-1}=rn_1=rN_c\exp[-(E_c-E_T)/kT], \tag{8}$$

$$(dn_T/dt)_0=-rn_1N_T=-rN_TN_c\exp[-(E_c-E_T)/kT]. \tag{9}$$

A semilogarithmic plot of the experimental values of either τ or $(dn_T/dt)_0$ *versus* $1/T$ should therefore yield a straight line of slope $(E_c-E_T)/k$. In addition the trap density may be computed directly from the relationship

$$\Delta n_T\equiv(dn_T/dt)_0\tau=N_T. \tag{10}$$

Here we have defined an order of magnitude quantity Δn_T which will be useful in estimating the relative magnitudes of the charge relaxation in various configurations.

(b) $F>F'>E_T$. In this case n_s' is much greater than n_1 and n_T is very nearly equal to N_T. Thus to this approximation equations (5) and (6) become

$$(dn_T/dt)_0=-rN_Tn_1;\quad \tau^{-1}=rn_s';$$
$$\Delta n_T=-N_Tn_1/n_s'=-N_T\exp[-(F'-E_T)/kT].$$

Therefore, the relaxation signal associated with this mode of relaxation will be extremely small compared to that of configuration (a). This follows from the fact that before and after shifting the quasi-Fermi levels, the trap remains essentially completely filled.

(c) $E_T>F>F'$. For this case n_s' is very much less than n_1 and n_T is much smaller than N_T.

Equations (5) and (6) become

$$\tau^{-1}=rn_1;\quad (dn_T/dt)_0=r(n_s'N_T-n_Tn_1)$$
$$\approx-rN_cN_T\exp[-(E_c-F)/kT].$$

Hence

$$\Delta n_T = N_T(\exp[-(E_T-F')/kT]-\exp[-(E_T-F)/kT]) \approx -N_T \exp[-(E_T-F)/kT].$$

Here, as in case (b), the transient effects are small.

For the three configurations we have considered, there are two transitional configurations wherein F or F' coincides with E_T. When F' lies on E_T, one obtains

$$\tau^{-1}=2rn_1; \quad (dn_T/dt)_0=-rN_Tn_1; \quad \Delta n_T=-\tfrac{1}{2}N_T.$$

When F lies on E_T, one obtains

$$\tau^{-1}=rn_1; \quad (dn_T/dt)_0=-\tfrac{1}{2}rN_Tn_1; \quad \Delta n_T=-\tfrac{1}{2}N_T.$$

Summarizing the process II relaxations, it may be said that in any case wherein the condition

$$F \geq E_T \geq F'$$

is satisfied, the temperature variation of either τ or $(dn_T/dt)_0$ should allow one to determine experimentally the trap activation energy. In addition, the product $\tau(dn_T/dt)_0$ should always give the trap density within a factor of two. The transitional cases are of considerable significance because there is reason to believe that quasi-Fermi levels for conduction electrons have a tendency to anchor themselves on traps.

The equations for the inverse processes wherein the quasi-Fermi level is pulsed upwards can be similarly derived. These cases represent relaxations wherein the traps are filled by electron capture from the conduction band. Hence, the channel resistance increases with time, and we therefore identify these relaxations with "process I." For such cases it can be shown that a simultaneous determination of trap activation energy and density is only possible for the case wherein the quasi-Fermi level for conduction electrons F' anchors on the trap. It will be shown subsequently that this condition is often achieved.

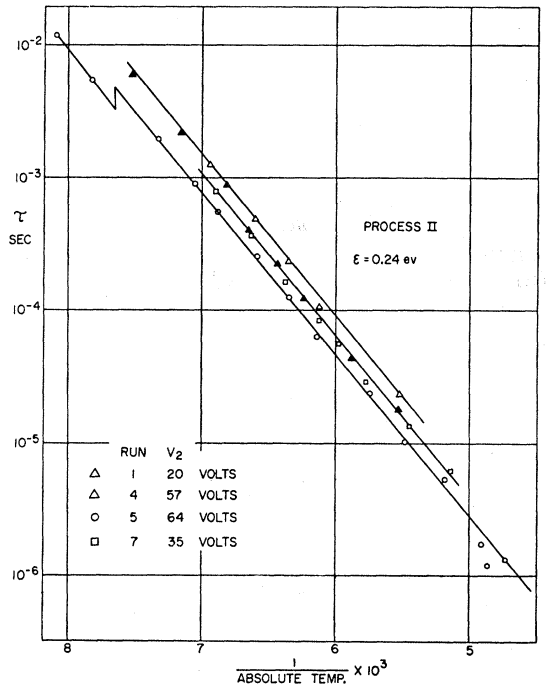

FIG. 4. Series of process II lifetime runs giving an activation energy of 0.24 ev. *Note added in proof.*—Run No. 4 is indicated by ▲.

