PHYSICAL REVIEW VOLUME 101, NUMBER 4 FEBRUARY 15, 1956

Surface States on Silicon and Germanium Surfaces*

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(Received November 9, 1955)

On silicon and germanium, steady-state and nonsteady-state *p*-type inversion layer conductance measurements can be understood in terms of two sets of surface states: one with a great density outside the oxide and the other with a smaller density at the semiconductor-semiconductor oxide interface. The interface states in silicon and germanium lie 0.455 and 0.138 ev, respectively, below the middle of the gap. There may also be interface states in the upper half of the gap; however, for their determination, measurement on *n*-type inversion layers would have to be made. The density of the interface states in silicon is about 1.4×10^{12} states/cm^2; the density in germanium is one-tenth this value. Various mechanisms of charge transfer through the oxide film are considered and compared with experimental data.

INTRODUCTION

In the last few years, a great amount of work[1–10] has been done on semiconductor surfaces. Silicon or germanium, unless it has not been exposed to oxygen, is covered by an oxide film. On the oxide film there are adsorbed gas atoms or molecules of the surrounding ambient. This structure gives rise to a complex set of localized electronic states. At the present time it seems exceedingly difficult to calculate this set of states by pure quantum mechanical means, especially since there are many unknown factors necessary to formulate such a problem. One does not know, for example, the thickness and structure of the oxide film. It also seems certain that there are some "defects" or irregularities at the interface of the semiconductor and the oxide. The difficulties of such a calculation can be visualized by studying the literature of the simpler problem of a clean semiconductor surface in a vacuum.[11–17] The results are very sensitive to small variations in the potential at the surface. These calculations predict that there may be localized electronic states in the energy gap at the surface. If these states are present, then their number is always equal to the number of surface atoms. These electronic levels will be called "Tamm states." In principle, there is the possibility of the existence of Tamm states at the semiconductor-oxide interface[18] and at the oxide surface. No experimental evidence for their existence has been found.

Adsorbed gas atoms on the surface[19,20] act quantum mechanically much like impurity atoms in the interior of the crystal. Adsorbed gas atoms will in general give localized electronic states. If there is a complete monomolecular layer of adsorbed gas atoms, then interactions will exist between neighboring atoms, and surface energy bands will be formed much like in a two-dimensional metal. These surface energy bands belong to electrons moving in the layer of adsorbed material. As long as the energy of these states is in forbidden zones of the underlying semiconductor, the wave functions will be damped exponentially into the semiconductor. In addition, if these surface energy bands are partly filled one may expect surface conduction. This type of conduction has not yet been reported.

In general, there will not be just one monolayer of adsorbed material. If there is less than one monolayer, then there will be less interaction between neighboring adsorbed atoms and the broadening of the surface bands will be less. If there is more than one monolayer, the surface bands will be broader. Imperfections in the oxide film or irregularities in the semiconductor-oxide interface, due to the misfit of the semiconductor and oxide lattice or impurity atoms in the interface originating from the etching solution, may be additional sources of surface states. In the present work, no evidence for states in the oxide film was found.

Next consider the effects of surface states. The occupancy of the surface states will be determined by the position of the Fermi level. In general, these states will be either positively or negatively charged. The sum of the charges in the various surface states will determine the direction and amount that the energy bands at the surface will be tilted. If the charge is negative, for example, the bands will be bent such as to repel electrons and to attract holes. For an *n*-type semi-

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* The work for this paper was supported in part by the Bureau of Ships, the Signal Corps, and the Air Force.

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conductor, this may give rise to a thin layer in which there are more holes than electrons. Such layers of different conductivity type than the bulk of the semiconductor are called inversion layers. Measurements of the conductivity of such inversion layers are an important method of investigating surfaces. This paper will be concerned with the interpretation of measurements of inversion layer conductance. Some of the measurements on germanium surfaces have already been reported.[6,7] This paper will be concerned mainly with silicon surfaces and only additional results on germanium will be given. Only *p*-type inversion layers on *n*-type material have been studied.

For coherence, use will be made of the charge in the inner surface states prior to the description of the method of determination.

SAMPLE PREPARATION AND MEASUREMENTS

In order to create an inversion layer on *n*-type silicon material, the surface must have a negative charge. The surface states have to be predominantly of the acceptor type. The only type of states that can be influenced readily are those arising from adsorbed atoms on the surface of the oxide. One might expect that adsorbed oxygen, fluorine, chlorine, bromine, and perhaps other gases tend to accept an electron. Only oxygen was investigated and found to behave in this manner, especially when present in the form of ozone. The silicon samples were etched in CP4, carefully washed in water, methyl alcohol, and carbon tetrachloride, and dried. The samples were then oxidized for approximately one hour in a wet O_2 and O_3 mixture. Then the samples were kept in a dry atmosphere of dry O_2 and O_3 and an inversion layer on *n*-type material was observed. In the course of about six hours, the inversion layer conductance increased after which time it was stable. This surface treatment is approximately the same as for germanium.[6]

To measure the conductance of the inversion layer, the samples were cut in rectangular bars from a *p-n-p* type crystal. In the silicon samples, the *n*-region had a width of 0.075 cm and a resistivity of 1.1 ohm cm. The measurements were made in about the same manner as those described by Kingston[8] as shown in Fig. 1.

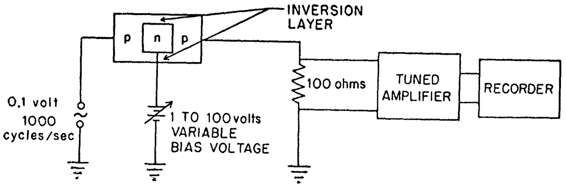

FIG. 1. Diagram of circuit used to measure conductance of inversion layers as a function of bias voltage.

RELATIONSHIP BETWEEN CONDUCTANCE OF INVERSION LAYERS, CHARGE IN SURFACE STATES AND POSITION OF FERMI LEVEL AT SURFACE

It was first shown by Brown[1] that it is possible to determine from the conductance of the inversion layer the total charge in the surface states and the position of the quasi-Fermi level at the surface. The calculations in the literature are either not accurate enough or those which have sufficient accuracy do not apply. The formulas derived below have proven to be simple and accurate enough for this work.

