PHYSICAL REVIEW VOLUME 84, NUMBER 1 OCTOBER 1, 1951

The Effects of Pressure and Temperature on the Resistance of $p-n$ Junctions in Germanium*

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(Received June 12, 1951)

According to Shockley's theory, the low voltage resistance, R_0, of a $p-n$ junction is proportional to $\exp(E_G/kT)$, where E_G is the energy gap. Measurements of the change with pressure of the characteristics of a junction in a single crystal of germanium indicate a change $\Delta R_0/R_0$ of 12.5 percent, corresponding to a change ΔE_G of about 3.1×10^{-3} ev, for a pressure change of 10,000 lbs/in². Analysis of measurements made at temperatures between 16.5°C and 20.5°C give values of E_G averaging about 0.72 ev. These values are in agreement with those obtained from the change in intrinsic resistivity with temperature and pressure.

I. INTRODUCTION

IN the energy level structure of the diamond-type lattice, such as that of silicon or germanium, the energy gap, E_G, between the valence-bond and conduction bands increases with decreasing atomic spacing and therefore with pressure.[1] Direct evidence for this effect comes from the increase in intrinsic resistivity with pressure as observed by Miller and Taylor.[2] Shifts of the energy bands with dilation have been related[3] to the mobilities of the conduction electrons and holes.

It is generally necessary to make measurements of intrinsic conductivity at elevated temperatures. On the other hand, Shockley's theory[4] of the $p-n$ junction indicates that the junction resistance should depend critically on E_G and thus on pressure even at room temperature. Some preliminary measurements, made both at the Bell Telephone Laboratories and at the University of New Hampshire, confirmed this effect.[5] Measurements have now been repeated under more carefully controlled conditions on a junction whose current-voltage characteristic is close to theoretical.[6]

The junction was formed by bombarding high-purity n-type germanium with α-particles. The effect of the bombardment is to produce acceptor centers and thus convert the n-type material to p-type in a depth corresponding to the range of the α-particles in the germanium. Probe electrodes were introduced so as to measure only that part of the voltage drop which occurs across the junction itself.

According to Shockley's theory,[4] current flowing at not too large reverse voltages consists mainly of holes which diffuse to the junction from the n-type side and electrons which diffuse to the junction from the p-type side. These currents depend on the concentration of holes, p_n, in the n-type and of electrons, n_p, in the p-type sides, both of which vary as $\exp(-E_G/kT)$. In the forward direction, holes flow from the p-side to the n-side and electrons from the n-side to the p-side. For not too large voltages in either direction, the expression for the total current flow is

$$I=I_p+I_n=I_0(\exp(eV/kT)-1), \qquad (1.1)$$

where

$$I_0=e[(D_pp_n/L_p)+D_nn_p/L_n], \qquad (1.2)$$

and e = electronic charge (1.6×10^{-19} coulomb), D_p = diffusion constant of holes in n-type material. D_n = diffusion constant of electrons in p-type material, L_p = diffusion length of holes in n-type material, L_n = diffusion length of electrons in p-type material, p_n = concentration of holes in n-type material, n_p = concentration of electrons in p-type material, V = difference of potential applied to junction, k = Boltzmann's constant (8.69×10^{-5} ev/deg), and T = absolute temperature.

Statistical theory shows that the product of the concentrations of holes and electrons without regard to impurities depends on E_G,[7] thus

$$n_pp_p=p_nn_n=A\exp(-E_G/kT), \qquad (1.3)$$

where n_n = concentration of electrons in n-type material. p_p = concentration of holes in p-type material.

Since n_n and p_p are substantially constant near room temperature in germanium, p_n and n_p must each vary with $\exp(-E_G/kT)$. Thus assuming that the other

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* The measurements of resistance under pressure were made with equipment built under contract between the University of New Hampshire and the Bureau of Ordnance of the Navy.

[1] G. E. Kimball, J. Chem. Phys. **3**, 560 (1935) (diamond); J. F. Mullaney, Phys. Rev. **66**, 326 (1944) (silicon).

