Properties of Grain Boundaries in Gold-Doped Germanium

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It has been found that grain boundaries produce a path of relatively low electrical resistance at temperatures below ~100°K in Ge whose bulk resistivity has been made greater than 10^3 to 10^5 ohm-cm by the addition of Au. A new permanent-magnet apparatus for measuring the Hall effect in semiconductors at low temperatures is described. The results of measurement of the Hall effect as a function of temperature in Ge samples containing grain boundaries of known orientation are given. A peak in the Hall coefficient observed in some samples is discussed in terms of a crude model. Preferential conduction along grain boundaries also occurs in high-resistivity Fe-doped Ge, but has not been observed in crystals containing coherent twin boundaries. A modification of Bardeen's theory of surface states is used in an attempt to account for the existence of the grain-boundary conduction phenomenon.

I. INTRODUCTION

IT has been known for some time[1,2] that a grain boundary in *n*-type germanium introduces a layer of high-resistance material localized at the boundary, with a reverse saturation characteristic symmetrical with respect to the direction of a voltage applied across the grain boundary. Photovoltages[2] were also observed which reversed direction when the light spot crossed the boundary. When the bulk Ge was converted to *p*-type by heat treatment, the localized resistance at the grain boundary disappeared.[2] These facts have been interpreted by Pearson[2] to indicate the presence of an abnormally high concentration of acceptors at the grain boundary, producing a *p*-type layer.

A series of experiments were performed by the Purdue group[3] in which the breakdown voltage, dc conductance, and frequency-dependence of the impedance were all measured as a function of temperature on *n*-type Ge samples containing grain boundaries. These measurements were made with the voltage applied across the grain boundary. The results were interpreted in terms of a potential barrier model in which acceptor levels with energies in the forbidden energy gap are concentrated at the grain boundary, distorting the position of the band edges in energy much as in Bardeen's theory of surface states.[4]

Recently it has been found[5] that there is a path of relatively low electrical resistance along a grain boundary through a Ge crystal whose bulk resistivity has been made greater than 10^3–10^5 ohm-cm by the addition of Au.[6] The investigations described here were made possible by the characteristic high resistivity at low temperatures in bulk Au-doped Ge, which permitted the relatively slight conduction of the sheath of space-charge surrounding the grain boundary to be revealed.

Most of the experiments to be reported here were Hall effect and resistivity measurements on bicrystals of Au-doped Ge. A separate section (Sec. IV) includes short descriptions of other experiments.

II. EXPERIMENTAL

A. Apparatus

A small cryostat containing a permanent magnet was constructed for the low temperature Hall effect experiments. The outside brass vacuum can, *A* (Fig. 1), $3\frac{1}{2}$ in. o.d., 5 in. high, was made in two parts, with a flange and gasket seal, *B*. A stainless steel tube, *C*, served both as a vacuum lead and also to suspend the cryostat from the Al lid, *D*, of a straight-sided commercial bench Dewar vessel, (not shown), which contained either liquid N_2 or liquid H_2. The bottom of the

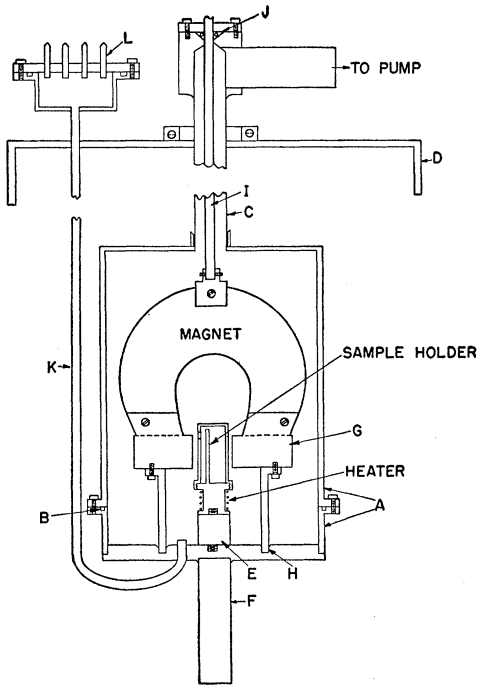

FIG. 1. The permanent-magnet vacuum Hall effect apparatus. The Dewar vessel surrounding the cryostat is not shown.

[1] K. Lark-Horovitz, National Research Council Report NDRC–14-585, 1945 (unpublished).
[2] G. L. Pearson, Phys. Rev. **76**, 459 (1949).
[3] Taylor, Odell, and Fan, Phys. Rev. **88**, 867 (1952).
[4] J. Bardeen, Phys. Rev. **71**, 717 (1947).
[5] A. G. Tweet, Phys. Rev. **96**, 828 (1954).
[6] W. C. Dunlap, Jr., Phys. Rev. **91**, 1282 (1953).

