only when the lower donor level was filled. However, a rough calculation of the Fermi level from the resistivity data indicated that it is "locked-in" at the 0.33 ev donor level, even at dry ice temperature. If there is only a negligible change in Fermi level in going from say 195°K to 77°K, then it would seem difficult to explain the data in terms of a two-level model. At present we have no alternative to suggest. If both resistivity and optical data were available for samples which could be made n-type by gold-doping, perhaps more complete information would be forthcoming on the energy level scheme in gold-doped silicon.

Response times of the gold-doped samples are of order 10 μsec.[3] No evidence was found in this work of long response times or quenching effects that would indicate the presence of stable traps even at 20°K.

I am indebted to E. A. Taft and F. H. Horn for furnishing the samples used here.

---

[3] E. A. Taft and F. H. Horn (private communication).

PHYSICAL REVIEW VOLUME 94, NUMBER 6 JUNE 15, 1954

Diffusion of Impurities in Germanium*

W. C. Dunlap, Jr.
General Electric Research Laboratory, Schenectady, New York

(Received February 26, 1954)

A method is described for the study of diffusion of impurities in semiconductors; results are obtained by the observation of the p-n junction formed as the diffusing impurity penetrates the specimen. Studies have been made upon germanium using this technique, and comparisons with the radioactive tracer method have shown the p-n junction method to give valid results. Measurements on indium, gallium, aluminum, arsenic, boron, phosphorus, antimony, and zinc are described. The diffusion coefficients of these elements in germanium range, at 900°C, from 10^{-12} cm^2/sec to 10^{-9} cm^2/sec. The activation energy for bulk diffusion in germanium is about 2.5 ev, or 57 000 cal/mole. Applications are given for the study of the p-n junction method to the study of surface and grain-boundary diffusion. The method has also been applied to the study of new elements and their electrical activity in germanium. It is concluded that the rapidity with which results can be obtained by the junction method, and its applicability to elements not conveniently available in radioactive form make it a valuable adjunct to the radioactive tracer method for studying diffusion.

INTRODUCTION

The problem of the diffusion of atoms through a crystalline lattice is an old one, and one which has been approached in many different ways, both theoretically and experimentally.[1] Most of the past work has been done on metals, and much of the recent work on metals has been done with the radioactive tracer technique.[2]

In the present study, a new method has been applied to the study of diffusion in semiconducting crystals. These crystals have the property that their electrical properties are determined, in most cases, by the presence of very minute traces of impurities. In many of these crystals, some impurities render them p type, whereas others make them n type semiconductors. The type of conduction refers to the carrier present; in n type semiconductors, the current is carried by electrons, in p type semiconductors, the current is carried by positive holes.

The type of carrier can be determined by several methods: (1) Hall effect; (2) thermoelectric measurements; and (3) rectification probe measurements. The latter two methods are particularly suitable to the present purpose, since the desired information can be made to apply to very localized regions of the specimen, by the use of fine whiskers for probes. In particular, the region of transition between p and n type material can be located with a high degree of precision, even though it may be localized very close to the surface of the specimen.

In the present work, diffusion has been studied by means of the change in type of conductivity. To do this, one chooses the base material to be one of the type opposite to that prevailing when the impurity has diffused in. Thus, for studying the diffusion of indium into germanium, one chooses samples of n type material, heats them in contact with indium, and measures the depth of the p-n junction formed by the diffusion of indium into the germanium.

The plan of the present work, then, was to put various impurity elements of interest in contact with germanium, and to diffuse them in at different tem-

---

* Preliminary accounts have appeared by W. C. Dunlap, Jr., **86**, 615 (1952); D. E. Brown and W. C. Dunlap, Jr., Phys. Rev. **86**, 616 (1952); and W. C. Dunlap, Jr., and D. E. Brown, Phys. Rev. **86**, 417 (1952).

[1] R. M. Barrer, *Diffusion in and Through Solids* (Cambridge University Press, Cambridge, 1951).

[2] For a discussion of the radioactive method, see R. Hoffman, in *Atom Movements* (American Society of Metals, Cleveland, 1951).

peratures for different times, in order to determine their diffusion coefficients as a function of temperature. Information about the lattice structure can be obtained by means of the equation:

$$D = D_0 \exp(-E/kT). \quad (1)$$

Here D_0 is a constant of the material, E is the activation energy for diffusion, and k is Boltzmann's constant. The activation energy is a measure of the stiffness of the lattice, since it is the energy jump that an impurity atom must acquire before it can make a motion into a nearby vacancy. Details of the theory of diffusion can be found in reference 1.

In particular, a study was made of the diffusion rates of donor as compared to acceptor atoms, and some interesting conclusions were drawn.

Attempts were also made to apply the *p-n* junction method to the study of other types of diffusion, such as surface and grain boundary diffusion.

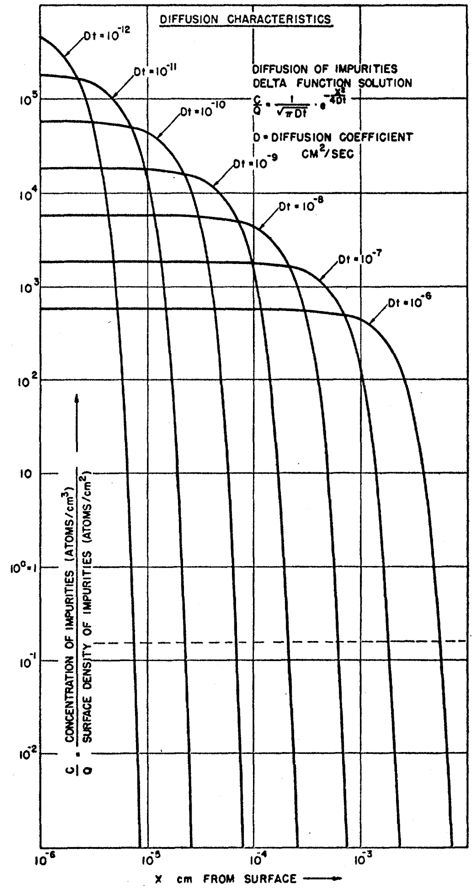

FIG. 1. Theoretical diffusion curves for one-dimensional diffusion, based upon the "constant-source" solution to the diffusion equation. The plot is on a log-log scale, with x being measured from the surface of the slab. The *p-n* junction, in the case of a semiconductor, is formed at the point where the curve crosses the horizontal line representing the impurity concentration in the base material.

