

that the neutron spends in the correlation range  $\kappa_1^{-1}$ . Hence Eq. (AII.8) may be written as

$$t_0 \gtrsim 10t'. \quad (\text{AII.9})$$

This relation shows that for negligible energy exchange, the relaxation time for the magnetic moment fluctuations should be much greater than the time spent by the neutron in traveling over a correlation range. The temperature dependence of the time  $t'$  is easily obtained from the relation  $(\kappa_1 r_1)^2 = \chi_1/\chi$ , giving

$$t' = (r_1/v)(\chi/\chi_1)^{1/2}. \quad (\text{AII.10})$$

The time  $t_0 = (\Lambda_1 \kappa^2) = \chi/(\lambda \kappa^2)$  may be estimated from the fact that at high temperatures  $t_0$  becomes a microscopic relaxation time which has been calculated<sup>3</sup> to be about  $20\hbar/J$ , where  $J$  is the interaction energy between a pair of spins. For  $T/T_c \gg 1$ ,  $\chi \rightarrow \chi_1$ , the paramagnetic susceptibility for noninteracting spins. Also, the im-

portant momentum transfers must be of order  $\hbar/r_1$ , since  $r_1$  then represents the range of the correlations. This determines the phenomenological constant  $\lambda$  and, assuming it to be temperature-independent, gives for the relaxation time  $t_0$  the estimate

$$t_0 \cong (20\hbar/Jr_1^2 \kappa^2)(\chi/\chi_1). \quad (\text{AII.11})$$

(The fact that we have here extrapolated results valid near  $T_c$  and for long times to much higher temperatures and microscopic times should not affect the order of magnitude of the results.) Our requirement for negligible energy exchange now reads

$$(20\hbar/Jr_1^2 \kappa^2)(\chi/\chi_1) \gtrsim 10(r_1/v)(\chi/\chi_1)^{1/2}. \quad (\text{AII.12})$$

Inserting the pertinent values, one sees that this condition is certainly fulfilled over the temperature range we have used and over the values for  $\kappa = k_0\theta$  corresponding to the small angles involved.

### Relaxation Time of Surface States on Germanium\*

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Two types of state exist at the surface of single crystal germanium; the first type, which is assumed to be at the semiconductor-oxide interface, is chiefly responsible for the carrier recombination process, while the second type, associated with the oxide structure and adsorbed ions, is believed to control the position of the Fermi level at the surface with respect to the electron band energy. The latter type of state has been studied by means of the "field-effect," or change in conductance with an applied field perpendicular to the surface. The results indicate that the relaxation or capture time of these states is much longer than that of the interface states, and is also extremely sensitive to surface treatment and ambient gas. In addition, some surface treatments lead to a distribution of time constants on the same surface over a range as large as six decades. Possible physical models for this behavior are discussed as well as its connection with excess or  $1/f$  noise.

#### INTRODUCTION

EARLY in the study of high-purity germanium as a semiconductor, it became apparent that the surface of the material had additional energy states for electrons beyond those normally expected in the bulk material. In particular, it was necessary to postulate electron levels in the gap both to explain metal-semiconductor rectification<sup>1</sup> and later to explain surface recombination velocity.<sup>2</sup> Direct evidence for the existence of such states was found by Shockley and Pearson,<sup>3</sup> who attempted to modulate the conductivity of a thin evaporated film of germanium by applying an

external electric field normal to the surface. Since the change in conductivity was only about 10% of what had been expected from the magnitude of the induced charge and the free carrier mobility, it was necessary to assume that there were localized levels at the surface which would absorb and thereby immobilize the majority of the induced charge. Recently, this experiment, the "field effect," has been studied in more detail on single crystal germanium slabs<sup>4-9</sup>; and, in conjunction with measurements of surface conductance on

\* The research reported in this document was supported jointly by the Army, Navy, and Air Force under contract with the Massachusetts Institute of Technology.

<sup>1</sup> J. Bardeen, *Phys. Rev.* **71**, 717 (1947).

<sup>2</sup> W. H. Brattain and J. Bardeen, *Bell System Tech. J.* **32**, 1 (1953).

<sup>3</sup> W. Shockley and G. L. Pearson, *Phys. Rev.* **74**, 232 (1948).

<sup>4</sup> J. Bardeen and S. R. Morrison, *Physica* **20**, 873 (1954).

