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 $1.4 \times 10^{12}$ states/cm$^2$ for silicon and ranges from $5 \times 10^{10}$ to $1.2 \times 10^{11}$ 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.

# 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 ($\sigma$) 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 $\sigma$ 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
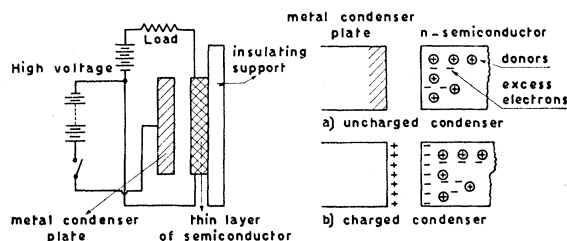


FIG. 1. Principle of the experiments on modulation by surface charges (from reference 1).

[1] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 29 ff.
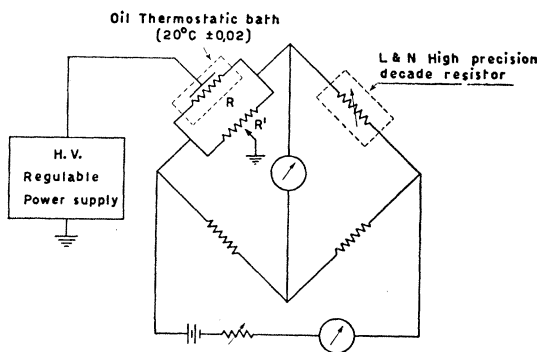[2] W. Shockley and G. L. Pearson, Phys. Rev. 74, 232 (1948).

FIG. 2. Circuit used in the experiments described in the text.

small amount from the preceding ones, giving rise to a sort of hysteresis loop.

(3) In Sb, a multivalent semimetal with electron and hole conduction and a very high, normally positive Hall effect (as in our specimen), an increment in the electron density causes $\sigma$ to increase with a linear behavior.

## 2. EXPERIMENTAL TECHNIQUE

Figure 2 shows the circuit used in the measurement of the conductivity modulation.

The specimen, of resistance $R$, is mounted on an arm of a high-sensitivity ($\sim 10^{-6}$) Wheatstone bridge. The regulable high-voltage power supply provides a transverse electric field which induces a large surface charge on the specimen. In order that this induced charge represent a measurable change in the average carrier density, the specimens used were thin metallic films. These were formed by evaporation of the metal in vacuum ($10^{-5}$ mm Hg) on best quality white mica substrates, not predegassed and held at room temperature.[3]

The thickness of the evaporated layers was evaluated by using a spectrophotometric titration against a specimen of known metal content.[4] Figure 3 illustrates the
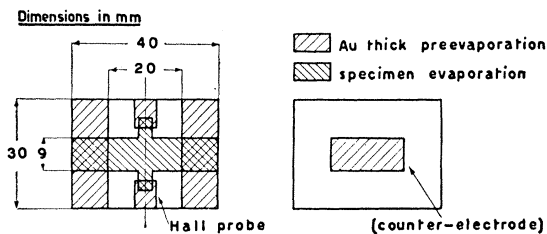


FIG. 3. Shape and size of the specimens. The diagram on the left is a front view; that on the right is a back view.

[3] Bonfiglioli, Coen, and Malvano, J. Appl. Phys. (to be published).

[4] A Beckman spectrophotometer was used to observe: for Au, the reddish color developed by reducing $AuCl_3$ with $SnCl_2$; for Bi, the orange yellow color due to a complex with KI; for Sb, the blue violet color due to the action of phosphomolibdotungstic acid. The results of such methods were satisfactory and good confidence may be given to the thicknesses indicated in the curves of Figs. 5, 6, 7, and 8.

shape of the specimen used. As insulating supports we used the best quality white mica because in this way we could easily obtain a transverse electric field of $10^6$ volts/cm, the right order of magnitude for measurable effects with evaporated films of good metals.

