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Water-Vapor-Induced *n*-Type Surface Conductivity on *p*-Type Germanium*

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By utilizing a direct reading instrument it is possible to measure the *n*-type surface conductance of the *p*-type germanium in an *n-p-n* junction transistor as a function of relative humidity, ambient gas, and surface treatment. The results of these measurements indicate that the leakage conductance from the emitter to the collector may be predicted on the basis of a constant electron density at the surface which is independent of the applied bias but a critical function of the oxidation of the surface and the adsorbed gas. This conductance exhibits a transient character upon change in applied bias which may be correlated with similar transients in the conductance of a thin germanium crystal upon application of an external applied field. This comparison establishes that the inversion layer is caused by ionization of surface impurities rather than migration of ions along the surface. From the results of the experiments it is postulated that the density and type of carrier at the surface of an etched germanium crystal are a function of the surface treatment and gaseous ambient rather than the acceptor and donor density of the bulk germanium.

INTRODUCTION

EARLY in the study of the junction transistor[1] it was observed that the experimental behavior was not in complete agreement with the theory. In particular, variation of the ambient surrounding the semiconductor was found to cause anomalous changes in the electrical characteristics. These discrepancies, which were attributed to the surface of the semiconductor, were first studied by Brown[2] who explained one of the more troublesome phenomena, channeling. A channel consists of a thin layer of *n*-type material on the surface of the *p*-type base region of an *n-p-n* germanium junction transistor and produces an ohmic path from the emitter to the collector. Brown determined that this *n*-type inversion layer could be attributed to the presence of excess positive charge on the surface of the germanium as a result of the applied voltage between the *n*- and *p*-type regions of the transistor. He further showed that once the charge has been established by the applied bias, the unit can be immersed in a temperature bath (−78°C) and the charge stabilized. The conductance of the channel is then found to decrease with increasing bias until the excess positive charge on the surface is completely neutralized by ionized acceptors in the space-charge region beneath the surface. At this bias no conduction electrons are necessary to neutralize the surface charge and the channel "pinches off." In general this effect was found to be produced in the presence of water vapor although alcohol and other vapors produced similar results.

The work to be described in this paper is a quantitative study of the room temperature behavior of the channel in the presence of moist nitrogen and oxygen. Brown experienced difficulty in making bridge measurements of channel conductance at room temperature due to instability; therefore a direct reading instrument was used which made possible instantaneous measurements. In addition, the moisture content of the gas used as ambient was controlled precisely, in order to reduce these instabilities and obtain a quantitative relation between conductance and vapor pressure. The preliminary results already reported[3,4] have been modified and extended and, it is hoped, give a further insight into the structure of the surface as well as an explanation of some of the anomalies of junction diode and transistor behavior.

EXPERIMENTAL APPARATUS

1. Conductance Measurement

The circuit of Fig. 1 was used to obtain a direct reading of channel conductance as a function of the voltage, ambient, and surface treatment. Here the *n*-type emitter and collector are maintained at ground potential for dc. A low-impedance 1000-cps oscillator supplies a measuring signal across the series combination of the channel and an adjustable load resistor. The signal is then amplified and detected by a tuned amplifier and the output read directly as channel conductance after reference to a calibration chart. Since the maximum rms voltage across the channel is 0.1 volt, the power dissipated is at most 2 microwatts corresponding to a channel conductance of 2×10^{-4} mhos. The high selectivity of the amplifier allows measurements as low as 10^{-7} mhos without interference from

FIG. 1. Channel conductance measuring apparatus.

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

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[1] Shockley, Sparks, and Teal, Phys. Rev. **83**, 151 (1951).

[2] W. L. Brown, Phys. Rev. **91**, 518 (1953).

[3] R. H. Kingston, Phys. Rev. **93**, 346 (1954).

[4] R. H. Kingston, Phys. Rev. **94**, 1416 (1954).

stray ac pickup or noise. Additional electrical measurements are described in the section on experimental results.

2. Humidity Control

In the preliminary experiments wet or dry nitrogen or oxygen were supplied by either bubbling the gas through water or passing it through a BaO drying tube. Later, when it was found that the amount of moisture was a critical quantity a system was devised for maintaining a selected set of relative humidities over the sample. This was accomplished by circulating the gas in a closed system over a saturated aqueous salt solution and through the chamber containing the specimen. The gas was circulated by a pump having a tight seal from the atmosphere and the apparatus was kept under a small partial pressure to prevent leakage of air into the system. The salt solution bottles and the sample chamber were kept in a water bath to maintain thermal equilibrium, since a slight difference in sample temperature and salt-bath temperature would produce a reasonable discrepancy in relative humidity over the sample. The salts used with their relative humidities are given in Table I. These were found in the International Critical Tables[5] and were chosen to have a negligible variation in relative humidity over the range of temperature, 20 to 30°C. The humidities were checked in the system with a standard dew-point indicator and found to be accurate within 2 to 3 percent.

Table I. Saturated aqueous salt solutions.

Salt	Relative humidity (percent)
LiCl	15
$MgCl_2$	32
K_2CO_3	43
NaBr	58
NaCl	75
$BaCl_2$	88

3. Sample Preparation

The data to be discussed were taken on bars from several *n-p-n* germanium grown-crystals. Specifically, those of Figs. 2 and 3 are from production type crystals kindly supplied by the Bell Telephone Laboratories and having dimensions and resistivities similar to those used by Brown. The remaining data were observed with a special crystal having a wide *p*-type base region thus facilitating accurate measurements of base width and resistivity. The constants for this crystal were determined by the methods of Goucher and Prince[6] and are given in Table II. The transistor structures were prepared by cutting the crystal into bars, wet-lapping with 600-mesh carborundum, and attaching nickel leads to the ends with antimony-tin solder. After etching in CP-4, the base contact was made by bonding a 0.002-in. gallium-doped gold wire to the base region. One advantage of the special wide-base crystal was the ease with which the bond could be located at the center of the base region. In the production-type crystals, having approximately 0.002-in. base width, the gold alloy region generally overlapped onto the collector material giving excess collector to base reverse current at high humidities, thus limiting the reverse biassing range. The samples, after bonding were rinsed in carbon tetrachloride, alcohol, and distilled water, mounted on a glass-taper lead assembly, and placed in the experimental chamber.