<sup>5</sup> G. G. E. Low, *Proc. Phys. Soc. (London)* **B68**, 10 (1955); **B68**, 1154 (1955).

<sup>6</sup> R. H. Kingston and A. L. McWhorter, *Phys. Rev.* **98**, 1191 (1955).

<sup>7</sup> W. L. Brown, *Phys. Rev.* **98**, 1565 (1955); **100**, 590 (1955).

<sup>8</sup> H. C. Montgomery and W. L. Brown, *Phys. Rev.* **98**, 1565 (1955).

<sup>9</sup> S. G. Kalashnikov and A. E. Yunovich, *J. Tech. Phys. (U.S.S.R.)* **25**, 952 (1955).

junction transistor structures,<sup>10-13</sup> the details and behavior of these surface states are more clearly understood. These experiments indicate that there are two distinct classes of surface states on germanium. The first type, which are thought to be located at the germanium-germanium oxide interface, are chiefly responsible for the surface recombination process, while the second type, which probably arise either from adsorbed ions or imperfections in the oxide layer, are believed to control the position of the energy bands at the surface with respect to the Fermi level. This paper will be largely concerned with the relaxation times of the latter type of state as determined from field-effect measurements.

### FIELD-INDUCED SURFACE CONDUCTANCE

Consider the germanium surface depicted in Fig. 1, where the bulk material has intrinsic conductivity and the surface is *n*-type due to the surface treatment and ambient.<sup>14</sup> If an external field is now applied as shown, then one expects more electrons to be drawn to the surface to terminate the field and the surface will become even more *n*-type. These extra electrons will produce an increased conductance along the surface which may easily be measured if the sample is a thin slab. One might think that the change in conductance would be given simply by the product of the induced carrier density and the bulk mobility of the electrons. Actually, the behavior of the conductance is much more complicated, both because of surface states and the finite recombination lifetime of excess carriers in the sample.

Consider first the lifetime effect. If the conductance is measured immediately after application of the field, the carrier distribution at the surface will not satisfy the equilibrium relationship between hole and electron density. Thus, in Fig. 1, the initial charging current supplied to the surface from the bulk will consist of holes leaving and electrons arriving in the ratio

$$I_p/I_n = p\mu_p/n\mu_n,$$

where *p* and *n* are the bulk carrier densities. After a time long compared with the over-all recombination time of the sample, the ratio of added electrons to removed holes must be given by  $n_s/p_s$ , the ratio of the electron and hole densities at the surface. Hence, if an inversion layer exists at the surface, the incremental conductance would actually change sign. In Fig. 1, for example, if the bulk material were *p*-type, then the conductance would initially decrease since holes would be removed from the surface. After recombination equilibrium, however, the conductance would be

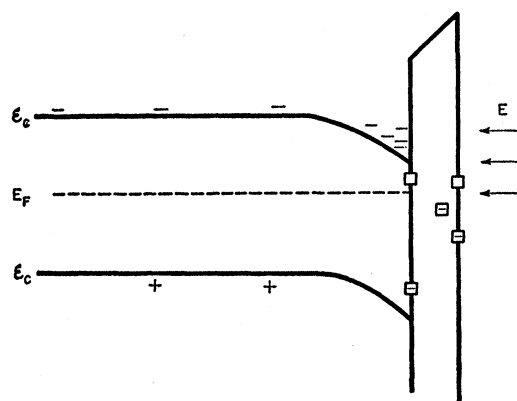


FIG. 1. Intrinsic germanium with *n*-type surface layer and applied external field.

greater since the negative charge would be supplied by extra surface electrons. Such effects have been studied by Low<sup>5</sup> and have also been observed both in this laboratory and by Montgomery and Brown.<sup>8</sup>

After the recombination transient the net occupancy of the recombination centers has changed from its initial value before application of the field. The induced negative charge at the surface is supplied by an increase in electron density both in the conduction band and in the recombination centers. Since the electrons trapped in these states do not contribute to the conductivity, the change in conductance produced by the external field is consequently reduced. This trapping effect has been measured both in the field effect experiment<sup>7,8</sup> and in "channel" measurements on *p-n-p* junction transistor structures.<sup>12</sup> The results, taking into account the reduction in mobility of carriers in the surface well,<sup>15</sup> give a probable density of recombination states of the order of  $10^{11}/\text{cm}^2$  for an etched surface.