In Fig. 2, the energy bands at the surface are drawn. Since a voltage is applied between the *p*-type inversion layer and the underlying *n*-type semiconductor, no single Fermi level exists and the semiconductor is described by two quasi-Fermi levels $-q\varphi_n$ and $-q\varphi_p$. φ_n is approximately a constant in the *n*-type region and φ_p is constant in the inversion layer region. No attempt was made to calculate the behavior of φ_n in the inversion layer region and φ_p in the *n*-region since this would require a knowledge of the lifetimes in the material including the surface recombination velocity. In Fig. 2, φ_p describes the occupancy of the surface states in the lower half of the energy gap. Brattain and Bardeen[3] suggested this as a reasonable assumption and it is indeed borne out by the following experiments.

The conductance g of a square of inversion layer is given by

$$g = q\mu_p p, \tag{1}$$

where q is the electronic charge, μ_p is the average mobility of the holes in the inversion layer, and p is the number of holes per cm^2 of *p*-type skin. The mobility depends on the width of the inversion layer because the mean free path of holes is of the order of the thickness of this layer and a large amount of scattering occurs at the surface. Hence, μ_p is a function of the applied bias voltage V_a, the position of the quasi-Fermi level with respect to the middle of the band[21] ϕ_s, and the charge density ρ_d arising from ionized donor atoms. μ_p has been calculated by Schrieffer.[22] Thus, p in Eq. (1) and the total space charge in the interior of the semiconductor must be calculated. The space charge is equal but of opposite sign to the charge in the surface states. The position of the Fermi level in the interior of the sample is taken as a reference for the potential Ψ. The line in the middle of the forbidden gap[21] is used to define the potential of the sample. (In Fig. 2, the potential energy $-q\Psi$ of an electron and not the potential Ψ is shown.) In the three regions of Fig. 2, the space charge ρ as a function of potential is given by the following expressions:

Region I, $\Psi_n \geqslant \Psi \geqslant 0$:

$$\rho = \rho_d - qn_i \exp(q\Psi/kT), \tag{2}$$

where n_i is the intrinsic concentration of electrons, ρ_d is

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[21] More accurately, by the middle of the band we mean that position at which the Fermi level would lie if the semiconductor were intrinsic.

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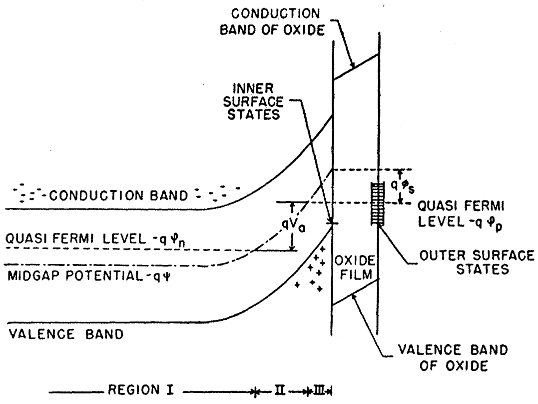


FIG. 2. Energy band and surface state structure at semiconductor surface.

the charge resulting from ionized donors, k is Boltzmann's constant, and T is the absolute temperature. In (2), the charge resulting from holes has been omitted, since for a reverse biased junction the holes are extracted from the n-type material within one diffusion length from the junction. Ψ_n is the potential far within the n-region of the semiconductor. Ψ_n and ρ_d are related by the equation

$$\rho_d = qn_i \exp(q\Psi_n/kT). \tag{3}$$

Region II, $0 > \Psi \geqslant -V_a$:

$$\rho = \rho_d. \tag{4}$$

The contribution of electrons and holes is very small compared to ρ_d and has therefore been omitted.

Region III, $-V_a > \Psi \geqslant -V_a - \phi_s$:

$$\rho = \rho_d + qn_i \exp[-q(\Psi + V_a)/kT]. \tag{5}$$

The space charge consists of ionized donors and free holes. The contribution from free electrons can again be omitted.

Poisson's equation is used to calculate the field at the surface. Poisson's equation,

$$d^2\Psi/dx^2 = -(4\pi/\epsilon)\rho(x) \tag{6}$$

(where ϵ = dielectric constant), can be written

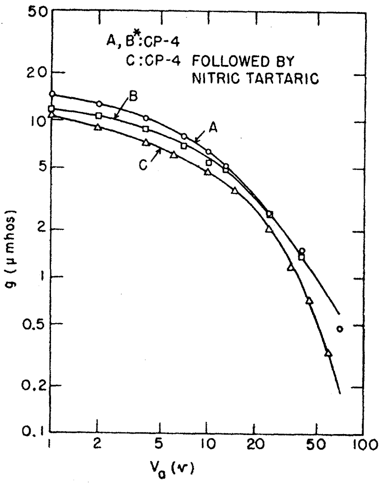
$$EdE = -(4\pi/\epsilon)\rho(\Psi)d\Psi, \tag{7}$$

where $E = -d\Psi/dx$. Substituting Eqs. (2), (4), and (5) into Eq. (7) and integrating the left-hand side from $E=0$ to $E=E_s$ (field at the surface) and the right-hand side from $\Psi = \Psi_n$ to $\Psi = -V_a - \phi_s$, we obtain

$$E_s^2 = \frac{8\pi}{\epsilon}\left\{\rho_d\left(|V_a| + |\Psi_n| + |\phi_s| - \frac{kT}{q}\right) + qn_i\frac{kT}{q}\exp\left(\frac{q|\phi_s|}{kT}\right)\right\}. \tag{8}$$

In (8), the absolute magnitude signs have been introduced so that the equation may be used without checking whether the quantities Ψ_n, ϕ_s, V_a are positive or negative in their definitions. The total space charge Q in a cylinder with unit cross section is given by Gauss' theorem which relates Q and E_s.

$$Q = (\epsilon/4\pi)E_s. \tag{9}$$



* Temperature for B 5°C above room temperature

FIG. 3. Steady-state inversion layer conductance as a function of bias voltage (silicon).

