

The energy per unit volume of the cylinder is

$$\bar{E} = \pi R^2 8\pi (16\pi^2 R^2 T)^{-1} \int_0^{2T} \int_0^{2\pi} 4\pi F \sigma R d\varphi dz. \quad (96)$$

integration

$$\bar{E} = \sum_{m=1}^{\infty} \frac{1}{2} \pi^2 I_s^2 \omega_{2m-1}^2 i H_1^{(1)} \left[i(2m-1) \frac{\pi}{T} R \right] \times J_1 \left[i(2m-1) \frac{\pi}{T} R \right]. \quad (97)$$

Using this and (90), (91), and (95), one obtains after

Surface States on Silicon and Germanium Surfaces*

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Interface states are found in the upper half of the energy gap of silicon and germanium. On weakly oxidized surfaces, they lie 0.42 and 0.13 ev above the intrinsic position of the gap with approximate densities 10^{11} to 10^{12} and 10^{10} to 10^{11} for silicon and germanium, respectively. On well-oxidized surfaces, interface states are found approximately 0.44 to 0.48 ev and 0.18 ev above the intrinsic position of the gap with densities of around 10^{12} and 10^{11} to 10^{12} for silicon and germanium, respectively. At large bias voltages, high electric fields exist in the oxide film. Changes in the structure of the interface states in the upper half of the gap of silicon are found. A model is given which can account for the experimental observation.

INTRODUCTION

IN a previous paper,¹ measurements of inversion layers on *n*-type germanium and silicon have been reported. This paper represents an extension of reference 1 to measurements of inversion layers on *p*-type germanium and silicon. Essentially, the same notation and terminology will be used. From the steady state and nonsteady state measurements, it has been deduced previously that on both germanium and silicon there is a very high density of surface states on or near the surface of the oxide film (outer surface states) and a much smaller density at the interface of the semiconductor and the semiconductor oxide film (interface states). The outer surface states appear to result from adsorbed atoms of the surrounding ambient gas. The measurements of the interface states have been interpreted in terms of one localized state 0.138 ev and 0.455 ev below the middle of the gap for germanium and silicon, respectively. The densities were approximately 10^{11} states/cm² for germanium and 10^{12} states/cm² for silicon.

In the meantime, other contributions from workers in the field have appeared in the literature which deal directly or indirectly with a determination of the interface states.²⁻⁸ The work of Bardeen *et al.*³

essentially confirmed the previous finding for interface states in the lower half of the gap of germanium. It appears, however, that in addition to these localized states there is a continuous distribution of surface states near the middle of the forbidden gap. The total number of these distributed states is considerably smaller than that of the localized ones.³ Measurements of interface states by conduction measurements of inversion layers are difficult and sometimes even impossible for states lying close to the center of the forbidden gap. In such measurements, the charge in the interface states as a function of the quasi-Fermi level for holes or electrons is deduced from "pulsed" conductance measurements as a function of bias voltage. If the quasi-Fermi level describing the distribution of the majority carriers in the surface layer is close to the middle of the gap, then the conductance of the inversion layer is very small. The saturation current flowing across the junction between the inversion layer and the bulk of the material gives rise to an ohmic drop in the inversion layer so that the bias voltage between the bulk of the semiconductor and the inversion layer is not constant along the base region of the *n-p-n* and *p-n-p* type semiconductor bars. The inversion layer technique is, therefore, not easily applicable for states near the middle of the band gap. In addition, as will be shown, the occupancy of the interface states may not be described by the quasi-Fermi level for majority carriers if the ratio of the capture cross for electrons and holes is unfavorable.

* Supported in part by the Bureau of Ships.

¹ Statz, deMars, Davis, and Adams, Phys. Rev. **101**, 1272 (1956).

² W. L. Brown, Phys. Rev. **100**, 590 (1955).

³ Bardeen, Coover, Morrison, Schrieffer, and Sun, Phys. Rev. **104**, 47 (1956).

⁴ W. H. Brattain and C. G. B. Garrett, Bell System Tech. J. **35**, 1019 (1956).

⁵ C. G. B. Garrett and W. H. Brattain, Bell System Tech. J. **35**, 1041 (1956).

⁶ Many, Margoninski, Harnik, and Alexander, Phys. Rev. **101**, 1433 (1956).

⁷ Harnik, Many, Margoninski, and Alexander, Phys. Rev. **101**,

1434 (1956). [See also contribution by Many, Harnik, and Margoninski to appear in *Proceedings of the Conference on the Physics of Semiconductor Surfaces, University of Pennsylvania, Philadelphia, Pennsylvania, June, 1956* (to be published)].

⁸ H. C. Montgomery and W. L. Brown, Phys. Rev. **103**, 865 (1956).

This paper deals with measurements on inversion layers on *p*-type germanium and silicon. Measurements and results which are analogous to those reported on *p*-type inversion layers on *n*-type material in reference 1 will be described only briefly and reference 1 should be consulted for details. In this paper, observations at high bias voltages are reported and interpreted. In most measurements, ammonia was used as the ambient gas to produce stable inversion layers. It is known that water vapor also gives inversion layers on *p*-type material. However, it appears that current can also flow in the water film, especially at higher bias voltages.^{9,10} Thus, the true conductance arising from the inversion layer alone is obscured. If there is a thick and coherent adsorbed film on the surface, the holes (or electrons) which have been transferred from the semiconductor to the film are apparently free to move when an electric field is applied which has a component in the plane of the water film.⁹ Ammonia at room temperature adsorbs in a film not coherent enough for this type of conduction to take place. However, it is very interesting to observe an increasing component of such a current in the ammonia film as the temperature is lowered, approaching the point of condensation of ammonia. For the measurement at -10°C which is reported below, acetylene was used instead of ammonia to produce an inversion layer. Electric conduction in the acetylene film has not yet been observed. From the measurements on *n*-type inversion layers, one can again deduce that there is a high density of outer surface states. There are also interface states in the upper half of the gap. For germanium, the energy level of these states coincides approximately with the one reported by Many *et al.*⁷ by interpretation of measurements of surface recombination velocity as a function of the position of the Fermi level at the surface. This agreement indicates that the interface states are indeed also the surface recombination states as has been postulated previously.^{1,11} Montgomery and Brown⁸ have reported that there are no localized surface states in the upper half of the gap in disagreement with the findings of the authors and Many *et al.*⁷ The reason for the discrepancy may lie in a different surface preparation but is at present not understood. Except for certain disagreements among the various workers, the structure of the interface states on etched surfaces is essentially known. The next phase of the work will be concerned with the identification of the interface states in terms of certain defects in the interface. In a first step in this direction the changes of the structure of the interface states has been studied as a function of the degree of oxidation and high bias voltages. Simple models will be used for the interpretation of the findings.