After prolonged application of the field, it is generally found that the conductance of the sample decays to its original zero field value. This decay, however, takes from 0.01 second to many minutes depending upon the surface treatment. This long time relaxation is attributed to additional surface states in or on the oxide layer,<sup>4,12,13</sup> whose energy and density are a critical function of the gaseous ambient and surface treatment. These latter states are thus distinguished from the surface recombination centers by their long time constant and in addition by their much larger density, which must be greater than  $10^{13} \text{ cm}^{-2}$  in order to neutralize the applied field without a perceptible shift in the Fermi level. It is these long time constants which are of immediate interest, both for the information they give about the surface structure and for their possible connection with excess or  $1/f$  noise.

### EXPERIMENT

The germanium used for the experiments was in the form of slabs, about  $0.5 \times 0.25 \times 0.01$  inch, cut from

<sup>10</sup> W. L. Brown, Phys. Rev. **91**, 518 (1953).

<sup>11</sup> deMars, Statz, and Davis, Phys. Rev. **98**, 539 (1955).

<sup>12</sup> Statz, Davis, and deMars, Phys. Rev. **98**, 540 (1955).

<sup>13</sup> R. H. Kingston, Phys. Rev. **98**, 1766 (1955).

<sup>14</sup> Such an *n*-type surface may be produced by water vapor, for example, as was shown by Brattain and Bardeen.<sup>2</sup>

<sup>15</sup> J. R. Schrieffer, Phys. Rev. **97**, 641 (1955).

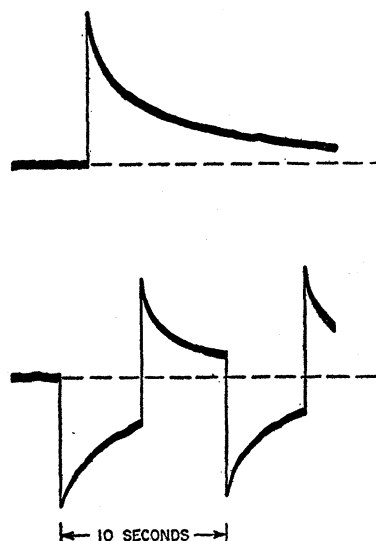


FIG. 2. Conductance vs time for etched surface in dry nitrogen. Upper trace: step function response. Lower trace: square wave response.

single-crystal material which was nearly intrinsic at room temperature. Ohmic contacts were attached along the ends of the sample and a plane metal electrode was placed approximately 0.01 inch from the surface under study. After etching the germanium, the whole assembly was placed in a glass chamber which could be supplied with various gases and water vapor. The conductance measuring circuit was similar to that used by Low,<sup>5</sup> except that it incorporated dc coupling and amplification for observation of the long time relaxation effects. The electrode voltage was either a square wave or a sine wave of up to 400 volts peak value, at frequencies from  $10^{-2}$  to  $10^3$  cps, thus producing at the surface a maximum field of approximately  $10^4$  volts per cm.

Initial experiments were performed using a square-wave voltage on the electrode to determine the transient response. Typical results are shown in Fig. 2 for an etched surface in dry nitrogen. The top trace, of approximately 20 seconds duration, is the response to a 300-volt step function applied to the electrode. The lower trace shows the response to a 300-volt peak-to-peak square wave of 10-second period. In this case the conductance decreases upon application of a positive field indicating a *p*-type surface. The time scale is too long to observe the initial recombination time transient, so that the initial pulse height is a measure of the quasi-static conductance after any trapping in recombination centers. No detailed data were taken on the amplitude of this initial conductance change, although the results are qualitatively in agreement with those of Montgomery and Brown.<sup>8</sup> In addition to the unusually long time of the observed transients, the decay in all cases is found to be nonexponential. The initial relaxation is rapid, but with increasing time the apparent time constant increases, giving more nearly a logarithmic rather than exponential law. One might suspect a nonlinear phenomenon. However, with the exception of a

near-intrinsic surface, the response was found not only to be symmetric with opposite field polarities, as in Fig. 2, but also to vary linearly with applied field. The nonlinearity in the near-intrinsic case is expected since here the surface conductance is near its minimum value and will increase for a small induced charge of either sign. (It is this minimum point which supplies a reference for the determination of the interface state densities.<sup>7,8</sup>)