As part of the work, a systematic study was made of the *p-n* junction method as compared to the radioactive tracer method, for reliability, accuracy, and rapidity.

METHODS OF MEASUREMENT

A basic assumption in this work was that of one-dimensional geometry; that is, the penetrations dealt with were always small compared to the lateral dimensions of the samples, and to the thickness of the samples. It was also assumed that the initial impurity distribution, at time zero, was zero except at the surface of the sample. This we can call the "constant-source"[3] problem, if we assume we are dealing with a constant number of impurity atoms Q present in or on the sample.

The diffusion equation is:

$$D[\partial^2 C(x)/\partial x^2] = \partial C(x)/\partial t, \quad (2)$$

where D is the diffusion coefficient, $C(x)$ is the concentration of the diffusing impurity; $C(x)$ is related to the total Q by the relation

$$Q = \int_0^\infty C(x)dx. \quad (3)$$

The solution of the diffusion equation for the constant-source problem is

$$C(x) = Q(\pi Dt)^{-\frac{1}{2}} \exp(-x^2/4Dt). \quad (4)$$

A plot of the form of the advancing diffusion front at various times (actually the parameter $(Dt)^{\frac{1}{2}}$ makes a more useful one for plotting) is shown in Fig. 1. Both the concentration and the distance are on a logarithmic scale. On this scale the shape of the curve does not change with time. The curve is simply translated down and to the right. The concentration representing that of the impurities in the base material is shown as a straight horizontal line. At the point where the curve crosses this line, the *p-n* junction occurs. If the *p-n* junction depth is x_0, and the base concentration C_0, then

$$x_0 = 2(Dt)^{\frac{1}{2}}\{\ln[Q/C_0(\pi Dt)^{\frac{1}{2}}]\}^{\frac{1}{2}}. \quad (5)$$

For example, if $C_0 = 10^{16}$, $Q = 10^{17}$, $(Dt)^{\frac{1}{2}} \sim 10^{-3}$ cm, then we can approximate

$$x_0 \approx 8(Dt)^{\frac{1}{2}}. \quad (6)$$

The quantity C_0 is easily determinable with good accuracy from Hall effect measurements. While the Hall measurement gives actually the density of electrical carriers, for germanium at room temperature these are all ionized, so that this is also the number of impurity centers.

$$C_0 = 7.4 \times 10^{18}/R, \quad (7)$$

where R is the Hall coefficient in cm³/coulomb.

---

[3] See reference 1, p. 44.

It is seen from Eq. (6) and Eq. (5) that the *p-n* junction moves very nearly according to a $\sqrt{t}$ law. This gives a means of checking the theory experimentally.

For exact solutions for the diffusion coefficient from Eq. (4), a method of successive approximations has been used. Since the complicating term $(Dt)^{\frac{1}{2}}$ enters logarithmically into the solution for D, the process rarely requires more than two such steps. Indeed, for an accuracy satisfactory in many experiments, a simple guess at C_0, Q, and D suffices to give D accurate to better than a factor of 2.

Another diffusion problem to which the present one is related is the "step-function" problem. In the application of this method, the diffusing impurity is present in large quantities at the plane $x=0$. As diffusion proceeds, the diffusing impurity enters the crystal, but the concentration at the surface presumably does not change. This method leads to the following solution of the diffusion equation.

$$C(x)=C_0'\{1-\mathrm{erf}[x/2(Dt)^{\frac{1}{2}}]\}, \qquad (8)$$

where C_0' is the concentration at the surface.

For the case that we have here, $C=C_0$, $x=x_0$, with $C_0 \ll C_0'$, the error function can be replaced by the form:

$$\exp(-x^2)/\pi^{\frac{1}{2}}x. \qquad (9)$$

Thus, the solution in the step-function case reduces to the form very similar to that for the constant-source case,

$$x_0 \approx 2(Dt)^{\frac{1}{2}}[\ln(C_0'/C_0)]^{\frac{1}{2}} \approx 6(Dt)^{\frac{1}{2}}, \qquad (10)$$

if $C_0' \sim 10^{20}$, $C_0 \sim 10^{16}$. It is interesting that for many practical cases, the "constant source" and the "step-function" approximations yield the same result [compare Eqs. (10) and (6)].

In general, we are not able to use the step-function solution for measurements of diffusion by the depth of the *p-n* junction. The major reason is that the quantity of diffusing impurity must be kept small. This is important because we wish the entire layer from the surface to the *p-n* junction to be a true diffusion zone. This means, presuming that the impurity may alloy with or dissolve into the germanium, that all secondary phases, alloy regions, etc., must be negligible in thickness compared to the true diffusion zone. If the amount of impurity is limited to a few micrograms/cm^2, simple calculations show that the "alloy zone" is actually thin compared to the diffusion zone.