The $R'$ potentiometer allowed for static compensation of leakage currents which might flow through the dielectric. As a matter of fact such currents, if uncompensated, would give rise to a potential difference across the specimen, simulating a real variation of resistance. At the beginning and at the end of each measurement, with the bridge battery disconnected, the absence of any galvanometer deflection when applying the transverse electric field was checked. As a matter of fact, no detectable leakage current took place in the mica under the strongest field used in our experiments.

It is important to remark that the "geometrical" difficulties encountered when working on thin films (see reference 3) were entirely absent for Sb films; their thicknesses were relatively high (400–4000 A); Sb does not easily agglomerate and furthermore the "active" surface was the one directly facing the freshly cleaved
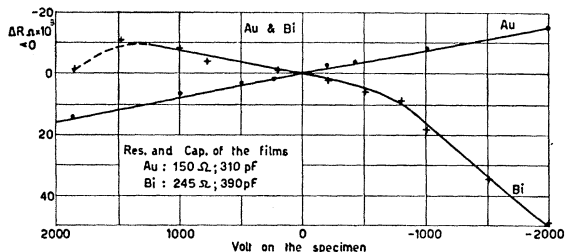


FIG. 4. $\Delta R$ effect in Au and Bi. (1 pf $= 10^{-12}$ farad.)

plane of mica. In any case, most of our deductions make no use of the precise thickness knowledge.[5]

## 3. EXPERIMENTAL RESULTS

The experimental results are given in Figs. 4–8. Figure 4 shows for Au and Bi the absolute variation in the specimen resistance $\Delta R$ as a function of the voltage $V$ applied across the mica condenser. The sign of resistance change and of the voltage on the specimen is indicated. For example, in Au we have $\Delta R < 0$ ($\sigma$ increasing) for a negative voltage on the specimen (electron "injection"). The dashed part of the curve for Bi concerns points (corresponding to great positive charges on the surface) that are affected by a much wider scattering of values than all the other ones, for unexplained reasons. Figure 5 shows the same effect for Sb specimens of various thicknesses. Figure 6 shows the relationship between $(1/R)(dR/dN)$ and $R$ for all the Sb specimens and indicates the constancy of $dG/dN$. $\Delta N$ is then the total number of electrons "injected"

[5] The paper referred to[3] explains the reasons why Hall coefficient and thickness are not quoted for Au and Bi specimens of Fig. 4; as a matter of fact these quantities are not very significant for very thin films.

into the specimen as given by the trivial relationship $e\Delta N = CV$, where $e$ is the electronic charge and $C$ is the measured capacity of the metallized mica sheet. Figures 7 and 8 show the Hall effect[6] and conductivity of Sb specimens as a function of thickness ("chemical," i.e., "mean" thickness).

## 4. DISCUSSION OF THE EXPERIMENTAL RESULTS

In the following discussion we shall consider separately the three cases of gold, antimony, and bismuth. Unfortunately we are not able at present to give a theoretical justification of the results; nevertheless, in some cases we can show the inconsistency of some simple hypotheses, limiting therefore the domain of a possible future theory.

*Case of Gold.*—In this case we can easily show that the experimental behavior of the conductivity modula-
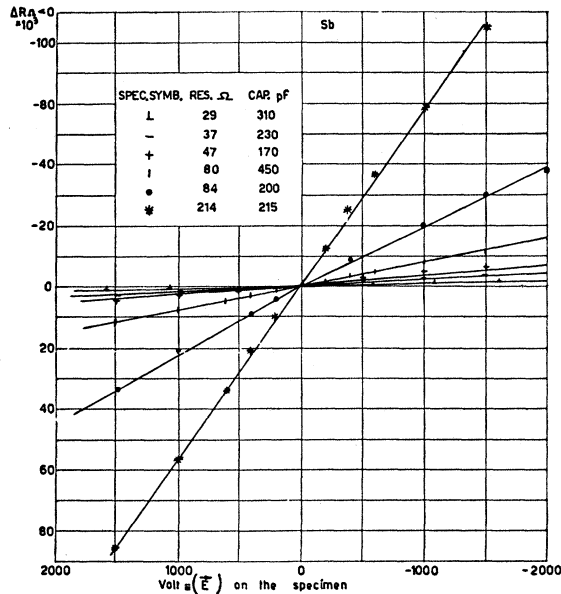
FIG. 5. $\Delta R$ effect in Sb. (1 pf $= 10^{-12}$ farad.)