As mentioned, the charge in the surface states per unit area is $-Q$. Next the number of holes in the inversion layer is calculated. The density of holes $\bar{p}$ in region III as a function of potential is

$$\bar{p} = n_i \exp[-q(\Psi + V_a)/kT]. \tag{10}$$

The total number p per unit area is

$$p = \int_{\text{Region III}} \bar{p}dx = \int_{-V_a}^{-V_a-\phi_s} \bar{p}\frac{1}{d\Psi/dx}d\Psi. \tag{11}$$

The quantity $d\Psi/dx$ can be obtained from (8). The field at an arbitrary position in region III is obtained by replacing ϕ_s by ϕ $(= -\Psi - V_a)$. When the variable of integration is changed from Ψ to ϕ, Eq. (11) can be written

$$p = \int_0^{\phi_s} \frac{n_i \exp(q|\phi|/kT)d\phi}{\left(\frac{8\pi}{\epsilon}\right)^{\frac{1}{2}}\left\{\rho_d\left(|V_a| + |\Psi_n| + |\phi| - \frac{kT}{q}\right) + qn_i\frac{kT}{q}\exp\left(\frac{q}{kT}|\phi|\right)\right\}^{\frac{1}{2}}}. \tag{12}$$

Equation (12) can be easily integrated if the quantity ϕ in the bracket under the square root is omitted. In practice, this simplification is a very good approximation. Limits for the true value of p can be obtained. If one integrates (12) by setting the considered term in ϕ equal to zero, the denominator will always be too small and the integral will be too large. Similarly, if ϕ in the considered term is always set equal to ϕ_s (the largest value that ϕ takes in the interval of integration), the denominator will be too large and the integral will be too small. Thus,

$$\begin{aligned}&\left(\frac{\epsilon}{2\pi}\right)^{\frac{1}{2}}\frac{1}{q}\left\{\rho_d\left(|V_a|+|\Psi_n|+|\phi_s|-\frac{kT}{q}\right)\right.\\&\quad\left.+\frac{kT}{q}qn_i\exp\left(\frac{q}{kT}|\phi_s|\right)\right\}^{\frac{1}{2}}\\&\quad-\left(\frac{\epsilon}{2\pi}\right)^{\frac{1}{2}}\frac{1}{q}\left\{\rho_d\left(|V_a|+|\Psi_n|+|\phi_s|-\frac{kT}{q}\right)\right.\\&\quad\left.+\frac{kT}{q}qn_i\right\}^{\frac{1}{2}}<p<\left(\frac{\epsilon}{2\pi}\right)^{\frac{1}{2}}\frac{1}{q}\left\{\rho_d\left(|V_a|+|\Psi_n|-\frac{kT}{q}\right)\right.\\&\quad\left.+\frac{kT}{q}qn_i\exp\left(\frac{q}{kT}|\phi_s|\right)\right\}^{\frac{1}{2}}-\left(\frac{\epsilon}{2\pi}\right)^{\frac{1}{2}}\\&\qquad\qquad\times\frac{1}{q}\left\{\rho_d\left(|V_a|+|\Psi_n|-\frac{kT}{q}\right)+\frac{kT}{q}qn_i\right\}^{\frac{1}{2}}.\qquad(13)\end{aligned}$$

In order to check the reliability of (13), conductance values were converted to values of ϕ_s, using either of the two limits. The error is the larger, the smaller the bias voltage and the smaller the conductance. For $V_a=2$ volts, and a conductance measurement of 10 micromhos, the two determinations of ϕ_s differed by 0.002 volt.

All experiments were carried out with samples cut from the same crystal (1.1 ohm cm n-type silicon, and 8 ohm cm n-type germanium as in references 6 and 7). Thus, ρ_d is always the same. The most extensive calculations have been made for room temperature (296°K). A series of bias voltages V_a was chosen. Then at each bias voltage a curve of channel conductance as a function of ϕ_s was plotted, using Schrieffer's[22] mobility values. For convenience, Schrieffer's two parameters β and B are given in the present notation by

$$\beta=\frac{1}{q\tau}\left\{\frac{m\epsilon}{8n_i}\exp\left(-\frac{q|\phi_s|}{kT}\right)\right\}^{\frac{1}{2}},$$

$$B=\frac{\rho_d}{qn_i}\frac{q}{kT}(|V_a|+|\Psi_n|+|\phi_s|)\exp\left(-\frac{q|\phi_s|}{kT}\right),$$

where τ and m are the relaxation time and effective mass as in Schrieffer's paper. Thus, for a conductance value measured at a given voltage, ϕ_s can be determined immediately. Similar graphs are made for the same set of voltages V_a showing the charge Q as a function of ϕ_s.

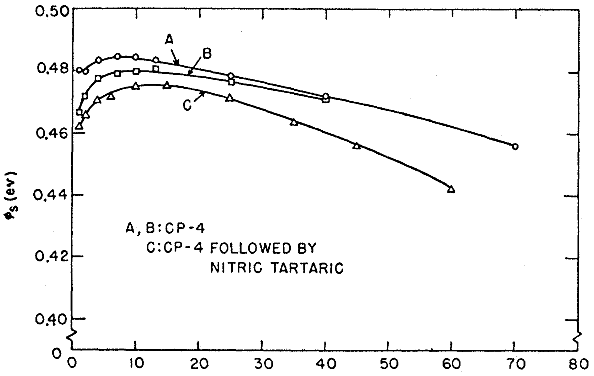


FIG. 4. Quasi-Fermi level at surface as a function of bias voltage (for the conductance curves of Fig. 3).

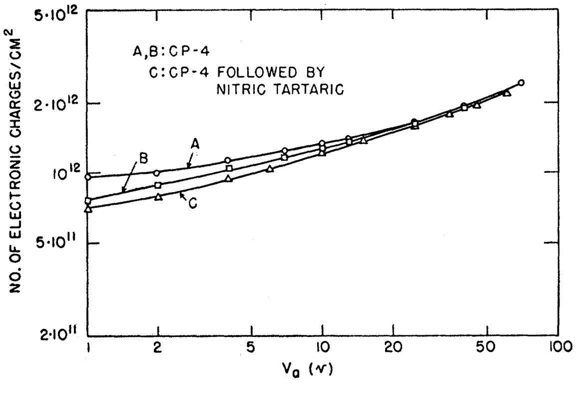


FIG. 5. Total charge in surface states as a function of bias voltage (for conductance curves of Fig. 3).