EXPERIMENTAL RESULTS

The results of a series of runs are shown in Figs. 4–9. The pertinent mode of relaxation is marked on each figure. The curves shown pertain to a series of runs made over a period of several weeks on the same channel. The normal experimental procedure was to cool the sample to liquid air temperature and to make measurements as the sample slowly warmed to room temperature. Experimental values of dV/dt are converted to dn/dt by the relationship

$$dn/dt=(l/\omega I_c\mu_n eR_i^2)(dV/dt).$$

The parallel displacements of the curves from one run to the next can arise from a combination of factors such as gradual change in trap density, progressive shifting of the surface Fermi level by aging effects in the slow states, and differences in pulse amplitude for different runs. Figures 4 and 5 both show an apparent activation energy of 0.24 ev. The product of τ and $(dn_T/dt)_0$ for these curves gives a constant value for each run ranging from 3 to 9×10^{10} cm^{-2}. This behavior is strongly suggestive of configuration (a) or its two transitional cases. Moreover, the relaxation processes themselves seldom exceed more than 10 to 20% of the initial channel resistance R_i. Thus we are led to expect that the actual shift in quasi-Fermi level is fairly small and that the Fermi level remains fairly close to the trap. Since it is not known whether the free surface is p or n type, the question arises whether this is an electron trap located 0.24 ev from the conduction band or a hole trap located an equal distance from the valence band. There are several reasons for believing that this is an electron trapping process. If the surface were p type with the Fermi level near the trap, then the application of the reverse biasing pulse would immediately reduce the concentration of free holes at the surface, i.e., the quasi-Fermi level for free holes is pulsed upward. The trap must then tend to empty. Thus, by charge neutrality the channel concentration of free electrons must drop to compensate for the loss of holes generated during the relaxation process. This process will then cause the channel conductance to decrease with time and we would observe a process I relaxation. This mechanism will hold as long as the number of free holes is small compared to the normal number of free electrons in the channel. It can be shown that this is always the case in the temperature range considered. Thus, it is evident that if this trap were

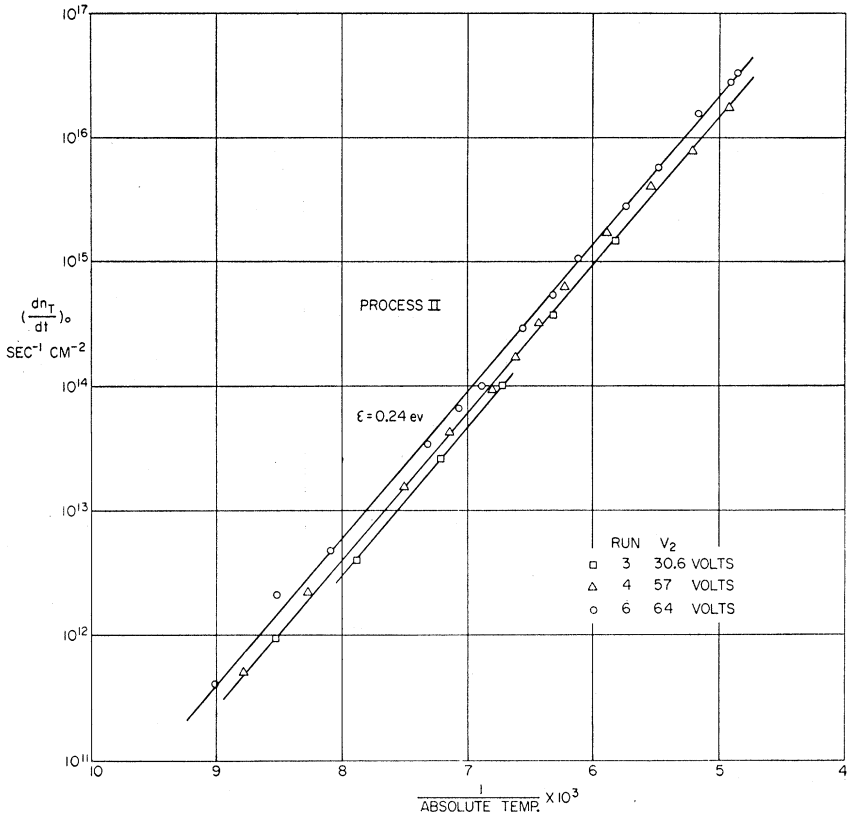

FIG. 5. Series of process II initial slope runs giving an activation energy of 0.24 ev. *Note added in proof.*—In the key, Run No. 6 should read 5.