⁹ Eriksen, Statz, and deMars, J. Appl. Phys. **28**, 133 (1957).

¹⁰ J. T. Law, Proc. Inst. Radio Engrs. **42**, 1367 (1954).

¹¹ W. H. Brattain and J. Bardeen, Bell System Tech. J. **32**, 1 (1953).

In the first section, the extent to which the quasi-Fermi level for majority carriers describes the occupancy of the surface states is briefly investigated. A treatment of this problem has, in principle, already been given by Brattain and Bardeen¹¹; however, their formulas are not readily applicable for an investigation of the limitations of the present method of determining interface states.

STATISTICS OF SURFACE TRAPS

Consider, for example, a single energy level at the surface in the upper half of the gap (Fig. 1). The bulk material is supposed to be *p*-type, and there is an inversion layer which has been biased in reverse by a voltage V_a . The trap will be characterized by two quantities c_n and c_p which will be defined as the probability that an electron or a hole will be captured by one empty or filled surface trap, respectively, per unit time and unit concentration of electrons or holes at the surface. The fraction f_t of surface states occupied can then be expressed in terms of the concentration of electrons n and of holes p at the surface by the equation

$$f_t = \frac{(c_n/c_p)n + p_1}{(c_n/c_p)(n + n_1) + (p + p_1)}. \quad (1)$$

This equation was derived by Shockley and Read¹² for trapping states in the bulk. The quantities n_1 and p_1 are defined by

$$\begin{aligned} n_1 &= N_c \exp[(E_t - E_c)/kT], \\ p_1 &= N_v \exp[(E_v - E_t)/kT]. \end{aligned} \quad (2)$$

In Eq. (2), N_c and N_v are the effective number of states in the conduction and valence band, E_c and E_v are the energies of the band edges at the surface, E_t is an effective energy of the surface state, k is Boltzmann's constant, and T is the absolute temperature. Because of the small density of the interface states, it is assumed that these states can only be occupied by an electron of plus or minus spin but not by two electrons. Under this assumption, E_t is not the true energy level of the trap but is related to it by the formula

$$E_t = E_t(\text{true}) - kT \ln 2. \quad (3)$$

If the applied voltage V_a is of the order of one volt or more and if the surface velocity is not extremely high, the quasi-Fermi level for holes $-q\phi_p$ lies above the surface level and consequently $p \ll p_1$. If, furthermore, $p_1 \ll (c_n/c_p)n$, then

$$f_t = \frac{n}{n + n_1} = \frac{1}{1 + \exp[(E_t + q\phi_n)/kT]}. \quad (4)$$

In Eq. (4), $-q\phi_n$ is the quasi-Fermi level of electrons and the occupancy of the surface traps is given by a

¹² W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952).

regular Fermi distribution where the Fermi level is replaced by the quasi-Fermi level for electrons. In the interpretation of pulsed conductance measurements, the validity of Eq. (4) has been assumed. The restriction $p_1 \ll (c_n/c_p)n$ can be written with the aid of Eq. (2) and the relation $n = N_c \exp(-q\phi_n - E_c)/kT$:

$$\frac{N_v c_p}{N_c c_n} \exp\left(\frac{E_v - E_t + q\phi_n + E_c}{kT}\right) \ll 1. \quad (5)$$

If all energies are now measured from the intrinsic position of the gap at the surface, and E_{ic} and $-E_{iv}$ are the separation of the conduction and valence bands from the intrinsic position, then

$$N_v/N_c = \exp[(+E_{iv} - E_{ic})/kT]. \quad (6)$$

Inserting Eq. (6) into (5) gives

$$c_p/c_n \ll \exp[q(\phi_s + \phi_T)/kT], \quad (7)$$

where $q\phi_s$ and $q\phi_T$ are the distances of the Fermi level and the effective trap level respectively from the intrinsic position of the Fermi level. Equation (7) holds for n -type inversion layers on p -type material. ϕ_s and ϕ_T are positive in the present definition when the Fermi level $-q\phi_n$ and the effective trap level are in the upper half of the gap. For a p -type inversion layer on n -type material, the corresponding condition may be written

$$c_n/c_p \ll \exp[-q(\phi_s + \phi_T)/kT]. \quad (8)$$

ϕ_s and ϕ_T are negative when the quasi-Fermi level $-q\phi_p$ and the effective energy level are in the lower half of the gap.

Some measurements of c_p/c_n for germanium are available in the literature.⁵⁻⁷ In all cases, except possibly for one state in the lower half of the gap, c_p is found to be larger than c_n which means that condition (8) is satisfied for states in the lower half of the gap. The upper half of the gap needs more detailed consideration. Evidence will be given for states lying approximately 0.130 eV above the middle of the gap. From Eq. (3) the effective trap level for these states will be 0.112 eV above the middle of the gap. In order to insure that these states are always occupied according to a Fermi distribution with $-q\phi_n$ replacing the Fermi level, Eq. (7) has to be satisfied for the smallest ϕ_s value. Further below in Fig. 10, a run is shown in which the lowest measured ϕ_s value equals 0.088 volt. Thus, condition (7) reduces to

$$c_p/c_n \ll 2600.$$

According to Many *et al.*,⁷ for this particular surface level $c_p/c_n \approx 30$, and thus the interpretation of the present measurements is justified. No values for c_p/c_n are yet available for silicon. However, for distributed states close to the middle of the gap a situation may arise where Eq. (7) or (8) no longer holds. From Eq. (1)