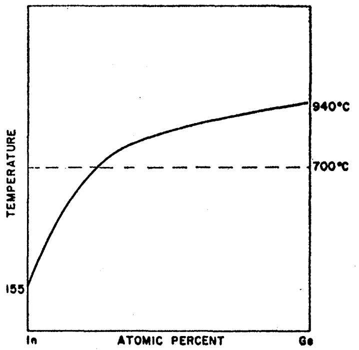

FIG. 2. Phase diagram showing the liquidus curve of indium-germanium.

For example, if 5 micrograms of indium are heated in contact with 1 cm^2 of germanium wafer, at 700°C, it can be estimated from a phase diagram, such as that of Fig. 2, that at that temperature the indium will dissolve germanium until a concentration of $\sim$20 percent indium is reached. This will mean an "alloy zone" of about 2 microns. In the design of the experiment then, one must heat for a sufficiently long time so that the diffusion distance x_0 is large compared to micron. This is hardly a limitation, since much larger diffusion distances than this must be used to attain reasonable experimental accuracy.

The fact that the surface layer, even though liquid initially, attains a state very shortly in which the impurity is in saturated solid solution with the germanium, means that we can be sure that the observed *p-n* junction arose by diffusion and not by liquid penetration.

Thus, for measurement purposes, one uses techniques that are somewhat complementary to those used when junctions are made for technical purposes.[4] There the "step-function" solution is more applicable, because large amounts of impurity are applied, there is a considerable penetration by solution and alloying, and usually conditions are chosen to make the diffusion zone thin in comparison with the alloy region. In technical fused junctions, also, the "recrystallization" region plays a major part, whereas, for measurement work, it can be neglected, as long as Q is small.

The step-function solution may apply to diffusion in a grown *p-n* junction, where the impurity of interest changes its concentration abruptly as a result of the doping procedure used. McAfee, Shockley, and Sparks[5] studied diffusion in germanium using such junctions. In their work, the motion of impurities was studied through the changes of capacity of the *p-n* junction used as a rectifier. Although in principle the same problem could be studied by the *p-n* technique dealt with in the present paper, there is a major drawback, the lack of a reference for measurement. In the case of measurements from the surface, the surface itself serves as a convenient base. In the grown junction, there is no such base. Although a base from which to measure can be set up, all the schemes for doing so that have been envisioned to date, suffer from such

---

[4] A discussion of "fused-impurity contact" or "alloy" junctions is given by J. S. Saby and W. C. Dunlap, Jr., Phys. Rev. **90**, 630 (1953).

[5] McAfee, Shockley, and Sparks, Phys. Rev. **86**, 137 (1952).

poor accuracy that much of the validity of the measurement is lost.

The work of McAfee, Shockley, and Sparks revealed an interesting discrepancy between the diffusion coefficients determined by their method, and those determined by the present method. The discrepancy appears to depend upon the fact that no surface was close to the point of diffusion in their *p-n* junction bars, whereas diffusion actually proceeds from the surface in the present method. The discrepancy is about a factor 1000 smaller diffusion coefficient in their measurements, than in those found from the present type measurement.

EXPERIMENTAL

Samples

The diffusion studies reported here were made, in the main, with single crystal samples of germanium, some kindly furnished by R. N. Hall, others made by the author. These samples were in the form of flat plates, cut square, ground, polished, and etched. For the study of donor elements, high-resistivity *n* material was often used for starting material, and the thermal conversion arising from the diffusion heating was used to give *p* type specimens of about 1 ohm cm resistivity.

For the study of acceptor elements, generally, low-resistivity *n* type material, in the range 0.1–0.2 ohm cm was used. These values were used to minimize thermal conversion effects such as occur with higher-resistivity samples.

Determination of the Depth of the *p–n* Junction

Determination of the depth of the *p-n* junction was generally done by cutting off the sample at a small angle, generally 5 or 10°, and measuring the distance along the slope from the original surface to the junction.

The method requires the use of flat, highly polished plates. These were accurately ground, and the angular surface was also prepared, using the hand grinding machine shown in Fig. 3. The hand grinder contains a piston of polished, hardened steel, turning in a cylinder of similar metal. The sample is mounted on an end piece, which may be a flat, or it may be a beveled piece of the proper angle. Some preliminary information is generally needed so that the cut is deep enough and of the right angle that the junction is actually exposed, and at a suitable distance for accurate measurement.

A problem that may be severe in some cases, is the warpage of some germanium surfaces at high temperatures of diffusion. This effect is, presumably, similar to that reported by Gallagher,[6] namely that the stress of supporting their own weight, while inside a cylindrical tube, at temperatures of 900°C or so for periods of days can lead to a curvature of the originally flat surface. Again, this does not appear as an error of alarming degree for measurements of the accuracy desired here. However, support for the sample on a flat surface is generally desirable.

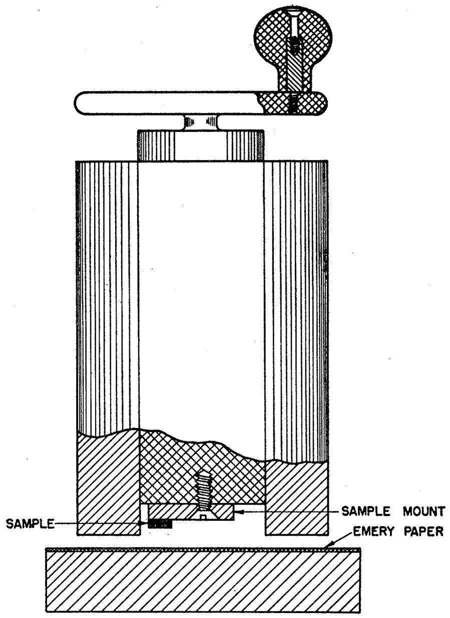

FIG. 3. Cut-away view and section of hand-operated precision grinder used in diffusion measurements, both in the radioactive tracer work and in the *p-n* junction work.

