AN INVESTIGATION OF THE ELECTRICAL CONDUCTIVITY OF GERMANIUM WHISKERS

by

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B.S., Louisiana State University, 1957

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

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KANSAS STATE UNIVERSITY
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1966

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INTRODUCTION

Germanium whiskers were grown by a vapor reduction process developed by Ruth, Marinace, and Dunlap (1) in the investigation of vapor-deposited single-crystal germanium. These authors noted that under certain conditions the growth of whiskers occurred, but no investigation of the electrical properties of the whiskers was reported. Although whiskers of several semiconducting materials have been grown, and investigations into the growth mechanisms and mechanical properties conducted, there has been found no reference in the literature to determinations of the electrical properties of semiconducting whiskers.

The investigation of a semiconducting system is frequently simplified by assuming a one dimensional, one electron model. In terms of this model, an attempt is made to determine the forbidden energy band, the majority and minority carrier concentrations and types, mobilities, and the energy levels within the forbidden energy band.

A fundamental experiment is to determine the electrical conductivity as a function of the absolute temperature. If the temperature range is sufficiently large, the forbidden energy gap can be calculated from the data, and certain information about the impurity levels inferred. Such determinations are the subject of the present paper. Other important experimental determinations, such as the Hall coefficient, were not attempted in this preliminary investigation, due to the technical problems presented by the small size of the whiskers.

WHISKER GROWTH

Growth Procedure

The whisker growth was obtained by the temperature reduction of GeI_2 into GeI_4 and germanium. The reaction used was

$$2GeI_2 \rightleftharpoons Ge + GeI_4$$

which proceeds to the right upon decreasing the temperature. Heated gaseous iodine was introduced into a reduction tube, where it was caused to pass over germanium chips maintained at 600° C., a temperature favorable to the formation of both GeI_2 and GeI_4. A seeded glass substrate was introduced into the reduction tube at 400° C., where free germanium atoms were obtained according to the above reaction.

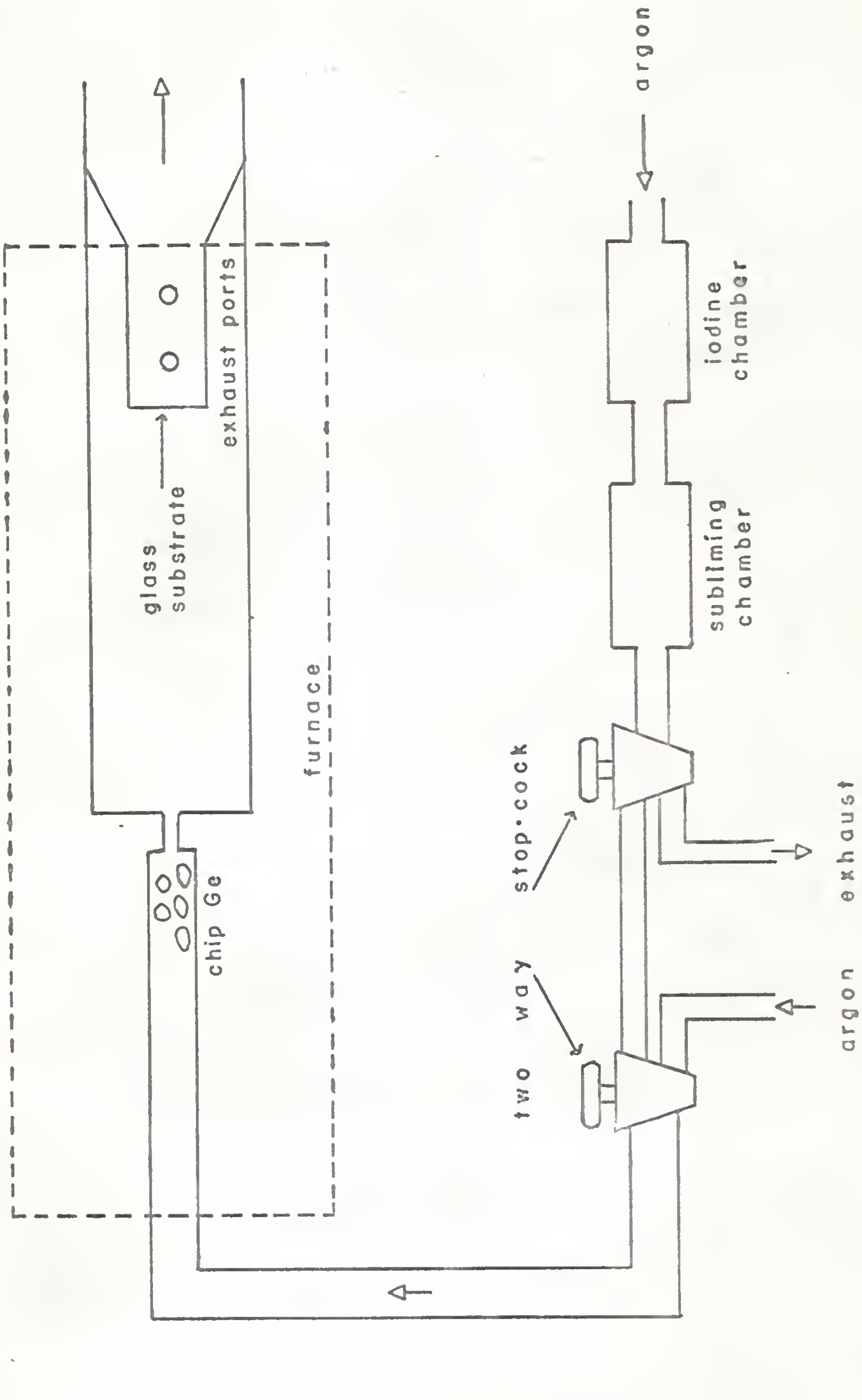
A reduction tube, constructed of Corning Pyrex glass (Plate I), was enclosed in an electrical furnace provided with two independently controlled temperature regions. The system was designed so that either gaseous iodine and argon, or argon alone, could be introduced into the reduction tube.