On the basis of these observations it seemed apparent that the decay phenomenon could be explained in terms of a set of traps having a distribution of time constants. In physical terms one might think of different small regions of the surface relaxing exponentially with different time constants associated with the local capture times of the traps. While it is possible to analyze the relaxation transient into a sum of simple exponential decays, a more accurate technique is to determine the amplitude of the conductance variation produced by an applied sinusoidal electrode voltage. The relative response of the conductance as a function of the frequency of the driving signal will give the same information as an analysis of the transient. Data of this form were obtained by applying to the electrode a constant amplitude sine wave, approximately 400 volts peak to peak, in the frequency range from  $10^{-2}$  to  $10^3$  cps. The response was found to be linear over this range of frequencies and also over a ten-to-one change in amplitude. For frequencies between 1 and  $10^3$  cps, the peak-to-peak conductance change was read on an oscilloscope, while below this frequency the deviations were read on a voltmeter connected to the output of the dc amplifier.

The results for a typical run are shown in Fig. 3, in this case for a freshly-etched surface exposed to dry nitrogen, with the response normalized to unity at 1000 cps. As discussed in the previous section it is important that the sample recombination lifetime be short, for otherwise injection effects may give an anomalous response at high frequencies. This was accomplished by sandblasting the back surface of the slab, thus lowering the lifetime to the order of 5 microseconds for the

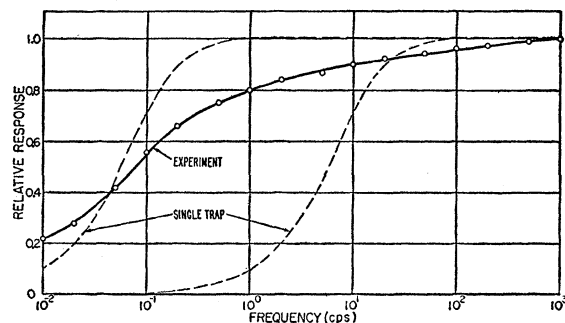


FIG. 3. Typical frequency response for a freshly etched surface in dry nitrogen. The dashed lines indicate two possible responses if the states all had the same time constant.