on the p side we would then expect a process I relaxation for the reasons just stated. However, the observed wave form is that of process II; hence we are led to believe that in this case we are dealing with an electron trap of activation energy 0.24 ev and density of 3×10^{10} to 9×10^{10} cm^{-2}. The electron capture cross section of this trap may then be computed from the equation

$$r_n=\sigma_n v_T, \tag{11}$$

where v_T is the thermal velocity. In the absence of a more detailed analysis of the variation of the thermal velocity with respect to crystal orientation we shall take the electron mass equal to its free mass.

The fact that the measure values of τ vary at most by a factor of 2 in succeeding runs made over several weeks with pulse biases varying from 20 volts to 64 volts leads one to suspect that the condition $F\geq E_T\geq F'$ is satisfied. Assuming configuration (a) to be the case and taking representative values of τ and $(dn_T/dt)_0$ at 170°K, one obtains from Eqs. (8)–(11)

$$N_T=8\times10^{10}\text{ cm}^{-2},\quad E_c-E_T=0.24\text{ ev},$$
$$r_n=3.2\times10^{-8},\quad \sigma_n=4.3\times10^{-15}\text{ cm}^2.$$

We note that in the case of either of the transitional configurations wherein F or F' are assumed to lie on E_T, the true value of N_T would be twice the value given

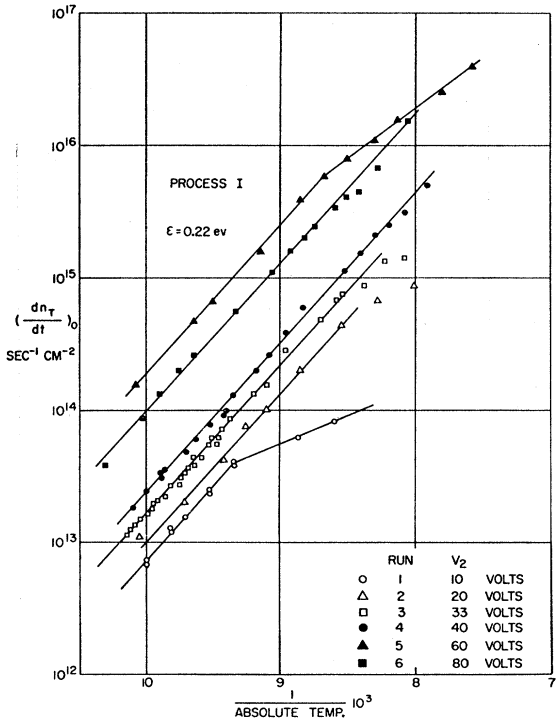

FIG. 6. Series of process I initial slope runs giving an activation energy of 0.22 ev.

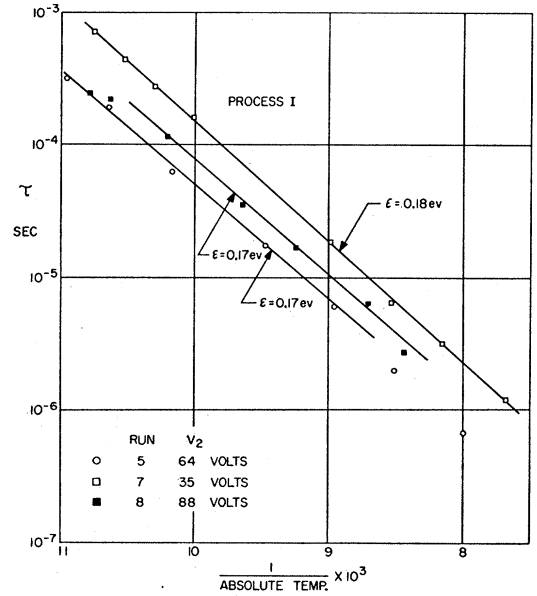

FIG. 7. Series of process I lifetime runs giving an average activation energy of 0.17 ev.

above. It is believed that the parallel displacements of τ and $(dn_T/dt)_0$ values illustrated in runs 4 and 5 (Fig. 4) and run 3 (Fig. 5) arise from a shifting of either F or F' with respect to E_T as the temperature varies. The exact details of this mechanism are not yet understood. The above values are to be compared with the level determined by Statz *et al.*[13] of density 10^{10} to 10^{11} cm^{-2} located 0.21 ev from the conduction band.

