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Diffusivity and Solubility of Copper in Germanium

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The diffusivity and solubility of Cu in Ge have been investigated as a function of temperature in the temperature range 700°–900°C, both by resistivity and radio-activity methods. The average diffusivity is $2.8\pm0.3\times10^{-5}$ cm^2/sec in this temperature interval. The solubility shows a maximum of 4.0×10^{16} atoms of copper cm^{-3} at about 875°C. The precision is not sufficient to determine an activation energy for diffusion. However, calculations based upon a theory of Wert and Zener, indicate an activation energy of about 4000 cal. The "thermal conversion" effect in Ge is explained by a temperature-dependent solution and precipitation of Cu. It is suggested that the acceptor and diffusional properties of Cu in Ge can be accounted for by decreased electron affinity of Cu at higher temperatures.

INTRODUCTION

During the development of germanium rectifiers, Scaff and Theuerer[1] found that it was possible to modify reversibly the electrical conductivity of germanium by heat treatment. Later, they carried out a more detailed study[2] of this phenomenon, which they termed "thermal conversion." They proposed that their observations could be explained either by a change in solubility of an acceptor impurity or of lattice defects introduced by the heat treatment.

More recent experiments by Fuller, Theuerer, and van Roosbroeck[3] established the additional fact that thermal conversion is attended by rapid diffusion of a *p-n* boundary from the germanium surface into the interior when *n*-type germanium of resistivity above approximately 1 ohm cm is heated to conversion temperatures. They determined the rate of diffusion and the solubility of a postulated acceptor, termed "thermal acceptor," as a function of temperature.

Still later work by one of the authors established by means of surface cleaning procedures that the thermal acceptor was usually present on the surface as an impurity and that surface cleaning prevented or greatly retarded the conversion of high-resistivity germanium. Attempts to find surface impurities which would reproduce the effects observed, pointed strongly to copper as the acceptor impurity.[4,5] This identity was securely established by means of experiments carried out by Fuller and Struthers[6] through the use of radioactive copper-64.

The purpose of this article is to give more precise results on the solubility and the diffusivity of copper in germanium and to show how these results are able to account for the changes which occur in the resistivity of germanium upon heat treatment. Two methods of determining diffusivity, one based on the measurement of electrical resistivity[7] and the other on radioactive copper, are described and the results compared. In Sec. II methods for determining the solid solubility of copper are described and results given. A discussion of the role of copper in the "thermal conversion" effect is given in Sec. IV. A discussion of the results is given in Sec. V which shows good agreement with the theory of interstitial diffusion proposed by Wert and Zener (see reference 24). An anomaly between the electrical and diffusional behavior of copper is discussed on the basis of recent results on the mobility of copper ions in germanium. The final quantitative results presented for the diffusivity differ appreciably from those previously given.[3]

I. DIFFUSION OF COPPER IN GERMANIUM

The diffusivity of copper in germanium has been determined by two independent methods. One is based on electrical resistance and assumes that each copper atom contributes a constant number of carriers. The other makes use of radioactive copper-64 and involves no assumptions. As will be shown, the agreement between the two methods is well within the estimated errors.

A. Test of Fick's Law

When the times required to reach a fixed arbitrary copper concentration c are determined at successively greater distances, Fick's second law, $\partial c/\partial t=D\partial^2c/\partial x^2$, requires that x vary linearly with the square root of the time t. The movement of a *p-n* junction in a slab of *n*-type Ge of homogeneous resistivity enables this

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[1] H. C. Torrey and C. A. Whitmer, *Crystal Rectifiers* (McGraw-Hill Book Company, Inc., New York, 1948), pp. 365–67.

[2] H. C. Theuerer and J. H. Scaff, J. Metals **191**, 59 (1951).

[3] Fuller, Theuerer, and van Roosbroeck, Phys. Rev. **85**, 678 (1952).

[4] This work also showed that water, except for carefully distilled samples, contained sufficient impurity to convert high-resistivity germanium.