Cu sample holder had a heater of No. 30 Constantan wire, resistance 50 ohms. A Cu radiation shield in fairly good thermal contact with the heater, enclosed the sample. The sample holder was electrically insulated from the sample by a thin sheet of mica glued on with *GE*7031 cement. The stainless steel heat leak, *E*, connected the sample holder to a Cu post, *F*, which depended into the cooling bath.

The Alnico *V* magnet, with its soft iron pole pieces, *G*, gave a flux of ~1400 gauss at the center of a gap $\frac{5}{8}$ in. across and $\frac{5}{8}$ in. square. The magnet could be rotated in a race, *H*, by means of the rod, *I*, which passed through an O-ring seal, *J*, at room temperature. The leads for the sample, heater and thermocouple came up through the tube, *K*, to a header, *L*. The gasket for the low-temperature vacuum seal was a torus of 0.050-in. In wire. A Welch Duoseal forepump was used to evacuate the cryostat, since only a rough vacuum was required to isolate the sample sufficiently from the cooling bath. Heat leaks from above were reduced by gluing a 1.5-in. thick plug of Styrafoam to to the under side of the lid, *D*. Openings in the lid, not shown in the drawing, provided a means of filling the Dewar flask. The lead wires were all 0.010-in. Cu Formex coated. The thermocouple wires were continuous to avoid stray thermal and contact emfs. They were brought out of the header through a seal of DeKhotinsky cement. The measurements of voltage were made with a Minneapolis-Honeywell vibrating reed electrometer. Sample temperature was measured by a (AuCo)−(AgAu) thermocouple,[7] read on a Rubincon Portable Precision Potentiometer. A heater power of ~5 watts raised the temperature of the sample to 200°K when the cooling bath was liquid N_2. When the apparatus has been precooled with liquid N_2, 2 liters of liquid H_2 are sufficient to cool it and maintain the sample at ~27°K for at least 6 hours.

The functioning of the apparatus, which has been in operation for over 8 months, has been checked against samples of Ge measured by W. C. Dunlap, Jr., and the results agree within 25 percent.

B. Procedure

Bicrystals of *n*- and *p*-type bulk Au-doped Ge were pulled from the melt using two [100] seeds bound symmetrically on either side of a Mo wedge. If the axis of rotation of the angle β between the two seed crystals is a [110] direction, then the resulting ingot is usually as shown in Fig. 2(A). β was approximately 10° in all the work to be reported here except when stated otherwise. If a wafer is cut from the ingot, as shown by the dotted lines in Fig. 2(A), the path of the grain boundary across the wafer seen from above is almost always as shown in Fig. 2(B) with the angle γ between 20° and 60°. However, if the axis of rotation of the angle β is a [100] direction, then the grain boundary very seldom departs from planarity, and the appearance of a wafer cut from such an ingot is usually as shown in Fig. 2(C).

[7] The author is indebted to J. F. Youngblood of this laboratory for the thermocouple.

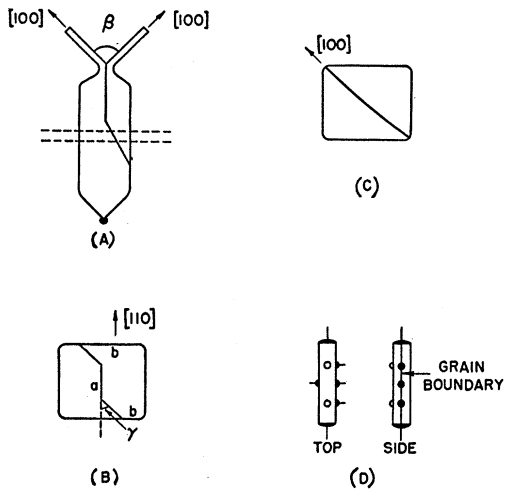

FIG. 2. (A) Schematic drawing of a bicrystalline ingot. (B) A wafer cut from the ingot in (A) along the dotted lines, and viewed along the ingot axis. (C) Same as (B) except that the axis of β is the [100] direction instead of [110]. Note that the grain boundary in (C) does not have the same orientation as section *b* of the grain boundary in (B). (D) Schematic drawing of Hall wafer containing a grain boundary.

For the Hall effect measurements, wafers ~0.10 in. ×0.15 in.×0.40 in. were cut from the Ge bicrystals so as to leave the grain boundary exposed, and In contacts fused on, as in Fig. 2(D), under H_2. All samples were etched carefully after putting on the contacts. The resistance was measured at liquid N_2 temperature between the contacts placed on the top surface of the wafer (open circles) and each of the contacts on the grain boundary to see that the latter were not shorting to one another through a conducting surface layer on the high-resistance Au-doped Ge. (Such shorting effects are often observed in high-impedance samples but can be avoided by careful handling after etching.) The samples were then attached to the sample holder with *GE*7031 cement which, when dry, provides moderately good thermal contact and excellent electrical insulation. The thermocouple was soldered directly to one of the contacts initially used to check for surface leakage and the apparatus closed, evacuated, and cooled.

Voltages were checked for linearity as a function of current magnitude and direction of flow through the whole temperature range of the measurements.