Table II. Constants of special *n-p-n* crystal

Base width	0.015 cm
Emitter resistivity	0.6 ohm-cm
Collector resistivity	10 ohm-cm
Base resistivity	3.3 ohm-cm
Acceptor density—N_A—(base)	1.1×10^{15} cm^{-3}
Fermi energy—ϕ_p—(base)	0.095 volt

EXPERIMENTAL RESULTS

Prior to the measurements on the samples discussed above, a plastic-encased transistor was measured with the conductance meter and found to give excellent agreement with Brown's low-temperature results. At room temperature, however, it was not possible to obtain a steady-state reading of channel conductance except at very low biases where the data were at the limit of sensitivity of the meter and also difficult to reproduce. Higher instantaneous readings of conductance could be obtained with a sudden reduction in applied bias after prolonged application, but the reading decayed in a few seconds to a negligible value.

The behavior of the bare *n-p-n* bars in a moist ambient was quite different from that of the plastic-encased transistors. At room temperature, in a sufficiently moist ambient, the channel conductance exhibited a reproducible steady-state value over a wide range of biases. The values of conductance were approximately inversely proportional to applied voltage and increased with humidity. Also a transient phenomenon was observed wherein the conductance decreased abruptly upon increase in bias and then increased to the new steady-state value with a time constant of the order of a second, with a small but measurable drift for the order of a minute. A similar transient was observed upon decrease in bias, the conductance increasing abruptly and decreasing to the new value. (The wide variation in time constant with humidity reported previously[3] is not observed when the conductance is measured directly. The early data was obtained by observation of the floating potential of the open-circuited emitter, after application of bias to the collector. The time constant measured was therefore that time in which the channel conductance

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[5] *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1926), Vol. 1, p. 67.

[6] F. S. Goucher and M. B. Prince, Phys. Rev. **89**, 651 (1953).

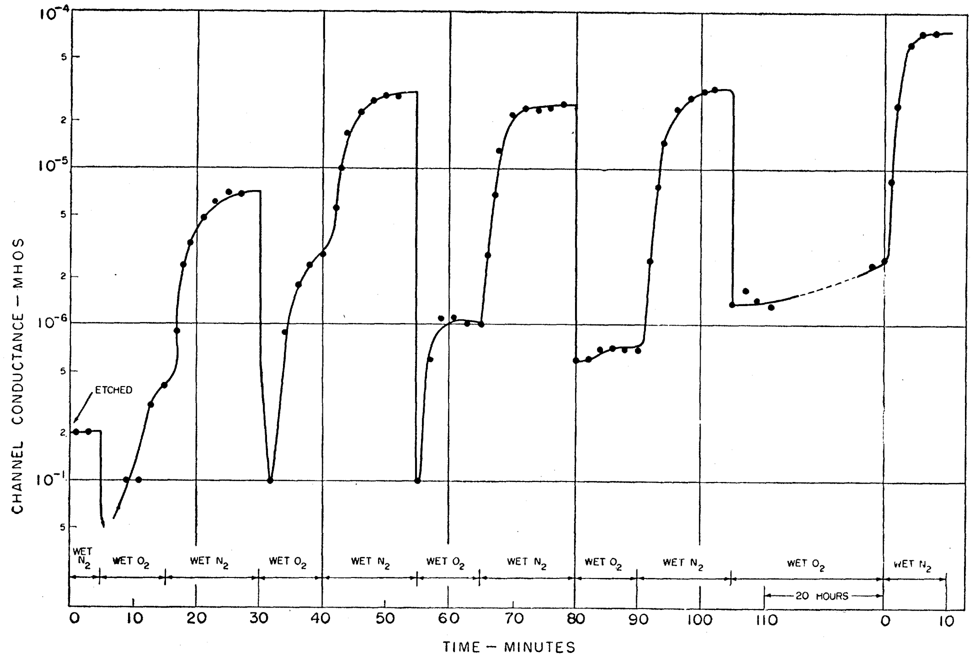

FIG. 2. Channel conductance *vs* time for wet oxygen and nitrogen exposure after etch with hydrofluoric acid.

increased by an amount comparable to the leakage conductance of the emitter circuit. Thus, for increasing channel conductance, corresponding to increasing humidity, the time for establishment of the floating potential decreased, since the emitter conductance is generally much smaller than that of the channel.) With the exception of some qualitative observations below, it was not possible to measure the channel conductance at low temperature on the bare units since freezing of the moisture on the surface of the bar produced erratic results.

Returning to the equilibrium behavior at room temperature, it was soon found that the early data had two serious shortcomings. First, the humidity, which was controlled by bubbling nitrogen through a variable-temperature water bath, was not sufficiently reproducible. Second, and most important, the data were found to be a critical function of the amount of oxidation of the germanium surface. That is, after the bonding and cleaning operation, exposure to oxygen produced an irreversible increase in channel conductance for a given relative humidity in nitrogen.