[5] Experiments by W. P. Slichter and E. D. Kolb, Phys. Rev. **87**, 526 (1952), likewise showed similar effects of impurities, notably copper, on the surface of Ge. Recently, Seiler, Geist, Keller, and Blank, Naturwiss. **40**, 56 (1953) have found a surface impurity to be responsible for thermal conversion. Cu is mentioned as a possibility. Recent experiments by R. A. Logan, Phys. Rev. **91**, 757 (1953), have further confirmed the role of copper as a surface impurity. See also George Finn, Phys. Rev. **91**, 754 (1953); W. C. Dunlap, Jr., Phys. Rev. **87**, 190 (1952); S. Mayburg and L. Rotondi, Phys. Rev. **91**, 1015 (1953).

[6] C. S. Fuller and J. D. Struthers, Phys. Rev. **87**, 526 (1952).

[7] Variations of this method are given in references 3 and 26. See also R. N. Hall and W. C. Dunlap, Jr., Phys. Rev. **80**, 467 (1950); W. C. Dunlap, Jr., Phys. Rev. **87**, 615 (1952).

one-dimensional relation to be tested for copper. This is because the *p-n* junction marks a boundary at which the electron concentration just equals the hole concentration introduced by the copper atoms. The carrier concentration is simply derived from the relation

$$1/\rho = q(n\mu_n + p\mu_p), \qquad (1)$$

in which ρ = resistivity in ohm cm; $q = 1.60\times10^{-19}$ coulombs; n,p = number of electrons or holes per cm^3, respectively; μ_n,μ_p = mobility of electrons or holes in cm^2/volt sec, respectively. Since for our purposes the minority carrier concentration is negligible compared to the majority carrier concentration, (1) may be written,

$$1/\rho_n = qn\mu_n, \qquad (2)$$

$$1/\rho_p = qp\mu_p, \qquad (3)$$

where now ρ_n and ρ_p are the resistivities of *n*-type and *p*-type germanium, respectively. The mobilities,[8] μ_n and μ_p at 25°C, the temperature of measurement, were taken as 3900 and 1900 cm^2 per volt sec, respectively, for high-resistivity germanium. In the calculations, these mobilities were corrected for impurity scattering by means of empirical curves determined by Debye and Conwell and independently by Prince.[9]

In the present instance, the resistivity ρ_n of the original *n*-type specimen provides n from (2). This is equal to the number of holes per cm^3 at the boundary which in turn is proportional to the number of copper atoms per cm^3. It is therefore a simple matter to determine the distances and times for equal concentrations of the diffused copper.

To test this relation two specimens ($0.8\times0.8\times0.25$ cm) of *n*-type single-crystal germanium[10] of uniform resistivity (ρ at 25°C = 0.7 ohm cm) were cleaned of surface impurities by grinding on fresh, dry Aloxite No. 400 abrasive paper. The exposed faces were treated with 1 percent (by weight) copper nitrate solution and each specimen was subjected to a series of heatings for known times in helium. Two runs were made, one at 815° and one at 915°C. After each heating, a cross-sectional cut was made perpendicular to the slab face in order to expose a fresh *p-n* boundary. This was necessary in order to avoid edge effects. The amounts removed did not affect materially the heat-up time curves. A heat-up time correction, chosen so as to meet the condition of zero distance at zero time, was applied to all points. No correction for cooling was required because of the rapid quenching to near room temperature in less than 1 second. The corrections used were 20 seconds at 815°C and 10 seconds at 915°C. The *p-n* boundary penetration distances were determined by means of a sharpened tungsten wire which served as a rectifying probe. Distances were measured to ±0.0001 cm by means of a micrometer eyepiece and microscope.

Plots of $\sqrt{t}$ against x, the penetration distance, are shown in Fig. 1. It is seen that Fick's relation is followed within the error of the experiment, namely, about ±2 percent in the time t.