The main part of the tube, enclosing the germanium chips and the glass substrate, was initially purged of atmospheric gases by bringing the furnace to the operating temperatures, and introducing a flow of commercial grade, untreated argon into the tube for twenty-four hours. Crystalline iodine was then placed in the iodine chamber shown in Plate I. In order to purify the iodine, an argon flow was directed into the iodine chamber, with the two way stop-cock in the exhaust position, and the chamber heated until all of the iodine had been sublimed. The stop-cock was then turned so that the flow was directed into the reduction tube, and the iodine that had condensed in the sublimation chamber was heated and thus introduced into the

EXPLANATION OF PLATE I

Diagram of reduction tube used in whisker growth.

PLATE I


argon
iodine chamber
subliming chamber
stop-cock
exhaust
two way
argon
exhaust ports
glass substrate
furnace
chip Ge

chamber as gaseous iodine.

After the iodine had been completely sublimed into the reduction tube, the furnaces were maintained at operating temperatures with the argon flow for an hour to permit the reaction to be completed. The free iodine was then purged from the system.

The substrate, a Pyrex glass cylinder flattened on the end, was seeded by first depositing, by the method described above, a thick layer of germanium, then removing some of the deposit by rubbing with emery paper, and finally etching in CP-4. This left an etched surface on the glass, where small particles of germanium could be seen embedded in the surface. The seeding was originally designed as a cleaning procedure, and it is not known whether or not this had an effect on the whisker growth. However, the only large whisker yield occurred immediately after this operation, and the seeding was assumed to be significant.

Results

The whiskers were grown on the end and sides of a Pyrex glass cylinder, approximately 1 cm in diameter, the growth covering approximately 2 cm of the cylinder. The growth was most dense along the end of the cylinder. The whiskers generally extended perpendicularly outward from the glass surface, although other directions were observed, including some samples growing parallel to the surface of the cylinder.

A single sample was used in X-ray analysis to determine structure and composition. It was found to be composed of germanium, with the growth axis along the 211 direction. The identification was made by Dr. R. D. Dragsdorf of Kansas State University. Davis and Lever (2), who used a method similar to that described above to obtain germanium whiskers, analyzed many samples by X-ray techniques, and concluded that the growth direction was random.

CONDUCTIVITY MEASUREMENTS

Resistance Measurements

In order to make measurements of the total resistance of the whiskers, they were placed on glass slides, where contacts of Eccobond silver compound were made to the ends. The contacts were designed to hold the ends of the whiskers firmly against the slides. To improve thermal conduction the exposed segments between the contacts were covered with Dow Corning Silicone vacuum grease. Iron-constantan thermocouples, mounted in a similar manner, were placed near to the whiskers to measure the temperature of the surface of the glass slides.

Each glass slide bearing a whisker and thermocouple was mounted in a metal dewar, designed to permit both heating and cooling (Plate II). The dewar was connected to a vacuum forepump, to reduce the condensation of water vapor at low temperatures. The entire system was shielded to reduce 60 cycle noise.