This effect was studied in more detail and a typical experimental curve is shown in Fig. 2. At the beginning of the run, the sample was etched in hydrofluoric acid which is assumed to remove all but the last few layers of oxide on the surface. The sample was then exposed to wet nitrogen, approximately 75 percent relative humidity, and the reverse bias set at approximately 1.0 volt. The ambient was then varied as shown along the time axis, the moisture content of the oxygen being the same as that of the nitrogen. There are two pertinent conclusions to be drawn from this graph. First, as noted above, the channel conductance increases monotonically with exposure to oxygen, when measured either in an oxygen or nitrogen ambient. This is further confirmed by the lack of any conductance increase if the sample is left in wet nitrogen for several hours after the hydrofluoric acid etch. Second, the channel conductance in wet oxygen is generally an order of magnitude lower than in wet nitrogen at the same time in the oxidation process. The gradual rise to equilibrium upon change from oxygen to nitrogen is probably caused by the speed at which the oxygen on the surface is removed, however the abrupt decrease in conductance upon re-exposure to oxygen in the initial cycles is as yet unexplained. After the last long oxygen exposure, the curves of Fig. 3 were obtained in the same ambients. The expected inverse voltage behavior is evidenced here along with the previously cited decrease of conductance in the oxygen ambient.

To obtain an accurate measurement of the channel conductance as a function of relative humidity, the circulating system was used with nitrogen, since, from Fig. 2, the surface was known to be stable in such an ambient. As mentioned in the previous section, it was desirable that the base layer of the transistor be wide enough to assure accurate measurements of the width and the resistivity of the *p*-type base material. Therefore the special crystal described in Table II was utilized and the sample had cross-sectional dimensions of 0.096 by 0.108 cm. The data of Fig. 4 were taken at a temperature of 24°C and were reproducible over all voltages and humidities. To avoid the effects of any slight oxidation throughout the experiment, the bar was initially exposed to oxygen for several hours to establish a stable layer. In addition to the data of Fig. 4, measurements taken in wet N_2 after different exposure times to oxygen always gave the same shape curves with an overall shift in magnitude corresponding to the changes observed in Fig. 2. It was not possible to obtain these data immediately after the hydrofluoric acid etch, however, since, in this condition, the conductance meter was not sensitive enough to give a reading for biases greater than about one volt. Neither was it possible to measure the wet oxygen ambient conductance, except on a well-oxidized surface, since the changes in conductance due to oxidation obscured the changes due to applied bias. Similar data was obtained using helium in place of nitrogen, indicating that the nitrogen only acts as a carrier for the water.

The channel capacitance was measured at several humidities by means of a substitution type circuit operating at 700 kcps. The reverse capacitance of the emitter and collector in parallel were first measured in a dry nitrogen ambient and then in the desired humidity, the difference between the two readings giving the contribution of the channel. This capacitance was found to be a definite function of humidity in agreement with the theory discussed in the next section. The experimental points for 88 percent relative humidity are plotted in Fig. 9 in modified form in conjunction with the theoretical treatment.

Since the relaxation phenomena should give information about the mechanism of channel formation, it was studied in more detail with the circuit of Fig. 5(a). The two batteries and switch at the center of the figure allow a step of voltage to be applied to the base and the battery at the left supplies a small current through the channel so that the output voltage to the scope is directly proportional to the channel conductance. Using a step voltage of approximately 0.1 volt, the conductance transient, shown at the right was found to have the same time constant over the range of bias voltages used in the previous data. The time of decay to half of the peak value varied from about 1.0 second at 32 percent humidity and decreased to the order of 0.1 second at 100 percent humidity. By cooling the chamber containing the transistor while moist nitrogen was flowing, it was also possible to observe a 1.0-second transient at temperatures as low as −25°C. Since the chamber wall was at a much lower temperature than that measured on the transistor with a thermocouple, the effective humidity was probably quite low and the result is only significant insofar as it indicates presence of the transient at temperatures well below freezing.

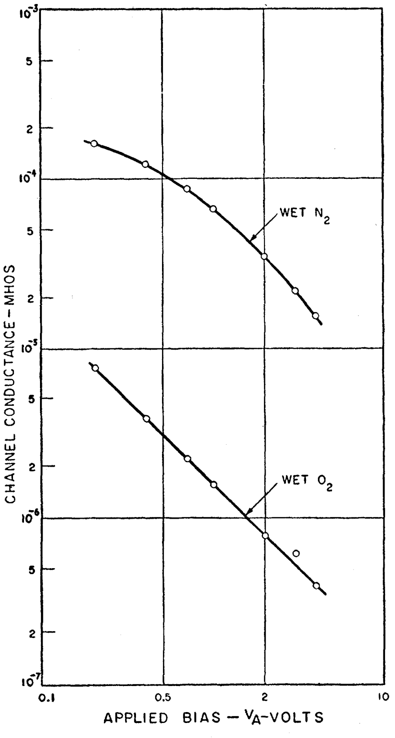

FIG. 3. Channel conductance *vs* applied voltage in wet oxygen and nitrogen after treatment shown in Fig. 2.

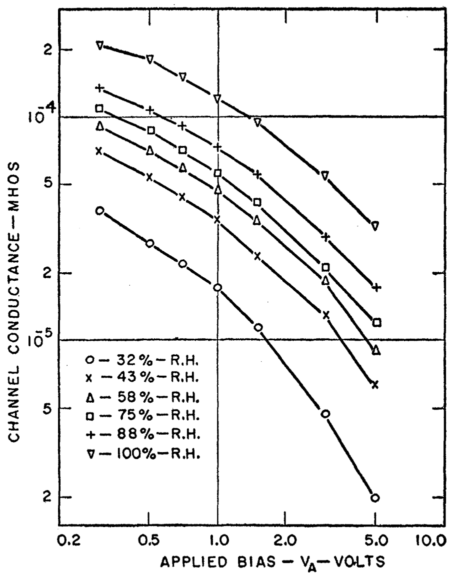

FIG. 4. Channel conductance *vs* applied bias on an oxidized surface for several values of humidity in a nitrogen ambient.