III. RESULTS AND DISCUSSION

A. Preliminary

In Fig. 3 is shown a schematic drawing of a wafer cut from a bicrystal of *p*-type Au-doped Ge whose orientation is that of Fig. 2(B). Solid circles indicate the position of fused In contacts on one surface of the

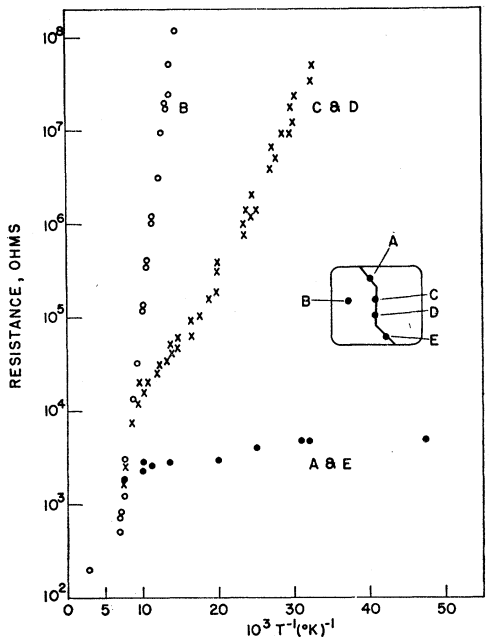

FIG. 3. Preliminary measurement showing qualitatively the grain boundary conduction phenomenon in Au-doped Ge. The inset gives the disposition of contacts on a sample of the orientation shown in Fig. 2(B). Curve B is of the form $e^{+\varphi/kT}$, where $\varphi=0.15$ ev, characteristic of the lower Au acceptor state in Ge. Curves labeled C and D, and A and E show the short-circuiting effects of the grain boundary.

wafer. The other surface has had an overall contact of In fused to it. The data points represent resistance measurements made with a Volt Ohmyst ohm-meter between the large area contact and the dot contacts in turn, through the bulk Ge (contact B), and through the various sections of the grain boundary (contacts A, C, D, and E) Curve B is an exponential of the form $e^{+\varphi/kT}$, where $\varphi=0.15$ ev, the energy associated with the lower gold acceptor state in Ge.[6] The curve labeled C and D has a slope corresponding to a φ of 0.04 ev. The extreme short circuiting effect of the conducting sheath concentrated at the grain boundary seen on the sections of crystal labeled A and E occurs for a considerable range of angle γ, defined in Fig. 2(B). On this wafer, $\gamma\sim40°$. These data, taken on a single wafer, together with similar data on many other samples, constitute evidence that the electrical properties of the grain boundary are a function of the orientation of the boundary, since all other conditions in the growth of the ingot are presumably identical.

The data also indicate the necessity for avoiding the inclusion of sections of grain boundary containing jogs when preparing a Hall wafer. All the Hall effect measurements were made on wafers in which the grain boundaries were believed to be free of jogs, as was inferred by viewing the straightness of their peripheries under a low-power (100×) microscope. However, the presence of internal irregularities in the wafers cannot be ruled out.

It is not uncommon for very-small-angle grain boundaries to spread out from the main boundary as tributaries from a river, sometimes in considerable profusion. These boundaries all separate crystals of misorientation less than 1° as measured by x-ray Laue photographs,[8] and can be revealed only by rather careful etching. About five wafers containing these tributary boundaries were measured by the technique used in obtaining the data for Fig. 3. No short-circuiting of the bulk Au-doped Ge because of the presence of the very small angle boundaries was found in these wafers up to resistances of 100 megohms. However, no wafers containing such tributary boundaries were used for Hall effect measurements.

B. Resistivity and Hall Coefficient

In this section data are presented on the reduced resistivity and reduced Hall coefficient of two wafers of p-type Au-doped Ge containing grain boundaries. The sign of the carriers in the grain boundary con-

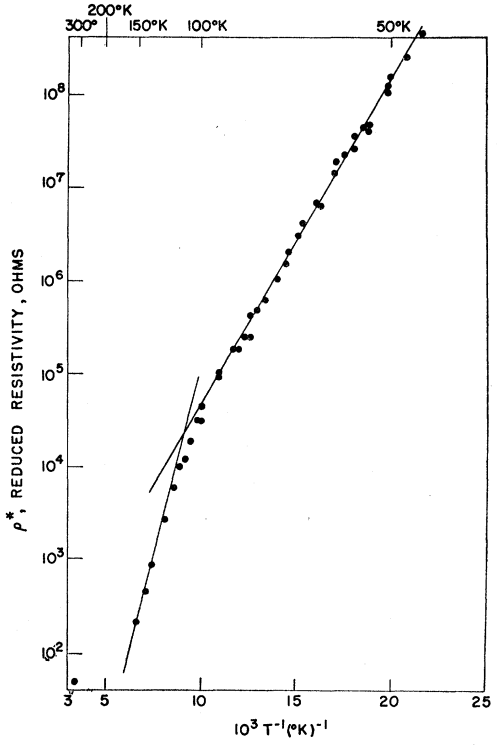

FIG. 4. Reduced resistivity, ρ^*, for a sample of Au-doped Ge containing a grain boundary such as a in Fig. 2(B). Above 100°K, ρ^* is of the form $e^{+\varphi/kT}$, where $\varphi=0.15$ ev, characteristic of the lower Au acceptor state in Ge. Below 100°K, it is of the same form, with $\varphi=0.07$ ev, representative of φ's observed for other samples with the same orientation of grain boundary. Above ~125°K, the true resistivity of the bulk Ge may be obtained by multiplying ρ^* by the sample thickness, $t=0.25$ cm.