Figure 4 shows the arrangement for making the tests on detection and location of the *p-n* junction. The test probe was mounted on a micromanipulator originally designed for work with point-contact transistors, and having a sensitivity of 0.1 mil per division.

Most of the measurements were made with a thermoelectric probe as the detector of the *p-n* junction. The point used was a tungsten carbide needle, sharpened to a fine point. The needle was mounted in a pin vise, close to a small heating coil. The base of the sample and the pin vise were connected to a recording dc millivoltmeter, whose direction of deflection indicated the type of germanium.

Some considerations in the use of the method are:

1. The diffusion coefficient depends upon the square of the *p-n* junction depth, and care must be exercised all through the measurement for best results.
2. The junction depth is determined from the distance to the junction, relative to the point of intersection of the ground surface and the original surface. This location had to be done visually, through the binocular microscope; the location is based upon the difference in visual appearance of the original polished surface and the new ground surface. The larger the angle for the cutting, the more clear the line of intersection; and, conversely, attempts to increase sensitivity by decreasing the angle of grinding are partially self-defeating because of increased fuzziness of the line of intersection.

---

[6] C. J. Gallagher, Phys. Rev. 88, 721 (1952).

3. Considerable attention must be given the location of the *p-n* junction itself. Besides the expected uncertainties due to roughness of the ground surface, there is a tendency of ground surfaces on the *n* type material to show up *p* type. This leads the measured value of the junction depth to be somewhat too small for measurements on donors, too large for acceptors. The effect is minimized if low-resistivity material is used for the base.

4. It is estimated that the *p-n* junction depth can be measured to about 10 percent accuracy at 10 mils penetration, 25 percent at 1 mil penetration. In most experiments, the heating time was chosen to produce penetrations of at least 1 mil.

Evaluation of Q

It is assumed that the quantity Q, the total number of impurity atoms deposited on the sample/cm^2, remains constant, in order to use Eq. (4) and its derivatives. This assumption is in general not valid. Evaporation often leads to departure of much of the volatile impurities in the first few seconds or minutes of heating, and surface diffusion can also lead to a spreading of the impurity around the sample. Evaporation, followed by chemical reaction or diffusion, can lead to a loss of most of the impurity into the walls of the heating chamber, in this work, quartz.

A virtue of the method used here, however, is the insensitivity of the method to the exact value Q. This point was demonstrated experimentally in the following way. Two similar specimens of germanium were prepared, each evaporated with radioactive antimony at the same time, in the same way. A third similar specimen was also used, but unevaporated. One evaporated specimen was sealed in a quartz tube by itself, the other two in another quartz tube. Both tubes were heated together at the same temperature, for the same time. The tubes were cut open, and each sample was measured for penetration of the *n* type layer into the *p* type base. All three were equal, to ±10 percent. Thus, the pure sample acquired from the evaporated one sufficient antimony to receive the same depth of junction. Likewise, the loss of antimony did not prevent the junction being at the same depth as in the sample heated by itself.

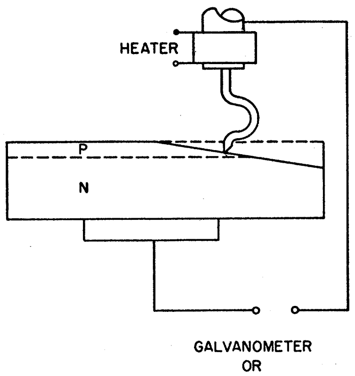

FIG. 4. Schematic diagram showing the method used for locating the *p-n* junction on germanium samples.

The loss of impurity from the sample has been checked for a number of the important impurities, particularly antimony, zinc, and indium, which were available in radioactive form. It was found by etching out the insides of the quartz tubes used for heating, and checking both samples and etching residues, that at least 50 percent of antimony could be found on the sample after the typical diffusion experiment, heating at 850°C for 16 hours. Zinc, however, and particularly indium, combine with or diffuse into the quartz walls at such a rate that only a small fraction of the originally deposited material is found on the sample. Attempts to counteract this by increasing Q may well lead to errors because of increased alloy penetration, contamination and roughening of the surface, etc.

Further information on the evaluation of Q is given under the headings for each impurity in the next section.

OTHER FACTORS IN DIFFUSION EXPERIMENTS

Two important factors for all diffusion experiments are the exact manner of heating the specimens, the atmosphere, and the type, uniformity, and degree of temperature control and measurement of the furnaces used.

The diffusion measurements were carried out almost exclusively with small quartz tubes to hold the samples and protect them from oxidation. Each sample was sealed in a separate quartz tube, about 4 inches long and $\frac{3}{8}$ inch in diameter. These tubes were all cleaned in hydrofluoric acid and well rinsed and dried before sealing in the samples. They were then baked out at 350°C, and 15 cm pure dry argon added. The tubes were then sealed off. Cleanliness of the tubes was of extreme importance, but very difficult to guarantee. Because of the extreme sensitivity of germanium to impurities, even a trace of an element that diffuses faster than the one under study may lead to a completely erroneous result.

The furnaces in which the heating was done were nichrome wound, tubular furnaces, with a single winding whose density of turns increased towards the ends to compensate for end losses. These furnaces were found to hold up well for long periods when used at temperatures of 1000°C and below. The length, 24 inches, was sufficient to furnish a zone about 6 inches long in which temperature was uniform to several degrees C.