STEADY-STATE INVERSION LAYER CONDUCTANCE

In Fig. 3, the steady-state conductance of an inversion layer on silicon as a function of bias voltage is shown for three sets of measurements. One of the silicon samples (Fig. 3, curve C) was first etched in CP4 and then treated with nitric and tartaric acids. The mixture of nitric and tartaric acids is presumably not an etch for silicon; the only effect is a further oxidation of the surface. The measurements were difficult because of the slow drift of conduction as well as the time required to reach the steady-state conduction. At each voltage, up to one hour or more was required for the inversion layer to approach a steady-state conductance value. Thus, one day was required for one run. The runs were made by first increasing and then decreasing the voltage. Only if the two readings at each point coincide can one be certain that the inversion layer did not change during the measurements. In Fig. 4 the position of the quasi-Fermi level with respect to the middle of

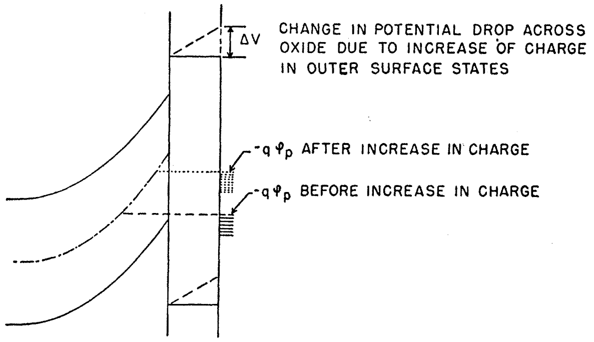


FIG. 6. Diagram of change in potential drop across oxide film resulting from change in charge in outer surface states.

the gap, i.e., ϕ_s, is shown as a function of the bias voltage. In Fig. 5 the total charge in the surface states is shown as a function of the bias voltage. The results are very similar to those obtained for germanium.[6,7] ϕ_s is again approximately constant for each run. However the deviations from a constant are greater than for germanium. The charge in the surface states again increases monotonically with V_a. The results must be interpreted—neglecting deviations of ϕ_s from a constant—as a high density of surface states. It seems certain that the calculated increase in ϕ_s for voltages below approximately 10 volts is not a real effect. In nonsteady-state measurements to be described below ϕ_s values are also found to be too small when they are determined from conductance values at bias voltages below approximately 10 volts. The authors have found the same but smaller effect for inversion layers on germanium. At the present time, the cause of this effect is not clear. The decrease of ϕ_s for voltages larger than approximately 10 volts seems to be a real effect. Two explanations can be given. First, the total density of surface states is finite. With this interpretation, the density can be calculated as the change in the number of electrons divided by the change in the quasi-Fermi level, and is found for curve *A* of Fig. 3 to lie in the vicinity of 3×10^{13} states/cm^2 volt. Secondly, a finite thickness of the silicon oxide film can give the same result. As in germanium, the states at the silicon-silicon oxide interface are by far not numerous enough to give a constant ϕ_s. In these experiments, no evidence for states in the oxide film is found. The large density of states therefore is outside the silicon oxide. Assume that their density is infinite so that the quasi-Fermi level is quenched with respect to the position of these dense states. When the voltage is increased, the negative charge in the outer surface states increases as can be seen from Fig. 5. Thus, the field in the oxide film as well as the potential difference between the inner side of the oxide and the outer surface change as indicated in Fig. 6. Since, for this interpretation, the quasi-Fermi level is assumed to be quenched with respect to the surface states at the outer surface, the position of the Fermi level at the interface must change.

The effects due to a finite density of states and the finite thickness of the oxide film will add; however, an upper limit for the thickness of the oxide film can be obtained by assuming an infinite density of states outside. In order to get accurate results, the fact that the charge in the interface states changes somewhat with the position of the quasi-Fermi level must be considered. By assuming a dielectric constant of 3.78 (fused quartz[23]) for the silicon oxide film, the electric field in the film can be calculated except for an additive constant. In Fig. 7, ϕ_s as calculated for run *A* of Fig. 3 is corrected for the potential drop by the addition of ΔV to the value obtained for ϕ_s from the conductance measurement. Because of the undetermined additive constant in the electric field E, ΔV is arbitrarily set equal to zero at $V_a=70$ volts. The thickness of the film is assumed to be 10 A. The curve for ϕ_s is nearly constant from 15 to 70 volts. This graph indicates that the silicon oxide film on this sample is not thicker than 10 A. For the other curves of Fig. 3, different values of thickness are obtained. For curve *C*, where the surface was oxidized with nitric and tartaric acids, the upper limit for the thickness is considerably greater. For germanium[6] there is almost no decrease in ϕ_s; however, the charge in the surface states is also much smaller. The same thickness of oxide film, therefore, gives a much smaller potential drop and the magnitude of this drop is probably not within the accuracy of the determination of ϕ_s and no reliable upper limit for the thickness of the oxide film can be given. A thickness of 10 A or less is certainly compatible with the measurements.

NONSTEADY-STATE CONDUCTANCE OF INVERSION LAYERS

In silicon, a similar transient effect is observed as in germanium when the bias voltage is switched from one value to another. If the voltage is switched from a value V_1 to a value V_2 with $V_2>V_1$, the conductance immedi-

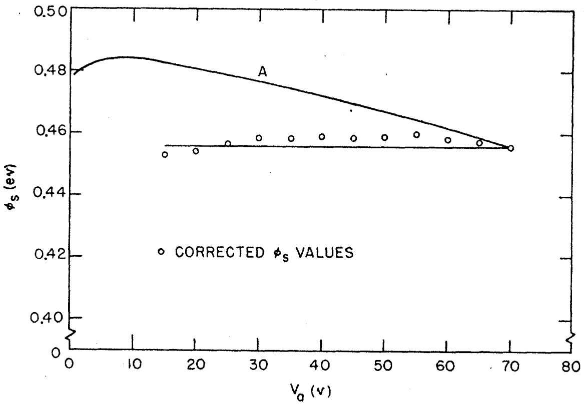


FIG. 7. Quasi-Fermi level corrected for potential drop in oxide film (silicon).