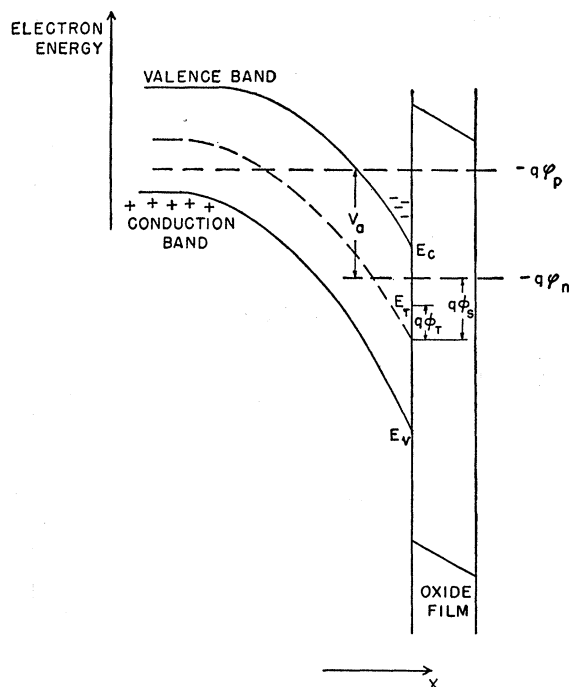


FIG. 1. Energy bands at surface representing n -type inversion layer on p -type material.

for $c_n/c_p \rightarrow 0$, it follows that $f_t = 1$ because $p \ll p_1$. Therefore, the states in this case will be occupied irrespective of the value of ϕ_s . Similarly for states in the lower half of the gap for $c_n/c_p \rightarrow \infty$, it follows that $f_t = 0$; therefore, the states will be empty irrespective of ϕ_s .

EXPERIMENTAL PROCEDURES

The sample preparation and the measurement techniques were essentially the same as in reference 1. Grown-junction silicon and germanium n - p - n type bars of near quadratic cross section with a circumference of about 1 cm were used. The widths of the p -regions were 0.065 and 0.0355 cm for the germanium and silicon bars respectively. Contacts were made by alloying suitably doped gold wires to the three regions. Inversion layers on the p -type regions were produced by first etching the samples in a solution of HF and HNO₃, washing and drying them, and then exposing them to dry ammonia. In some of the experiments to be reported, the samples were oxidized in wet oxygen and ozone before the exposure to ammonia. The measuring circuit was identical to the one given in reference 1. A dc bias was applied to the base region. The conductance was determined by applying a small ac voltage of 1000 cycles/sec between emitter and collector and measuring the resulting ac current through the inversion layer. For the fast time constants it was found advantageous not to use a recorder as in reference 1 but to use an oscilloscope. Thus, the response time of the measuring system could be brought to about

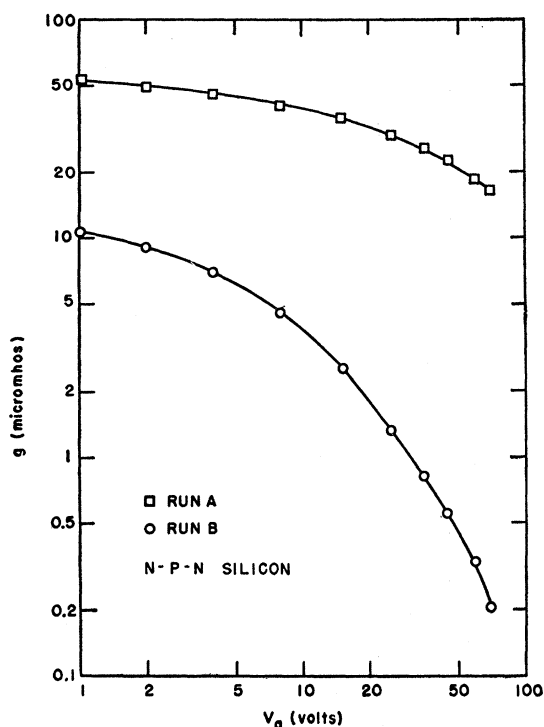


FIG. 2. Steady-state conductance of *n*-type inversion layers on *p*-type silicon versus bias voltage.

10^{-2} sec. The accuracy of the electrical measurements was in general about $\pm 2\%$; however, for the very lowest inversion layer conductances (close to pinch-off) the error may have approached 10% .

STEADY-STATE CONDUCTANCE OF INVERSION LAYERS

After applying a bias voltage, a certain time which depends upon temperature and the degree of oxidation is required to establish a steady-state conductance

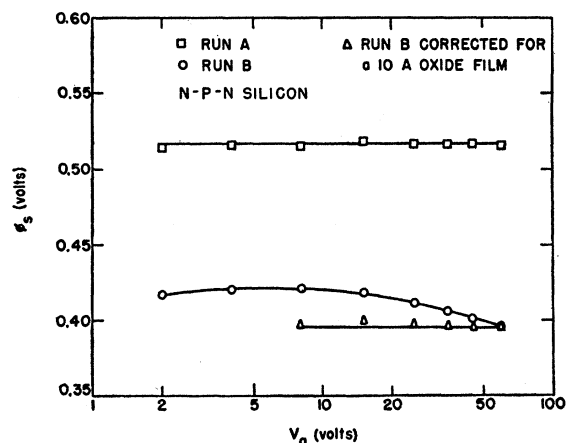


FIG. 3. Position of quasi-Fermi level versus bias voltage for the steady-state conductance measurements of Fig. 2.

value. In Fig. 2, steady-state conductance measurements of *n*-type inversion layers on 11 ohm cm *p*-type silicon are shown as a function of bias voltage. In run B, the surface was oxidized in oxygen and ozone. In Fig. 3, the position of the quasi-Fermi level as a function of bias voltage is shown for both runs. In Fig. 4, the total charge in the surface states as a function of bias voltage is shown. The findings indicate again that the total density of states is very high and that ϕ_s determines the occupancy of the surface states. Thus, Eq. (7) must also hold for the outer surface states, imposing restrictions on the possible ratios of c_p/c_n . At higher bias voltages, the decrease of ϕ_s with bias voltage is again interpreted as resulting from the potential drop across an oxide film.¹ By correcting for the voltage drop across an oxide film of 10 Å, the curve of ϕ_s versus bias voltage becomes horizontal. The slight increase of ϕ_s for small bias voltages is similar to that found