Temperatures were controlled from iron-constantan thermocouples, placed very close to the sample tube. These couples were used only for control of the regulators. Actual furnace temperatures were obtained periodically during the diffusion run, by use of a separate calibrated thermocouple. This was one of a group of six iron-constantan thermocouples, each used for a short period of time, discarded, and replaced by a new calibrated thermocouple. This procedure was done in order to avoid errors due to drift in calibration of thermocouples. All thermocouples were calibrated by the thermal standards section of the General Engineering Laboratory, General Electric Company.

The furnaces were all regulated by means of Brown Pyrovane electronic controllers. To each had been added an "anticipator," consisting of a dummy thermocouple, and a flashlight bulb. This device, which is a standard one, permits a greater degree of control of furnace temperature, if properly used. Even with these precautions, it was found very difficult to maintain a uniform measured temperature in a diffusion furnace for a period of a week or so at, say, 900°C, with uncertainties of less than ±2°C. The over-all temperatures specified are thought to be accurate to about ±5°C.

COMPARISON OF THE *p-n* JUNCTION METHOD WITH THE RADIOACTIVE TRACER METHOD

It was desirable to compare diffusion results obtained with the *p-n* junction method, with results on the same specimens obtained with the radioactive tracer method. For this purpose several wafers of single crystal germanium were ground to a high degree of polish and flatness, and coated with a thin evaporated layer of antimony, about 1000A thick. This antimony was Sb^{124}, a radioactive isotope with half-life of 60 days. The samples were heated in the usual way at temperatures ranging from 600 to 900°C. The heating times were chosen to give a reasonable penetration; because of the difficulty of removing thin layers accurately, the penetration was chosen to be at least several mils on all samples.

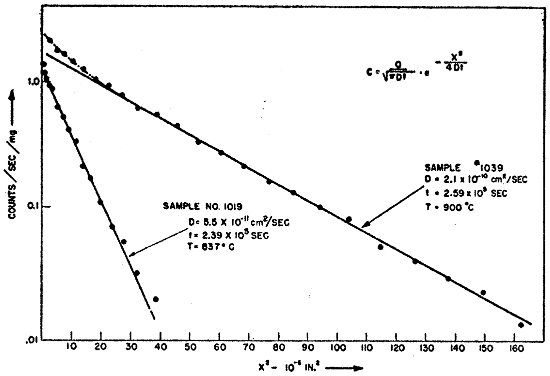

FIG. 5. Diffusion results on germanium obtained by radioactive tracer technique using Sb^{124}. The counting rate per unit weight of germanium is plotted against the square of the distance from the surface. According to Eq. (4) of the text, this should be a straight line. The diffusion coefficient is determined only by the slope of the line.

The samples were then ground on the grinder of Fig. 3. The grinding head was the one normal to the axis, so that the layers parallel to the surface could be removed. The face opposite the one to be ground off was first itself ground slightly to minimize effects of lack of parallelism. The activity was also removed from the opposite face and all the edges. Layers generally 0.2–0.3 mil were removed at a time. The amount removed was determined by micrometric measurements of the sample and base to which it was waxed. Also the weight of this combination was measured after each grinding. Weighing was found to give the most accurate results.

The grinding was done into sheets of fine grade emery paper. Care was taken that all the ground material was actually in or on the paper. The activity of the paper was determined by placing in a standard position in a scintillation counter, using an anthracene crystal for counting beta rays.

No corrections were made for the absorption of the activity in the powder while on the paper. It was found that if the layers removed were equal in thickness, the absorption would introduce a constant factor to be applied to give the correct activity. This corresponds to a translation of the log activity *versus* x^2 curve without change of slope and hence without effect on D.

The activity in the sample could be reduced to an absolute basis by using standards consisting of dilute solutions placed on similar pieces of emery paper, dried and coated with plastic to prevent loss of loose material.

The results of the radioactive tracer studies are summarized in Figs. 5 and 6. Figure 5 shows the counting rate per unit weight of germanium removed, plotted against the square of the distance from the original surface. This is based upon the formula of Eq. (4) and the assumption that the counting rate is proportional to the concentration of the antimony in the germanium. The good linearity in Fig. 5 is an excellent check on the validity of the theory.

Each time the surface was ground off, the new surface was checked for *p-n* characteristic, using the thermoelectric test method. Finally, the *p-n* junction was reached. This depth was then recorded, and the diffusion coefficient determined from Eq. (5). The results are indicated in Fig. 6. It can be seen that there is good agreement between the two methods. In general, the *p-n* junction method gave slightly smaller values of D than the tracer method. This might be ascribed to the slight effect that the surface has in contributing p type material. This would minimize the penetration, and give smaller D.

In principle it is possible from the absolute concentration of antimony to answer the question as to whether the diffusing antimony atoms are all electrically active. The good agreement between the two methods of measurement is one indication of this. Actually, direct comparison is difficult because of the large errors of determining the absolute antimony concentration in thin layers, particularly when the concentration is varying rapidly.

MEASUREMENTS ON THE VARIOUS IMPURITIES

Antimony

In this section is given a short discussion of the particular techniques applicable to each element.

In the case of antimony, which was more extensively studied than any other element, the major problem was determination of Q. Most the work with antimony was done with radioactive antimony 124. Use of the radioactive tracer is convenient for measurement of Q, even though the standard techniques for getting D by the tracer method are replaced by the *p-n* junction method.

When ordinary antimony was used, the evaporation was usually done upon a glass slide holding the sample. The slide was weighed on a micro balance before and after evaporation. Generally, the weights involved were about 10 microgram/cm^2, or about 200 microgram for the typical slide.

Because of the good retention of antimony on the sample, the values of Q obtained were relatively significant, and Eq. (5) could be used with safety.