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[23] Technical Report No. 57, Laboratory for Insulation Research, Massachusetts Institute of Technology, January, 1953 (unpublished).

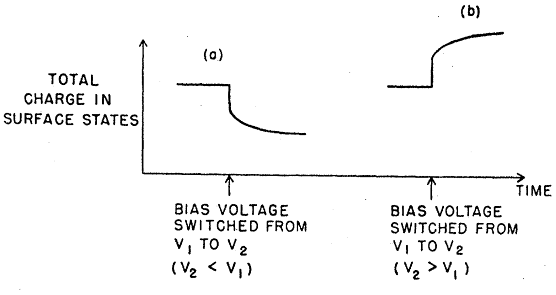

FIG. 8. Schematic representation of change in charge as a function of time after switching bias voltage.

ately drops to a low value and then slowly rises to a new equilibrium value. The drop is so fast that it cannot be resolved by the equipment, i.e., faster than 10^{-2} sec. The slowly rising conductance approaches the new equilibrium value with a time constant which lies between a few minutes and about one hour depending on the preparation of the surface. In general, the time constant is greater the longer the sample surface has been exposed to a mixture of wet or dry O_2 and O_3. The wet mixture seems more effective in increasing the time constant. Similarly, if the voltage is switched from a value V_1 to a value V_2 with $V_2 < V_1$, then the conductance first rises in a very short time and then slowly decreases again to approach a new equilibrium value. The total charge in the surface states can be calculated along these curves and is shown schematically in Fig. 8. The interpretation is again[7] that there are two sets of surface states, one with a short time constant and the other with a long time constant. The surface states with the long time constant are assumed to be located at the surface of the silicon oxide film, those with the short time constant at the interface.

Before proceeding with the determination of the interface states, it is worth stating that in experiments with *p*-type inversion layers on germanium or silicon there is no evidence for more than one set of slow states, in contrast to the case of water-induced inversion layers on *p*-type germanium.[24,25] In Fig. 9(a), a typical conductance curve for a *p*-type inversion layer on germanium is shown. The voltage is switched at $t=0$ from 10 to 31 volts. The conductance goes to zero for a period of time after switching and then recovers and approaches a new equilibrium value. In Fig. 9(b), a plot of $g_\infty - g$ (g_∞ = equilibrium conductance at 31 volts) is made. In Fig. 9(c), the total equilibrium charge at 31 volts minus the total charge in the surface states at arbitrary time is shown. In Fig. 9(d), the curve becomes exponential when the charge in the inner surface is subtracted from the total charge. In other cases where the conductance does not go to zero after switching, curves analogous to Fig. 9 are equally good exponentials.

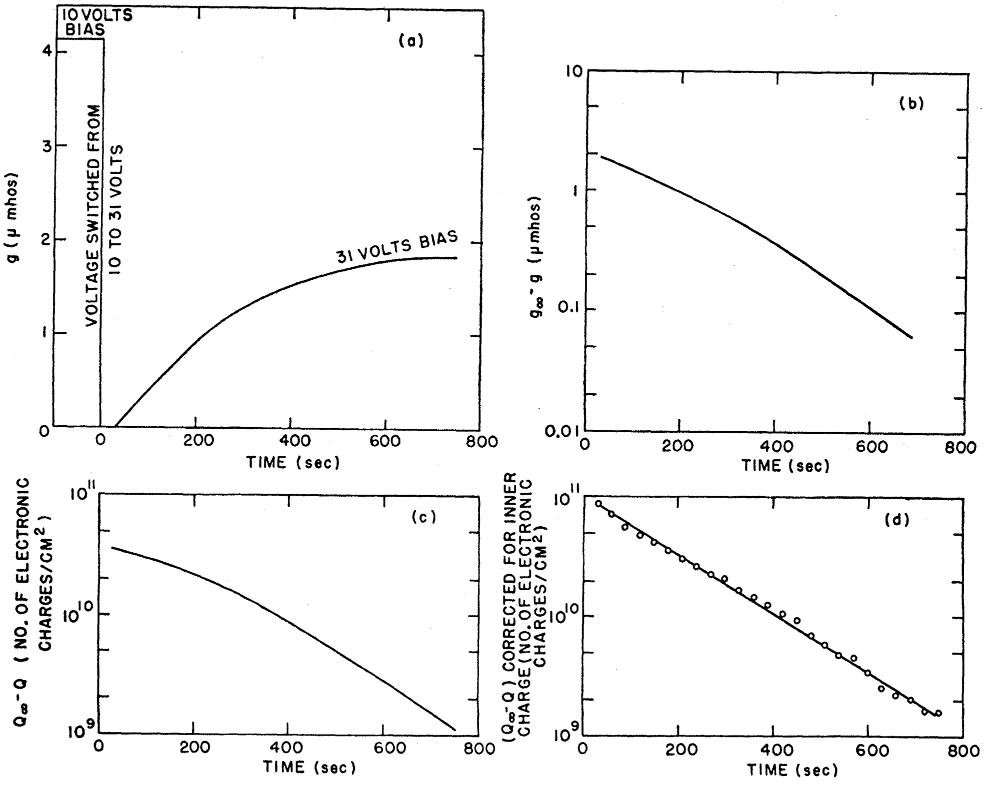

FIG. 9. Change in conductance and charge in surface states for an inversion layer on germanium.

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[24] R. H. Kingston and A. L. McWhorter, Phys. Rev. 98, 1191(A) (1955).
[25] A. L. McWhorter, Phys. Rev. 98, 1191(A) (1955).