B. Procedures for Determining Diffusivity

1. *Resistance Method*

Specimens for this method, were cut as cross sections from single-crystal germanium prepared by zone leveling.[11] The sections were 0.625 cm thick and roughly circular in shape of average radius 1.9 cm and ranged in resistivity (*n*-type) from 14.1 to 38.1 ohm cm at 25°C. Copper was applied as a 1 percent by weight nitrate solution to one surface of each of five specimens of the germanium, which were previously carefully cleaned of surface impurities.[12] In this manner, a very thin layer of metallic copper was deposited on one face of each specimen. Each specimen was then heated on a freshly split mica support in a resistance-type furnance with the copper treated surface toward the mica. The specimens and the mica support could be introduced into the furnance and removed therefrom in a time of about 1 second. Heating was carried out in

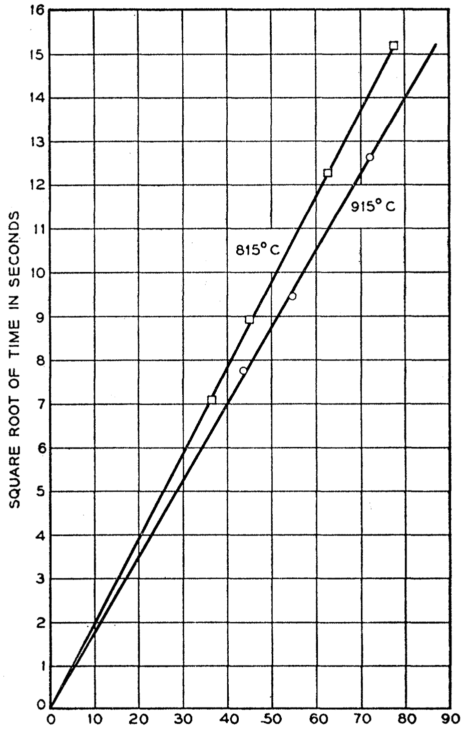

FIG. 1. Plots of diffusion distance against square root of time to reach a fixed concentration at 815° and 915°C.

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[8] J. R. Haynes and W. Shockley, Phys. Rev. **85**, 678 (1952).

[9] M. Prince, Phys. Rev. **92**, 681 (1953); P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954); Esther Conwell, Proc. Inst. Radio Engrs. **40**, 1327 (1952).

[10] G. K. Teal and J. B. Little, Phys. Rev. **78**, 647 (1950).

[11] W. G. Pfann and K. W. Olsen, Phys. Rev. **89**, 322 (1952).

[12] The purpose of cleaning was to minimize diffusion from the back and side surfaces.