A similar experiment was performed using a configuration similar to that used by Pearson and Shockley[7] to investigate surface states on germanium. In Fig. 5(b), the conductance of a thin slab of high resistivity *p*-type germanium is measured as a function of the electric field applied perpendicular to the surface. The sample was etched in the same manner as the transistor, and by means of the plane parallel electrode an electric field of approximately 10 000 volts per cm could be applied by closing the switch in the diagram. The conductance change was displayed on an oscilloscope by observing the voltage across the load resistor. The behavior of the conductance upon application of the field was indistinguishable from the behavior of the

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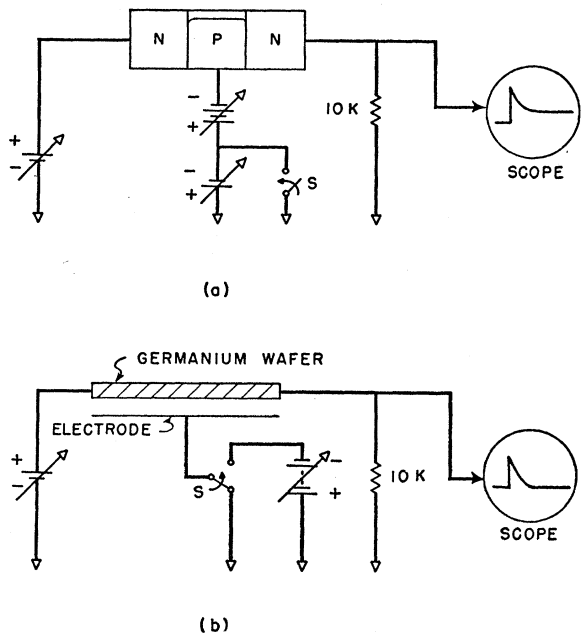
[7] G. L. Pearson and W. Shockley, Phys. Rev. **74**, 232 (1948).



(a)

(b)

Fig. 5. Circuits for measuring relaxation time (a) for the channel and (b) for the field-effect.

channel except that after the occurrence of the transient sketched at the right of the figure, the conductance returned to its original value.[8] The decay times also behaved in the same manner with humidity and temperature, and in this case the value of 1.0 second was found to hold not only for low humidities but also for a completely dry ambient. The structure of this decay curve and that of the channel have not been studied in detail and there is evidence that neither is a simple exponential. At least in the case of the channel, there is an observable drift toward equilibrium for the order of a minute. The significance of these observations on the field effect will be discussed in connection with the physical model of the channel.

In addition to the above information several other observations are of interest. One is the occurrence of an extraneous channel conductance under conditions of surface contamination. If the sample was not carefully cleaned after the bonding operation the conductance was found to decrease with applied bias until a bias of several volts was reached, at which point the conductance became constant and independent of further increases in bias. Accompanying this effect was an abnormal increase in the reverse current supplied to the emitter and collector regions. Since this anomaly could always be eliminated by etching in hydrofluoric acid, carefully rinsing in distilled water, and reoxidizing the surface, it might well be caused by ionic surface conduction similar to that discussed by Law.[9] Finally it should be noted that under the above clean conditions, the dc reverse current from the *n*-type to the *p*-type material increased by at most 5 microamperes from its dry value at the highest measuring voltages and the highest humidity. This means that the load resistances in the conductance-measuring circuit were shunted by a minimum of one megohm, thus producing a negligible effect on the accuracy of the reading.

THEORETICAL MODEL

In an earlier publication[3] the inverse voltage behavior of the channel was explained by assuming constant electron mobility and a fixed impurity level having a time constant comparable to the relaxation times observed. Later, at the suggestion of H. Brooks of Harvard University, the mobility was taken proportional to the effective thickness of the channel[4] on the basis of calculations of mobilities in thin films.[10] Concurrent with this revision of the theory, Schrieffer[11] presented detailed calculations of mobility in a channel, and the following theory utilizes results which he kindly made available previous to publication.

By using the model of Fig. 6, similar to that used by Brown, the channel is represented by the electrons in the potential well just beneath the surface. $\mathcal{E}_i$ is the electrostatic potential corresponding to the Fermi energy for intrinsic material, and the potentials, ϕ_p and ϕ_s, are the deviations of the quasi Fermi levels from the intrinsic value for holes in the bulk and electrons at the surface, respectively. These last two quantities and V_A, the applied bias, will be expressed in volts. The channel conductance may be converted to a specific surface conductance in mhos per square by the relationship,

$$g = G/WC, \qquad (1)$$

where G is the channel conductance, g, the specific surface conductance, C, the circumference, and W, the width of the *p*-type base region. The specific conductance

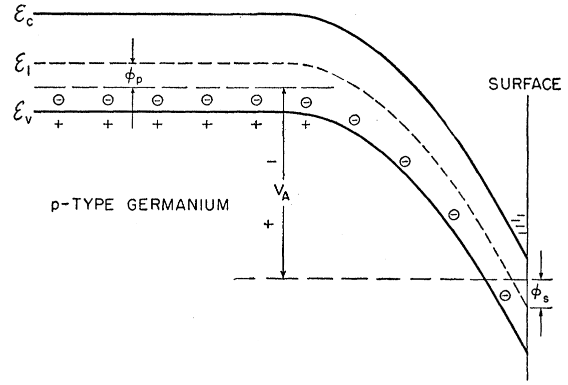


Fig. 6. Energy band configuration at surface of *p*-type germanium.

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[8] This transient phenomenon has been observed independently by D. T. Stevenson of this laboratory and S. R. Morrison of the University of Illinois (private communication).

[9] J. T. Law, Proc. Inst. Radio Engrs. 42, 1367 (1954).

[10] E. H. Sondheimer, Advances in Phys. **1**, 11 (1952).