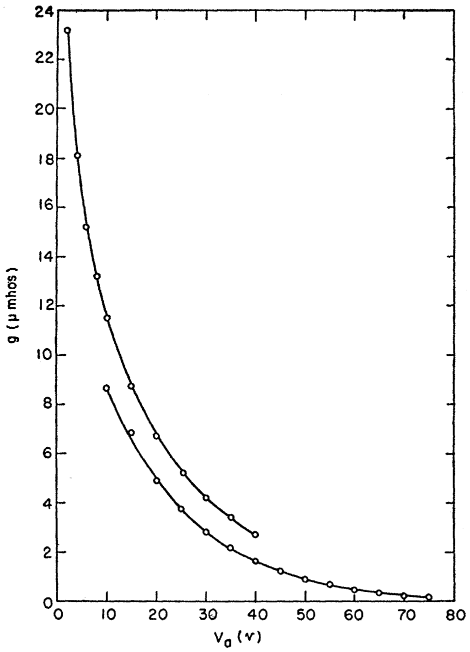

FIG. 10. Nonsteady-state conductance curves for an inversion layer on silicon.

There may be some nonexponential behavior if the time constants are very short. These cases have not been investigated. The fact that for the investigated surfaces, the slow decay is approximated by one single exponential term indicates that there is only one set of slow states. Consequently, no states in the oxide will be assumed for the interpretation of the present experiments.

Since the charge in the surface states outside the oxide changes so slowly in silicon, it was possible to record an entire conductance curve as a function of voltage without changing the charge in the outer states to a measurable extent. An $x-y$ recorder was used in the present experiments. The voltage was first increased to a value at which the conductance was zero, i.e., pinch-off, and then the curve was traced back. If the elapsed time during such a measurement did not exceed 10 sec, then the two are not distinguishable. It was desirable to cover experimentally a large range in ϕ_s values. In the example of Fig. 10, the voltage was increased from 10 to approximately 75 volts where the conductance vanished. ϕ_s decreased from the equilibrium value ϕ_{s0} to a very small value. (The formulas are not accurate for the vicinity of pinch-off. A more detailed treatment would follow closely the work of Prim and Shockley[26] on field-effect transistors, but for this paper an exact description of pinch-off is not essential.) Next the bias voltage was changed to 40 volts, and after a long time (almost sufficient to establish the equilibrium conductance) the voltage was decreased in a short time to 2 volts and the conductance was recorded. In order to be certain that the charge in the outer surface states does not change, the voltage was immediately increased from 2 volts to 40 volts and the conductance recorded. These conductance readings for the runs from 40 volts to 2 volts and from 2 volts to 40 volts must coincide. While the bias was held at 40 volts, the charge outside the oxide film built up until ϕ_s approached the equilibrium value for 40 volts which is somewhat less than the corresponding value for 10 volts. In decreasing the voltage from 40 volts to 2 volts, ϕ_s increased and became considerably larger than the equilibrium value for 10 volts. Thus a large range in ϕ_s was covered. The charge in the outer surface states is, of course, different for the runs from 10 volts to 75 volts and from 40 volts to 2 volts.

In order to convert the measured curves into plots of charge in inner surface states *versus* position of quasi-Fermi level, the charge in the outer surface states must be subtracted. In principle, this can be done only by the trial-and-error method. However, from the work of Brattain and Bardeen[3] one already knows that the states lie far away from the middle of the energy gap. Therefore it can be assumed that at pinch-off the interface states in the lower half of the gap are full. When the (negative) charge in the surface states at pinch-off is subtracted from the smaller (negative) charge at an arbitrary value for ϕ_s, a charge with positive sign interpreted as resulting from holes in the inner surface states is obtained. For example, the circles shown in Fig. 11 correspond to the run starting at 10 volts (Fig. 10). The corresponding charge for the run from 40 volts to 2 volts was obtained in the following way. At the value for ϕ_s at 40 volts, the number of holes in the inner surface states is known from the run between 10 volts and 75 volts. Thus for this particular ϕ_s value the charge in the outer surface states can be determined, since the total charge in the surface states is known. The charge in the outer surface states does not change; thus the number of holes in the inner surface states as a function of ϕ_s is known for the run between 40 volts and 2 volts (points shown as triangles in Fig. 11). The points in Fig. 11 immediately suggest that there is just

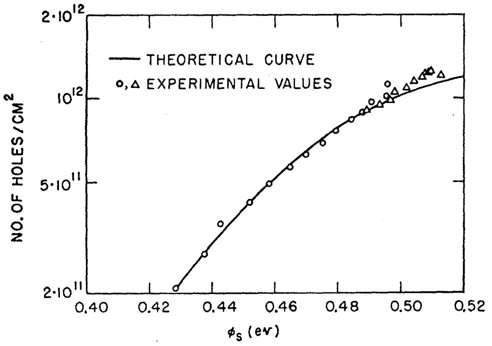

FIG. 11. Number of holes in inner surface states as a function of the position of the quasi-Fermi level for silicon.

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[26] R. C. Prim and W. Shockley, Trans. Inst. Radio Engrs. Prof. Group on Electron Devices, *PGED-4*, 1 (Dec. 1953).

one state below the middle of the gap. To determine the energy of this state the distribution function must be known.

From the curve of Fig. 11, there are much fewer interface states than surface atoms. Therefore it seems reasonable to assume that the surface states can be empty or occupied by either one electron with plus spin or one electron with minus spin, but not with two electrons of opposite spin. If the states are localized, as must be assumed from their density, the second electron would have a different "one-electron" energy from the first electron because of electrostatic interaction. The Fermi distribution function therefore has the form

$$f=\frac{1}{1+\frac{1}{2}\exp[(E-E_F)/kT]}. \tag{15}$$

In (15), E is the energy of the surface state and E_F the Fermi energy. In the present notation, the number of holes in the surface states is

$$p_s=\frac{N_s}{1+2\exp[q(\phi_L-\phi_s)/kT]}. \tag{16}$$

In (16), ϕ_L is the position of the surface level with respect to the middle of the gap. In Fig. 11, the solid line represents (16) with $N_s=1.4\times10^{12}$ cm^{-2} and $\phi_L=0.455$ volt. The theoretical curve fits the experimental points quite well. If one assumes the usual Fermi distribution in which two electrons, one with plus and one with minus spin, can be accommodated, then a different position $\bar{\phi}_L$ is obtained. Obviously, (16) becomes the usual Fermi distribution $1/\{1+\exp[(q/kT)(\bar{\phi}_L-\phi_s)]\}$, when $\phi_L=\bar{\phi}_L-(kT/q)\ln2$. Thus, if the usual Fermi distribution is used, the energy level of the states lies 0.472 volt below the middle of the gap. From measurements at one temperature it is, in principle, impossible to determine which distribution function applies.