tion cannot be justified simply considering the expression for the bulk conductivity,

$$\sigma = en\mu, \qquad (4.1)$$

where $n$ is the density of carriers, $\mu$ the mobility[7] that in a metal depends on $n$ itself. As a matter of fact, let us now take into account that in our experiment $n$ is function of $x$, a coordinate normal to the flat faces of the film. The conductance $G$ of the film may be ex-

[6] Bulk values are taken from W. F. Leverton and A. J. Dekker, Phys. Rev. **80**, 732 (1950).

[7] It is not an easy matter to decide which kind of mobility (Hall, microscopic, etc.) is the right one in formula (4.1); because we do not know the role possibly played by trapping in our specimens. In any case, the conclusions are not sensibly altered by this uncertainty.
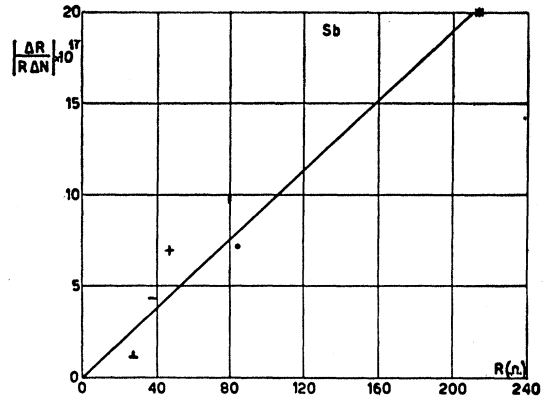
FIG. 6. $dR/R\Delta N$ (i.e., relative variation of resistance per injected electron) in Sb specimens.

pressed, therefore, as

$$G = \frac{be}{l} \int_0^t \mu(n[x])n[x]dx, \qquad (4.2)$$

where $b$, $l$, and $t$ are the width, length, and thickness of the specimen. The variation of conductance is then

$$\Delta G = -\frac{\Delta R}{R^2} = \frac{e}{l^2}\left(\mu + n\frac{d\mu}{dn}\right)\Delta N, \qquad (4.3)$$

where $\Delta N$ is the total number of electrons added to the film.

Inserting into (4.3) the experimental data taken from Fig. 4 and from measurements of the capacity of the specimen and the mobility (4 cm²/volt sec) (see reference 3), we get

$$\left(n\frac{d\mu}{dn}\right)_{EF} = +5.5\frac{cm^2}{volt\ sec}. \qquad (4.4)$$

However, the conductivity $\sigma$ of a monovalent metal can also be expressed as

$$o = ne^2\tau/m_{eff}, \qquad (4.5)$$

where

$$\tau \sim 1/P \sim 1/\rho(E_F),$$

and where $P$ is the scattering probability per unit time and $\rho(E)$ is the density of states in the conduction band,
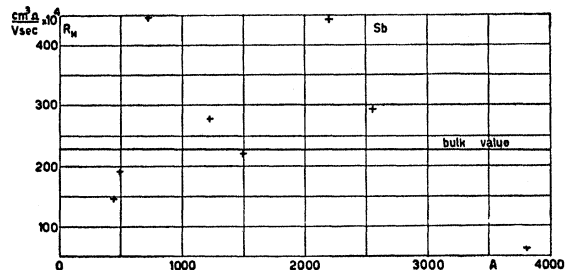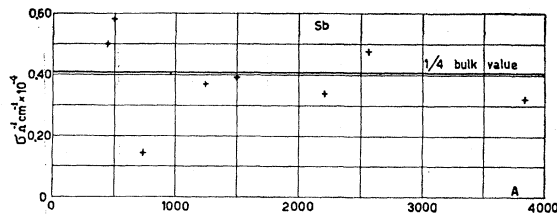
FIG. 7. Hall coefficient of Sb specimens.