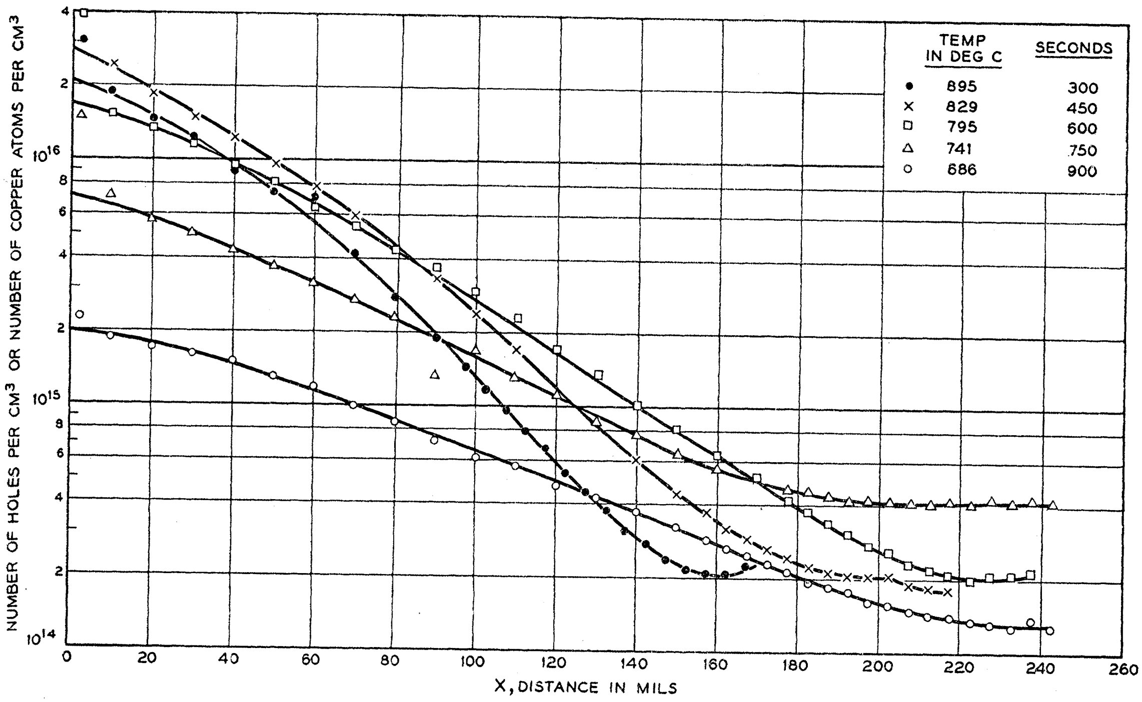

FIG. 2. Penetration curves for Cu in Ge at various temperatures as determined from resistivity.

a quartz tube in an atmosphere of pure helium at temperatures ranging from 700° to 914°C. The heated specimens were quenched by sliding onto a heavy steel block at room temperature. By means of a thermocouple in contact with the thin mica support, the temperature rise of each specimen was determined as a function of time during the entire heat treatment cycle. From the curves so obtained, mean effective temperatures, T_e, were determined by the method of Ham,[13] using graphical integration and assuming an activation energy for diffusion of 8000 calories (0.35 ev).

TABLE I. Diffusivity and solubility of copper in germanium from penetration curves.

T_e(°C)	D(cm²/sec) ×10⁵	C_0(Cu atoms/cm³) ×10⁻¹⁵
680[a]	2.7	2.7
686	3.0	2.1
741	2.4	6.6
770[a]	3.2	8.0
780[a]	2.7	19.0
785[a]	3.6	26.0
795[a]	2.7	17.0
829	2.2	27.2
880[a]	3.1	36.0
895	2.9	20.8
900[a]	2.5	47.0

[a] Radiotracer determinations.

Bars 0.125×0.125×0.625 cm were next cut perpendicular to the plane faces of each specimen. Without injury to the ends, solder was applied to them to form ohmic contacts for the passage of current. Each bar was mounted in turn on a traveling stage under a microscope in such a manner that contact could be made along the sides of the bar at measured distances from the ends. A sharp tungsten probe was employed for the contact and the distance was measured to ±0.002 cm by means of a micrometer screw. Thus, with a current of 1 milliampere flowing down the bar, the change in potential at each point along the bar, and therefore the change in resistivity could be measured. A type-K potentiometer was used to measure potential differences. Potential differences were taken in steps of 5, and sometimes 10 mils, along all four sides of each bar and the results averaged for the resistivity calculations.

The number of holes per cm³ added at each step during the diffusion is given by the sum of the electron concentrations of the original n-type germanium specimens [Eq. (2)] and the hole concentrations corresponding to the resistivity at each step along the test bars as derived from Eq. (3). The assumption (justified later on in this paper) is made here that one hole is introduced by each diffusing copper atom.

From plots, at each mean effective temperature, of the number of copper atoms per cm³ as a function of distance into the specimen, C_0 the surface copper concentration, and D the diffusivity were determined

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[13] J. L. Ham, Trans. Am. Soc. Metals **31**, 877 (1943). The value of ΔH^* of 8000 cal assumed in these calculations is probably high, but large errors can be tolerated without appreciable influence on T_e.

by a method suggested by Bardeen.[14] This consists of matching the penetration curves, with log distance plotted *vs* log concentration, to the curve obtained by plotting, on log-log paper to the same scale, erfc$u$ against u, where erfc$u$ is

$$1-\frac{2}{\sqrt{\pi}}\int_0^u \exp(-\beta^2)d\beta.$$

C_0 then corresponds to the point where erfc$u=1$ and D is derived from the point where $u=x/[2(Dt)^{\frac{1}{2}}]=1$.

