



**LB-885**

**ELECTRICAL MEASUREMENTS**

**ON GERMANIUM**

**RADIO CORPORATION OF AMERICA  
RCA LABORATORIES DIVISION  
INDUSTRY SERVICE LABORATORY**

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## Electrical Measurements on Germanium

### Introduction

There are three room-temperature electrical measurements that give quantitative information about germanium quality. These are resistivity, Hall coefficient and minority-carrier lifetime. On large ingots and single crystals, the resistivity is desired as a function of distance along the specimen. The use of automatic scanning and recording equipment speeds this measurement. The Hall coefficient can be determined by d-c or a-c measurements on a bar of germanium placed in a magnetic field. In either case, a single probe connected to one side of the specimen can be used to measure the Hall voltage, thus speeding the sample preparation. The lifetime is measured by the decay of photo e.m.f. as a function of distance between a line of illumination and a point probe on the germanium surface. This surface must be carefully prepared in order to get lifetime values characteristic of the bulk material. A fourth measurement, the thermal e.m.f., is useful primarily in giving qualitative information as to the conductivity type of the germanium, that is, whether it is p-type or n-type. The resistivity scanning equipment can also be used for this measurement with very slight modification.

### General Discussion

Electrical measurements are the best tests of germanium quality as to purity and device utility. The significance of the electrical parameters is stated very briefly in this section. More specific information on interpretation of the measurements is included in the subsequent sections. Further information can also be found in Chapters I and III of Shockley's book.<sup>1</sup>

Assuming constant mobility ( $\mu$ ), the electrical resistivity ( $\rho$ ) or its reciprocal, the conductivity ( $\sigma$ ), is a direct measure of purity over a considerable range of impurity con-

centration. Although more care must be used in interpreting the results obtained for polycrystalline material, resistivity measurements have important applications here as well as for single crystals. The Hall coefficient ( $R$ ) measures purity more directly since in many cases no assumptions have to be made about the carrier mobility. The Hall effect is also less subject to grain boundary disturbances. Combined with a resistivity determination, it gives a value for the mobility. The sign of the Hall coefficient specifies the conductivity type (p or n). Hall measurements are less convenient to make than resistivity determinations because of the magnetic field and the special sample preparation required.

<sup>1</sup>W. Shockley, ELECTRONS AND HOLES IN SEMICONDUCTORS, Van Nostrand, N.Y., 1950.

## Resistivity or Conductivity

For germanium at 300 degrees K (27°C or 81°F) conductivity is directly proportional to impurity concentration in the range 0.1 to 10 mho/cm ( $\rho = 10$  to 0.1 ohm-cm). The range of strict proportionality can be extended to higher purity material by decreasing the temperature in order to diminish intrinsic behavior. For lower purity material, the temperature may be increased to accentuate thermal scattering relative to impurity scattering. Fortunately, the aforesaid 100 to 1 range is that of most interest for germanium as used in transistor devices; furthermore, the conductivity is a monotonically increasing function of impurity concentration considerably outside this range. This bulletin will, therefore, be concerned only with room-temperature measurements. Convenient calibration points to keep in mind for the proportionality between impurity content and conductivity are

$$x_D = 3.9 \times 10^{-8} \text{ mol-fraction of donor}$$

impurities per mho/cm of conductivity

$$x_A = 8.2 \times 10^{-8} \text{ mol-fraction of acceptor}$$

impurities per mho/cm of conductivity

in n- and p-type material respectively at 300 degrees K. These values apply where one conduction electron arises from each donor impurity atom or one hole from each acceptor impurity atom (or equivalent lattice defect).

By definition, resistivity involves the determination of the potential drop in a sample of known geometry carrying a known current. Here the primary concern is with the special problems relating to germanium purification where it is important to know the resistivity as a function of length along an ingot or crystal. Since this determination is performed frequently, techniques have been developed to speed the work. The heart of the equipment is an automatic scanner which drives a probe along the sample. The potential drop as a function of distance is plotted by a synchronously driven recorder.

The crystal scanner along with its as-



Fig. 1 - Equipment used in resistivity measurements.

Associated electrical equipment is shown in Fig. 1. It consists of several parts, the most important of which are the specimen support, the probe, and the probe holder. These may be readily distinguished in the photograph.

The specimen support was designed to provide adjustment of the specimen along the three major axes with respect to the probe. The same leads that are used for carrying current through the specimen are also used for securing it to the support. These leads are copper wire soldered to the ends of the crystal.

The support will accommodate a wide variety of crystals including those with compound curvature and with cross-sectional changes along their length.

The probe is a hardened steel rod 1/8 inch in diameter, tapered at the tip and rounded to a 1/32 inch radius. It is weighted in order to insure good contact between the probe and crystal. The probe is carried along in an insulated holder which in turn is driven by a screw cut with eight threads per inch. Two synchronous motors are available, the desired one being selected by meshing an idler gear.

Model 610 Synchron motors are used with the gear reduction supplied. Their speeds are 1 and 8 r.p.m. so the linear probe speeds available are 1/8 and 1 inch per minute. The higher speed is normally used, the lower one being employed when greater resolution is needed.

The probe holder engages the screw by means of a pin which can be retracted to permit sliding the carriage manually to any point along the specimen.