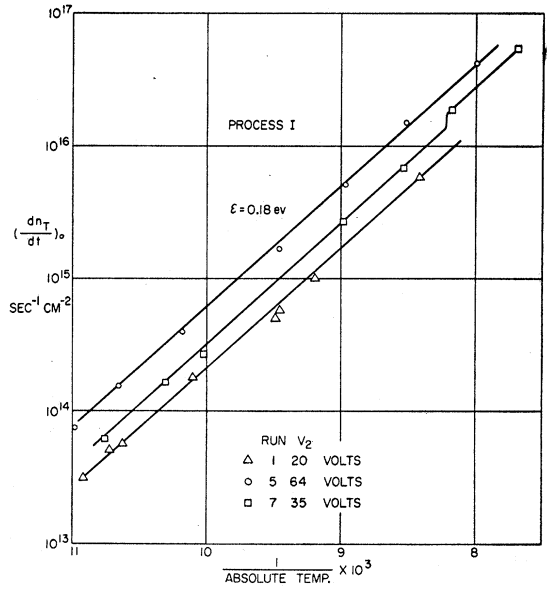

FIG. 8. Series of process I initial slope runs giving an activation energy of 0.18 ev.

[13] Statz, deMars, Davis, and Adams, Phys. Rev. **106**, 455 (1957).

The results of a series of runs wherein the oscilloscope showed process I relaxations are shown in Figs. 6, 7, and 8. Figure 6 shows the values of $(dn_T/dt)_0$ obtained from vacuum measurements after exposing the surface to strong ozone ambient. We may therefore assume that these curves represent the relaxation process wherein a hole trap reacts with the valence band. We find an activation energy of 0.22 ev for this process. Since the values of τ were poorly defined in these runs, they were not recorded; hence trap density and cross section cannot be evaluated here. The abrupt changes in slope noted in Fig. 6 presumably denote shifts of the Fermi level to new configurations possibly involving additional trap levels.

Figures 7 and 8 show τ and $(dn_T/dt)_0$ for another series of process I runs, and by similar analysis one obtains for the most probable values:

$$N_T=6\times10^{10}\ \text{cm}^2,\quad E_T-E_v=0.17\ \text{ev},$$
$$r_p=1.2\times10^{-6},\quad \sigma_p=2\times10^{-13}\ \text{cm}^2.$$

It should be noted that the density of this trap is approximately the same as that of the 0.24-ev level, whereas the cross section is surprisingly large. The agreement between the slopes of the τ and $(dn_T/dt)_0$ values for this level is quite gratifying.

From the foregoing it would appear that the 0.22-ev and the 0.17-ev levels are hole traps interacting with

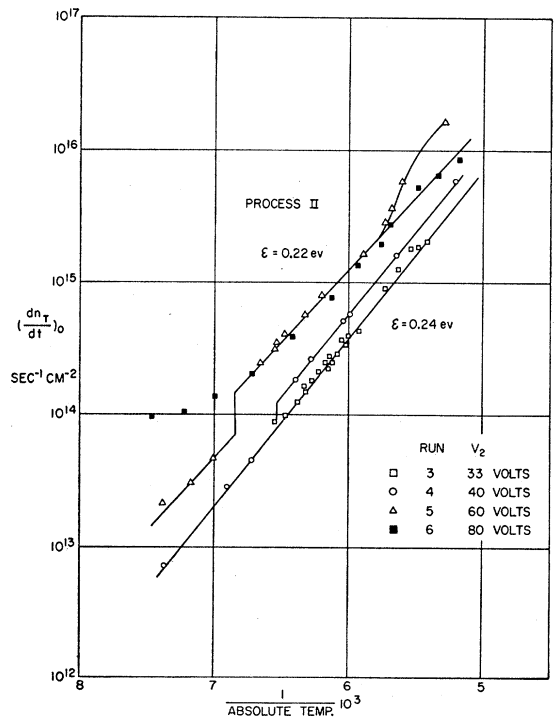

FIG. 9. Series of process II initial slope runs illustrating parallel shift of lines during a run. Energy values dubious because of limited range of values of $(dn_T/dt)_0$.

the valence band. Statz *et al.*[14] have reported a level of approximate density 10^{11} cm^{-2} located 0.20 ev from the valence band. Bardeen *et al.*[2] have also determined a trap of density 1 to 3×10^{11} cm^{-2} at the same energy.