[11] J. R. Schrieffer, Phys. Rev. **94**, 1420 (1954).

may then be written:

$$g=qN\mu_{\mathrm{eff}}, \tag{2}$$

where q is the electron charge, N, the number of electrons per unit surface area and μ_{eff} is the effective mobility of electrons in the channel. Assuming that the free electron charge at the surface is small compared with the charge produced by acceptor ions in the depletion layer, the electric field perpendicular to the surface may be calculated to be

$$E_s=[2qN_A(V_A+\phi_s+\phi_p)/\kappa\epsilon_0]^{\frac{1}{2}}, \tag{3}$$

from a solution of Poisson's equation. This expression is the same as that for the field at the center of an abrupt p-n junction. To determine N, the number of electrons per unit area, integration from the surface into the bulk gives

$$N=n_ie^{q\phi_s/kT}\int_0^\infty e^{-qE_sx/kT}dx=\frac{kT}{qE_s}n_ie^{q\phi_s/kT}=wn_ie^{q\phi_s/kT}, \tag{4}$$

where w is defined as the channel thickness and is the distance in which the electrostatic potential rises by kT/q or the electron density falls to $1/e$ of its value at the surface. Here, E_s is assumed constant over the important range of x or alternatively w is much less than the thickness of the space-charge layer. In terms of this thickness, Schrieffer's mobility calculation gives

$$\mu_{\mathrm{eff}}=3w\mu_n/l_s, \quad w\ll l_s, \tag{5}$$

where l_s is the mean free path for lattice scattering. When the appropriate terms in electron concentration and mobility are combined, the specific surface conductance is found to be proportional to the square of the channel thickness and consequently inversely proportional to the electrostatic potential between the bulk and the surface, $\psi=V_A+\phi_s+\phi_p$. The result is

$$g=\tfrac{3}{2}[k\epsilon_0(kT/q)^2(n_i/N_A)(\mu_n/l_s)e^{q\phi_s/kT}] \times(V_A+\phi_s+\phi_p)^{-1}. \tag{6}$$

It may be seen by inspection that, for voltages large compared to ϕ_s plus ϕ_p, the conductance varies inversely with applied bias if ϕ_s is held constant. Since the experimental data show a similar inverse relationship, the value of ϕ_s for each humidity has been obtained from the curves of Fig. 4 at large bias and the data replotted in Fig. 7 as specific surface conductance *versus* effective bias, $V_A+\phi_s+\phi_p$. In this calculation the mean free path is obtained from the relationship[12]

$$\mu_n=4ql_s/3(2\pi m^*kT)^{\frac{1}{2}}, \tag{7}$$

with the effective mass, m^*, 0.12 times the mass of the free electron,[13] giving l_s equals 8.8×10^{-6} cm at room temperature.

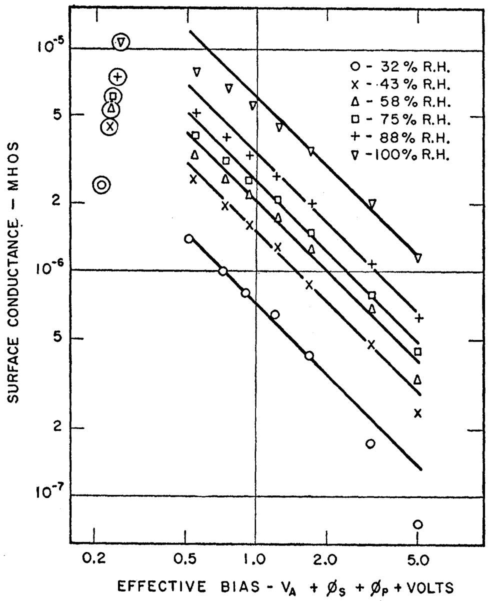

FIG. 7. Specific surface conductance *vs* effective bias. The solid lines are the theory for large bias and the circled points at the left, for zero bias.

Verifying the approximations, the calculated channel thickness, w, for an effective bias, $V_A+\phi_s+\phi_p$, of one volt, is

$$w=kT/qE_s=1.6\times10^{-6}\ \mathrm{cm}, \tag{8}$$

with E_s equal to 1.6×10^4 volt/cm from Eq. (3). Thus, except at effective biases less than one volt, taking the channel thickness much less than the mean free path for lattice scattering is a good approximation. As assumed for Eq. (4), this value for w is also much less than the space charge thickness. The free electron charge in the channel at the same bias may be calculated from Eqs. (2) and (5), giving

$$qN=gl_s/3\mu_nw=(5.1\times10^{-4})g\ \mathrm{coul/cm^2}, \tag{9}$$

where g is expressed in mhos. From the value of E_s, the charge of the ionized acceptors is found to be

$$Q_A=k\epsilon_0E_s=2.3\times10^{-8}\ \mathrm{coul/cm^2}, \tag{10}$$

again evaluated at one-volt effective bias. Referring to Fig. 7 and using Eq. (9), the free electron charge in the channel varies from 3.6×10^{-10} to 3.1×10^{-9} coulomb per cm^2, from the lowest to the highest humidity. This is seen to be much less than the charge due to the acceptor ions, thus agreeing with the assumption for the electric field at the surface.

In addition to this calculation at large applied bias, it is also possible to compute the channel conductance at zero applied bias for the values of ϕ_s previously obtained. This is accomplished by a numerical integration of Poisson's equation[14] and utilization of the effective mobility as calculated by Schrieffer.[11] These

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[12] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 277.

[13] B. Lax, International Conference on Semiconductors, Amsterdam, July, 1954 (to be published in Physica).

[14] R. H. Kingston and S. F. Neustadter (to be published).