A block diagram of the electrical circuits is given in Fig. 2. The control box for the specimen current can be seen in the right foreground of Fig. 1. A 400-ohm voltage divider across a 1.5-volt dry cell is used to set the crystal voltage drop to 0.5 volt. The crystal current is read on the panel meter having ranges of 1, 10 and 100 ma full scale. A polarity switch and on-off switches for the dry cell and the motor are provided.

From the circuit standpoint, the most important effect that may lead to unreliable results with a potential plotting system is rectification at the probe. The moving rectifier will have a constantly and erratically changing internal resistance which shifts the sensitivity of the potentiometer. This problem is especially

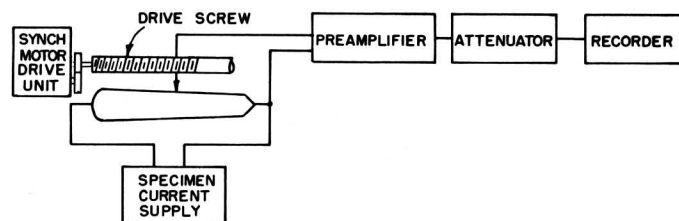


Fig. 2 - Arrangement for measuring resistivity.

serious when automatic recording of the potential is attempted. The solution is to use a preamplifier which presents a very high input impedance to the probe. If the input impedance is much greater than the internal impedance of the probe rectifier at any point in its path along the ingot, the recorder will indicate the correct potential. This input circuit is essential even if the recorder is of the self-balancing potentiometer type, notwithstanding the fact that such an instrument draws no current from the circuit at balance. Since the instrument will not drive up-scale unless there is some unbalance at its input, it is the unbalanced input impedance which is of interest. This is of the order of a few thousand ohms for many of the well-known electronic recording potentiometers commonly used. The problem is reduced by correct choice of the polarity across the crystal so that whatever bias appears across the probe rectifier will be in the forward direction. For an n-type crystal the common connection to the preamplifier should be the positive side of the crystal.

A simple and convenient method of attaining a high input impedance preamplifier without sacrificing scale linearity is to use a simple modification of a commercial vacuum tube microammeter, the RCA Ultra Sensitive Microammeter, Model WV-84A. This is used on its most sensitive current scale, 0.01  $\mu$ a, where it has 50 megohms input resistance. An input of 0.5 volt is required for full scale deflection; this provides approximately 100 millivolts across the meter movement. The exact value varies somewhat with different instruments. A double-pole switch is used to take the meter movement out of the circuit and connect in the input of an attenuator seen in Fig. 1 (on top of the recorder at the left). This attenuator is a tapped 10 K ohm resistor. The 500-ohm tap gives approximately the correct signal and impedance to feed the 0-5 mv Brown Recording Potentiometer which follows in the circuit. Final calibration

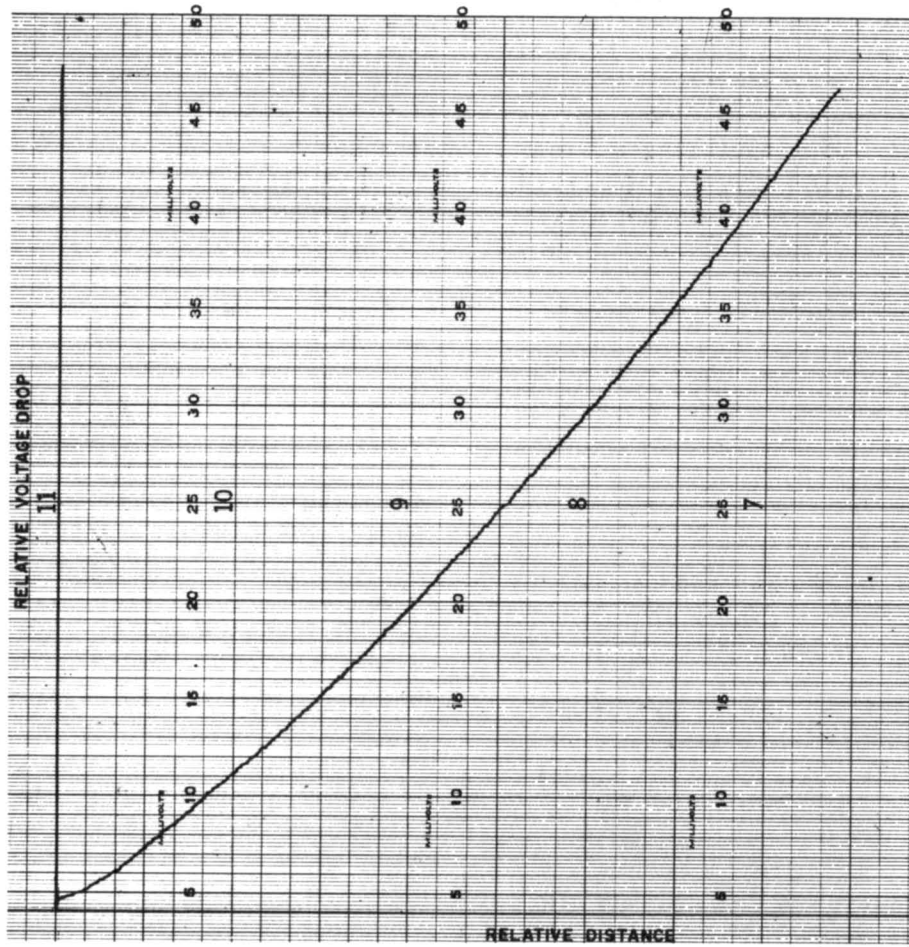


Fig. 3 - Typical resistivity scan.

adjustment is made by shunting the input terminals of the attenuator with the exact resistance required to give full scale deflection of the recorder for 0.5 volt at the probe.