Figure 9 illustrates a type of behavior which is sometimes encountered during the course of a run. This phenomenon indicates that the Fermi level does not always remain well anchored to the trap. All values of trap energy reported in this paper are based upon runs which give an essentially linear plot over a variation of at least three powers of ten in τ or $(dn_T/dt)_0$.

DISCUSSION OF RESULTS

The possibility must be considered that some or all of these processes represent bulk trap relaxations instead of true surface effects. To resolve this question an estimate must be made of the magnitude of possible bulk trapping effect in this geometry. It is therefore necessary to analyze the junction region in some detail. In Fig. 10 a series of typical values of R_0/R_i and R_0/R_F are plotted as a function of pulse bias V_2. The charge Q which is squeezed out of the junction by application of the pulse is then given by

$$R_0/R_i=N_i/N_0=1-Q/N_0.$$

The difference between the two curves is therefore Q_T/N_0, where Q_T is the amount of charge added or removed from the trap during the relaxation process. This quantity is plotted in Fig. 10 as a function of pulse bias for a typical run. If this process were due to a relaxation of bulk traps it would have to originate from those traps located in the depletion region of the junction. Assuming a uniform spatial density for such traps, it follows that the magnitude of Q_T would then be proportional to the width l of this region.

If one assumes that to a first approximation the diffused donor density in this region varies linearly with distance from the center of the junction, then it follows from well known principles[15] that l is proportional to $V^{\frac{1}{3}}$. This dependence has been verified by measurement of the channel capacitance as a function of bias. Therefore, the relaxation charge should vary as $V^{\frac{1}{3}}$, and one would expect a behavior as indicated by the dotted line in Fig. 10. It is evident that there is a marked discrepancy between the two curves; moreover, the experimental curve is strongly indicative of a surface relaxation phenomenon wherein considerable bias must be applied in order to cause a significant change in quasi-Fermi level at the surface. From this it would appear that bulk effects can be excluded.

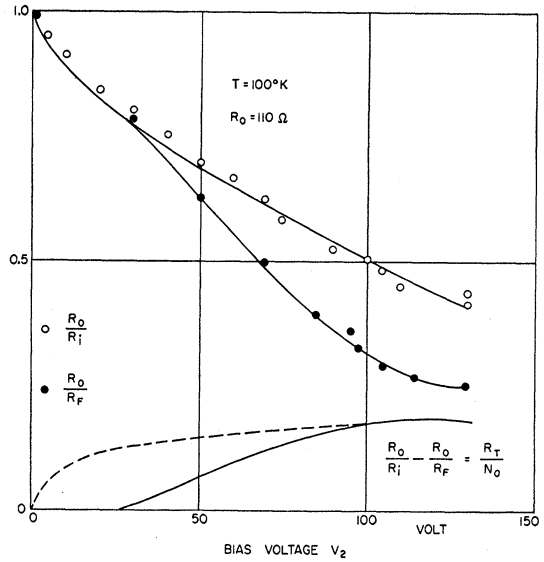

FIG. 10. Typical behavior of R_0/R_i and R_0/R_F. Lower set of curves illustrate actual behavior of Q_T/N_0 (solid line) and expected behavior if bulk trapping effects were dominant (dotted line).

From high-frequency field effect measurements on germanium at room temperature, Montgomery[16] has estimated that the relaxation times of the dominant fast states are of the order of or less than 10^{-8} sec. The values for τ for the 0.24-ev and the 0.17-ev levels extrapolate to room temperature values of 4×10^{-8} sec and 2×10^{-10} sec, respectively. Those values are not inconsistent with Montgomery's estimate.

ACKNOWLEDGMENTS

The writer wishes to express his appreciation to Professor John Bardeen and Dr. J. Robert Schrieffer for their many helpful discussions and continued interest throughout the course of this experiment. The writer is also indebted to R. J. Wilfinger for the design and construction of the electronics equipment and to S. R. Arnold for his assistance in preparing this manuscript.

[14] Statz, deMars, Davis, and Adams, Phys. Rev. **101**, 1272 (1956).

[15] W. Schottky, Mitteilung aus der Zentralabteilung der Siemen und Halske A.-G. Berlin-Siemensstadt 553 (1941).

[16] H. C. Montgomery, Phys. Rev. **106**, 441 (1957).