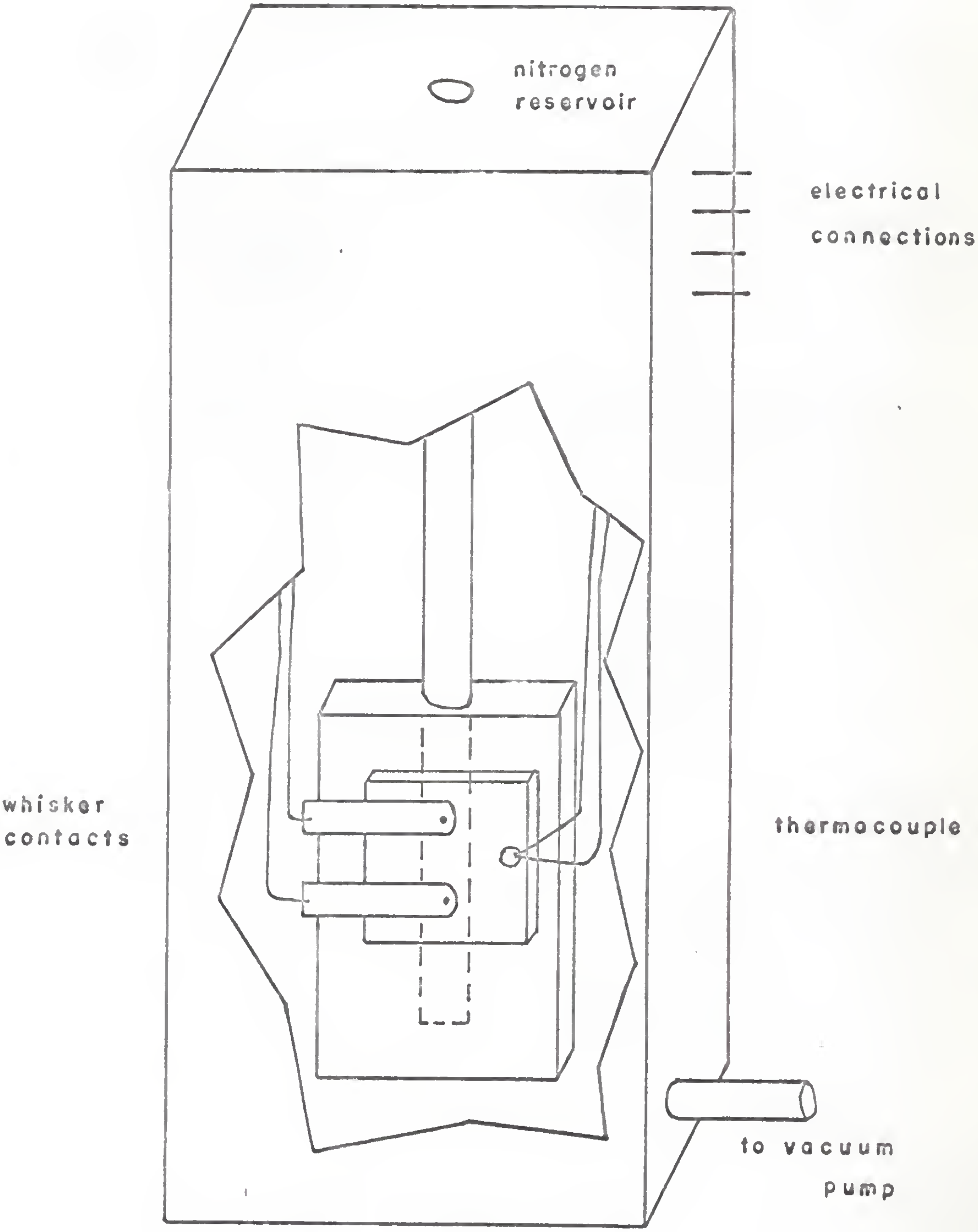
Resistance measurements were made over the temperature range -170° C. to 350° C., at approximately 15 degree intervals. Each set of measurements was started at the lowest temperature, and values were obtained continuously as the system slowly heated to the maximum temperature. Cooling was obtained by the use of liquid nitrogen, and heating by an electric heater.

The measurement of total resistance was made using an A.C. method. A low frequency alternating signal was applied across the whisker and a 1000 ohm

EXPLANATION OF PLATE II

Diagram of metal dewar used in measuring whisker resistance. A single whisker is located between the whisker contacts.

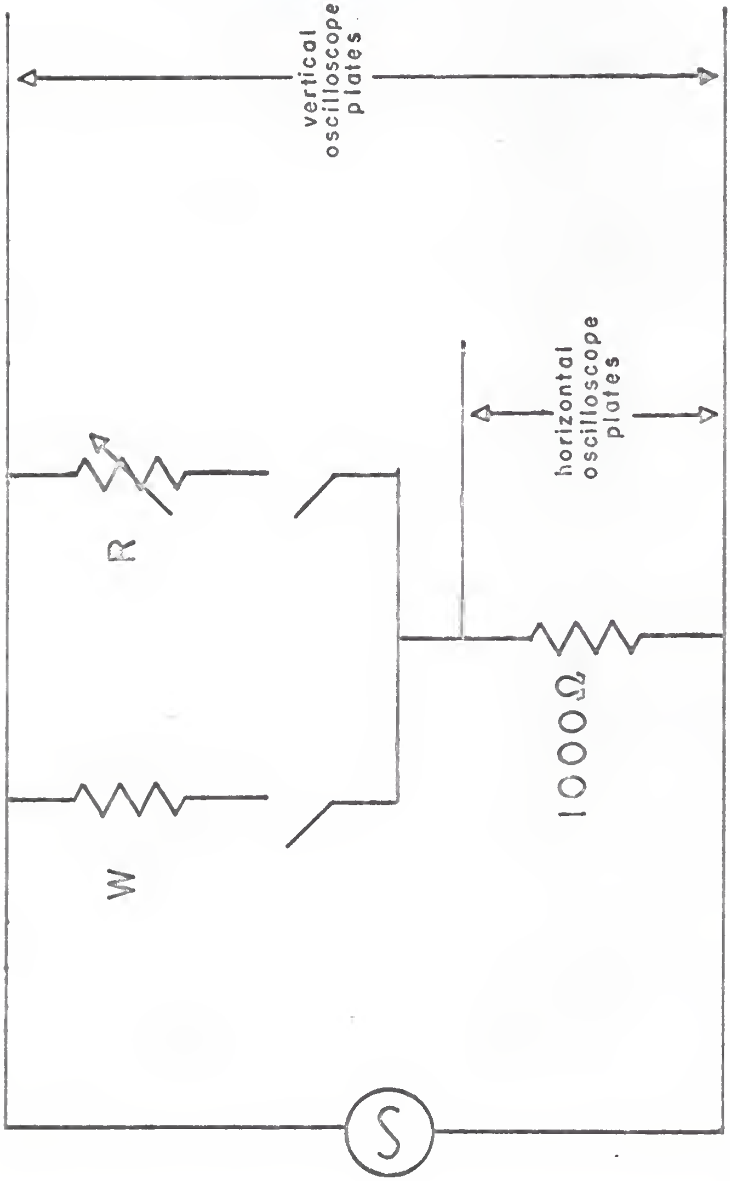
PLATE II


nitrogen reservoir
electrical connections
whisker contacts
thermocouple
to vacuum pump

EXPLANATION OF PLATE III

Diagram of the circuit used to determine the total resistance of the whisker.