In operation, the voltage across the sample is adjusted to about 0.5 volt, or slightly less, and the current noted for that voltage. The drive mechanism and recorder are started together and the potential plot is

made. If sufficient resolution is available, the same mechanism can be used to locate p-n junctions, plot potential variations in biased transistors of the grown crystal type, and so on. A typical potential plot is shown in Fig. 3.

Calculation of the resistivity can be simplified by using mechanical and nomographic aids. It is convenient to have a scale which transforms distance on the recorder chart to

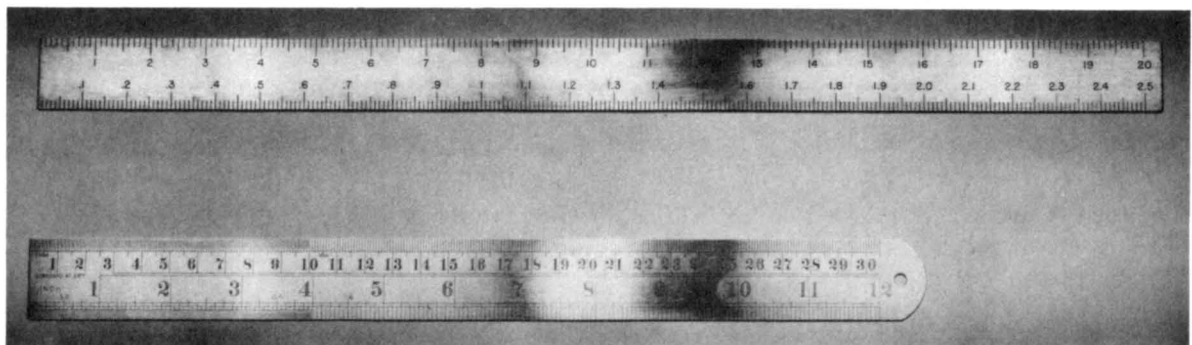


Fig. 4 - Special chart scale at top graduated in ingot centimeters for two different scanning speeds compared with standard scale.

distance along the crystal. This transformation is fixed by the relative drive speeds of the recorder and scanner, determined by synchronous motors. Fig. 4 shows such a scale compared with a standard ruler. The upper and lower calibrations give crystal centimeters in terms of chart length for the two scanner speeds available.

Fig. 5 illustrates the use of a mechanical slope-calculator. Its base line is laid tangent to the curve at the desired point such as A.

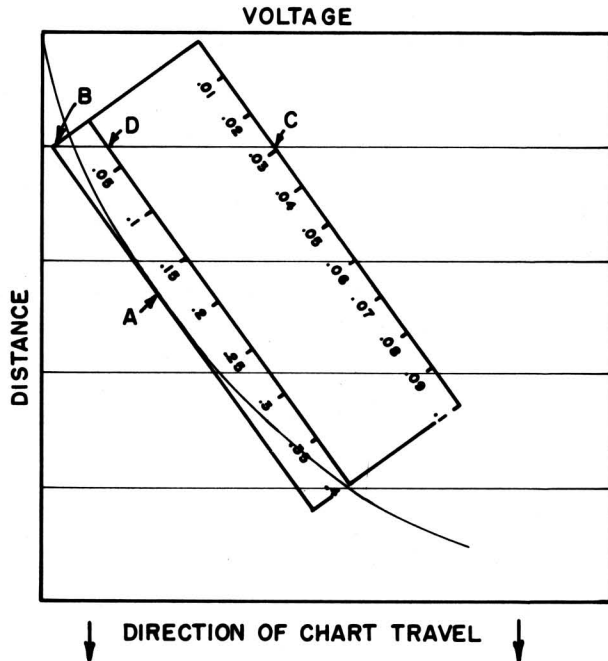


Fig. 5 - Use of slope calculator.

The calculator is slid along its base line until the origin B rests on a horizontal chart line. The slope in volts per crystal centimeter is given by the reading C where the upper scale is intercepted by the same horizontal chart line. Slopes greater than 0.1 must be read on the lower scale. When the horizontal chart line intersects both scales they agree (points C and D).

Fig. 6 shows a nomograph used to obtain the resistivity without calculation using the slope value obtained as above. A straight edge is laid between this slope on scale S (point A) and the diameter on scale d (point B). In the case of ingots prepared in a crucible of standardized size, point B may be obtained via scale L which relates length along the ingot

to its diameter in terms of an established taper:  $d = 0.0302 L + 1.512$  where d and L are in centimeters. The intersection of the straight edge with scale Q is marked (point C) and this point is joined to the correct current value on scale I (point D). The intersection of the new straight edge position with scale  $\rho$  gives the resistivity (point E).

It is also possible to measure resistivity by using a two-probe method in which the voltage drop is measured across two probes spaced a fixed distance apart on the current-carrying crystal. This double probe is then moved the length of the crystal by the motor mechanism. This method gives the resistance directly without the necessity of calculating the slope.