[8] The author wishes to thank Mrs. A. Cooper of the Metallurgy Research Department for these x-ray measurements.

duction was p-type for both wafers. This has been the case for all samples studied, even when the bulk Ge was n-type. The significance of the use of the term "reduced Hall coefficient" is the following. For a normal Hall wafer,[9]

$$R=10^8V_Ht/HI,$$

where the Hall coefficient, R, is in cm³/coulomb when the Hall voltage V_H is in volts, the sample thickness t, is in cm, the magnetic field, H, is in gauss and the current, I, is in amperes. This formula is applicable to a homogeneous sample when the sample thickness is a measurable quantity. However, in the case of the grain boundary space-charge layer conduction in Au-doped Ge, the thickness of the conducting layer can only be estimated and the density of carriers is almost certainly a function of the perpendicular distance from the grain boundary. Consequently, it is difficult to see the physical significance of R. But if one defines R^*, the reduced Hall coefficient, as $R^*\equiv 10^8V_H/HI$, then all the quantities on the right side of the equation are measurable. R^* is the reciprocal of the total charge/cm² of sample, provided the volume density of charge is a function only of the perpendicular distance from the grain boundary, and the mobility is not a function of position in the Hall wafer. In p-type Au-doped Ge, at room temperature R^*t is the Hall coefficient of bulk Ge, since now the fraction of the current carried by the grain boundary space-charge sheath is not detectable. At sufficiently low temperatures, R^* is the reciprocal of the total charge/cm² of grain boundary associated only with the grain boundary conduction. At intermediate temperatures, when comparable fractions of the current are carried by bulk Ge and grain boundary, a quantitative interpretation of R^* is difficult. However, in this temperature range there are other more fundamental difficulties in interpreting the measurement, as will become evident, and hence no detailed treatment at this time seems profitable.

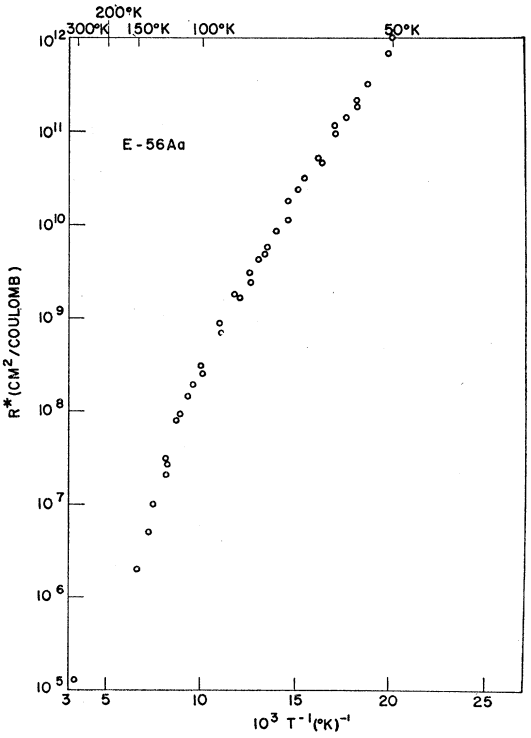

FIG. 5. Reduced Hall coefficient, R^*, for the sample of Fig. 4. The true Hall coefficient of the bulk Ge above ~125°K may be obtained by multiplying R^* by $t=0.25$ cm.

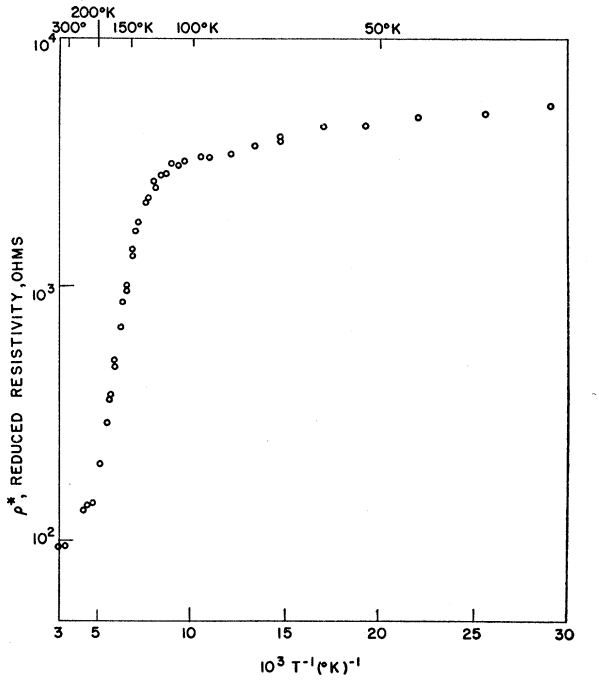

FIG. 6. Reduced resistivity for a sample of Au-doped Ge containing a grain boundary as in Fig. 2(C). Above ~150°K, true bulk resistivity $\rho=\rho^*t$, $t=0.21$ cm.