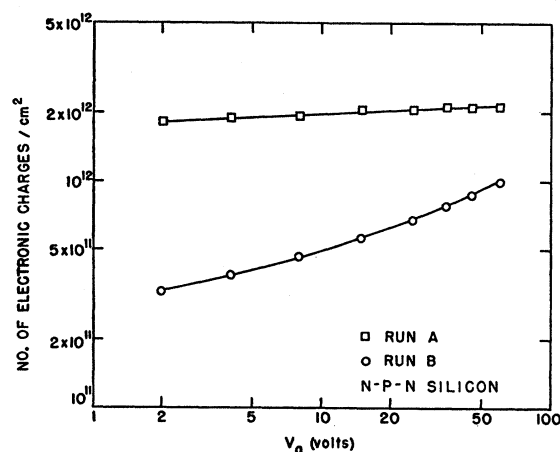


FIG. 4. Total charge in surface states versus bias voltage for the steady-state conductance measurements of Fig. 2.

on *p*-type inversion layers on both silicon and germanium, and is not yet understood. The curve of ϕ_s versus bias voltage is very nearly horizontal for the unoxidized sample, indicating a thin oxide film. This behavior substantiates the explanation of a voltage drop across an oxide film. The contribution from a finite density of surface states to the decrease of ϕ_s with increasing bias voltage appears negligible.

In Figs. 5, 6, and 7, corresponding curves are shown for an *n*-type inversion layer on an eight ohm cm germanium sample. The surface of the germanium had not been oxidized in wet oxygen and ozone. Conductance curves for *n*-type inversion layers on *p*-type germanium have been measured previously by Kingston¹³ up to a bias voltage of five volts. His voltage range was limited because of water-induced excess currents on the surface. The measurements again show that the quasi-Fermi level $-q\phi_n$ determines the occupancy of the surface

¹³ R. H. Kingston, Phys. Rev. 98, 1766 (1955).

states and that the total density of surface states is high, in agreement with the findings of Kingston. The ϕ_s curve does not decrease with bias voltage over a long enough range to give a satisfactory determination of the thickness of the oxide film.

NONSTEADY-STATE CONDUCTANCE OF INVERSION LAYERS

The principal idea underlying these measurements is the recording of a curve of conductivity *versus* bias voltage in a time which is short compared to the relaxation time of the slow (outer) surface states but fast compared to the relaxation time of the recombination states. This is readily done in the case of silicon because the long relaxation time is many minutes to an hour. It is somewhat more difficult for the case of germanium which with our surface treatments may

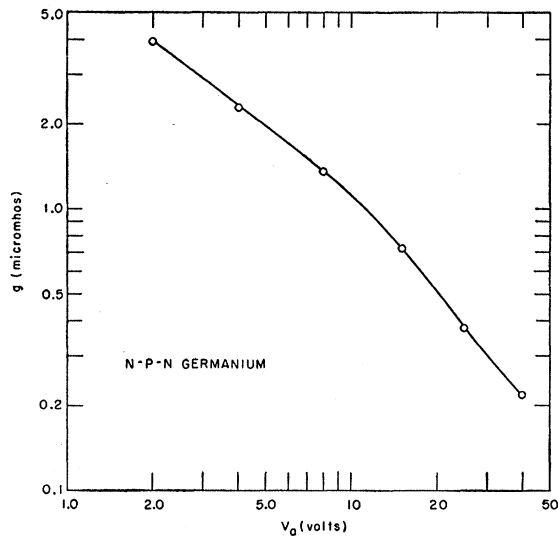


FIG. 5. Steady-state conductance of *n*-type inversion layer on *p*-type germanium *versus* bias voltage.

have relaxation times of the order of one second and more. Measurements on germanium are usually made point by point as described previously.¹⁴ Along such a conductance curve, the charge in the slow surface states is constant and the charge in the interface states is in equilibrium with the bulk of the material. To eliminate the constant charge in the outer surface states, the total charge in the surface states at pinch-off is subtracted from the individual charge values, as before.

In both silicon and germanium, differences will be found before and after oxidation of the surface. In Fig. 8, the number of electrons *versus* ϕ_s in the upper half of the gap of silicon is shown for an unoxidized surface. The solid line is a theoretical curve assuming 7.8×10^{11} states/cm² at an energy 0.42 eV above the

¹⁴ Statz, Davis, and deMars, Phys. Rev. **98**, 540 (1955).

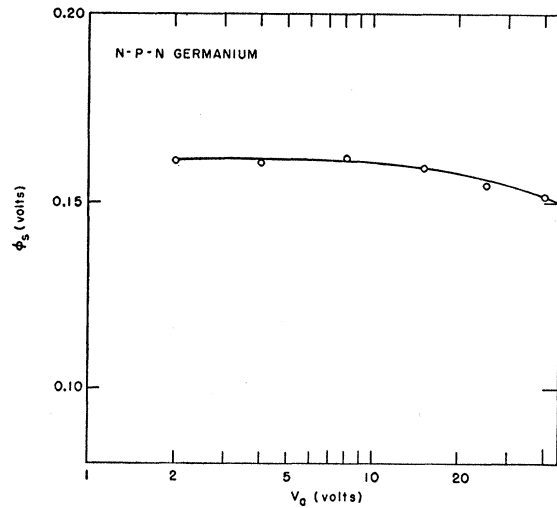


FIG. 6. Position of quasi-Fermi level *versus* bias voltage for the steady-state conductance measurements of Fig. 5.

intrinsic position in the gap. After oxidation in wet oxygen and ozone, curves as shown in Fig. 9 were obtained. One of the solid lines corresponds to a state 0.48 eV above the intrinsic position in the gap with a density of 1.4×10^{12} states/cm². This case has been found only once. The other solid line corresponds to an energy level of 0.44 eV above the intrinsic position of the gap with a density of 8.4×10^{11} states/cm². The latter energy value is characteristic for most of the oxidized samples.

A similar observation is made in germanium. In Fig. 10, the number of electrons *versus* ϕ_s is shown for a germanium surface before oxidation. The solid line corresponds to a state 0.13 eV above the middle of the gap with a density of 1.05×10^{11} states/cm². The energy value of this state corresponds approximately to that reported by Many *et al.*⁷ which has been deduced from measurements of surface velocity as a function of ϕ_s .