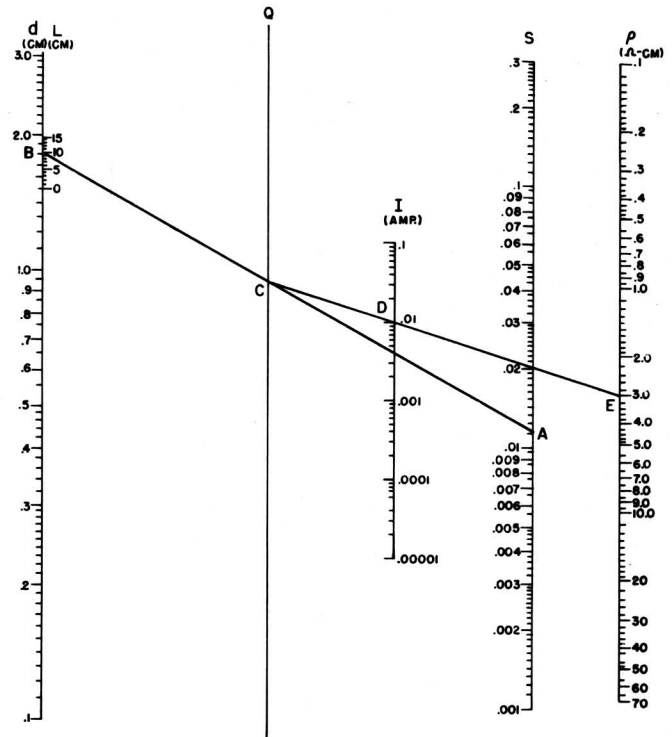


Fig. 6 - Resistivity nomograph.

For lower purity polycrystalline ingots, in which there are large fluctuations in resistivity due to grain boundaries and segregation, the one-probe method is preferable because the process of taking the slope brings in a visual averaging process which is likely to give a more realistic value of resistivity. Neither of these methods is subject to error due to voltage drops across the lead connections to the sample.

### Thermal E.M.F.

With minor modifications, the same mechanical scanning mechanism can be used to measure the thermoelectric potential along a crystal, and hence obtain information about the conductivity type (p or n). If a heated probe is touched to the surface of the semiconductor, the probe will go positive or negative with respect to an unheated soldered contact on the crystal accordingly as the semiconductor is n-type or p-type. A convenient way of providing a heated probe is firmly to attach the heating unit from a small pencil type soldering iron to the upper end of a brass rod acting as a probe. The lower end of the rod carries a small hardened steel ball for contacting the specimen. A temperature differential of 100 degrees C between hot and cold contacts on the crystal can easily be achieved. Since the thermoelectric power,  $dE/dT$ , is of the order of hundreds of microvolts per degree for good semiconductors, this gives an e.m.f. of 10 to 50 millivolts. This potential can be measured directly on the recording potentiometer, without the high impedance preamplifier since the thermal e.m.f. is a low impedance generator. It is convenient to bias the recorder with a fixed potential so that zero e.m.f. falls at mid-scale. Then up-scale readings indicate n-type material, down-scale readings indicate p-type.

### Hall Coefficient

The Hall effect deals with the transverse voltage that is produced when a conductor carries current in a magnetic field as shown vectorially in Fig. 7. The Hall coefficient  $R$  is defined by the equation

$$V = R \frac{IH}{t}$$

where  $V$  is the voltage produced when the current is  $I$ , the magnetic field is  $H$  and the thickness is  $t$ . In practical units,

$$R = 10^9 \frac{V t}{I H} \text{ (cm}^2\text{/coulomb)}$$

where the quantities on the right hand side of

the equation are measured in volts, centimeters, amperes and gauss, respectively.

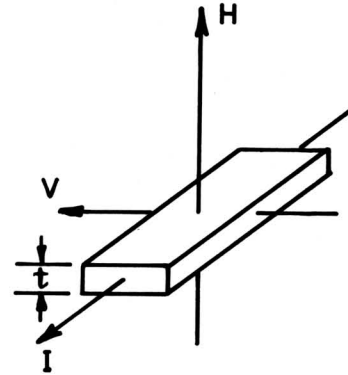


Fig. 7 - Hall effect for positive carriers.

For germanium in the resistivity range  $\rho = 10 \text{ ohm-cm}$  to  $0.1 \text{ ohm-cm}$ , the Hall coefficient ( $R$ ) is insensitive to temperature change near room temperature and is related to the carrier concentration by the simple expression

$$R = \frac{3\pi}{8} \frac{1}{ne}$$

where  $n$  is the carrier concentration (electrons or holes per  $\text{cm}^3$ ) and  $e$  is the carrier charge ( $\pm 1.6 \times 10^{-19}$  coulombs). Thus the sign of  $R$  gives the sign of the carriers (holes or electrons).

Since the conductivity is given by

$$\sigma = ne\mu$$

the product  $R\sigma$  is almost equal to the mobility ( $\mu$ ) and is called the Hall mobility. The true mobility is  $8/3\pi$  times greater or

$$\mu = \frac{8}{3\pi} R \sigma \text{ (cm}^2\text{/volt-sec.)}$$

Measurement of the Hall coefficient is relatively easy for germanium since for reasonable values of the variables,  $V$  will be of the order of millivolts. Three basic measuring circuits may be employed: d.c., single frequency a.c. or double frequency a.c. The last is undesirably complex for the present purpose.<sup>2</sup>

<sup>2</sup>B. R. Russell and C. Wahlig, "A New Method of Measuring Hall Coefficients", *Rev. Sci. Inst.*, Vol. 21, pp. 1028-1029 (Dec. 1950).