PLATE III


vertical oscilloscope plates
horizontal oscilloscope plates
R
W
1000Ω
S

standard resistor was placed in series (Plate III). The voltage drop across the whisker and the standard resistor together was displayed on the vertical axis of an oscilloscope, and the voltage drop across the standard resistor alone on the horizontal axis. For reference, the oscilloscope screen was fitted with a transparent plastic front, which had a simgle straight line scratched along a diameter, and which was free to rotate smoothly directly in front of the screen.

For each determination, the whisker was put into the circuit and the signal applied. Since the 1000 ohm standard resistor was small with respect to the whisker resistance (on the order of one megohm), the resulting oscilloscope trace was approximately a voltage-current plot, the slope of this curve giving the total resistance of the whisker. The whisker was then replaced in the circuit by a variable resistor, a one percent decade box. The line on the oscilloscope was adjusted to the same slope, using the scored front-piece as a reference. The whisker resistance was then read directly from the decade box.

The whiskers used in obtaining the conductivity curves were photographed using the Leitz microscope, and the magnification of each photograph determined. The photographic images were measured using a scaled traveling microscope, providing an estimate of the whisker dimensions.

Results

Values of the electrical conductivity at several temperatures were calculated for each whisker, using the total resistance and the dimensions, according to the definition

$$\sigma = (1/R)(L/A), \tag{1}$$

where R is the resistance, L the length, and A the cross-sectional area. The natural log of the conductivity was plotted against one thousand times the reciprocal of the absolute temperature for each of the whiskers (Plate IV). Low temperature values of conductivity obtained by Debye and Conwell (3) for pure bulk germanium samples were plotted on the same graph for comparison, as were high temperature values obtained for similar samples by Morin and Maita (4).

In the intrinsic conduction region, the conductivity is related to the forbidden energy gap E_1 by the equation

(2) $$\sigma = \sigma_0 \exp(-E_1/2kT),$$

where k is Boltzmann's constant, T the absolute temperature, and σ_0 approximately a constant at high temperatures.

At high temperatures, the conductivity curves become linear, and the forbidden energy gap may be determined from the slope of the resulting straight line, if the material is clearly in the intrinsic region of conduction.

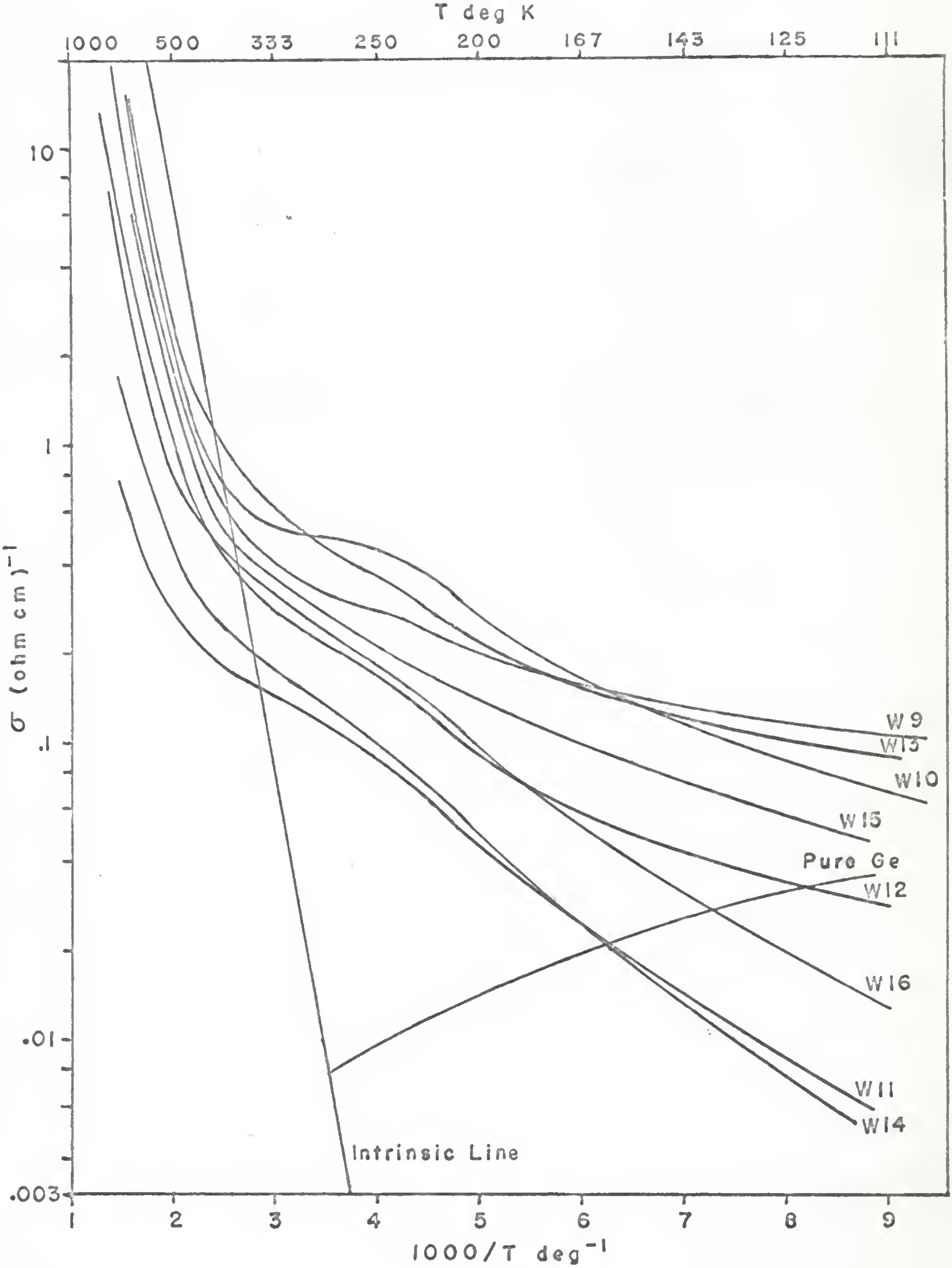
The high temperature region of the conductivity curves has been expanded on a separate graph (Plate V) for the purpose of calculating the width of the forbidden energy gap E_1. The value of E_1 was determined in each case from the slope of the tangent to the conductivity curve at 608° K.