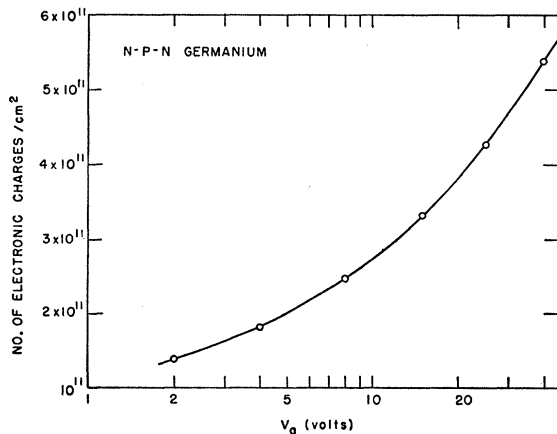


FIG. 7. Total charge in surface states *versus* bias voltage for the steady-state conductance measurements of Fig. 5.

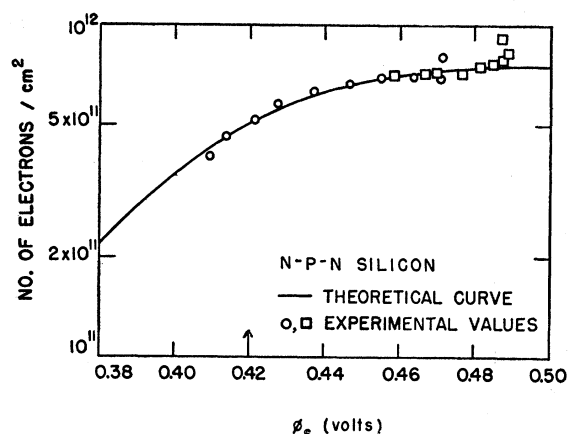


FIG. 8. Number of electrons in interface states in upper half of gap versus the position of the quasi-Fermi level for silicon.

In Fig. 11, various curves are shown which correspond to different degrees of oxidation. The energy level of the states for curves *A* and *B* is approximately 0.175 eV and for *C* more than 0.18 eV above the intrinsic position in the gap. The approximate densities of surface states are 2.7×10^{11} , 6×10^{11} , and 1.6×10^{12} for runs *A*, *B*, and *C*, respectively. Run *A* corresponds to an oxidation time of 15 sec at 160°C, *B* to 30 sec at 160°C, and *C* to 20 sec at 220°C. The longer the time of oxidation and the higher the temperature the more surface states are present. Because of the relatively high density of states, the range of the ϕ_s values is small and considerable errors are possible. Especially in run *C*, it is difficult to determine with certainty whether there is a distribution of states or discrete states. Sometimes there are indications of distributed states close to the conduction band as can be seen, for example, from Fig. 10. At present, it is not clear whether the states at 0.13 eV

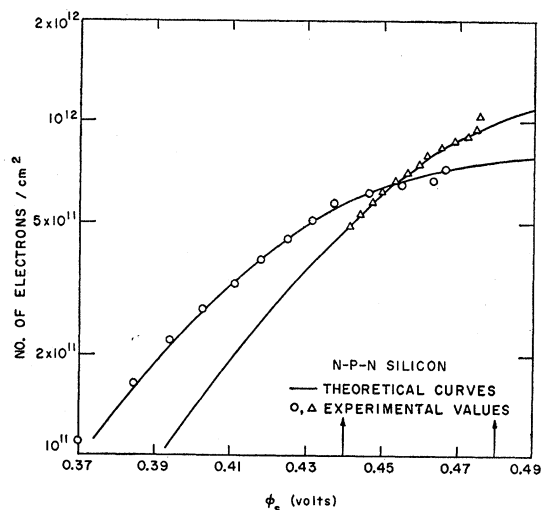


FIG. 9. Number of electrons in the interface states in upper half of gap versus the position of the quasi-Fermi level for silicon, after oxidation.

which are found on unoxidized surfaces shift in energy upon oxidation to a higher level with increased density. In silicon, there is at least some evidence from data to be discussed below that the low-lying states are always present but become obscured by the high density of the high-lying states.

EFFECTS OF HIGH ELECTRIC FIELDS ON INTERFACE STATES

When the bias voltage between the inversion layer and the bulk material is made very large, certain effects are observed which will be shown to be due to changes in the structure of the surface states. These changes have been studied in detail for *n*- and *p*-type inversion layers on silicon. First the experimental observations will be described and then possible explanations will be discussed.

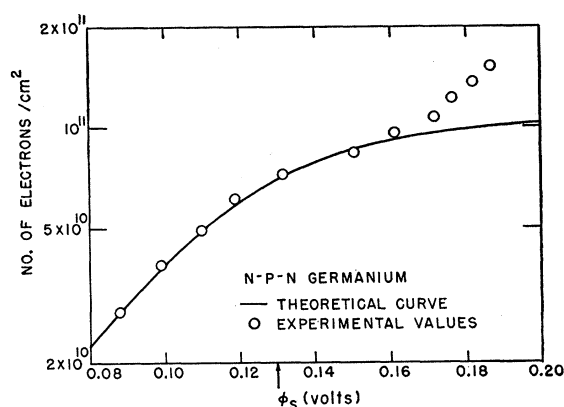


FIG. 10. Number of electrons in the interface states in upper half of gap versus the position of the quasi-Fermi level for germanium.

The conductance curves of Fig. 12 show these effects for *p*-type inversion layers on *n*-type silicon. The conductance curves are "pulsed," i.e., the bias voltage is changed so rapidly that the charge in the slow surface states cannot change. Run *A* corresponds to increasing bias voltage, and run *B* to decreasing bias voltage. For run *A*, between 70 and 80 volts bias, there appears to be an anomalous decrease in conductance. Around 90 volts the inversion layer pinches off. The interesting new feature is the fact that the curves *A* and *B* do not coincide. Apparently, during the anomalous decrease of the conductance certain changes take place. This may be seen from an experiment in which the bias voltage is pulsed only up to 70 volts. Upon subsequently decreasing the bias voltage the two conductance curves thus obtained are identical. The changes which take place occur faster with increasing bias voltage. For curve *A* of Fig. 12 these changes took place in a time short as compared to the time in which the bias voltage was pulsed up. Often, changes take place which do not occur fast enough to show up in anomalous decrease

in conductance. If the bias voltage is held for some time at a value corresponding to pinch-off, when the bias is decreased, a curve *B* is traced out which may lie below *A*. If an *A* curve is selected which has no anomalous conductance drop and where the changes in the surface states occur while the inversion layer is pinched off, the structure of the interface states in the lower half of the gap can be determined from such a run. Within the experimental error, there is no change in the structure of these states when one compares the interface states as deduced from runs before and after the changes in the total charge in the surface states.