With either the d-c or the a-c method, a single probe may be employed at the center of the crystal, thus simplifying the sample preparation. Instead of a second opposing contact, a voltage divider is connected across the ends of sample and adjusted for balance with no magnetic field. This convenience is obtained at the expense of a loss in sensitivity by a factor of two since the voltage ( $V'$ ) measured this way is one half the Hall voltage ( $V$ ) in the formulas. Thus, for this method of measurement

$$R = 2 \times 10^8 \frac{V' t}{I H}$$

Fig. 8 shows the arrangement for d-c measurements. A magnet of several thousand gauss and one-inch diameter pole pieces is convenient. It may be electrically energized or permanent. If the latter, it should be convenient to remove the sample from the magnetic field to balance the voltage divider. Sample dimensions of about 1 mm thick, 2 mm wide and 1 cm long are convenient. The length should be at least three times the width to reduce interference from the end contact on the Hall voltage. End contacts are easily applied by soldering using soft solder and an acid flux. The center contact should be soldered, too, although a pressure contact may be used if a suitable holding jig is employed. Since the manually-

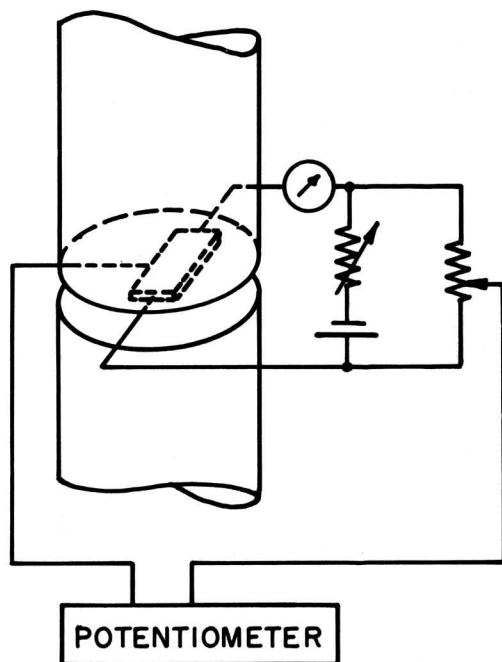


Fig. 8 - D-C Hall effect arrangement.

balanced potentiometer is read only at balance, where it has a very high input impedance, this contact resistance is not critical. Readings should be taken for both directions of sample current and the results averaged to minimize the effects of residual asymmetries. The crystal current should be read with the sample in the magnetic field since the latter affects the crystal resistance.

The advantages of a-c measuring techniques are mostly ones of convenience. A direct reading output meter may be employed and the value is automatically the average of both current directions in the sample. Fig. 9 gives the arrangement for a-c measurements. Less hum pickup is usually obtained with the center

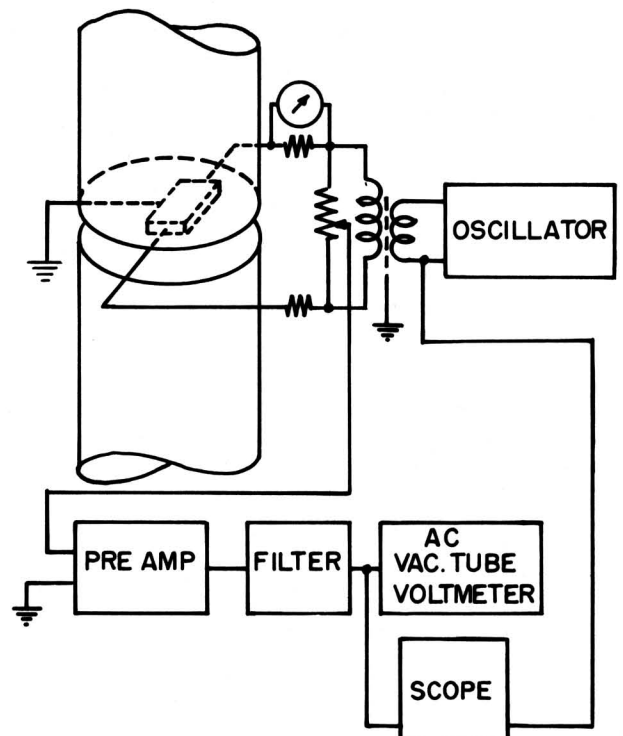


Fig. 9 - A-C Hall effect arrangement.

crystal contact grounded and the signal taken from the voltage divider. The oscillator should be connected through a transformer which is chosen and connected so as to minimize capacitance coupling from primary to secondary. Since the a-c current meter will probably have appreciable resistance, it is best to preserve balance by adding a resistor as shown.

It will often be found in using the one-probe method that the output contains appreciable amounts of second harmonic that cannot be

balanced out with the voltage divider. This is due to harmonic generation by the end contacts which are not strictly ohmic. The voltage divider does not carry this harmonic component. A solder of 49% lead, 49% tin and 2% antimony will minimize rectification at the contacts for n-type germanium. Any residual harmonics can be reduced by filtering.