Fig. 8. Conductivity of Sb specimens.

to be calculated at $E_F$, the top of the Fermi distribution.[8]

Combining (4.1) and (4.3) we find with a simple calculation[9]

$$\left(n\frac{d\mu}{dn}\right)_{E_F} = -\frac{\text{const}}{\rho^2}\left(\frac{d\rho}{dE}\right)_{E_F}\cdot\frac{dE_F}{dn}(\text{const}>0). \quad (4.6)$$

But $dE_F/dn>0$, and for a monovalent metal, such as Au, the density of states at the top of the Fermi distribution is an increasing function of the energy. Therefore, the left-hand side of (4.6) becomes negative, a result in striking contrast with (4.4).

In order to explain this discrepancy, we are compelled to refuse the above simple theory and to accept one of the following assumptions:

(a) Because of the different geometrical and physical conditions of the two surfaces of the film and (or) a contamination of the more external part of the film by foreign atoms (Mo, O, N, etc.) the electron mobility of electrons in Au is greater near the mica than near the external face.

(b) We are studying the purely surface phenomenon, i.e., the added electrons moving near the surface have a greater mobility ($\sim$10 cm²/volt sec) than the bulk ones ($\sim$4 cm²/volt sec) as though the former were guided by "surface waves" (see Peierls).[10]

Case of Antimony.—In this case the negative conclusions of the above calculations cannot be repeated

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[8] N. F. Mott and H. Jones, Theory of the Properties of Metals and Alloys (Clarendon Press, Oxford, 1936), p. 257.

[9] It has been assumed that $m_{\text{eff}}$, the effective mass, does not depend appreciably on $n$.

[10] R. E. Peierls, Quantum Theory of Solids (Oxford University Press, New York, 1953), Vol. 2, p. 117.

here, because the expression analogous to (4.3) is formed now by six terms, whose magnitude and sign cannot be easily predicted. In fact, Sb conducts both by holes and electrons (in equal number) and together with the electron mobility we have to consider a hole mobility; furthermore, the analytical expression for $\Delta G$ contains also some sort of cross terms that further complicate the calculations.

However, as all our specimens are affected by the same "surface mobility" $dG/dN$ (see Fig. 6), even when the conductivity varies greatly from specimen to specimen (see Fig. 8), we are likely to accept an explanation in terms of a surface rather than a volume effect.

Case of Bismuth.—In the Bi case, we are faced with the same difficulties as in Sb: conduction by holes and by electrons. But there is another feature of the "transverse field effect" that further complicates the problem: the nonlinear behavior of $\Delta R$ versus $V$. The explanation of this fact may possibly reside in some distortion of the crystal lattice, which may explain also the nonreversible variation of $R$ upon application of the electric field. These lattice distortions that take place possibly only at the true metal surface, may be caused by the changed electronic density, which affects the cohesion energy of the metal. Actually this change of density is very conspicuous in the surface zone. For instance, if the added electrons are confined in a thickness of a few angstroms we can have a variation of the conduction electron density which may reach 100%. If this point of view is correct many other parameters, that depend on the cohesion energy (melting point, vapor pressure, lattice constant, etc.), may suffer appreciable modifications.

We hope in the near future to report further on these questions that still remain open, performing new experiments with the help of more suitable techniques in order to throw some light on these difficult problems.

The points that should be cleared up are the following: (1) the possible role played by surface states in the metals considered; (2) the independence (or dependence) of the $\Delta R$ effect on the current flowing in the specimen; (3) a more careful investigation of the irreversible effect in Bi, using also Bi with a normal Hall effect coefficient.