The forbidden energy gap is itself a function of temperature, and using the values given by Smith (5), the value of E_1 for pure bulk germanium at the temperature chosen is .60 ev. The values obtained experimentally are listed below in Table I, together with the whisker identification and radius.

EXPLANATION OF PLATE IV

Graph of ln σ, plotted against 1000/T, for each of the whiskers measured.

PLATE IV


T deg K
1000
500
333
250
200
167
143
125
111
10
1
.1
•01
.003
σ (ohm cm)$^{-1}$
W 9
W13
W10
W15
Pure Ge
W12
W16
W11
W14
Intrinsic Line
1
2
3
4
5
6
7
8
9
1000/T deg^{-1}

EXPLANATION OF PLATE V

Graph of $\ln \sigma$ vs 1000/T for high temperatures. A straight line fit is made in the intrinsic region, for the purpose of determining the forbidden energy gap.

PLATE V

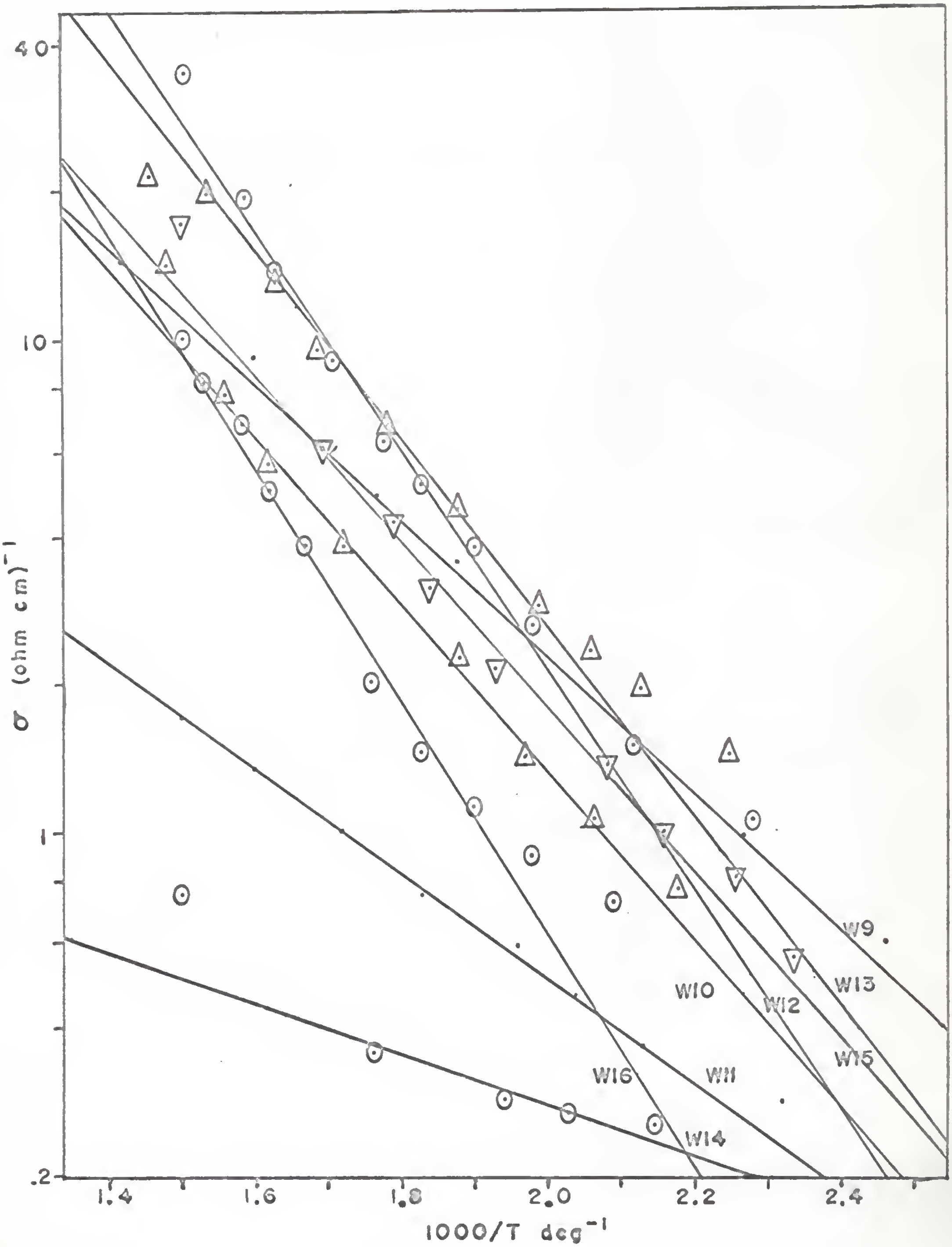

40
10
1
.2
σ (ohm cm)⁻¹
1.4
1.6
1.8
2.0
2.2
2.4
1000/T deg⁻¹
W9
W10
W11
W12
W13
W14
W15
W16

Table I. Comparison of the calculated forbidden energy gap E_1 and the radius.