A tuned amplifier may be used as the filter. In particular, use of a synchronous detector type amplifier is attractive because the synchronizing signal is available from the oscillator. Care must be taken, however, that the amplifier does not respond to harmonics, a common situation even in narrow band amplifiers. A simple filter that has proved useful is an inductance and capacitance tuned to parallel resonance at the measuring frequency and connected in series with a resistance ten times their resonant impedance. The input signal is fed across the series combination and the output is taken from the tuned circuit.

### Lifetime and Diffusion Length

n-type germanium conducts electricity primarily because of the free electrons in the conduction band of energy. A smaller concentration of free holes in the valence band of energy is normally in equilibrium with these electrons. Both the electrons and the holes contribute to the conductivity according to their respective mobilities. In germanium the electron mobility is 2.1 times the hole mobility. Except for this, the holes may be regarded as carriers equivalent to electrons with a positive instead of a negative charge. Germanium has the property of being readily injected with minority carriers in excess of the equilibrium number. Thus in n-type germanium, excess holes may be introduced through a p-n junction or a metal probe. Hole injection is the principal function of the emitter in a transistor. The excess minority carrier concentration decays exponentially with time due to recombination with carriers of the opposite sign. The decay constant or lifetime is an important parameter in determining transistor performance. It is simply related to a quantity called the diffusion length  $L$  which is the mean distance that the

holes diffuse before recombination. A complete symmetry exists between p- and n-type germanium and the above considerations apply to p-type material where the roles of electrons and holes are interchanged.

The method to be described<sup>3</sup> measures diffusion length  $L$  directly. The results are readily converted to lifetime values since

$$L^2 = D\tau$$

where  $D$  is the diffusion constant.  $D$  in turn can be obtained directly from the mobility using the relationship

$$D = kT\mu/e.$$

Using the accepted values of drift mobility for germanium at room temperature,  $D$  comes out to be 44 cm<sup>2</sup>/sec for holes and 92 for electrons. There are various ways of measuring lifetime and diffusion length. Although some are more accurate than the one to be described, this method is best suited for routine application.

The apparatus required is shown schematically in Fig. 10. The lamp used is a ribbon filament type taking 40 watts at 8 volts (General Electric Co. type 5A/T8/1S.C. - 8v) and is powered by an 8-volt storage battery. The shutter is used to chop the light to enable a-c amplification. The center of rotation should lie in the plane determined by the optical axis and the filament and the shutter apertures should be sectors formed by radii from this center. Any convenient shutter speed will do, but a chopping frequency of 600 cps or higher will aid in eliminating 60 cps interference. The first lens should be of wide aperture.

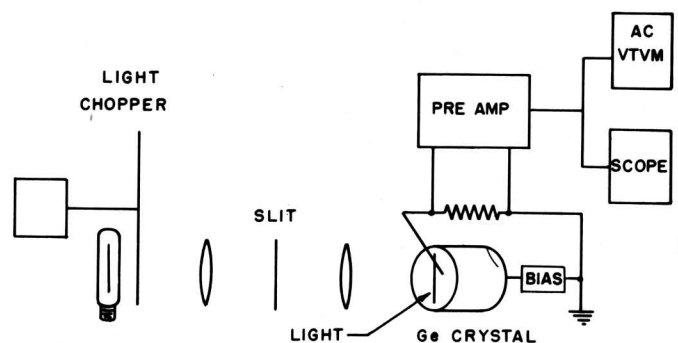


Fig. 10 - Arrangement for measuring lifetime.

<sup>3</sup>First described by L. B. Valdes at the Electron Device Conference, Durham, New Hampshire, June 1951.

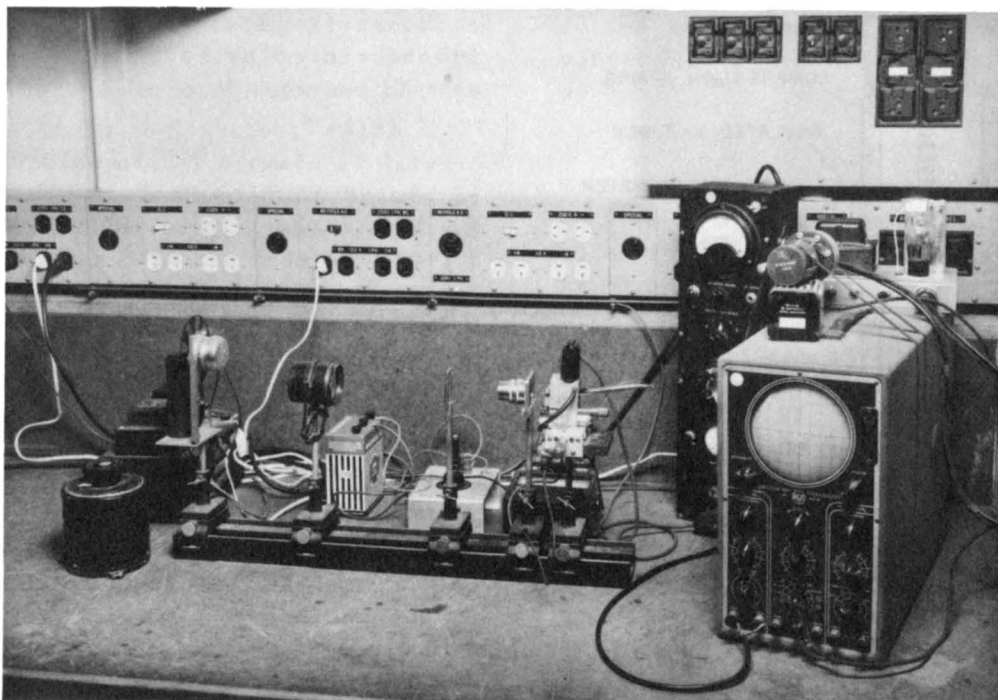


Fig. 11 - Equipment used in lifetime measurements.