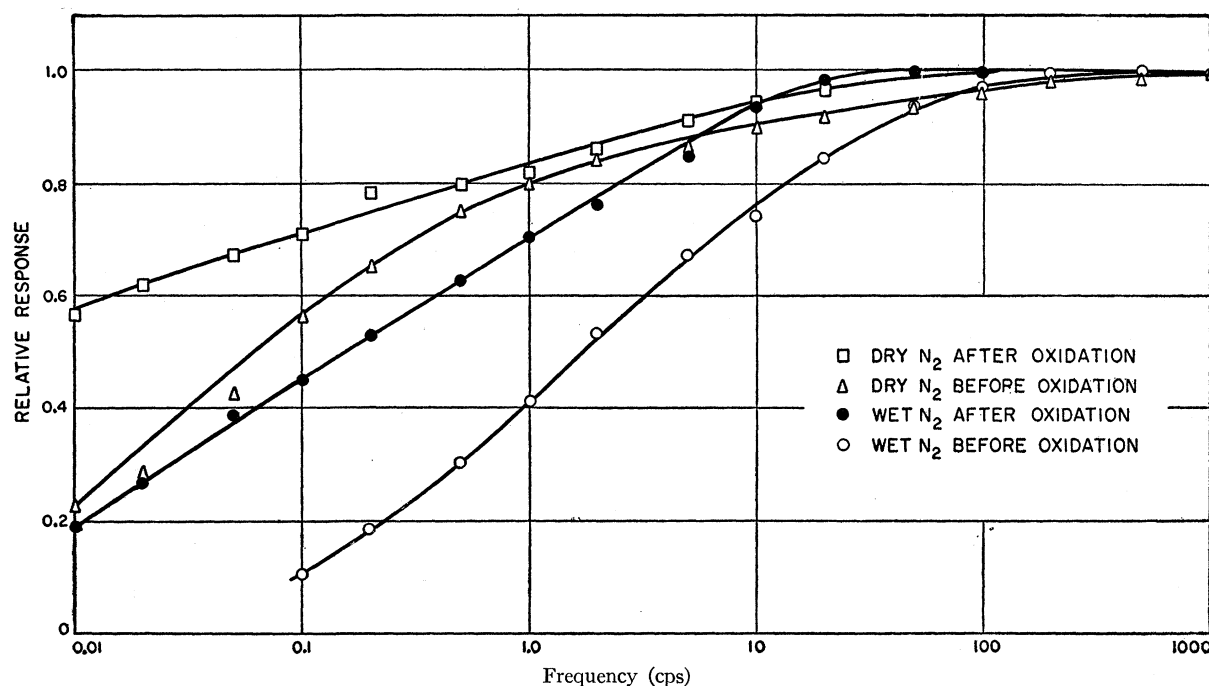


FIG. 4. Response for several surface treatments. All curves are normalized to unity at 1000 cps.

dimensions used. The dashed lines in Fig. 3 represent the response to be expected if all the traps had the same time constant, corresponding to a simple exponential decay in the transient case. As expected from the transient behavior, the frequency response or system function does not fit the curve for a single trapping time, but instead falls very gradually over many decades of frequency, still continuing in this case at  $10^{-2}$  cps. Similar frequency response curves were taken after various surface treatments. It was known from the transient behavior that the relaxation time was a critical function of gaseous ambient and surface history. Exposing a freshly etched sample to oxygen or air for several hours, for example, would always increase the decay time quite markedly. Also, for both a freshly-etched surface and a well-oxidized surface, wet nitrogen produces a more rapid relaxation than dry nitrogen. The effect of the water vapor is actually strong enough to counteract the effect of the oxidation: the decay for an oxidized surface in wet nitrogen is faster than for a freshly-etched surface in dry nitrogen. Typical frequency response curves for these cases are shown in Fig. 4. The "before oxidation" curves could not be obtained until approximately one-half hour after etching, since the surface was relatively unstable during the initial period and the steady drift in conductance made low-frequency measurements impossible. By observation of the transient response, however, it was found that during this period, the time constant increased from a small value, of the order of several milliseconds, to a value in the 0.1-second range when

the surface became stable enough to measure. The terms "before oxidation" and "after oxidation" should only be taken to mean before and after exposure to oxygen. At the present time the chemical behavior of a surface after etching and exposure to oxygen is not well understood. However, a similar change in surface properties with time is observed in other measurements such as surface conductance<sup>13</sup> and contact potential.<sup>2</sup>

A few measurements made in a vacuum of about 0.1 mm Hg indicated that the decay rate does not differ markedly from that in one atmosphere of dry nitrogen, but the results are only qualitative. A better understanding of the chemistry of the surface would be needed to make quantitative data meaningful. Even more interesting is the fact that measurements made in a nitrogen ambient at temperatures close to that of liquid nitrogen showed a faster decay than at room temperature. This last result must be considered somewhat tentative because the role of trapping<sup>16,17</sup> in these experiments is not completely known. Since illumination had no strong effect on the behavior, it is believed that the observations are valid. In any case, as observed both in this work and work on *n-p-n* junctions,<sup>13</sup> there is no appreciable change in the relaxation time for a wet surface as the temperature is lowered below the freezing point of water.

#### ANALYSIS OF DATA

Since the distribution of time constants of the trapping states is desired, it is necessary to convert the

<sup>16</sup> Fan, Navon, and Gebbie, *Physica* **20**, 855 (1954).

<sup>17</sup> H. A. Gebbie and K. Blodgett, *Phys. Rev.* **100**, 970 (1955).

frequency response or system function data to a function  $g(\tau)$  which gives the number of states per unit trapping time. If one considers the response due to a large density of states of one time,  $\tau$ , the system function will be

$$dS = g(\tau) \left( \frac{j\omega\tau}{1+j\omega\tau} \right) d\tau. \quad (1)$$