Arsenic

Arsenic was studied less extensively than antimony. In most of the experiments, a tiny speck of arsenic was simply added to the quartz tube at the time of sealing. Equation (6) was used to determine D.

Phosphorus

A similar procedure to that of arsenic was used in the case of phosphorus. In these three cases above, ordinary cp chemicals were found to be of adequate purity. Their segregation characteristics and diffusion coefficients are such that the only element likely to cause trouble is one of the other two, and it would have to be present as a rather high percentage impurity to cause much trouble.

Zinc

For the zinc measurements, Zn^{65} was available, and some work was also done with high purity Johnson-Mathey zinc (about 99.99 percent). Unfortunately, zinc was found to be one of the elements most likely to disappear into the walls of the quartz tube during heating. Equation (6) was used.

Gallium

Gallium was deposited as an evaporated film on most of the samples. Weighing of the film was used for most of the experiments. Gallium has a lower vapor pressure than indium or zinc, but much of it is still lost to the quartz at the higher temperatures of diffusion heating.

Equation (5) and Eq. (6) were both used for measurements on gallium.

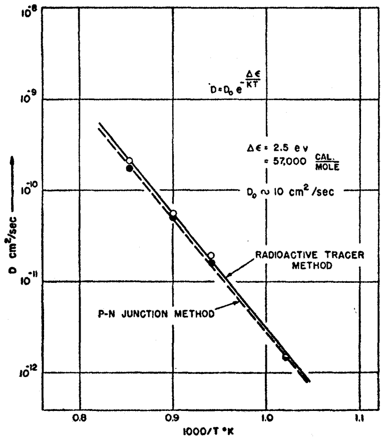

FIG. 6. Diffusion coefficient of antimony in germanium plotted *vs* the reciprocal temperature. Results were obtained both by the *p-n* junction method and radioactive tracer method on the same samples. Agreement between the two methods is seen to be good.

Aluminum

A number of attempts were made to determine the diffusion coefficient of aluminum into germanium, without success. The troubles apparently lay in the oxidation of the very small amounts of aluminum deposited by evaporation on the samples. Very high resistance layers were generally observed when probe tests were attempted on these surfaces.

Indium

As in the case of antimony, most of the work with indium was done with radioactive material, in this case In^{114}, which has a 48-day half-life. The surface activity of the sample before diffusion again could be used for accurate determination of the initial Q. In the case of indium, however, so much of the indium was lost to the quartz during diffusion, that the utility of this value is questionable. Equation (5) was used, however, on the belief that at most temperatures the indium would not be lost so fast that the initial penetration, which determines the final penetration, to a great extent, is that given by the initial Q, Eq. (5) was used for most of the work.

Boron

Boron was deposited pyrolytically upon the germanium samples. Although weighings were made in order to determine Q, it was found more precise to determine thickness of the films from their interference properties. For this purpose, one of the samples was etched at one end to remove the boron, using hot concentrated nitric acid for a few minutes. This made a region where the fringe depth was zero. By counting fringes, and comparing with a standard step gauge for interference colors, a good estimate could be obtained for the Q in the case of boron.

RESULTS OF THE p-n JUNCTION MEASUREMENTS

Tests of the $\sqrt{t}$ Relation

The $\sqrt{t}$ relation that follows from Eq. (4) was tested using radioactive antimony. The results obtained are shown in Fig. 7. It is seen that the agreement with the $\sqrt{t}$ law is only fair. The initial penetration follows this law quite closely. The deviations are probably due to the loss of antimony from the system by evaporation and diffusion. Thus, these effects appear to be a limitation on the accuracy of the measurements.

Results of Measurements on Various Impurities

Figure 8 shows results obtained on the various impurities at temperatures ranging from 600°C to 900°C. The lines describe the results to a good approximation, considering the rather large errors in measurement of x_0, the uncertainty in Q values, uncertainties in temperature measurement and control, and other effects already discussed.

The lines shown are nearly parallel, and have a slope about the same found for antimony by the radioactive tracer method, i.e., 2.5 ev, or 57 000 cal/mole.

Boron appears to give somewhat anomalous results, in contrast to all the others. Boron diffusion appears to be rather rapid at high temperatures, slow at low temperatures; thus the activation energy appears to be higher. A possible reason for this behavior lies in the fact that boron does not alloy easily with germanium, as do all the other elements studied here. Thus, some of the slowness of diffusion at the lower temperatures, may be due to lack of good "contact" between the film of boron and the crystal.

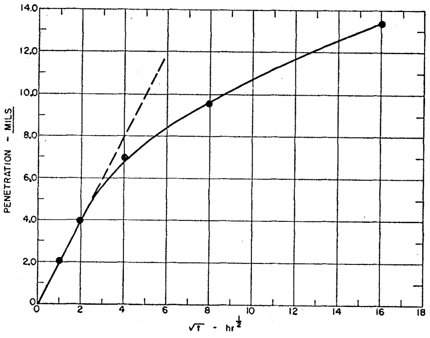

FIG. 7. Penetration of the p-n junction into germanium as a function of time of heating. The dashed line is the theoretical $\sqrt{t}$ law predicted by diffusion theory. Agreement is considered fair.