[2] P. H. Miller and J. Taylor, Phys. Rev. **76**, 179 (1949); and Julius H. Taylor, Phys. Rev. **80**, 919 (1950).

[3] W. Shockley and J. Bardeen, Phys. Rev. **77**, 407 (1950); **80**, 72 (1950). The data reported here were discussed in the second of these.

[4] W. Shockley, Bell System Tech. J. **28**, 435 (1949).

[5] W. Shockley, *Electrons and Holes in Semiconductors* (Van Nostrand Company, Inc., New York, 1950), p. 309 and following.

[6] For a comparison between theory and experiment of the current-voltage characteristic of a junction formed in a different way see Teal, Sparks, and Buehler, Phys. Rev. **81**, 637 (1951); Croucher, Pearson, Teal, Sparks, and Shockley, *ibid.*

[7] See, for example, reference 5, p. 245. Actually, the factor A varies as T^3, but this variation is slow compared with the exponential.

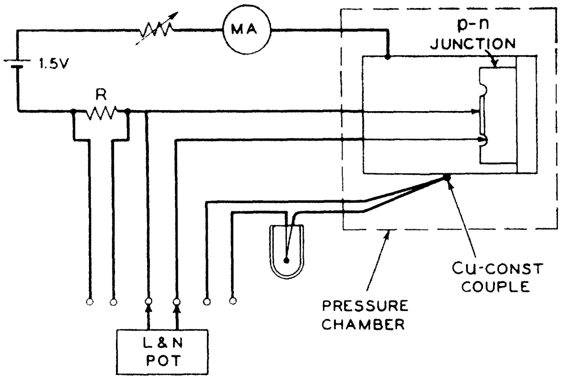

FIG. 1. Circuit diagram of measuring equipment.

factors do not vary rapidly with temperature, $I_0 \propto \exp(-E_G/kT)$. The expected increase of E_G with pressure will be evidenced by a decrease in I_0 and an increase in junction resistance. The current I_0 is closely related to the resistance, R_0, and in the low voltage limit,

$$R_0 = (kT/eI_0). \tag{1.4}$$

In subsequent analysis we use R_0, which can be obtained rather directly from the experimental data, rather than I_0, to estimate the variation of E_G with pressure. Thus we take

$$R_0 = A \exp(E_G/kT) \tag{1.5}$$

and assume that the effect of changes in A with pressure is negligible compared with changes in E_G. Because of the large value of the exponent[8] ($E_G \sim 0.72$ ev, $kT \sim 0.025$ ev), a very small percentage change in E_G will have a large effect on R_0.

II. PREPARATION OF THE $p-n$ JUNCTIONS

The $p-n$ junctions were prepared by bombarding high purity n-type germanium with α-particles.[9] A disk 0.3 cm in diameter and 0.05 cm thick was cut from an ingot of single crystal germanium having a resistivity of 8 ohm-cm. One side was bombarded for 72 hours with a collimated beam of 5.3-Mev polonium α-particles amounting to 6×10^9 particles per square cm per hour. This converted a surface layer 1.9×10^{-3} cm deep to p-type, thus forming a $p-n$ junction at this depth below the surface.

After electroplating rhodium electrodes on either side of the disk, the electrode on the n-type surface was soldered to a brass disk suitable for mounting in a type A transistor shell. A small circular cut about 0.01 cm in depth was then made through the remaining rhodium electrode, the p-type layer of germanium, the $p-n$ junction, and into the n-type germanium thus forming a circular $p-n$ junction 0.16 cm in diameter with ohmic electrodes attached. The germanium surface formed by the circular groove was etched with a mixture of hydrofluoric and nitric acids to clean off the debris and give the $p-n$ junction a high reverse voltage characteristic.

The completed sample was mounted in a standard type A transistor shell as shown schematically in Fig. 1. Phosphor bronze spring contacts bear on the p-type rhodium electrode, and on the n-type germanium at the bottom of the circular groove. A third electrical connection is made through the metal shell to the rhodium electrode on the n-type germanium. This permits potential probe measurements directly across the $p-n$ junction without introducing errors due to potential drop in the body resistance of the n-type germanium.