The problem of the unknown thickness of space-charge sheath at the grain boundary and its nonuniform density also occurs in the calculation of sample resistivity. The reduced resistivity, $\rho^*\equiv V_sw/Il$. It is in ohms when V_s, sample voltage, is in volts and the sample current, I, is in amperes. The quantities w and l are the sample width and separation of the voltage probes, respectively. At temperatures where the grain boundary charge sheath carries a negligible fraction of the sample current, ρ^*t is the true sample resistivity.

The results of measurements of the reduced resistivity, ρ^*, and reduced Hall coefficient, R^*, on a sample cut from a bicrystal of Au-doped Ge containing a section of grain boundary such as a in Fig. 2(B) are shown in Figs. 4 and 5. The steeper slope at temperatures above 100°K corresponds to a φ of 0.15 ev and is characteristic of the lower Au acceptor level in Au-

[9] W. Shockley, *Holes and Electrons in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), pp. 211–215.

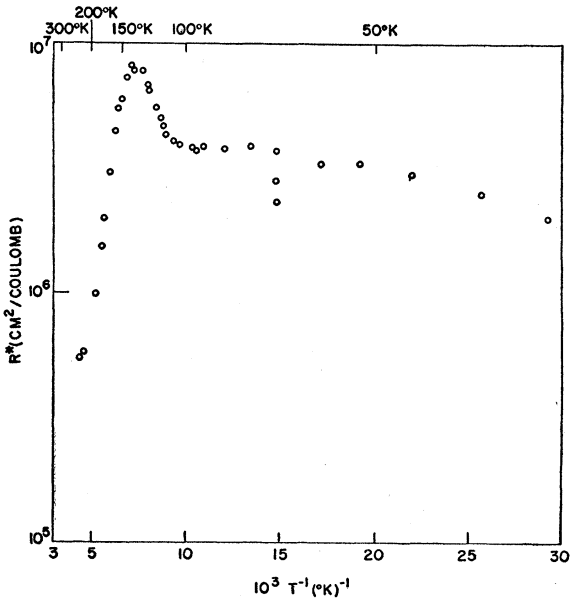

FIG. 7. Reduced Hall coefficient, R^*, for the sample of Fig. 6. Above ~150°C, true bulk Hall coefficient, $R=R^*t$, $t=0.21$ cm. Note the peak in the Hall coefficient.

doped Ge. The curve changes slope to 0.07 ev below about 80°K, which is representative of values of φ ranging from 0.03 ev to 0.07 ev seen in similar samples taken from other ingots.

Plots of reduced resistivity and reduced Hall coefficient for a sample cut from an ingot whose grain boundary is as shown in Fig. 2(C) are given in Figs. 6 and 7. Note that even though the resistance of this sample is similar in temperature dependence to that of the sections marked A and E on Fig. 3, these grain boundaries do not have the same orientation.

The peak in the reduced Hall coefficient in Fig. 7 has been observed in all five samples taken from ingots similar to the one whose measurements are reproduced here. It is believed to be characteristic of all grain boundaries with this orientation.

C. Discussion of Hall Effect Measurements

The proper interpretation of the Hall effect data is uncertain, quite aside from the difficulty connected with nonuniform carrier density mentioned in Sec. III. B. This uncertainty is made particularly evident by the marked maximum in the Hall coefficient in Fig. 7. It is extremely unlikely that the carrier concentration, no matter how it is distributed across the thickness of the sample, should increase as the temperature decreases, which is the conclusion one is led to if he assumes that $R=1/nec$, the usual interpretation.[9] Consequently further interpretation of the data is necessary.

Consider an idealized model of a Hall wafer of Au-doped Ge containing a grain boundary as composed of two homogeneous p-type regions, such as in Fig. 8(A). Let the first region represent the bulk Ge in which the resistivity increases rapidly with decreasing temperature and the mobility is limited by thermal vibrations, increasing as the temperature decreases. In the second region, which we will identify with the very much thinner grain boundary space-charge sheath, assume that the resistivity remains relatively constant with decreasing temperature and that the mobility is limited by impurity and dislocation scattering, decreasing as the temperature decreases.[10]

When a current, I, flows in such a composite sample in the presence of a magnetic field, H, [Fig 8(A)], in general a circulating current will flow through the Hall contacts between regions 1 and 2 in the plane of the figure, because of the difference between the Hall mobilities, and hence the Hall voltages, characteristic of the two regions.