In further investigation of the interface states in the lower half of the gap, a systematic variation was found

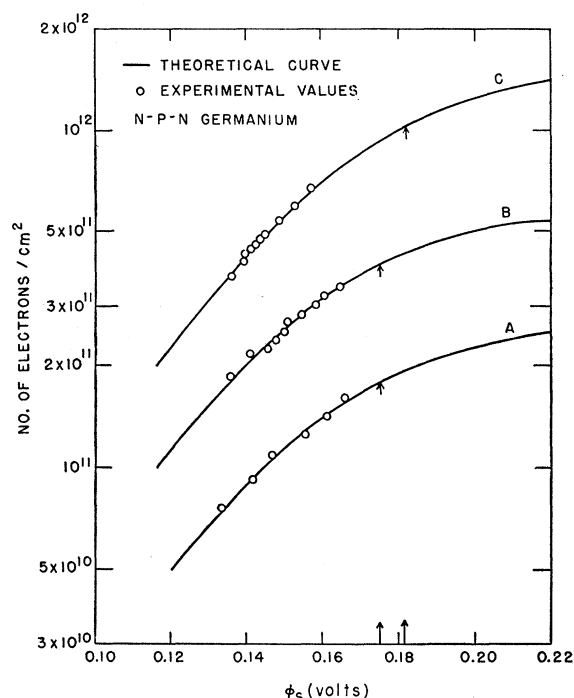


FIG. 11. Number of electrons in interface states in upper half of gap versus the position of the quasi-Fermi level for germanium, after oxidation for various times and temperatures.

in the apparent energy level, but not in density, with the equilibrium conductance of the inversion layer from which a pulsed run is started. Investigations of this effect are not yet conclusive and it is not clear at present whether there is a true change in the energy level with the charge in the outer surface states or whether the assumed mobility¹⁵ is grossly in error. In making the above statement that there are no changes in the structure of the surface states in the lower half of the gap, the apparent shift in the energy of the levels with equilibrium conductance has been considered and corrected for. To date, there has been no indication of a corresponding change in the energy level of the states in the upper half of the gap.

¹⁵ J. R. Schrieffer, Phys. Rev. **97**, 641 (1955).

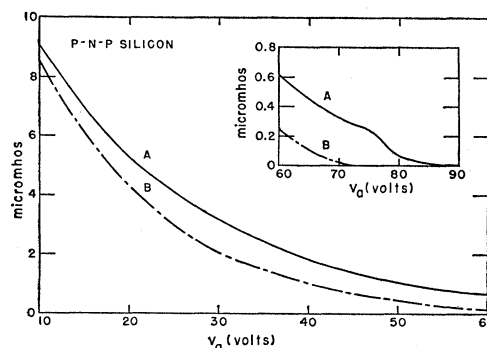


FIG. 12. Pulsed inversion layer conductance curves showing "anomalous" decrease in conductance at high bias voltage (*p-n-p* silicon).

Inversion layers on *p*-type silicon behave somewhat differently. Changes similar to those described above were observed only when the surface was oxidized in wet oxygen and ozone prior to exposure to ammonia. Three pulsed conductance curves for inversion layers on 11 ohm cm silicon are shown in Fig. 13. Curve *A* again was recorded while increasing the bias voltage. Between 130 and 140 volts, an anomalous decrease in conductance was observed. Upon decreasing the bias voltage, curve *B* was obtained. Curve *C* was obtained upon decreasing the bias voltage after it was held at 160 volts for one minute. The relaxation time of the outer surface states was 24 minutes in this particular case. The main difference in the behavior lies in the fact that curve *C* crosses both curves *A* and *B* in the low-bias-voltage region and has the highest conductance in this range. The different slopes of curves *A*, *B*, and *C* are due to different densities of interface states. In Fig. 14, several runs of charge in interface states versus ϕ_s are shown after application of a high bias voltage. The curves are not smooth and indicate inhomogeneities. It is seen that the number of surface states is drastically reduced after the high bias voltage was

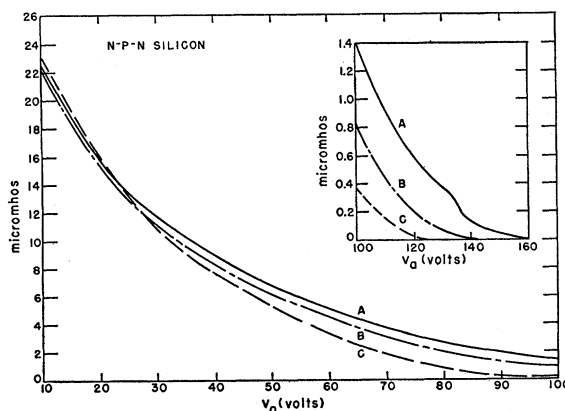


FIG. 13. Pulsed inversion layer conductance curves showing anomalous decrease in conductance at high bias voltage (*n-p-n* silicon).