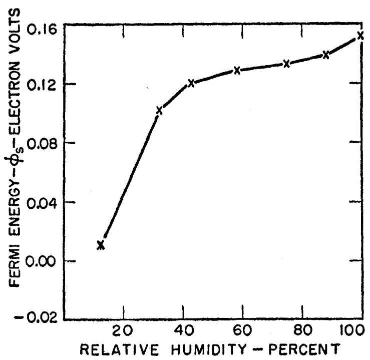

FIG. 8. Values of ϕ_s obtained from Fig. 7 for a well-oxidized surface in moist nitrogen.

calculated points are circled on Fig. 7 and show good agreement with the extrapolated conductance data at low biases. The zero-bias value of conductance cannot be measured directly, of course, since under this condition there is no longer a high impedance isolating the p-type from the n-type regions of the semiconductor.

Thus, for a given ambient, as the bias is increased, the positive charge on the surface increases with E_s, such that ϕ_s is maintained constant. The value of ϕ_s, based on this model, has been plotted in Fig. 8. The lowest point, at 15 percent relative humidity, is only an estimate based on readings taken below one-volt bias, where there is no assurance that the conductance obeys the inverse voltage law.

In calculating the channel capacitance it is first necessary to consider that the data were measured at 700 kcps so that the period of the applied voltage is much shorter than the observed relaxation time of the channel. For this reason it will be assumed that the positive charge on the surface producing the channel is fixed and the only charge which changes with the applied signal is that produced by the acceptor ions, N_A, the electrons in the channel, N, and any charge residing in surface recombination states, similar to those proposed by Brattain and Bardeen.[15] This assumption is the same as that made by Brown[2] for the treatment of the channel at low temperatures. The capacitance per unit area may be written

$$C_1/A = dQ/dV_A, \tag{11}$$

where dQ is the change in charge per unit area at the surface or by neutrality the change in acceptor charge at the inside of the space charge region. Now ψ, the electrostatic potential between the bulk and surface is given by $V_A+\phi_s+\phi_p$; therefore,

$$d\psi = dV_A + d\phi_s, \tag{12}$$

since ϕ_p is a constant. By referring to Fig. 6, it may be seen that if V_A is increased, then the corresponding increase in ψ is diminished by a decrease in ϕ_s, since the reduction in the number of electrons at the surface must be accompanied by a shift in the Fermi energy toward the valence band. This shift in ϕ_s occurs instantaneously since the electrons in the channel are in equilibrium with the n-type material in the emitter and collector regions. Similarly it is assumed that any electrons in surface recombination centers will be released in a time short compared to the period of the applied frequency, as done by Brattain and Bardeen.[15] The change in charge with a change in ψ may be found by writing

$$dQ = qN_A dx, \tag{13}$$

where dx is the change in width of the space charge region. But if the space charge widens by this amount, then ψ at the surface must increase by

$$d\psi = E_s dx. \tag{14}$$

Combining Eqs. (13) and (14) gives

$$C_0/A = dQ/d\psi = qN_A/E_s,$$

where C_0/A is also the capacitance obtained for an abrupt p-n junction between p-type material of acceptor density, N_A, and n-type material of infinite conductivity. To find the true capacitance dQ/dV_A it is necessary to find the relationship between dQ and $d\phi_s$. The charge in the channel may be written

$$Q = -q[wn_i + n_{a0}]e^{q\phi_s/kT}, \tag{15}$$

where n_{a0} is the density of electrons in donor type surface states when ϕ_s is zero, as defined by Brattain and Bardeen.[15] It is assumed that the acceptor type states are completely filled and they are therefore neglected. The change in charge is then

$$dQ = -[wn_i + n_{a0}]q^2 e^{q\phi_s/kT} d\phi_s/kT, \tag{16}$$

and rewriting, using Eq. (8), gives

$$dQ = -[n_i + n_{a0}/w]qe^{q\phi_s/kT} d\phi_s/E_s. \tag{17}$$

The true channel capacitance, C_1/A, may then be found from

$$C_1/C_0 = dV_A/d\psi = [1 + (wN_A e^{-q\phi_s/kT}/wn_i + n_{a0})]^{-1}. \tag{18}$$

Since the channel is, in reality, a distributed RC transmission line, it was necessary to correct the above expression by the factor

$$\frac{C_{\text{meas}}}{C_1} = \frac{1}{2x}[\tanh x(1 - \tan x \tanh x) + \tan x(1 + \tan x \tanh x)][1 + (\tan x \tanh x)^2]^{-1},$$

where

$$x = (wC/8G)^{\frac{1}{2}}, \tag{19}$$

which is the effective capacitance as measured from both ends of an RC line having a total conductance, G, and total capacitance, C. The best fit with the data was

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[15] W. H. Brattain and J. Bardeen, Bell System Tech. J. 32, 1 (1953).

found if the contribution of n_{a0} was neglected, and Fig. 9 shows the three theoretical curves and the experimental data corresponding to a relative humidity of 88 percent and $\phi_s = 0.14$ volt. A similar agreement was found for the same humidity with a partially oxidized sample having a value of ϕ_s of 0.10 volt. Since the surface states were found to have no effect on the measured capacitance as expected from Eq. (18), then either they do not maintain equilibrium with the conduction band at 700 kcps or their density is too small to affect the result. In this latter case, from Eq. (18),

$$n_{a0} \ll w n_i = 5 \times 10^7 \text{ cm}^{-2}, \tag{20}$$

which is a factor of 10^4 smaller than the same quantity estimated by Brattain and Bardeen.[15]

DISCUSSION

The pertinent results of the experiment and theory may be summarized as follows: (1) The variation of channel conductance and capacitance may be explained on the basis of a constant ϕ_s at the surface determined by the ambient and the oxidation of the surface. (2) Whenever the applied bias is changed, the channel conductance shows an instantaneous change followed by a gradual relaxation to a new steady-state value. (3) The magnitude of ϕ_s, or consequently the free-electron density at the surface, increases with oxidation and also with water vapor pressure. (4) Moist nitrogen produces a value of ϕ_s approximately 0.1 volt higher than oxygen of the same moisture content on a surface having the same oxide layer thickness.