This may be recognized as the response of a simple  $RC$  high-pass filter whose transient response is a simple exponential decay with time constant  $\tau = RC$ . Now, assuming that the response of individual regions of the surface with different trapping times is additive, the normalized system function may be represented as

$$S(\omega) = \int_{\tau_1}^{\tau_2} g(\tau) \frac{j\omega\tau}{1+j\omega\tau} d\tau \left[ \int_{\tau_1}^{\tau_2} g(\tau) d\tau \right]^{-1}, \quad (2)$$

where  $g(\tau)$  is defined above and  $\tau_1$  and  $\tau_2$  are the limits of the distribution. For a given  $S(\omega)$  it is possible to solve Eq. (2) for  $g(\tau)$  by using Stieltjes transforms. However, since such a formal procedure requires numerical integration of the data, it is perhaps more instructive to consider three simple types of distribution for  $\tau$ ; namely, a single trapping time, a uniform distribution, and a hyperbolic distribution, given respectively by

$$g(\tau) = \delta(\tau - \tau_0), \quad (3a)$$

$$g(\tau) = k, \quad (3b)$$

$$g(\tau) = k/\tau. \quad (3c)$$

Integration of Eq. (2) with these functions gives, respectively,

$$S(\omega) = j\omega\tau_0 / (1+j\omega\tau_0), \quad (4a)$$

$$S(\omega) = 1 - [j\omega(\tau_2 - \tau_1)]^{-1} \left[ \ln \left( \frac{1+j\omega\tau_2}{1+j\omega\tau_1} \right) \right], \quad (4b)$$

$$S(\omega) = [\ln(\tau_2/\tau_1)]^{-1} \ln \left( \frac{1+j\omega\tau_2}{1+j\omega\tau_1} \right). \quad (4c)$$

The first form is shown in Fig. 3 by the dashed lines and obviously does not behave properly. The second solution also falls off too rapidly with decreasing frequency, most of the decrease occurring in the neighborhood of  $\omega = 1/\tau_2$ . The last form turns out to give the best approximation to the experimental data. If  $\tau_2$  is several orders of magnitude greater than  $\tau_1$ , the magnitude of  $S(\omega)$  is found to take the form

$$|S(\omega)| \approx [\ln(\tau_2/\tau_1)]^{-1} \ln(\omega\tau_2) \quad (5)$$

for

$$\omega\tau_1 \ll 1 \ll \omega\tau_2.$$

Near  $\omega = 1/\tau_2$  and  $1/\tau_1$  the function approaches zero and unity asymptotically. Now log  $\omega\tau_2$ , if plotted on

Figs. 3 or 4, would be simply a straight line with constant slope, in close agreement with experiment. In fact, it may be shown that a line tangent to this function along its straight portion intersects the zero and unity ordinates at the frequencies  $\omega = 1/\tau_2$  and  $1/\tau_1$ , respectively. Thus the distribution of time constants is given very nearly by  $1/\tau$  for all cases, with the limits of the distribution determined as above. Actually, for such a slowly varying function an approximate relation between  $g(\tau)$  and  $S(\omega)$  may be derived (see Appendix), which is

$$g(\tau) \propto -\frac{1}{\tau} \left[ \omega^2 \frac{d^2|S|}{d\omega^2} \right]_{\omega=1/\tau} = \frac{1}{\tau} \left[ \frac{d|S|}{d(\ln\omega)} - \frac{d^2|S|}{d(\ln\omega)^2} \right]_{\omega=1/\tau}. \quad (6)$$

for  $\omega\tau_1 \ll 1 \ll \omega\tau_2$ .

Analyzing the data on the basis of this formula gives the results in Table I. The trap distributions follow a hyperbolic law within experimental error, with the exception of Case III, dry nitrogen before oxidation. Here, application of Eq. (6) yields a density given by  $1/\tau^{0.75}$ , as a consequence of the negative curvature apparent in Fig. 4. The limits of the distribution,  $\tau_1$  and  $\tau_2$ , were obtained from the intersection of the straight portion of the system function with the zero and unity axes. The values of  $\tau_2$  in parentheses are only estimates since it was necessary to extrapolate beyond the lower frequency limit, while the  $\tau_1$  value in Case III is only an upper limit since the response is still rising at 1000 cps.

## DISCUSSION

The slow time constants observed in these experiments are believed to be a measure of the rate at which electrons are transferred between the bulk and states in or on the oxide layer. For the sake of discussion, consider the decay of excess electrons from the conduction band into the surface states (the reverse rate may be shown to be equivalent by detailed balancing arguments). The limiting process for this decay could be either the transition rate of the electron to existing states, as in a normal trapping process, or the rate of creation of new levels. The latter must be considered as a possibility since new states may be created either by the adsorption of additional molecules or by a chemical reaction between species present on the surface. However, adsorption as the rate-limiting process may be ruled out because the time constants are not strongly