III. EXPERIMENTAL PROCEDURE AND RESULTS

The fundamental experimental data obtained in this study are the potential differences across the $p-n$ junction during passage of a fixed dc current of about 30 microamperes in both the forward and the reverse directions under varying conditions of temperature and pressure. As shown in Fig. 1, a Leeds and Northrup type K potentiometer in conjunction with a selector switch was used to measure the $p-n$ junction potential difference, as well as the voltage drop in the standard resistance R, and the thermoelectric voltage of a copper-constantan thermocouple soldered to the junction case.

Pressure was applied in a steel cylinder containing an axial chamber 0.875 inch in diameter and 3.0 inches long. The outer surface of the cylinder was jacketed with copper around which passed copper cooling and heating coils. The heating current was controlled by a thermostatic element in good thermal contact with the copper jacket as tap water circulated through the cooling coils. The temperature inside the test chamber, as measured by the copper-constantan thermocouple, could be regulated to a few hundredths of a degree by this means. The test chamber was filled with SAE No. 10 oil which transmitted the pressure applied by a hand-operated pump of 0.125 inch piston diameter. Pressure was measured by a bourdon gauge which was calibrated against a "dead weight" piston at frequent intervals. The readings were accurate to ± 25 lb/in.^{2} over a range from 0 to 10,000 lb/in.^{2}

The three leads from the $p-n$ junction and the two from the thermocouple were brought out of the pressure chamber through a 0.125-inch diameter copper tube, the inner end of which had been flared to about twice its diameter. The leads were sealed into the copper tube with De Khotinsky cement, the flare serving to support a conical wedge of cement against the outward thrust of the oil. The tube passed through two pairs of split steel disks, separated by a Neoprene washer, which were compressed by a plug threaded into the pressure chamber. Outward movement through the pressure seal was prevented by a metal collar soldered to the copper tube.

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[8] Reference 5, p. 22.

[9] W. H. Brattain and G. L. Pearson, Phys. Rev. **78**, 646 (1950); and W. E. Johnson and K. Lark-Horovitz, Phys. Rev. **76**, 442 (1949).

Two series of measurements were made. In the first series, the resistance of the $p-n$ junction ($R=V/I$) was measured as a function of temperature for a constant current of 30.91 microamperes in both forward and reverse directions while pressure was varied in steps of 2000 lb/in.^{2} from atmospheric to 10,000 lb/in.^{2} (The analysis in terms of the rectification theory is given in Sec. IV.) As shown in Fig. 2, R increased with pressure and decreased with temperature for both the forward and reverse directions of current flow. At 17 degrees centigrade the increase in resistance between one atmosphere and 10,000 lb/in.^{2} is 26.7 percent in the reverse direction, and 13.6 percent in the forward direction, while at 21 degrees centigrade the increases are 23.8 and 11.0 percent, respectively. At one atmosphere the decrease in resistance between 17 degrees centigrade and 21 degrees centigrade is 43.4 percent in the reverse direction, and 26.1 percent in the forward direction, while at 10,000 lb/in.^{2} the decreases are 44.7 and 27.8 percent, respectively.

In the second series of measurements, the resistance of the $p-n$ junction was measured as a function of pressure at a fixed current of 30 microamperes and a constant temperature of 18.55 degrees centigrade. The data, which are shown in Fig. 3, indicate an increase in resistance of 18.5 percent in the reverse direction and an increase of 11.5 percent in the forward direction between one atmosphere and 10,000 lb/in.^{2}, the change being approximately linear. The data of this series are considered the more reliable for determining the effects of pressure, since the current was determined with greater accuracy and the temperature stabilization appeared to have been more successful.