Figure 8(B) shows a crude equivalent circuit for this situation. V_1 and V_2 are the Hall voltages which would be developed across regions 1 and 2, respectively, if

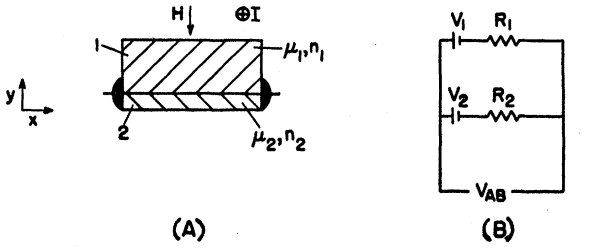

FIG. 8. (A) A crude model of a Ge sample containing two regions with different temperature-dependences of mobility (μ_1 and μ_2) and carrier concentrations (n_1 and n_2). Region 1 is identified with the bulk Ge and region 2 with the conducting layer localized at the grain boundary (see text). (B) Equivalent circuit of model in (A).

they were isolated from each other. R_1 and R_2 are resistances proportional to the (resistivity/thickness) ratio for the two regions. V_{AB} is the Hall voltage measured in the composite sample. From room temperature down to approximately 200°K, the bulk Ge short circuits the thin grain boundary layer, $R_2 \gg R_1$ and $V_{AB}=V_1$. At temperatures below ~100°K, $R_1 \gg R_2$ and $V_{AB}=V_2$: the grain boundary layer short circuits the high-resistivity bulk Ge.

However, $V_2 < V_1$ at low temperatures because of the different temperature dependences of the scattering mechanisms and hence at some intermediate temperatures, where $R_1 \approx R_2$, under conditions of constant sample voltage, V_{AB} must pass through a maximum.

H. Brooks[11] has given an elegant mathematical treatment of the ideas qualitatively described above, as follows. Referring to Fig. 8(A), remove all restrictions

[10] D. L. Dexter and F. Seitz, Phys. Rev. 86, 964 (1952).

[11] H. Brooks (private communication). The author is much indebted to Professor Brooks for permission to publish this summary of his analysis.

on the y-dependence of μ and n, the Hall mobility and carrier concentrations, respectively. Let $J_x(y)$ be the current density of the circulating current described above, which may now be a function of position in the direction perpendicular to the grain boundary. From the continuity equation,

$$\int_0^t J_x(y)dy=0,$$

where t is the sample thickness, since there are no sources or sinks in the wafer.

But

$$J_x(y)=\sigma(y)[E_H(y)-V_{AB}/w],$$

where $\sigma(y)$ is the conductivity of the Hall wafer, a function of position in the y direction as well as temperature. $E_H(y)$ is the Hall field, V_{AB} is the measured Hall voltage, and w is the sample width. Substituting for the Hall field,

$$E_H(y)=\mu_H(y)HE_z/c,$$

where E_z is the drift field and $\mu_H(y)$ is the Hall mobility, one obtains

$$V_{AB}=\frac{IH}{ec}\frac{\int_0^t n(y)\mu_H(y)\mu_D(y)dy}{\left[\int_0^t n(y)\mu_D(y)dy\right]^2}, \quad (1)$$

where μ_H and μ_D, the drift mobility, are not assumed to be the same. Equation (1) describes the circuit of Fig. 8(B) in the limit of two homogeneous regions.

The peak in Hall coefficient in sample E-46A2 occurs because under constant applied voltage, only the Hall voltage is temperature-dependent below ~100°K and its peak controls the peak in the Hall coefficient. On the other hand, there is *no* peak in the Hall coefficient of sample E-56Aa because the rapid decrease with falling temperature in sample current at constant sample voltage (see Fig. 4) completely overshadows the decrease in Hall voltage and so the Hall coefficient continues to rise as the temperature decreases. Equation (1) suggests that the continued decrease in Hall coefficient for sample E-46A2 as the temperature drops below 60°K may be evidence for the existence of layers of different mobility in the grain boundary space-charge sheath.

From Eq. (1) it can be shown that if the form of $n(y)$ in the space-charge layer surrounding the grain boundary is known, the ratio of the Hall mobilities in the grain boundary layer and the bulk Ge at the temperature of the maximum in the Hall coefficient can be calculated from the experimental data.