TABLE I. Limits of time-constant distribution for several surface treatments.<sup>a</sup>

|                                  | $\tau_1$ (sec)       | $\tau_2$ (sec)    |
|----------------------------------|----------------------|-------------------|
| I. Wet $N_2$ —before oxidation   | $3 \times 10^{-3}$   | 2                 |
| II. Wet $N_2$ —after oxidation   | $10^{-2}$            | $(10^2)$          |
| III. Dry $N_2$ —before oxidation | $< 2 \times 10^{-4}$ | $(10^2)$          |
| IV. Dry $N_2$ —after oxidation   | $6 \times 10^{-3}$   | $(3 \times 10^3)$ |

<sup>a</sup> Values of  $\tau_2$  in parentheses are estimated; see text.

pressure-dependent. The temperature insensitivity of the decay, on the other hand, makes it almost impossible for a chemical reaction to be the determining factor. Any reaction involving water can almost certainly be eliminated, even without the liquid nitrogen data, since there is no marked change as the temperature is lowered far past the freezing point. Thus slow electron transitions to existing levels seems to be the only reasonable explanation for the long time constants. More direct evidence that electron transfer is the rate-determining process has recently been obtained by Morrison<sup>18</sup> as a result of studying the change in dark conductance of a germanium sample after it had been exposed to light for various periods of time. The conductance change under these conditions is apparently produced by the same trapping process as in the field effect since the slow transients are similar. Morrison found that the initial rate of change of dark conductance is proportional to the number of carriers in excess of equilibrium, but increases only slightly with oxygen pressure.

In connection with Morrison's data it should be mentioned that he finds a fairly strong temperature dependence for the rate of decay of conductance in the field effect. His measurements between 20° and -59°C, when interpreted according to the aforementioned model, give an activation energy of 0.5 eV for  $\tau_2$ , the upper limit of the  $1/\tau$  distribution. The reason for the disagreement between Morrison's results and the ones presented here is not known. Conceivably, the difference in the preparation of the surfaces could be the answer. Morrison etched his samples with 10% HF, 90% HNO<sub>3</sub>, and then aged them for four weeks in air.

If the electron transfer to the surface states takes place by thermionic emission over the barrier in Fig. 1, then the  $1/\tau$  distribution could result from a uniform distribution of the barrier height over the surface. To show this, let  $E$  be the height of the barrier, so that

$$\tau = ae^{qE/kT},$$

where  $a$  is a constant. Then the number of traps with time constants in the range  $(\tau, \tau + d\tau)$  is given by

$$dn = \frac{dn}{dE} \frac{dE}{d\tau} d\tau = \frac{kT}{q\tau} \frac{dn}{dE} d\tau.$$

Hence,  $g(\tau) = dn/d\tau$  will be proportional to  $1/\tau$  in the range  $\tau_1 < \tau < \tau_2$  if  $dn/dE$  is constant in the range  $E_1 = (kT/q) \ln(\tau_1/a) < E < E_2 = (kT/q) \ln(\tau_2/a)$ . This is the same idea that has been used to obtain a  $1/f$  distribution in some theories of  $1/f$  noise.<sup>19</sup>

Since in the present work it has been found that the time constants are relatively independent of temperature, an attractive alternative to thermionic emission is

to assume that the electrons tunnel through the barrier of Fig. 1.<sup>20</sup> In this case, the distribution of time constants may be explained by a uniform distribution in barrier widths, since  $\tau$  would be given by

$$\tau = Ae^{Bw},$$

where  $w$  is the barrier width and  $A$  and  $B$  are constants. The proof is completely analogous to the one for thermionic emission. Such a uniform distribution of barrier widths could arise either from a uniform spatial distribution of traps over a range of distance in the oxide layer or from a variation of oxide layer thickness over the surface. For a variation of thickness from 20 to 40 Å, and a barrier height of one electron volt, the transition times may be shown to vary from the order of  $10^{-4}$  to  $10^4$  sec.<sup>21</sup> If the oxide layer does thicken appreciably "after oxidation," this picture would also explain the accompanying increase in time constants. It is also possible in the case of tunneling to obtain the desired  $1/\tau$  distribution by considering fluctuations in the barrier height along the surface.