In the paper on germanium,[7] the energy level has been determined with the usual Fermi distribution.

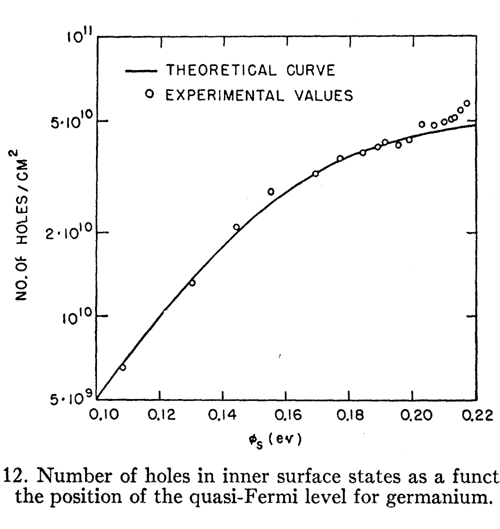

FIG. 12. Number of holes in inner surface states as a function of the position of the quasi-Fermi level for germanium.

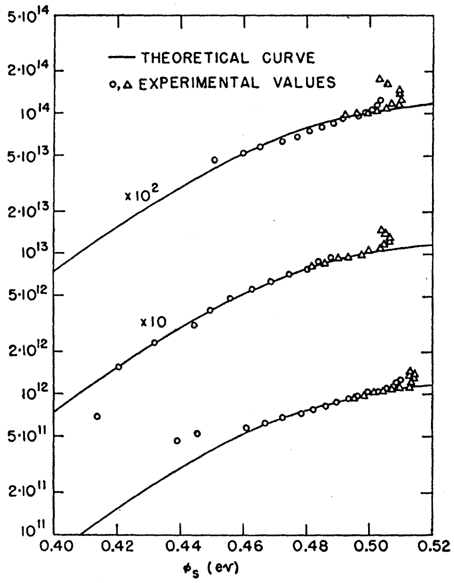

FIG. 13. Number of holes in inner surface states as a function of the position of the quasi-Fermi level for three silicon runs.

However, with the distribution (16) the level for the interface states for germanium becomes 0.138 volt below the middle of the gap. A curve showing charge *versus* ϕ_s for a germanium surface is given in Fig. 12. This plot covers a larger ϕ_s range than the curves previously reported.[7] The solid line in Fig. 12 is the theoretical distribution function (16) with $\phi_L=0.138$ volt and $N_s=4.8\times10^{10}$ states/cm² volt.

In Fig. 13, the results of other measurements made with the same silicon surface as that of Fig. 11 are shown. In these measurements, different voltage ranges are used. The solid curves in Fig. 13 are all identical with the one shown in Fig. 11. The curves do not fit as well as in Fig. 11 but are still satisfactory. The points which deviate from the theoretical curve at high ϕ_s values correspond to voltages below 10 volts. The same phenomenon is found in the steady-state curves; ϕ_s is too low at low voltages. No significance will be attributed to this behavior which has also been found in germanium for values obtained at low bias voltages. The accuracy of the energy level is probably ±0.015 volt. Since the number of states is much smaller than the number of surface atoms, the interface states cannot be of the Tamm type. In order to determine the origin of the interface levels, extensive measurements have to be made by adding impurity atoms to the etch and varying the type of etch. So far, for all samples from the investigated silicon crystal, approximately the same density and the same energy level for the interface states has been obtained. For germanium the density varied by approximately a factor of two.

It is believed that the interface states are related to the surface recombination of electrons and holes. It is interesting to note that the number of interface states

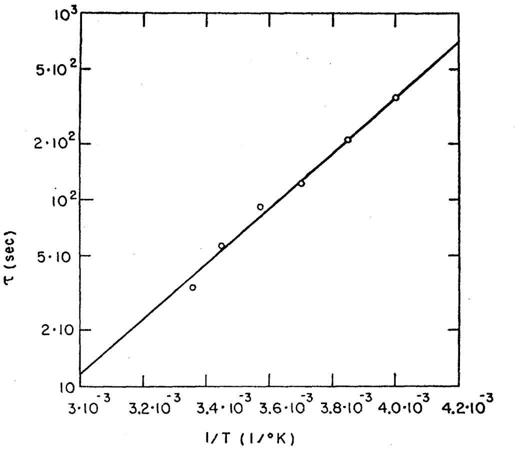

FIG. 14. Time constant as a function of temperature for germanium.

on silicon is of the order of ten times that of germanium. Also, the surface velocity for silicon is of the order of ten times that for germanium. This would appear to confirm the interpretation of these states as surface recombination levels. However, no measurements have yet been made to determine whether there are any states in the upper half of the energy gap.

CHARGE TRANSFER THROUGH OXIDE FILM

In order to determine how electrons or holes cross the oxide film, plots analogous to Fig. 9(d) have been made for a given germanium surface at various temperatures and the time constant τ determined. In Fig. 14, τ has been plotted as a function of $1/T$. The data are not accurate enough to determine if τ as a function of $1/T$ is of the form $\exp(+u/kT)$. The straight line in Fig. 14 corresponds to $u=0.3$ ev. There are two possible mechanisms to explain the transfer of electrons or holes through the film. First, the electrons or holes surmount a potential barrier in the oxide film. This barrier must be interpreted as the forbidden gap of the oxide film. Either holes can move through the valence band of the oxide, or electrons through the conduction band. For thin films, a conduction and valence band can no longer be defined rigorously. With the present model, do the experimental data allow a distinction between conduction through the valence band and conduction band of the oxide? For this problem, it is important that the steady-state conductance of the inversion layers can be explained by assuming that $-q\varphi_p$ determines the occupancy of the outer surface states. This fact indicates that these states communicate in some way with the holes in the semiconductor. This communication can be described as follows: The holes in the inversion layer at the interface attain equilibrium with the holes next to the interface in the valence band of the oxide. At the outer surface, the holes are in equilibrium with the outer surface states. If the quasi-Fermi level $-q\varphi_p$ at the interface is different from that at the outer surface, a current will flow through the oxide until $-q\varphi_p$ is the same throughout.