Figure 9 shows Hall mobilities for the two samples whose resistivities and Hall coefficients are presented

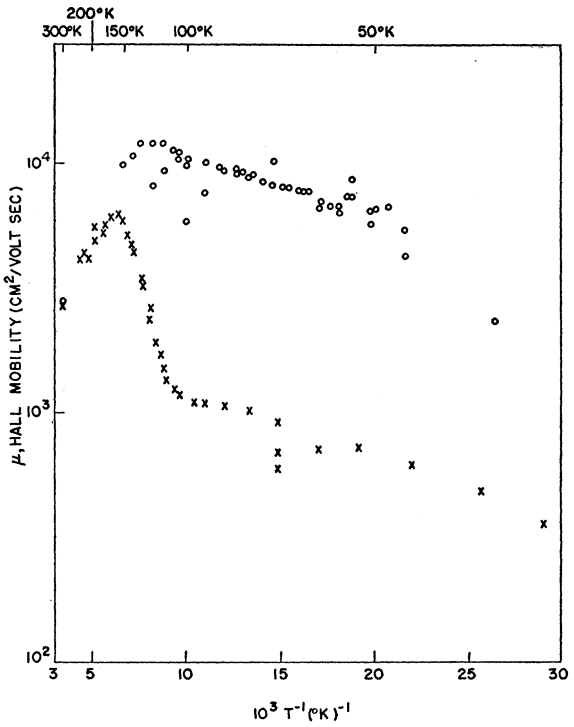

FIG. 9. Hall mobilities for samples of Figs. 4 and 6. ○ Sample of Fig. 4; × sample of Fig. 6. Note that for the calculation of the Hall mobility it is not necessary to know the thickness of the conducting layer.

in Figs. 4–7. The mobilities were calculated from the formula[9]

$$\mu=\frac{10^8\,V_H\,s}{H\;V_s\;w},$$

where μ is in cm²/volt sec if H is in gauss. V_H is the Hall voltage, V_s, the sample voltage, and s and w are, respectively, the separation of the resistivity and Hall probes. Both sets of data can be divided into three regions according to temperature. There is a high-temperature range in which the mobility is essentially that of the bulk Ge, which is carrying all the current. There is a low-temperature range in which all the current is confined to the space-charge layer at the grain boundary and the mobilities are characteristic of the carriers in this layer, subject to the limitations of interpretation imposed by the above discussion of the modification in Hall voltage encountered in composite samples. There is also an intermediate-temperature range, coincident with the neighborhood of the maximum in the Hall coefficient in one of the samples, in which the Hall voltage and mobilities have their peaks, reflecting the transition from one kind of conduction to the other. It is evident that in the sample with the low grain-boundary resistance, the shorting effect on the Hall voltage (or mobility) of the bulk Ge due to the presence of the grain-boundary space-charge layer

occurs at a higher temperature than for the sample in which the grain-boundary layer resistance remains greater than that of the bulk Ge down to a lower temperature. This is to be expected. However, there seems to be no *a priori* reason to believe that the Hall voltage associated with the low-resistance grain boundary should be lower than that of the higher-resistance grain boundary.

Although it is more difficult to interpret the data on the low-resistance grain boundary because of the drop-off in Hall coefficient at temperatures below ~60°K, the data for both samples between 60°K and 100°K, seem to be consistent with the presence of a considerable number of low-mobility carriers in the space-charge sheath at the grain boundary. No detailed interpretation of the data is attempted between 100°K and the peak at ~160°.

IV. ADDITIONAL EXPERIMENTS

(1) In order to check the possibility that the "grain boundary" conduction actually takes place in a precipitated phase of Au-rich alloy localized at the grain boundary, two bicrystals were grown doped with Au^{198} (β^-, 2.7-day). Autoradiographs of wafers such as that shown in Fig. 2(B) were made using Eastman autoradiographic plates "*t*-coating," but no additional fogging of the plates at the position of contact with the grain boundary was observed. The resolution of this method is very poor, however, and the experiments do not preclude the possibility that preferential segregation of the Au, as well as other impurities, occurs at the grain boundary.

(2) Another possibility is that preferential grain boundary diffusion[12] takes place when the fused In contacts are being put on, and that the rapidly diffused In is really responsible for the grain boundary conduction. However, by smearing Al-Ga paste on the ground surface of one face of a wafer and probing the opposite face with a point, preferential grain-boundary conduction could be detected quite readily on wafers which had had no heat treatment after growth.

(3) As mentioned previously, most of the experiments reported here have been performed upon bicrystals with angle β as defined on Fig 2(A) of 10°. However, crystals with twin boundaries have been grown and in these it was impossible to detect the presence of the boundary by electrical resistance measurements up to resistance of the order of 100 megohms.

(4) To examine the width of the conducting layer surrounding the grain boundary in a wafer of Au-doped Ge, an In contact was fused to the grain boundary region of a wafer cut from a bicrystal of Au-doped Ge. The resistance was then measured between this contact and a 0.001-in. W point set down at regularly spaced intervals on the surface with a micromanipulator. The measurements were made at liquid N_2 temperature with the surface of the wafer continuously immersed in liquid N_2. The spatial resolution of the experimental arrangement was improved by a factor of 10 by cutting the wafer at an angle of ~5° to the grain boundary and then probing across the etched surface of the wafer. The point was lifted from the Ge when moving it from place to place on the wafer to avoid scratching the surface. Considerable care was exercised to minimize effects associated with variations in point pressure. The width of the conducting layer is apparently not more than ~2μ, an experimental upper limit set by the width of the W point.

(5) It is of interest to know whether or not the phenomenon of grain boundary conduction is confined to crystals doped with Au. As a check, bicrystals of Fe-doped Ge[13] were grown, and it was found that the short-circuiting effects of a grain boundary occurred here as well.