Whisker	E_1	r
W-13	.74 ev	1.5×10^{-4} cm
W-10	.74	2.7
W-12	.74	2.8
W-16	.72	3.4
W-15	.71	4.9
W-09	.68	3.2
W-11	.52	4.5
W-14	.41	3.4

The calculated values of the forbidden energy gap E_1 are not in close agreement with the results for pure bulk germanium, but with the exception of W-11 and W-15, there appears to be a definite ordering of E_1 with radius, the larger energies corresponding to the smaller radii.

The shapes of the conductivity curves in the temperature region below the intrinsic temperature are unexpected, since in this range the curves obtained from pure bulk samples usually exhibit positive slopes (3).

Below the intrinsic temperature, the conductivity is a product of two factors, each dependent upon the temperature. Assuming a single type of carrier, and a single donor level at an energy E_d below the bottom of the conduction band in the forbidden energy gap, the conductivity may be expressed as (6)

$$\sigma = eun \tag{3}$$

where n is the electron density excited into the conduction band from the impurity level, and u is the electron mobility.

The electron density n is given by (6)

$$n = (2\pi mkT/h^2)^{3/4} n_d^{\frac{1}{2}} \exp(-E_d/2kT) \tag{4}$$

where n_d is the density of impurity levels at E_d, k is Boltzmann's constant, h is Plank's constant, T is the absolute temperature, and m is the effective mass. For a given crystal direction, this equation may be replaced by

(5) $$n = AT^{3/4}\exp(-E_d/2kT),$$

where A is a constant.

Although the expression for the mobility depends upon the scattering mechanism, in many cases the temperature dependence is given according to the power law (5)

(6) $$u = BT^{-s}$$

where B is a constant, and s is a parameter depending upon the type of scattering. For scattering due only to lattice vibrations, s is a small positive number, giving rise to the decrease of conductivity with increasing temperature of very pure bulk samples in the low temperature region (Plate IV). For scattering due to impurities, dislocations, or to surface effects, s may be either a positive or negative number. In general, mobilities due to different types of scattering do not add in a simple way, giving a single power law dependence of u on T. However, in some temperature regions, a single term may dominate, giving rise to a simple power law expression.

In the present case, the measurement of conductivities alone was not sufficient to determine the type of scattering present at low temperatures. However, all conductivity curves showed a simple power law dependence upon temperature in the temperature range from 100° K to 200° K, indicating the predominance of a single scattering mechanism in this region. Using graphical methods, it was possible to estimate the value of the parameter s in equation (6).

From equation (3), for a single type of scattering,

(7) $$\sigma = eun = CT^{4/3-s}\exp(-E_d/2kT),$$

where C is a constant. Taking the natural log of both sides,

$$(8) \qquad \log \sigma - \log T^{4/3-s} - \log C = (-E_d/2000k)(1000/T).$$

By subtracting from the graph of log σ vs 1000/T the graph of log T^p vs 1000/T, where p was allowed to vary in .1 steps, the value of s leading to the best straight line of equation (8) was found for each whisker. The results are tabulated in Table II.

Table II. Comparison of the calculated value of the parameter s and the whisker radius.

Whisker	s	r
W-11	-3.0	4.5×10^{-4} cm
W-14	-2.7	3.4
W-16	-2.4	3.4
W-10	-1.7	2.7
W-12	-1.2	2.8
W-15	-0.9	4.9
W-13	-0.6	1.5
W-09	-0.4	3.2

It will be noted that with the exception of W-09 and W-15, the values of the parameter s are ordered with respect to the whisker radius, a result similar to that noted in Table I. Since in all cases the value of the parameter s is negative, the predominant scattering mechanism in the temperature region considered is not that of lattice vibrations.

WHISKER CONTACTS

The electrical contacts to the whiskers used in obtaining the conductivity measurements were made by embedding the ends in Eccobond silver compound, and making pressure contacts by platinum tipped metal clips directly to the silver. The oscilloscope traces, or the I-V curves, of all of the whiskers mounted in this manner showed a decided curvature at low temperatures (Plate VI), indicating that the contacts were non-ohmic. A hysteresis loop was observed in some cases at low temperatures.

Generally the curvature was not the same for both the positive and the negative branches, and not in all cases smooth, implying that the non-ohmic behavior was inherent in the contact, rather than in the bulk resistance of the whiskers.

Since earlier experimenters (7) have observed ohmic contacts between germanium and certain metals, it was assumed that an improvement in the contact was possible, and efforts were directed toward this goal. The contact was assumed to be more ohmic when the oscilloscope trace was more linear. Many attempts were made, but since the results were inconclusive, only the last, and as applied to the above criteria, the best, has been included in this paper (8).