The phenomenological model of slow traps developed here to explain the field effect measurements can also explain  $1/f$  noise in single-crystal filaments of germanium. If it is simply assumed that there are a large number of traps with a  $1/\tau$  distribution of time constants, then a calculation of the conductivity fluctuations caused by the random filling and emptying of the traps gives both the desired  $1/f$  spectrum and the right order of magnitude for the noise.<sup>21</sup> The origin of the  $1/\tau$  distribution does not have to be known to obtain this result, but the characteristic temperature insensitivity of  $1/f$  noise again makes a tunneling process attractive. Reference 20 also contains a detailed analysis of the statistics of these slow traps in connection with the field effect measurements.

Throughout the paper the nonexponential conductance decays and the logarithmic frequency response of the field effect have been interpreted in terms of a distribution of time constants. To account for these same observations, Morrison<sup>18,22</sup> has proposed a nonlinear model with only one type of surface level and a single time constant. He gets a change in the instantaneous rate of decay of the conductance by means of a variation of the barrier height with the amount of charge trapped in the slow surface states. As has been emphasized previously, however, in the present work the change in conductance was found to be directly proportional to the applied field as long as the field strengths were kept below about  $10^4$  volts/cm. (Such fields produce a deviation in surface potential less than  $kT/q$ .) Doubling the voltage applied between the germanium and the electrode, for example, doubled the conductance change at every instant of time; a

<sup>18</sup> S. R. Morrison, Phys. Rev. **102**, 1298 (1956). The authors wish to thank Dr. Morrison for a preprint of his paper.

<sup>19</sup> A. van der Ziel, Physica **16**, 359 (1950); F. K. duPré, Phys. Rev. **78**, 615 (1950).

<sup>20</sup> A. L. McWhorter, Phys. Rev. **98**, 1191 (1955).

<sup>21</sup> A. L. McWhorter, Sc. D. thesis, Massachusetts Institute of Technology, 1955 (unpublished).

<sup>22</sup> S. R. Morrison, Phys. Rev. **99**, 1655 (1955).

change of polarity of applied field simply reversed the sign of the conductance change without altering the shape of the curve. Furthermore, a sinusoidal voltage applied to the electrode caused the conductance to vary sinusoidally at the same frequency with no harmonic distortion. This linearity means that the differential equation governing the process has to be linear, or at least linearized for small-signal deviations about equilibrium. However, as soon as one linearizes Morrison's equations, one immediately gets a simple exponential decay, so that his model cannot explain the low-field experimental results presented here. On the other hand, Morrison's model may well account for effects associated with large applied fields that produce a variation in the surface potential greater than  $kT/q$ , a situation which has not been investigated in this paper.

### CONCLUSION

The results of this study apply directly only to the types of surface treatment used. However, it is believed that the observed behavior is common to a broad range of surface treatments both on silicon as well as germanium. For instance, a similar transient behavior has been observed on sandblasted surfaces, although it has not been studied in detail. More detailed models of the surface must await further investigations of the structure and chemical behavior of the oxide layer. In particular, the variation of the time constants with temperature bears further study, but at present is hindered by a lack of knowledge of the detailed physical

and chemical processes occurring in the different temperature ranges.

### APPENDIX. DERIVATION OF EQ. (6)

Let  $g(\tau) = f(\tau)/\tau$ , where  $f(\tau)$  is now a slowly varying function. Then Eq. (2) of the text may be rewritten as

$$S(\omega) = N \int_{\tau_1}^{\tau_2} f(\tau) j\omega (1 + j\omega\tau)^{-1} d\tau, \quad (\text{A1})$$

where  $N$  is the normalizing constant. Differentiating both sides with respect to  $\omega$  leads to

$$\frac{dS}{d\omega} = N \int_{\tau_1}^{\tau_2} f(\tau) [j/(1 + j\omega\tau)^2] d\tau. \quad (\text{A2})$$

Since the term in brackets is approximately unity up to  $\omega = 1/\tau$  and falls rapidly to zero beyond this point, the result may be approximated by

$$\frac{d|S|}{d\omega} \approx N \int_{\tau_1}^{1/\omega} f(\tau) d\tau. \quad (\text{A3})$$

Differentiating with respect to  $1/\omega$  and rearranging terms gives the final result

$$f(\tau) = -\frac{1}{N} \left[ \omega^2 \frac{d^2 |S|}{d\omega^2} \right]_{\omega=1/\tau}, \quad (\text{A4})$$

which is utilized in Eq. (6) of the text.