With the possible exception of the data taken at 32 percent relative humidity, the results indicate that for electric fields at the surface up to 3×10^4 volts per cm, the positive surface charge varies in such a way as to maintain ϕ_s constant. This observation is further verified by the field-effect experiment where it was found that even in a dry nitrogen ambient it was not possible to produce a steady-state change in ϕ_s with applied external fields of the same order of magnitude. Before considering this behavior in detail, it is first necessary to consider the mechanism of charge establishment on the surface. Brown[2] postulated two possibilities for this phenomenon. First, mobile positive ions on the surface might drift onto the *p*-type material as a result of the applied field between the *n*- and *p*-type material; or second, neutral impurities on the surface might become positively ionized as a result of the departure from equilibrium of the underlying semiconductor. Now it is apparent that the relaxation effect observed with the channel is a result of the time dependence of one or the other of these processes. In fact, it was as a means of differentiating the two, that the field-effect experiment was carried out. Since there is no field parallel to the surface of the semiconductor in this experiment, it follows that the aforementioned second mechanism, is that which maintains ϕ_s constant. Therefore, since the relaxation times behave in the same manner for the channel, it is concluded that the positive surface charge is produced by ionization of impurity levels at the surface of the semiconductor. A further qualitative argument in favor of this mechanism is the lack of a pronounced change in the relaxation time as the temperature is decreased below 0°C. If the transient were attributable to mobile charges one would certainly expect a marked increase in relaxation time as the water on the surface solidified. These experiments do not eliminate the possibility of ionic migration, of course, and it is quite probable that, in cases of surface contamination, both mechanisms might be operative.

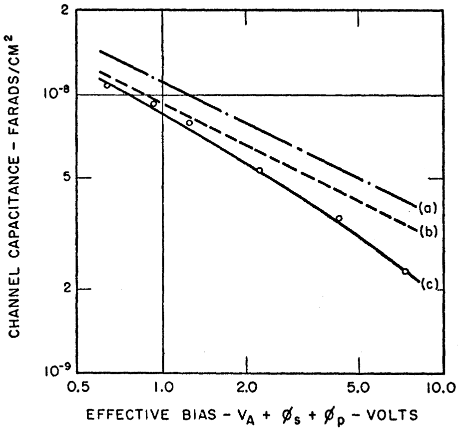

FIG. 9. Channel capacitance *vs* effective bias. (*a*) C_0/A, theory for a junction with infinite donor density, see text. (*b*) C_1/A, theory including effect of channel electrons, and (*c*), C_{meas}/A, theory and experiment including transmission loss.

Examining the relaxation phenomenon in detail, consider the behavior of the surface in Fig. 6, if the field is increased instantaneously by a sudden increase in V_A. As described in the capacitance treatment in the previous section, there must be an instantaneous decrease in the electron density in the channel, since the larger field must now be compensated by more positive charge. But this decrease, which corresponds to an abrupt decrease in channel conductance, is equivalent to a movement of the Fermi level toward the valence band. Consequently, any states at the surface will correspondingly lose electrons to the bulk and the experiments indicate that these states are dense enough to require a return to the original Fermi energy to maintain charge balance. Now, at first, one might suspect that the states which are producing this clamping of ϕ_s are the recombination centers proposed by Brattain and Bardeen.[15] That this is not the case is evident from the relaxation times observed, since it is inconceivable that such states would require the order of a second to reach equilibrium if they are to take part in the surface recombination process. An additional objection to clamping by recombination centers is the wide variation of ϕ_s with gaseous ambient. This would require that the state energy and density is a function of the ambient which is in complete disagreement with the aforementioned authors' observations. A much more plausible explanation is based on the occurrence of additional states either in or on the surface oxide layer. If one assumes a distribution of neutral and charged ions in this region which is directly related to the gaseous ambient, then the relative ionization will be a function of the position of the Fermi level of the underlying material. If their density is large enough then any small shift in this Fermi level will cause a large readjustment of charge distribution, electrons being transferred between the bulk germanium and the energy states of the ions. Quantitatively, consider that a change in electric field of the order of 3×10^4 volts per cm is found to produce a negligible change in Fermi energy from the experimental data. Now this change in field requires a net change in positive surface charge of 4×10^{-8} coulomb per cm^2 or a change in electron density of 3×10^{11} per cm^2. Since a monolayer of adsorbed ions on germanium has a density of about 10^{15} per cm^2, it is seen that only a small change in the position of the Fermi level would result in the required charge. It follows that the relaxation time may be attributed to the rate at which electrons may transfer between these ions and the bulk germanium and that the dependence of ϕ_s upon gaseous ambient and oxide layer thickness is associated with the ionization energies and densities of the ions present in or on the oxide layer.

It follows from the preceding arguments that items (3) and (4) in the summary of results can be explained on the basis of the position of the various energy levels associated with thickness of the oxide layer and the adsorbed species. Qualitatively, for a given oxide thickness, ϕ_s is highest for water vapor in an inert ambient and decreases with decreasing vapor pressure or addition of oxygen. The opposite extreme, ϕ_s most negative, or the surface most *p*-type, would be expected for dry oxygen, ozone, or hydrogen peroxide ambients. Such an effect is observed both by Brattain and Bardeen[15] in their contact potential measurements and by Christensen[16] in studies of *p*-type channels on *n*-type material. This behavior may be seen to conform with the idea that the more oxidizing or electronegative the ambient the lower the ϕ_s of the germanium surface. The rise of ϕ_s with increased oxide thickness, also observed by Brattain and Bardeen,[15] is not as easily explained but is undoubtedly connected with such problems as the deviation of the germanium dioxide from stoichiometry and any electrostatic field in the layer. An investigation of the structure of the oxide on the surface should explain many of these details.