Definition is not important and an ordinary condensing lens will do.<sup>4</sup> This lens images the filament which is about  $\frac{1}{4}$  inch long on a slit 0.002 inch wide with unity magnification. A second lens forms an image of the slit on the face of the crystal at a 3:1 reduction. Here good definition is required in addition to large aperture and an f/1.5, 1-inch movie camera lens is used.<sup>5</sup>

Provision is made for applying a pointed probe to the surface of the crystal and moving this assembly transverse to the optical axis by known amounts. The arrangement may be seen in the photograph, Fig. 11, and the mechanism is detailed schematically in the drawing of Fig. 12. Basically this is a platform spring loaded against a micrometer head. A toolmakers microscope base can also be utilized if available. A return connection to the crystal is also needed. A soldered contact is best, but a large area clamp will give equivalent results.

The measurement is made on the surface of the crystal. Since a diffusion length is desired

which is characteristic of the bulk material, care must be taken in preparing the surface to minimize surface recombination of the excess minority carriers introduced by action of the light. The surface of the crystal is ground flat if necessary on abrasive cloth and then given a finer finish by grinding with wet abrasive on glass. Only two grades of abrasive are needed. Aluminum oxide, supplied by American Optical Co. as No. 303 $\frac{1}{2}$ , is used first and No. 305 is used for finishing. This should leave a matte surface with no visible scratches; a higher polish is unnecessary for this purpose. Crystal flaws such as twin or grain boundaries will usually be clearly visible on this ground surface. The surface is then etched for one minute in a low recombination etch such as the CP-4 described by Haynes and Shockley<sup>6</sup> and rinsed with distilled water and then methanol. The etch is very corrosive and should be prepared, stored and used under a fume hood with care to avoid contact to the skin. The heat of reaction will be excessive in etching large pieces, but satisfactory results can be ob-

<sup>4</sup>Equally inexpensive is an f/1.9, 91.4 mm objective and mounting flange sold by Edmund Scientific Corp., 101 E. Gloucester Pike, Barrington, N. J. This eliminates mounting problems and gives satisfactory results.

<sup>5</sup>Wollensak Raptar.

<sup>6</sup>J. R. Haynes and W. Shockley, "The Mobility and Life of Injected Holes and Electrons in Germanium", *Phys. Rev.*, Vol. 81, p. 838 (March 1, 1951). Formula for the etch is 15 cc  $\text{CH}_3\text{COOH}$ , 25 cc conc.  $\text{HNO}_3$ , 15 cc 48%  $\text{HF}$  and 0.3 cc  $\text{Br}$ .

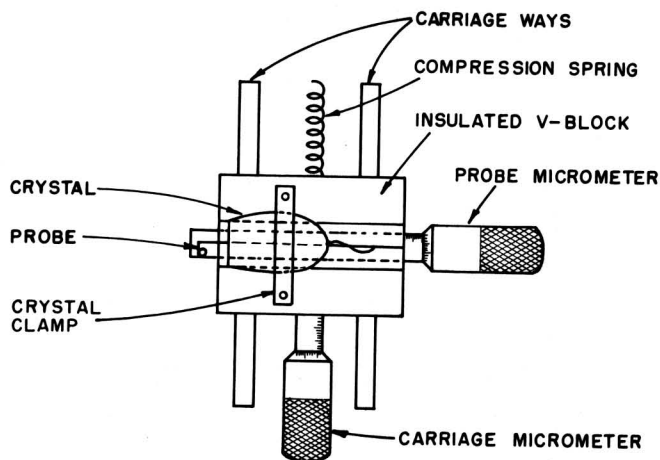


Fig. 12 - Schematic of crystal carriage for lifetime apparatus.

tained by water-cooling the exterior of the container. Polyethylene bottles which are commercially available make excellent containers for the etch although some other plastics can also be used. It should be stored in a well-capped bottle since the bromine is rapidly dissipated otherwise. Deterioration of the