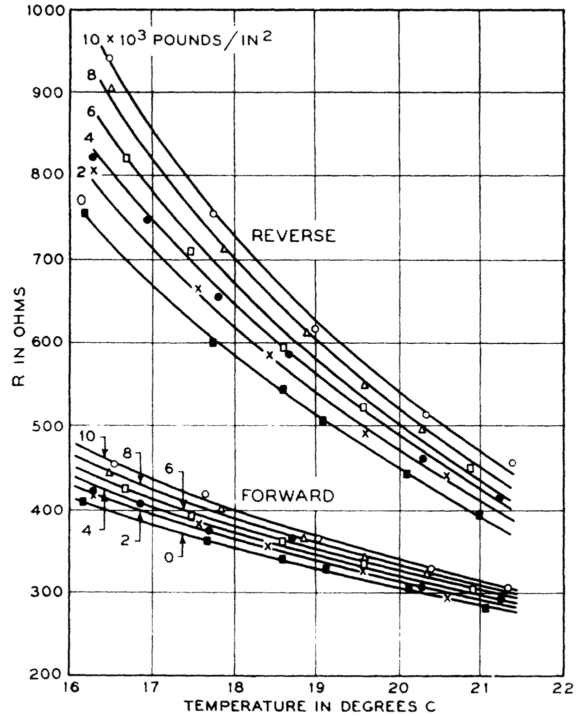

FIG. 2. Resistance (V/I) *versus* temperature characteristic of $p-n$ junction for a constant current of 30.91 microamperes in either direction. The pressures are as indicated.

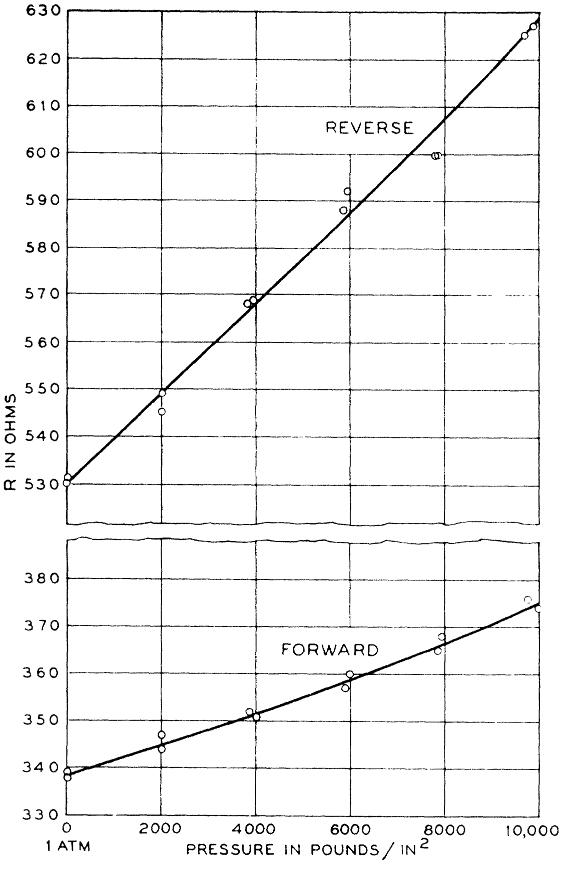

FIG. 3. Resistance (V/I) *versus* pressure characteristic of $p-n$ junction for a constant current of 30.00 microamperes in either direction and a fixed temperature of 18.85 degrees centigrade.

The resistances, which are plotted in Fig. 2 and Fig. 3, are the ratios V/I rather than the differential values dV/dI. From these we have estimated the differential resistances, R_0, for the limit $I\rightarrow0$, as described in the following section.

IV. ANALYSIS OF DATA

Resistance measurements were made for fixed values of the current in both the forward and reverse directions. For purposes of analysis we have extrapolated between these values to get the resistance, R_0, in the limit $I\rightarrow0$. This was done by the following method. By differentiating (1.1) with respect to I and then setting $V=0$ we find

$$R_0=(dV/dI)_0=(kT/eI_0). \tag{4.1}$$

In the following we shall use a reduced current $x=(I/I_0)$. We want to determine the resistance in the limit $x\rightarrow0$ from measurements made at small fixed values of x in both the forward and reverse directions.