For this case, the whisker was placed on a glass slide, and the center section covered with epoxy glue (Plate VII), and the glue allowed to dry. The exposed ends of the whisker were then copper plated, using a copper sulfate solution. The plating procedure was to place a drop of the solution on one end of the whisker, making contact to the drop by means of a hand held copper probe. Contact was made to the opposite end of the whisker by means of a small drop of mercury, in contact with a second probe. A current of about .4 ma was applied, and the plating continued until a thin coating of copper was visible on the end of the whisker. After the plating, a small drop of commercial quality electronic solder was applied to the ends of the whisker, painted silver leads completing the connection.

Although not entirely straight, the oscilloscope traces of the several samples tested were in general straighter than had been obtained by the

EXPLANATION OF PLATE VI

Photographs of the oscilloscope trace of W-16 at several temperatures:

Fig. 1	-173° C.
Fig. 2	-140° C.
Fig. 3	-94° C.
Fig. 4	-63° C.

PLATE VI

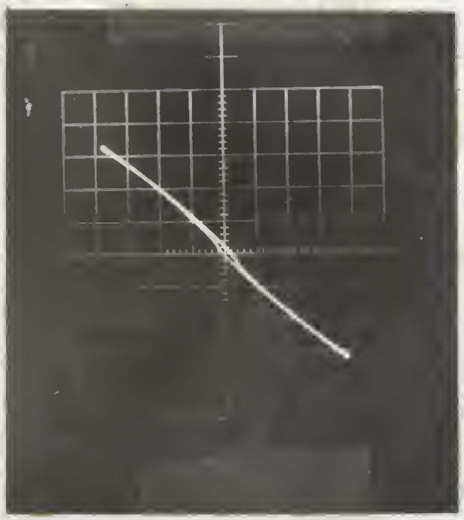


Fig. 1

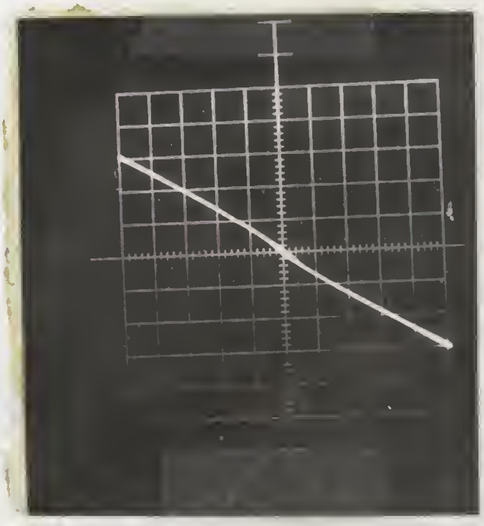


Fig. 2

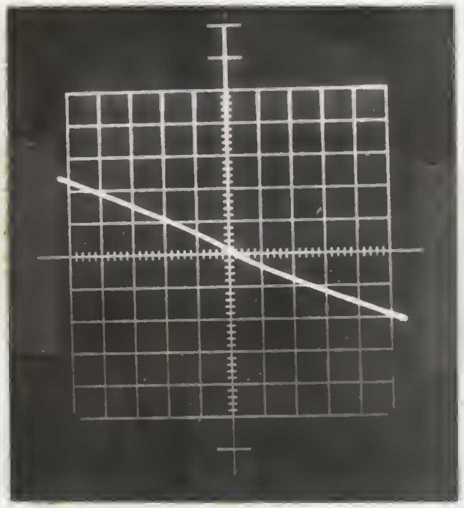


Fig. 3

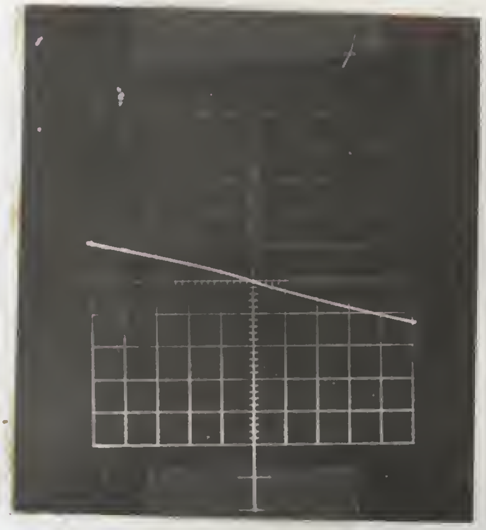


Fig. 4

EXPLANATION OF PLATE VII

Fig. 1	Mounted whisker as seen from below, looking through the glass slide.
Fig. 2	Mounted whisker as seen from above.
Fig. 3	Reference scale, in millimeters.

PLATE VII

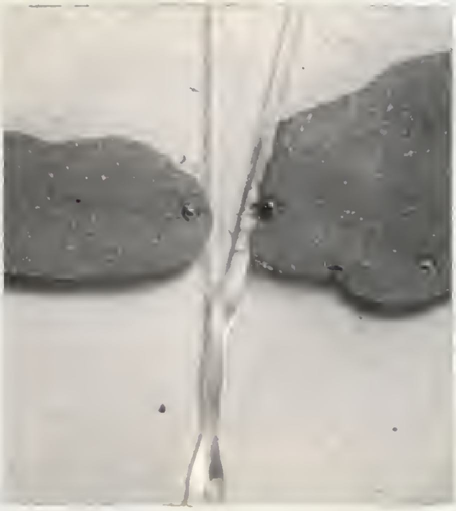


Fig. 1

Fig. 2

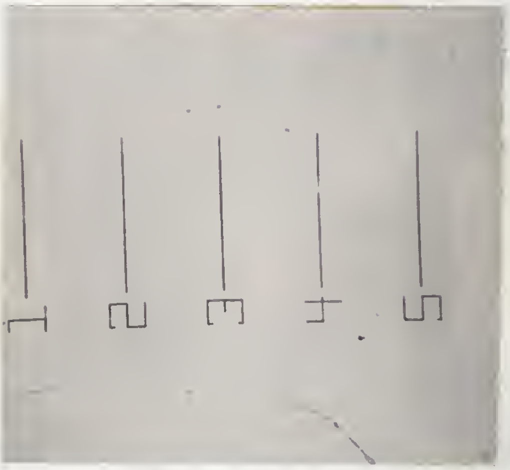


Fig. 3

earlier method, for a certain range of temperatures. However, the contacts did not have the physical stability of the Eccobond silver mounting, and contact was retained only in the region between approximately -50° C. and 200° C., a temperature range too small for conductivity curves to be very meaningful.