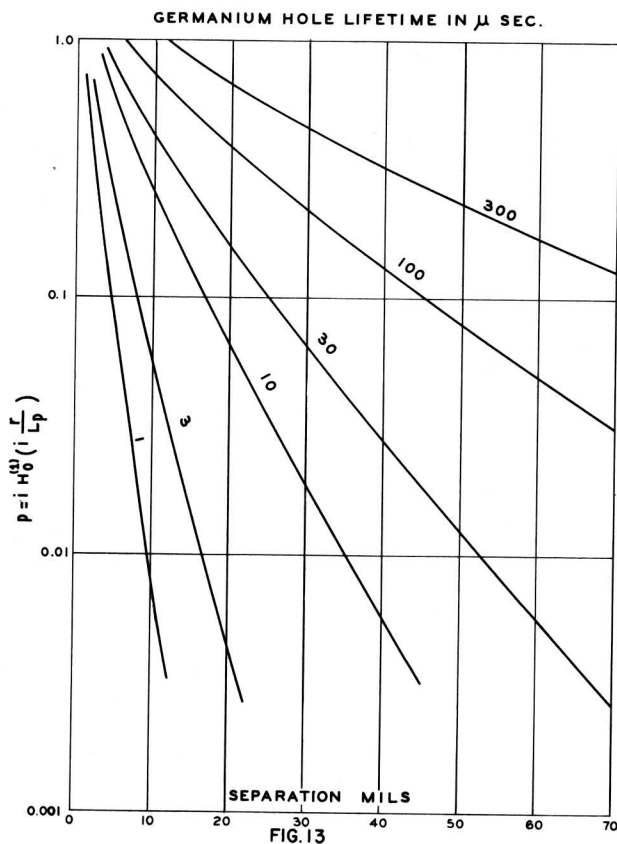


Fig. 13 - Lifetime calibration, 1-300  $\mu$ sec.

etch can be gaged by fading of its initial bright red color. A useful life of several days to one week is possible

After preparation of the surface, the crystal is clamped in its holder and the probe is placed in firm contact with the surface. The bias circuit shown in Fig. 10 is useful in determining when contact is made but is usually not used in the actual measurement. The electrical behavior of the contact may be stabilized by applying 10 to 30 volts a.c. in series with 50 ohms for one second between the probe and return connection. Either tungsten or phosphor bronze probes can be used since this does not constitute a forming treatment in the transistor sense.

A high input impedance is used at the pre-amplifier whose output is therefore proportional to the photo e.m.f. The signal is a maximum with the light on the probe and data are taken of output voltage as a function of distance. These are plotted on semi-log paper to the same scale as the calibration curves shown in Figs. 13 and 14. Since only relative amplitudes are significant on the ordinate scale, the cali-

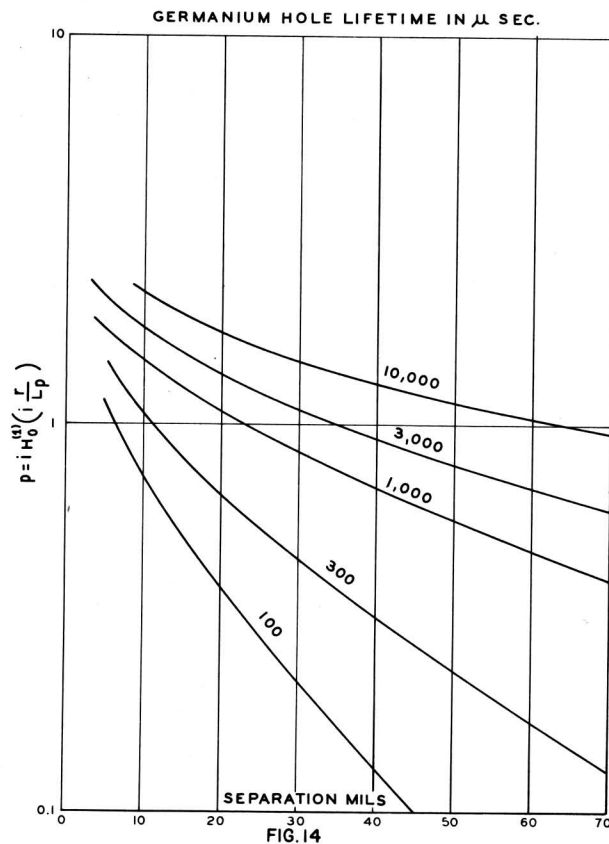


Fig. 14 - Lifetime calibration, 100-10,000  $\mu$ sec.

Calibration curves may be slid vertically over the data curves until a match is obtained. The lifetime is then taken as that used in the calculation of the particular calibration curve and marked on it.

The calibration curves were obtained by solving the differential equation for hole diffusion:

$$\nabla^2 p - p/L^2 = 0$$

where  $p$  is the excess hole density. The boundary conditions correspond to cylindrical symmetry since the line of illumination is the axis of a semi-cylinder of radiating flow lines if surface recombination can be neglected. The first order solution is a Hankel function.

$$p = i H_0^1(i r/L)$$

where  $r$  is distance from the line of light.

For various values of lifetime  $\tau$ , the corresponding values of  $L$  in mils were calculated using

$$L^2 = D\tau$$

each value of  $L$  then provided a curve of  $p$  vs  $r$  using the values of the Hankel function tabulated by Jahnke and Emde.<sup>7</sup>

For reliable results, it is necessary that the length of the line of illumination on the crystal and the distances from the point to the boundaries of the crystal be large compared with the spacing between point and light. It is also necessary that the width of illumination be small compared with this spacing. In practice, specimens  $\frac{1}{4}$  inch in diameter and  $\frac{1}{4}$  inch thick are adequate minimum dimensions. These are scanned over a distance of about  $1/16$  inch.

<sup>7</sup>E. Jahnke and F. Emde, TABLES OF FUNCTION, Dover Publications 1945, p. 236.

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