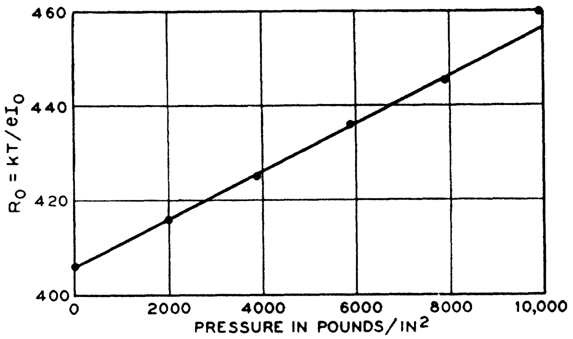

FIG. 4. Resistance extrapolated to $V=0$ *versus* pressure for $p-n$ junction at 18.85 degrees centigrade.

From (1.1) we have

$$(eV/kT)=\log(1+x)=x-\tfrac{1}{2}x^2+\tfrac{1}{3}x^3-\cdots. \tag{4.2}$$

The voltage/current ratio is

$$R=(V/I)=R_0(1-\tfrac{1}{2}x+\tfrac{1}{3}x^2-\cdots). \tag{4.3}$$

Let R_f be the resistance in the forward direction (x positive) and R_b be the resistance in reverse direction (x negative). Using (4.3) we find

$$R_b+R_f=2R_0(1+\tfrac{1}{3}x^2+\cdots),$$

or

$$R_0\simeq\tfrac{1}{2}(R_b+R_f)(1-\tfrac{1}{3}x^2\cdots). \tag{4.4}$$

The value of x to use in the correction factor can be obtained from

$$R_b-R_f=R_0(x+\cdots),$$

or

$$x\simeq 2(R_b-R_f)/(R_b+R_f). \tag{4.5}$$

Values of R_0 estimated from the values of R_b and R_f in Fig. 3 are shown in Fig. 4. The change in R_0 with pressure is approximately linear, and is approximately 1.25 percent for 1000 lb/in.²

If it is assumed, as seems reasonable, that the change in I_0, and thus of R_0, results almost entirely from the change in E_G with pressure, we have

$$\frac{R_0(P)}{R_0(0)}=\frac{\exp[E_G(P)/kT]}{\exp[E_G(0)/kT]}, \tag{4.6}$$

and for small changes

$$\Delta R_0/R_0\simeq\Delta E_G/kT. \tag{4.7}$$

A change $\Delta R_0/R_0$ of 1.25 percent corresponds to a change ΔE_G of about 3.1×10^{-4} ev at room temperature. The dilation for 1000 lb/in.² is about 7×10^{-5}, so that the rate of change of energy gap with dilation is about

$$dE_G/d\log v=-3.1\times10^{-4}/7\times10^{-5}=-4.5\text{ ev}.$$

This value is in good agreement with those based on earlier measurements on $p-n$ junctions quoted in reference (3) and also with those of Miller and Taylor based on changes in intrinsic conductivity with pressure.

The value of E_G can be estimated from the temperature variation of R_0. If $R_0(T)$ corresponds to the value of R_0 at temperature T at a fixed pressure, we have

$$\log[R_0(T+\Delta T)/R_0(T)]=-(E_G/kT)(\Delta T/T).$$

From the data of Fig. 2 we have estimated the values of R_0 given below:

$T=16.5$°C	$P=1$ atmos	$R_0=497$
$T=20.5$°C	$P=1$ atmos	$R_0=343$
$T=16.5$°C	$P=10{,}000$ lb/in.²	$R_0=590$
$T=20.5$°C	$P=10{,}000$ lb/in.²	$R_0=390$.

These values give $E_G=0.69$ ev for $P=1$ atmos and $E_G=0.75$ ev for $P=10{,}000$ lb/in.² It is not believed that the differences in E_G at the two different pressures are significant; a change of only about 0.003 ev is to be expected. These values of E_G are in reasonable agreement with the value 0.72 ev estimated from the change in intrinsic resistivity with temperature.

The observed pressure and temperature variations of the resistance of the $p-n$ junction are in good agreement with Shockley's theory of the current-voltage characteristic and previous estimates of the energy gap and its change with pressure. The measurements thus provide a further confirmation of the theory.