The capacitance data are in good agreement with the channel theory; however, the density of surface states required to fit the theory is in serious disagreement with the results of Brattain and Bardeen.[15] Upon further examination, this is not too surprising since their model neglects interaction of the ions on the surface with the Fermi level of the germanium. As for the estimated surface density obtained by Brown,[2] it is difficult to make a direct comparison since his model, utilizing a continuous distribution of states *versus* energy, does not lend itself to comparison with the aforementioned data which are based on a discrete level. It should be pointed out, incidentally, that Brown's theoretical calculation does not take into account the variation of mobility with applied bias and thus the numerical results are subject to some error.

These experiments lead to the postulate that ϕ_s at the surface of germanium is determined not by the donor or acceptor concentration in the bulk but by the oxide thickness and external ambient. This follows from a general extension of the process of the clamping of ϕ_s by the adsorbed ions, and is further verified by the field-effect experiment where it was found that no steady-state change in Fermi energy could be produced with either polarity of field in either a dry or moist ambient. In detail, consider the extreme case of a sample of *p*-type germanium of resistivity 1.0 ohm-cm, with an inversion layer at the surface corresponding to an *n*-type resistivity of 1.0 ohm-cm. This would require a value of ϕ_s at the surface of 0.11 volt and the internal field, E_s, at the surface may be calculated to be 1.5×10^4 volts per cm. But from the field-effect experiment, it is found that fields of this order of magnitude may be terminated by the charged ions in the surface layer with no measurable change in position of ϕ_s. Therefore, it follows that the ions present will determine the carrier density at the surface rather than the underlying donor or acceptor impurities. Just how generally this postulate may be applied is not certain; however, experiments of the type carried out by Morrison[17] should establish the range of validity.

As for the application of the experimental results to the behavior of germanium devices, it has been shown elsewhere[18] that the reverse leakage of a *p-n* junction diode in a moist ambient may be explained on the basis of the above model.

CONCLUSION

The channel conductance has been shown to depend upon a constant position of the Fermi level with respect to the electrostatic potential at the surface of the germanium crystal. The actual position of the Fermi level or the quantity, ϕ_s, is in turn found to be a function of the state of oxidation of the surface and the ambient to which it is exposed. Studies of the relaxation time of the channel and the surface conductance in a field-effect experiment indicate that ϕ_s is generally determined by the surface conditions and not by the acceptor or donor density of the bulk germanium.[19] Qualitatively, one might say that the impurity levels associated with the

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surface and adsorbate are dense enough to overcome the effects of the bulk impurities. One major difference, of course, is that these impurity levels require the order of a second to come to equilibrium with the bulk whereas the normal doping impurities reach equilibrium instantaneously as far as present physical measurements are concerned. Thus, a complete description of the properties of a germanium crystal requires a knowledge of the bulk resistivity and the equivalent surface resistivity. Just how and why the surface resistivity varies with ambient and surface treatment is therefore of utmost importance in the study of the electronic properties of germanium.

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Lattice Resistance to Dislocation Motion at High Velocity

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Dissipative effects at high velocities, resulting from coherent collisions of dislocations with the lattice sites, have been estimated and found to be too small to limit the dislocation velocity.

I. INTRODUCTION

A LONG-STANDING question in the theory of dislocations and in the application of the theory to mechanisms of plastic deformation is that which concerns the permissible velocities for motion of a dislocation in a crystal lattice. More explicitly, one would like to know whether or not the lattice presents large resistance to dislocation motion when the velocity is large. The answer to this question is of particular importance in the consideration of dislocation processes that depend on the ability of the dislocation to conserve kinetic energy over any considerable portion of its trajectory.

Leibfried[1] first considered the effect of the scattering of lattice vibration waves by dislocations as a resistive effect. This work was later critically evaluated and corrected by Nabarro[2] who concluded that resistive contributions from this mechanism would be negligible. The purpose of the present report is to investigate the inelastic collisions between the dislocations and the lattice sites. This effect was first proposed as an energy loss mechanism by Orowan,[3] but no quantitative estimates have yet been made for this dissipation. It is proposed to make an estimate here in terms of coherent dislocation oscillations.

Peierls[4] and Nabarro[5] have shown that the presence of the lattice provides a reference frame for a variation of the energy of a dislocation as a function of its position relative to the lattice points. These authors made an approximate calculation for an edge dislocation lying along a $\langle 100\rangle$ direction of a simple cubic crystal, and they deduced the energy per unit length, V, as a function of displacement x in the direction of the Burgers vector, to be of the form

$$V=E_0[1+\alpha\cos(4\pi x/b)], \tag{1}$$

where

$$E_0=Gb^2/4\pi(1-\nu),$$
$$\alpha=2\exp[-2\pi/(1-\nu)],$$

b is the Burgers vector, G is the shear modulus, and ν is Poisson's ratio. As the dislocation moves through the lattice it then experiences a sinusoidally varying force per unit length,

$$\begin{aligned} f&=-dV/dx\\ &=(4\pi/b)\alpha E_0\sin(4\pi x/b), \end{aligned} \tag{2}$$

in addition to any applied uniform driving force. At sufficiently high velocities this lattice force will produce an oscillation of the dislocation position about its mean position of uniform translation. The oscillation results in radiation of elastic energy by the dislocation and a resultant rate of energy loss which will give rise to a resistive force in its motion through the lattice.

The oscillatory driving force is probably overestimated by the Peierls-Nabarro calculation, but, since the purpose of this investigation is to obtain an upper estimate of the resistive force, it will not be inappropriate. The same comment applies to the assumption that the dislocation is always aligned in the lattice so

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