DISCUSSION

The shapes of the conductivity curves in the temperature region below the intrinsic temperature suggest that the samples have few donor or acceptor levels close to the conduction or valence bands, and that the significant carrier concentration in the extrinsic region is due to impurity levels far into the interior of the forbidden energy gap. This is suggested because the low temperature regions with the large negative slopes may be associated with an exponential increase of conduction carriers excited from a deep lying impurity level, and the change of curvature near the intrinsic temperature with the onset of saturation, or the complete ionization of the impurity levles.

The assumption made of impurity levels deep in the forbidden energy gap seems reasonable. It has been pointed out (7) that on the surface of any semiconductor there exist deep donor or acceptor levels, the number per unit area of these levels being approximately equal to the density of surface atoms. The occupation and position of these levels depends largely upon the condition of the surface. The presence of these surface levels has been shown to disturb the positions of the conduction and valence bands to a depth of 10^{-4} cm in germanium. The region of disturbance is known as the space charge region. If conduction occurs in the space charge region, the surface states will act as impurity levels, and the carrier mobility will be characteristic of the space charge region, being generally lower than in the bulk systems, due to scattering from the surface.

Since the radii of all of the whiskers were on the order of 10^{-4} cm, or approximately the same as the thickness of the space charge region found for large bulk samples, it is possible that the majority of the conduction occurred in this region, and the parameter s calculated above is a characteristic of the scattering due to the space charge region.

Scattering due to dislocations may have been an important part of the low temperature mobility. No estimate of such scattering can be made, since the dislocation density was not determined.

The low temperature conductivities may also have had some dependence on whisker orientation. The whiskers were subjected to uniaxial tensions due to the fixed end mountings, and since large piezo-resistance effects have been observed in bulk samples (5), similar effects would be expected in the smaller whisker samples. Since the growth directions of the samples used were not obtained, no estimate can be made of this effect.

In the intrinsic region, the energy levels on the crystal surface should have no effect on the carrier concentrations in the conduction process, and the determination of the forbidden energy gap E_1 made above should yield the bulk germanium values. The lack of agreement between the calculated value of E_1, and the value observed for bulk germanium, could not be explained by the thermal expansion of the whiskers. The ordering of this quantity with respect to the radius suggests, however, that the mobility, assumed constant in the calculations, may depend upon the radius.

There were several unavoidable experimental errors, which are listed below:

a. The whisker contacts were non-ohmic at low temperatures, and consequently a contact resistance, possibly temperature dependent, was measured in series with the total whisker resistance.

b. The oscilloscope traces were curved at low temperatures, making the measurement of resistance uncertain.

c. The whiskers were heated by the applied current, making the whisker temperature higher than that measured by the thermocouple.

d. The whisker dimensions were in error, since the radius was determined assuming the crystal to be a cylinder, and since the actual point of electrical contact to the silver was unknown, making the length uncertain. Errors in whisker dimensions would not effect the energy calculations.

If, as has been postulated above, the conduction process occurs largely in the space charge region, whiskers may provide a good system for the study of surface phenomena. The electrical contacts developed here are not suitable over a wide range of temperatures, but may prove useful for constant temperature surface investigations, such as the field effect experiment.

REFERENCES

1. Ruth, Marinace, and Dunlap, J. Appl. Phys., 31, 995 (1960).
2. Davis, M., and Lever, R. F., J. Appl. Phys., 27, 835 (1956).
3. Debye, P. P., and Conwell, E. M., Phys. Rev., 93, 693 (1954).
4. Morin, F. J., and Maita, J. P., Phys. Rev., 94, 1525 (1954).
5. Smith, R. A., Semiconductors, Cambridge University Press, 1961.
6. Wilson, A. H., The Theory of Metals, 2d ed., Cambridge University Press, 1953.
7. Handler, P., Semiconductor Surface Physics, Philadelphia University Press, 1957.
8. Dale, E. B., and Calvert, J. W., Rev. Sci. Instr., 35, 1719 (1964).

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Whiskers of germanium were grown by a vapor reduction process, where GeI_2 was caused to disassociate into Ge and GeI_4 in the presence of a seeded substrate.

The electrical conductivity of several whiskers was determined as a function of temperature, over a temperature range from -170° C., to 350° C. Conductivity curves were plotted, and the value of the forbidden energy gap was determined for each sample, in the intrinsic region of conduction. The extrinsic region of the conductivity curves did not follow the results obtained for pure bulk samples, and an attempt was made to explain the departure from bulk properties in terms of the small size of the whiskers.

The electrical contacts to the whiskers were found to be non-ohmic, and a method of making improved contacts to germanium whsikers, suitable over a limited range of temperatures, was developed.