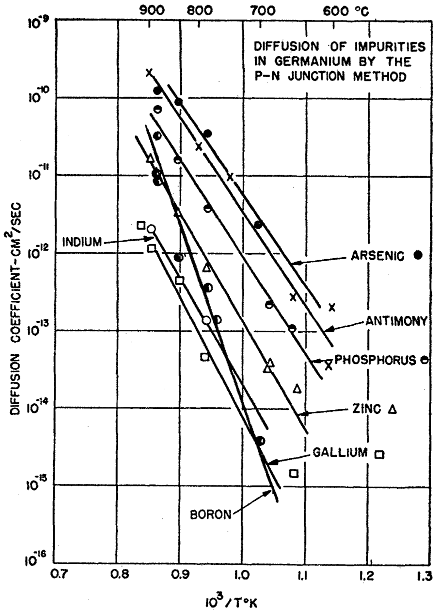

FIG. 8. Diffusion results for various elements, based upon p-n junction measurements.

DISCUSSION

Besides the activation energy E, another parameter of interest is D_0, the "frequency factor" in the diffusion equation. This value is obtained by extrapolating the diffusion curve to the axis $1/T=0$. From Fig. 6 it is found that D_0 is about 10 cm²/volt sec for germanium. A similar value is found from Fig. 7, although this is probably not as accurate.

A use of the experimental value of D_0 is in checking validity of diffusion data, as described by Nowick.[7] Thus, diffusion through cracks, imperfections, or other agencies than the pure bulk diffusion effect show up as a departure from the "Langmuir-Dushman equation,"[8] or one of its successors. The equation used by Langmuir and Dushman was

$$D_0 = a^2E/N_0h, \tag{11}$$

where a is the interatomic spacing in cm, E is the experimental activation energy, N_0 is Avogadro's number 6.06×10^{23}, and h = Planck's constant. Although this equation has been supplanted by more rigorous equations, most of them involving such parameters as the entropy of diffusion and the rigidity modulus, it still remains a useful tool for qualitative evaluation of diffusion data.

According to Eq. (11), D_0 for germanium should be about 0.3 cm²/sec. The agreement with the experimental extrapolated value of 10 cm²/sec is satisfactory, considering that in many cases of invalid data, the disagreement is many orders of magnitude.

---

[7] A. S. Nowick, J. Appl. Phys. **22**, 1182 (1951).

[8] I. Langmuir and S. Dushman, Phys. Rev. **20**, 113 (1922).

Another factor of importance in considering D_0 is the possibility of a temperature dependence of the activation energy E. If E has a component depending linearly upon the temperature,

$$E = E_0 + \alpha T, \tag{12}$$

then the expression for D should be written

$$D = D_0 e^{-\alpha/k} e^{-E_0/kT} = D_0' e^{-E_0/kT}. \tag{13}$$

Thus, in this case, the experimental D_0' actually contains the parameter (α/k) as well as the proper component D_0. There is some likelihood that there is such a temperature dependence of the activation energy.

Comparison of the Diffusion Coefficients

It is seen from Fig. 8 that the various elements differ greatly in their diffusion coefficients. In particular, the donors are seen to diffuse much more rapidly than the acceptors. This can be interpreted qualitatively in terms of Fig. 9. Here are shown the "Goldschmidt ionic radii" for various ionic charges, as determined from x-ray studies of compounds in which these elements assume different valencies. As is expected, the negative ions of an element are considerably larger than the positive ions. In germanium, of course, the donor ions become positively charged on giving up their electrons, whereas the acceptors become negatively charged. These differences, even apart from the natural differences of ionic radius for the various elements, lead naturally to higher diffusion coefficients for donor elements.

No great success has followed attempts to correlate to a higher degree the specific values of diffusion coefficient with the values of ionic radii. The ionic radii themselves do not apply well enough, and there is question as to whether the data on diffusion are accurate enough to justify serious attempts in this direction.

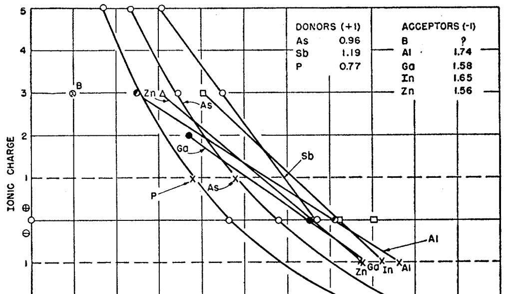

FIG. 9. Ionic radii for various ions of interest, determined from "Goldschmidt ionic radii." These values were obtained from various compounds of these elements and unfortunately do not have direct application without serious error to the substitutional solution of the elements in germanium, where their bonding relations are not the same as in their compounds. This hinders their use in more than rough correlations between ionic charge and diffusion coefficient.

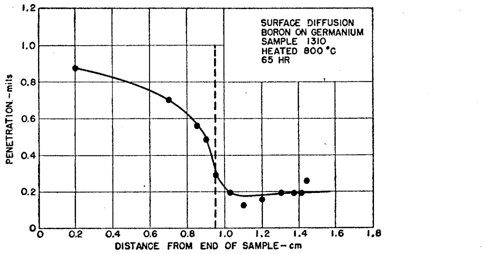

FIG. 10. Surface diffusion of boron on germanium. The plot of bulk penetration *vs* distance from end of boron coating indicated that appreciable time elapsed before sufficient boron reached points indicated, and thus before bulk penetration could proceed. Because of the large distances, however, it was concluded that surface diffusion proceeds at a rate probably 100 times the bulk penetration in this experiment.

APPLICATION OF THE *p-n* JUNCTION METHOD TO SURFACE AND GRAIN BOUNDARY DIFFUSION

Studies of Boron Surface Diffusion

Figure 10 illustrates some preliminary results on study of surface diffusion of boron on germanium, using the *p-n* junction method. The technique was as follows: polished samples on which boron had been deposited pyrolytically, were used. The boron was removed from about half the sample by etching in hot concentrated nitric acid. The sample was then sealed and heated at 800°C for 65 hours in argon. The sample was next ground off at a 5° angle, starting at the edge of the sample, in steps. After about eight of these steps, the sample had been cut beyond the point at which the boron layer had stopped.