The argument against conduction through the conduction band is the following: Assume conduction by electrons through the conduction band. The electrons in the conduction band of the oxide next to the interface are in equilibrium with electrons in the conduction band of the semiconductor, and, as above, $-q\varphi_n$ should determine the occupancy of the outer states. However, the experiments indicate that $-q\varphi_p$ describes the population of the outer states; thus, one may conclude that at the surface $-q\varphi_p=-q\varphi_n$. But this conclusion is contradicted by the following experimental observation. It was found that after admitting traces of water vapor, the conductivity of the inversion layers dropped immediately to low values. Measurements before and after admission of water vapor indicate that the time constant for charge transfer hardly changes. However, the model predicts a great change in the time constant. A more detailed consideration of the model shows that even $Q_\infty-Q$ [Fig. 9(d)] would be expected to deviate greatly from an exponential time dependence for all values of conductance. Thus, conduction through the conduction band is not consistent with experimental data. If conduction through the valence band is considered, then the time constant for charge transfer can be estimated numerically. From Fig. 14, it can be concluded that the valence band of the oxide lies 0.3 ev below that of germanium. With reasonable estimates for the other physical constants, the calculated time constants are much too small. Thus, this conduction model does not account for all the observed data.

The other possible mechanism is a modified tunneling process as first suggested by Kingston.[24] In the case of very thin oxide films, the wave functions of the outer surface states are expected to overlap to some extent the band functions of the valence band of the semiconductor and phonon-induced transitions may take place. It can be shown that the transition probability (suitably averaged over all states) of an electron from a full state in the valence band to an empty state in the outer surface states must have the same temperature dependence as $1/\tau$. Calculations of this transition probability have not yet been made. Such calculations are necessary in order to see if this mechanism of charge transfer through the oxide film is feasible.

CONCLUSIONS

The steady-state conductance of p-type inversion layers on germanium and silicon can be understood in terms of a high density of surface states outside the oxide film. From a careful analysis of the electrical data, it is possible, especially on silicon, to obtain an upper limit for the thickness of the oxide film. The non-steady-state conductance measurement on p-type inversion layers can be interpreted by assuming states located at the semiconductor-semiconductor oxide interface. The energy level of these states is 0.455 ev and 0.138 ev below the middle of the gap for silicon and germanium, respectively. The density on the investigated samples is 1.4×10^{12} states/cm^2 for silicon and ranges from 5×10^{10} to 1.2×10^{11} states/cm^2 for germanium.

The mechanism of charge transfer through the oxide film is not yet clear. Simple conduction through a conduction band or valence band in the oxide is unlikely. More work must be done to establish whether the wave functions of the semiconductor valence band overlap sufficiently those of the outer surface states so that direct transitions between these functions account for the charge transfer.

ACKNOWLEDGMENTS

The authors wish to thank Mr. L. G. Rubin for his help with the instrumentation. Thanks are also due to Miss J. Sullivan and Mrs. M. Sturm for carrying out the computations and for help in preparing the manuscript.

PHYSICAL REVIEW VOLUME 101, NUMBER 4 FEBRUARY 15, 1956

Modulation of Conductivity by Surface Charges in Metals

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(Received June 20, 1955; revised manuscript received November 21, 1955)

Experiments on conductivity modulation by surface charges in metals are reported. Because of the high density of carriers, it is necessary to work on thin films in order to get measurable effects. The experimental technique used and the results obtained are reported. Metals belonging to widely different groups (Au, Bi, Sb) have been tested, and peculiar features have been found. A tentative interpretation of these results is offered, and the nature of the information that could eventually be gained is pointed out.

1. INTRODUCTION

The modulation of conductivity by electrical charges added at the surface of a flat specimen by a transverse electric field was demonstrated for semiconductors in the early stages of the transistor program.[1] Figure 1, taken from reference 1, illustrates the principle of the experiment in a self-explanatory form. The low density of current carriers in a semiconductor makes the experiment relatively easy to perform. The information to be gained from the experimental results in such a case is concerned with the density of "surface states."[2]

Apart from the much greater difficulty of the experiment (due to the small effect to be expected in a substance with extremely high carrier density) there is no reason why such an effect could not be detected in metals.

The present paper reports some measurements performed on metals belonging to widely different groups: Au, Bi, Sb.

The main results may be summarized as follows:

(1) In Au, a noble (nonoxidizable) monovalent metal with purely electronic conduction (negative Hall effect) due to nearly free electrons, an increment in the electron density causes the conductivity (σ) to increase.

(2) Bi is in contrast a multivalent semimetal with electron and hole conduction and high, normally negative, Hall effect, extremely sensitive to impurity concentration: as a matter of fact, our specimen has a positive Hall effect coefficient, surely not due to mechanical strains in the evaporated layer, as shown by measurements on a bulk specimen. An increment in the electron density causes σ to decrease. In addition, in this case we must remark:

(a) The effect is not linear.

(b) In addition to a reversible effect, there seems to be an irreversible one. As a matter of fact, we get the experimental points of Fig. 4, if the voltage is continuously and very slowly increased; but if, starting from a certain value, we invert the sense of the variation of the voltage, we obtain different points, displaced by a

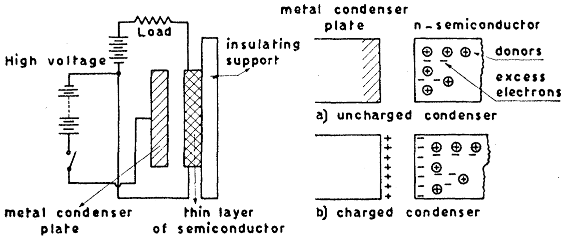

Fig. 1. Principle of the experiments on modulation by surface charges (from reference 1).

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[1] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 29 ff.

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