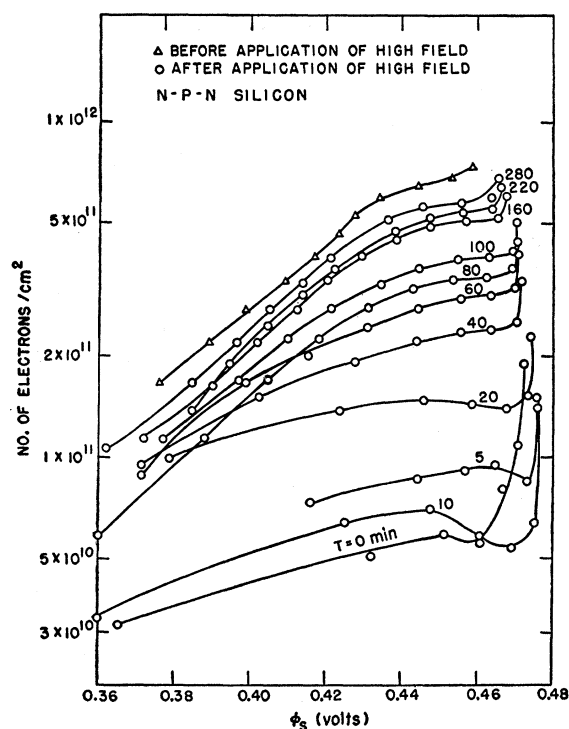


FIG. 14. Runs of number of electrons in interface states versus ϕ_s for silicon before and after application of high field.

applied. The surface states slowly recover their original density and energy level. The residual density of surface states may vary greatly. For the case of Fig. 14, this residual density is relatively small. The residual surface states usually have an energy level 0.42 eV above the intrinsic position of the gap. This level coincides with the one found before oxidation of the surface.

Next, consider the cause for changes in the structure of the surface states at high bias voltages. In the following section it will be shown that the electric field in the oxide film changes with bias voltage. Consider, for example, a *p*-type inversion layer on *n*-type material. As the bias voltage is pulsed up, the positive space charge inside the semiconductor becomes large. Since the bias voltage is changed fast, the charge in the outer surface states does not change and the increase in the positive space charge is compensated by a decreasing positive charge in the interface states or an increasing negative charge in the interface states. The average field in the oxide film will remain unchanged. The important point to consider is that only the average field remains the same. Since the space charge of positive donors is much wider than the average spacing between donors, the positive charge can be considered to be smeared out and giving a constant field at the interface. However, for a negative ion in the oxide film, the spacing of the charged interface states is many times larger than the distance of an ion from the interface.

The field that an ion will see depends critically upon its position relative to charged interface states. If an ion sits midway between the nearest charged interface states, it will see practically the full field due to the positive space charge. To illustrate this effect an example has been calculated. It has been assumed that there are 4×10^{11} positive donor atoms and holes making up the positive space charge and that there are 2.5×10^{11} evenly distributed negatively charged interface states. The electric field component normal to the interface has been calculated at several points in a plane parallel to the interface with a distance of 3 Å between the plane and the interface. The points at which the field has been calculated and the results are indicated in Fig. 15. For simplicity, the dielectric constant has been set equal to unity. It is seen that far away from the charged interface states, the field due to the positive space charge penetrates practically unattenuated into the oxide film. An ion in the interface will see the total field due to the positive space charge. Only after the distance of an ion from the interface is large as compared to the separation of the charged interface states will the field due to the space charge in the semiconductor be shielded, a case which in the presently investigated oxide films will not occur.

In Fig. 16, two models for these changes are illustrated. In both models, reference to oxidation mechanisms has been made because the above effect is found only on oxidized surfaces. However, in a more cautious interpretation, one should not identify the centers with oxygen but rather with some yet unknown lattice defect. Consider first the model shown in Fig. 16(a) and 16(b). It is assumed that O^- can diffuse through the oxide film. As it comes to the interface it creates a level in the upper half of the gap. If the Fermi level is above this energy, the center corresponds to mostly O^- ; if it lies below it, the oxygen is mostly neutral.

For an inversion layer on *n*-type material, there will be some O^- in and on the oxide film. As the bias voltage is made large, the positive space charge in the semi-

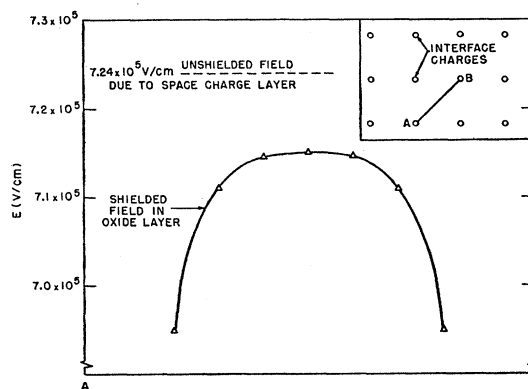


FIG. 15. Example showing penetration into oxide film of field due to space-charge layer.

conductor becomes large. As discussed above, the electric field in the regions between the interface states increases and O^- atoms are pulled to the interface [Fig. 16(a)].

Since both quasi-Fermi levels lie below the middle of the gap, O^- will be discharged. Thus, the total negative charge in the two types of surface states decreases and the conductance drops. This explains the experimental results for p -type inversion layers on n -type material.

Next consider n -type inversion layers on p -type material [Fig. 16(b)]. As the bias voltage is made large, the conductance of the inversion layer becomes small and the quasi-Fermi level $-q\phi_n$ approaches the middle of the gap. Only a few of the interface states will be charged. The field from the negative space charge has its full magnitude for ions in the interface and pushes the charged ions into the oxide film. Previously uncharged atoms will receive an electron since the Fermi distribution always assures the presence of a certain fraction of charged ions. Then these atoms also are pushed out by the field. This continues until all mobile ions are pushed out. Since each atom that is pushed out has a negative charge, the total positive charge in the surface states decreases by this process and the conductance of the inversion layer becomes lower. However, this is not the case when the quasi-Fermi level $-q\phi_n$ lies so close to the conduction band that all interface states are charged. Here, apparently, no change in the total charge in the surface states and the oxide film takes place when the negative ions move from the interface into the oxide film. Thus, for low bias voltages, the conductance curve C in Fig. 13 lies above curves A and B because the positive charge in the outer surface states has increased somewhat while the inversion layer was pinched off for one minute at 160 volts. This model requires that the decrease in the number of positive charges in the outer surface states equals the decrease in the number of interface states. This requirement is most conveniently checked by comparing the total charge in both types of surface states at pinch-off before and after the change in the interface states has taken place. Since at pinch-off the considered interface states are practically empty, the difference in the total number of charges has to equal the decrease in the number of interface states. In order to make such a test reliable, care has to be taken that the high bias voltage is applied for a long enough time so that significant changes occur, but also this period of time should still be short as compared to the relaxation time of the outer surface states. In one particular set of curves where this condition was reasonably well satisfied the change in the density of interface states was 2.4×10^{11} states/cm² as compared to a decrease in the number of charges in the outer surface states of 2.8×10^{11} charges/cm². Considering all possible sources of error this agreement is satisfactory.