(6) Hall measurements were made on pairs of wafers cut from the same ingot with their long directions at right angles to each other in a search for directional dependence of the mobility in the grain boundary conduction, but with no conclusive evidence that such a dependence exists.

V. CONCLUSIONS

The results of the measurements reported here are consistent with the existence of an array of acceptor levels localized at the grain boundary in a Ge bicrystal, with energies near the valence band. Electrons from the valence band may be trapped by these centers and the resulting holes confined to a space-charge layer surrounding the array of negatively charged acceptor levels. The difference in the temperature dependence of the reduced resistivity for the samples described here may possibly be related to a dependence of the energy of the acceptor levels with respect to the valence band upon the orientation of the grain boundary.

It is not clear what the source of the grain-boundary acceptor levels is. They may be related to the distorted and unsaturated valence forces discussed by Read,[14] in which case it is quite plausible that their energy should depend upon whether the dislocations in the grain boundary are pure edge or have a sizable screw component. On the other hand, impurities trapped at the grain boundary could be responsible for its acceptor action. This seems somewhat unlikely, however, in view of the available evidence concerning the binding energy of impurities to dislocations.[15,16]

[12] D. Turnbull and R. E. Hoffman, Acta Metallurgica **2**, 419 (1954).

[13] W. W. Tyler and H. H. Woodbury, Phys. Rev. **96**, 874 (1954).

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[15] A. H. Cottrell, *Relation of Properties to Microstructures* (American Society for Metals, Cleveland, 1952), p. 131.

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As might be expected, the temperature dependence of the mobility of the carriers in the grain-boundary space-charge sheath is such as to indicate that the principle scattering mechanism is impurity or defect scattering However, the marked difference between the mobilities (Fig. 9) of samples with different orientation of the grain boundary is not understood.

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Hot Electron Problem in Semiconductors with Spheroidal Energy Surfaces

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Shockley has derived the expression $E_c=(1.51)C_l/\mu$ for the critical electric field strength E_c at which the current-voltage relation in a semiconductor departs from Ohm's law. Here C_l is the velocity of longitudinal phonons and μ the conductivity mobility of the carrier. Experimental values of E_c for Ge and Si are from two to four times larger than those predicted by this formula. We therefore have extended the theory to take account ellipsoidal energy surfaces in the Brillouin Zone and scattering by shear modes of vibration. The effect of the more general effective mass tensor is to raise the theoretical value of E_c by a factor of about 2 for n-type Ge and 1.3 for n-type Si, whereas shear mode scattering lowers E_c by a factor that is between 1 and the value of the ratio of the velocity of transverse modes to that of longitudinal modes. Moreover, E_c should vary with the direction of the current. The present study still fails to close the gap between theory and experiment: the remaining discrepancy is possibly the result of neglecting intervalley scattering.

INTRODUCTION AND SUMMARY

THE deviation from Ohm's law in semiconductors such as Ge and Si in strong electric fields has been studied both theoretically[1–7] and experimentally[8,9] by many investigators. This problem has been called the "hot-electron" problem by Shockley because the average kinetic energy of the electrons in strong fields becomes larger than the usual thermal energy, so that the "electron temperature" becomes larger than the lattice temperature. There are, however, quantitative discrepancies between theory and experiment in some respects, such as in the value of the critical field E_c where the deviation from Ohm's law occurs. The experimental values in Ge and Si are about twice to four times larger than those obtained from the formula

$$E_c{}^s=1.51C_l/\mu. \tag{1}$$

The superscript s on E_c indicates that this value is obtained from the scalar effective mass theories, C_l is the longitudinal velocity of the phonons, and μ is the weak-field conductivity mobility of electrons.

Previous calculations have assumed spherical energy surfaces in the Brillouin zone. It is now believed that for n-type Ge and Si one must use spheroidal surfaces in discussing the electrical properties. Further, as has been pointed out by Adams[10] and by Herring,[11] shear waves are as important as pure compressional waves in the lattice scattering of electrons in these crystals. Therefore we have attempted to solve the hot-electron problem with the spheroidal model, including the effect of shear waves. A number of drastic approximations are made in solving the Bloch equation, and we finally get the expression for the critical field in the following form:

$$E_c=ASE_c{}^s, \tag{2}$$

where the factor A is an anisotropy factor and the other factor S results from the effect of the shear waves. When we neglect the effect of the latter, S equals 1, and when the mass component ratio $r=m_2/m_1$ is equal to 1, A becomes independent of the direction of the current vector and is also 1. The larger the departure of r from 1, the larger is the value of A. The factor S is a complicated function of the mass ratio r, the ratios of the characteristic coefficients of the deformation potentials of shear waves and of pure compressional waves, and the ratio $C=C_t/C_l$ of the transverse and longitudinal velocities of the acoustical modes of lattice vibration. However, the value of S is almost always between C and 1. This fact may be qualitatively understood, because both

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