The first thing noticed on checking the sample after diffusion was that the surface was *p* type. In a check experiment, with an *n* type sample in the same tube, the *n* type sample showed no corresponding *p* type layer. This is evidence that the *p* layer was due to boron surface diffusion, and not evaporation.

The depth of penetration was measured as a function of the distance from the original boron coating. This should give some measure of the time required to move along the surface, because the boron cannot begin its penetration into the bulk until it has diffused along the surface to the point in question.

The curve of Fig. 10 gives this bulk penetration as a function of distance along the sample. The location of the original boron coating is indicated by the dashed line. As expected, the penetration falls off rather rapidly in the region of this line and reaches nearly a constant value farther out. While it is rather difficult to estimate surface diffusion velocities from this type of data, it appears that surface diffusion proceeds, at 800°C, at a rate of about 100 times its average penetration into the bulk in this experiment, namely 1 or 2 mil/hr.

Similar studies can be made for grain boundaries. Even less has been done on this aspect of the work, however, than on surface diffusion. Again the best technique would probably involve measurement of bulk diffusion penetrations as a function of the distance along the grain boundary, measured from that point at which the impurity had been applied. From the preliminary work done in this field, however, it appeared that grain boundary diffusion was not sufficiently more rapid than bulk diffusion to make it possible to get good data easily.

OTHER WORK ON THE *p-n* JUNCTION METHOD FOR MEASURING DIFFUSION

In addition to the papers of the author (and D. E. Brown) on the measurement of diffusion by the *p-n* junction method, papers by Fuller and others on similar applications of the method have appeared. Fuller[9] measured diffusion of antimony, arsenic, indium, and zinc in germanium by the junction method, and obtained results in agreement with those of the author. Even more interesting, however, has been the application of the method to the very rapid diffusion of copper and lithium, both studied by Fuller *et al.*[10]

At this point we might mention the somewhat different though related methods of measuring diffusion coefficient described by Fuller. He assumed the step function solution, which we have seen is not completely valid for very small amounts of added impurity, but which should give satisfactory approximations.

In Fuller's technique, the diffusion coefficient is measured by study of two samples of germanium, both exposed to the same amount of impurity, as for example by exposing them together in a closed tube to the vapor of arsenic.

The two samples can be described by impurity concentrations C_1 and C_2, determined from conductivity or Hall measurement. The depth of the *p-n* junction is determined in the two cases to be x_1 and x_2. Application Eq. (8) leads then, according to Fuller, to the relation:

$$\frac{C_1}{C_2}=\frac{1-\mathrm{erf}[x_1/2(Dt)^{\frac{1}{2}}]}{1-\mathrm{erf}[x_2/2(Dt)^{\frac{1}{2}}]}. \tag{14}$$

If one then replaces the error function by its approximate value from Eq. (9), one finds for the diffusion coefficient the relation

$$4Dt=\frac{x_2^2-x_1^2}{\ln(C_1x_1/C_2x_2)}. \tag{15}$$

Thus, the diffusion coefficient is determined by the difference in the squares of the penetrations of the *p-n* junction for two different resistivities. It removes C_0 (or Q) as a variable in the measurement, but requires the measurement of two junction depths. Since the error in each "squared depth" is double the error in the depth measurement itself, additional care must be taken regarding accuracy of measurement.

An additional assumption involved in Fuller's approach is that C_0 remain constant during the diffusion. This is a rather doubtful assumption, since we have seen that the impurity either evaporates from the sample, and reacts with the walls, or it alloys with the germanium until there is no longer a second phase at the surface. Furthermore, if enough diffusing impurity is added until there is always a supply of impurity at the surface, then the penetration by the liquid alloy will, in general, be considerable, and will lead to erroneous ideas of the diffusion penetration.

The method of Fuller is somewhat similar to that in which the $\sqrt{t}$ law is assumed to be correct, the sample is diffused for two successive periods, and again the determination of two junction depths permits of the measurement of the diffusion coefficient without knowledge of the C_0, or Q value.

Results by the method of Fuller are best obtained by use of two samples having the greatest possible range of resistivity. As in all applications of the *p-n* junction method, accuracy is improved if the diffusion depth is as large as possible.

SUMMARY AND CONCLUSIONS

In the long history of the study of diffusion in solids, many physical properties have been used for indication of the extent of diffusion. The radioactive tracer, among the most modern of these, has also proved one of the most universally effective. In the field of semiconductors, however, it is possible to use the extreme sensitivity of the material to impurities, both in type and quantity, to establish a new and sensitive method for studying diffusion. Comparison of this *p-n* junction method with other methods, including the tracer method, shows that it has a distinct set of advantages, coupled with some disadvantages.

Among the advantages over the radioactive tracer method, the junction method can be used for some elements, like gallium, aluminum, and boron, which are either unobtainable in radioactive form, or are of such half-life that measurements are somewhat inconvenient.

Secondly, measurements with the *p-n* junction method are quite rapid. A measurement of diffusion coefficient requires only one measurement on the sample, namely the depth of the *p-n* junction. On the other hand, the tracer method requires a large number of time consuming operations and measurement before a corresponding value of similar precision is obtained.

A disadvantage of the junction method is the fact that is works only for electrically active elements. For inactive elements, it cannot be used at all. And of course, it is used only for semiconductors.

---

[9] C. S. Fuller, Phys. Rev. **86**, 136 (1952).

[10] C. S. Fuller and J. D. Struthers, Phys. Rev. **87**, 526 (1952); C. S. Fuller, Phys. Rev. **91**, 193 (1953).