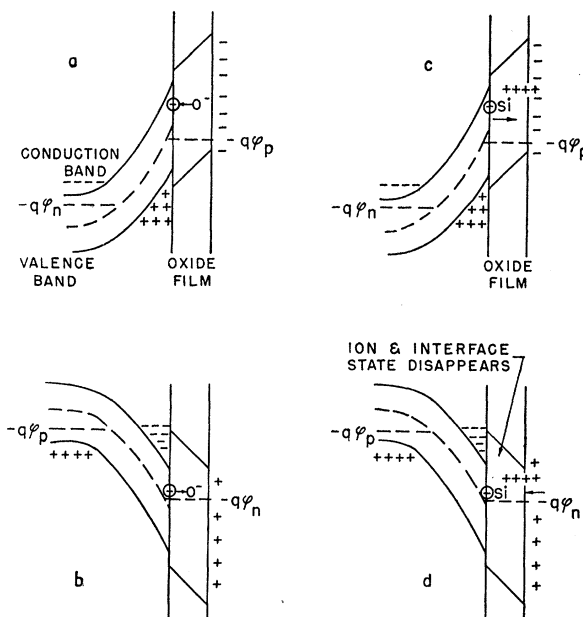


FIG. 16. Various models for explanation of conductance decrease at high bias voltages.

A similar qualitative explanation can be given by using the model shown in Fig. 16(c) and 16(d). Essentially Cabrera and Mott's theory of oxidation¹⁶ has been used. In Fig. 16(c), as the bias voltage is made large, Si^{++++} ions are pulled into the oxide film. They leave interface states in the upper half of the gap. In Fig. 16(d) with the field in the opposite direction, the ions are pulled back to the interface and ion and interface states disappear. Several objections can be made to this picture, however, and the most severe one is the above found equality of the number of interface states that disappear and the decrease in the number of positive charges in and on the oxide film. In the model of Fig. 16(c) and 16(d) the number of charges disappearing in and on the oxide film would be four times the difference in the number of interface states. It is thus certain that ions with multiple charges are not involved in the observed processes.

TIME CONSTANTS

As pointed out in reference 1 and elsewhere, when the bias voltage is switched from a certain voltage V_1 to another voltage V_2 with $V_2 > V_1$, the inversion layer conductance drops immediately to a low value and then slowly increases again to a new equilibrium value which is lower than the equilibrium conductance at voltages V_1 . The slow increase in conductance results from a build-up of the charge in the outer surface states. In Fig. 17, four plots are shown of $g_\infty - g(t)$ (g = conductance of inversion layer) as a function of

¹⁶ N. Cabrera and N. F. Mott, Repts. Progr. Phys. 12, 163 (1949).

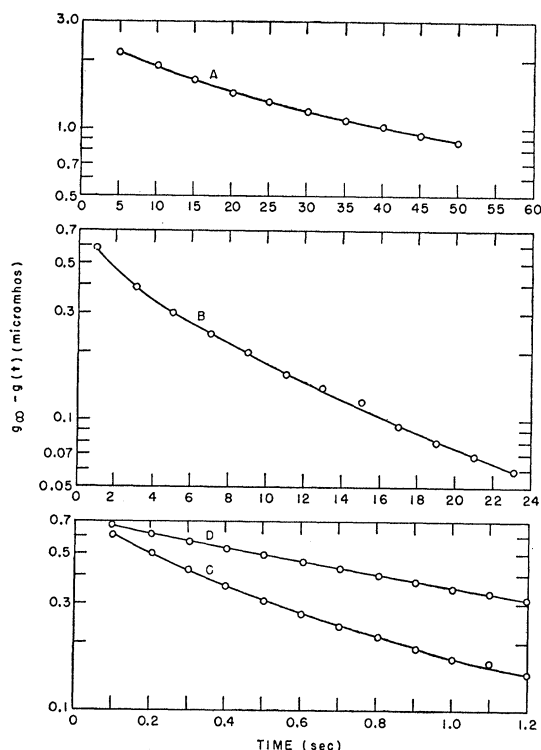


FIG. 17. Relaxation of inversion layer conductance after change in bias voltage.

time t . Figure 17 corresponds to n -type inversion layers on p -type material. Run *A* corresponds to an inversion layer on weakly-oxidized silicon and the curve shows a slight departure from an exponential form. Run *B* is for a well-oxidized germanium surface. Here, the curve is definitely nonexponential. Curve *C* is for a weakly-oxidized germanium surface. The decay is also nonexponential but faster compared to the well-oxidized surface. Curve *D* corresponds to a weakly-oxidized germanium surface at -10°C and it is seen that the "time constant" has become somewhat longer and the curve is nearly exponential. It would have been desirable to plot the charge in the outer surface states instead of the conductance as a function of time. The differences in the resulting curves are minor,

however, so that the extra work is not warranted. Two essentially different explanations have been given for the mechanism of charge transfer through the oxide film.¹⁷ In the present experiments the relaxation times are found to depend upon temperature so that an over-simplified temperature-independent tunneling mechanism must be rejected. However, since the band functions in the valence and conduction bands, and the outer surface states in general have different energies, phonons have to be involved to induce transitions between these two wave functions in their overlap regions. Thus, in a somewhat refined picture of tunneling, there is room for a temperature dependence. Also, from measurements in this laboratory there are definitely cases, especially for inversion layers on n -type silicon and germanium, where the charge in the outer surface states varies exponentially with time. The existing theories have been aimed particularly at explaining the nonexponential variation of the charge in the outer surface states. In this paper it will not be attempted to decide whether such a refined tunneling mechanism or a suitably extended model involving a potential barrier between the semiconductor and the outer surface states can satisfactorily explain all the various data. The behavior of germanium at -10°C suggests that perhaps residual water vapor was causing the nonexponential behavior at room temperature. If there are different surface states resulting, for example, from water and ammonia and if, furthermore, the over-all transition probabilities to the two surface states are different, then $g_{\infty} - g(t)$ should not be describable by a single time constant.

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¹⁷ R. H. Kingston and A. L. McWhorter, Phys. Rev. **103**, 534 (1956); S. R. Morrison, Phys. Rev. **102**, 1297 (1956); see also reference 1.