2. *Radiotracer Method*

Specimens, approximately 0.5 in. thick and 1 in. in diameter, were cut from n-type single-crystal germanium.[8] Radioactive copper[15] (Cu^{64}) was deposited on all surfaces by immersing the specimens for two minutes in a 0.1 percent (by weight) copper nitrate solution containing Cu^{64}. Diffusion anneals were carried out in helium gas in a quartz tube furnace at temperatures ranging from 680° to 900°C. The heated specimens were quenched in air by sliding onto a heavy steel block at room temperature. Blocks the full thickness of the specimen and $\frac{3}{8}$-in. square cross section were cut from the center of the heated samples, giving for the diffusion measurements specimens in which copper was diffused from two surfaces only. Grindings were taken, using No. 400 or No. 320 Aloxite paper, at measured distances from the surface of the block and the activity of the grindings measured by the usual counting techniques. The concentration of copper in the grindings was calculated from the activity making suitable corrections for absorption and decay, and the penetration curves plotted in the usual way. Because of the short half-life of Cu^{64} (12.8 hr) it was necessary to complete the work within 72 hours to obtain the desired counting precision.

3. *Diffusion Results*

In Table I are given the essential results from both the resistance and radiotracer measurements. Figure 2 shows the penetration curves obtained at each temperature by the resistance method, and Fig. 3 gives similar curves for the radiotracer results. In calculating diffusivity and surface concentration, corrections were applied to the penetration curves of Fig. 2 by subtracting from each ordinate the final concentration level approached in each case.[16] The corrected penetration curves fit the u, erfc$u$ curves within the error of experiment in all cases.[17] No such corrections are needed for the curves of Fig. 3 which descend normally.

When log D is plotted against $1/T$ in the usual manner to determine ΔH^*, the activation energy for diffusion, the scatter in the results as shown in Fig. 4 is too great to allow an accurate estimate of ΔH^* to be made. This is in spite of the fact that the precision of the determinations is rather good, namely a probable error of ± 10 percent, for this type of measurement. The average diffusivity of copper in germanium, taking all of the results, is $2.8\pm 0.3\times 10^{-5}$ cm²/sec, at all temperatures investigated. If we assume a maximum positive deviation of 2σ at 900°C and a maximum negative deviation of the same amount at 700°C, the maximum expected ΔH^* is 4900 cal. We may suppose the true value, therefore, to fall between 0 and 4900 cal.[18] Obviously a higher precision will be required to estimate ΔH^* more accurately than this.

II. SOLID SOLUBILITY OF COPPER IN GERMANIUM

Indirect determinations of the solubility of copper as a function of temperature are obtainable, as already

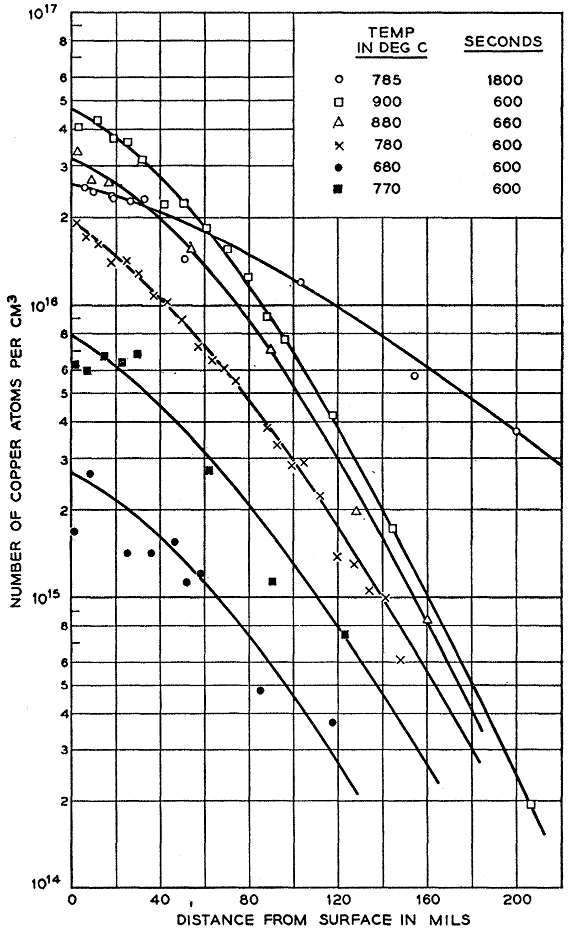

FIG. 3. Penetration curves at various temperatures determined by means of radioactive copper.

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[14] W. G. Pfann (private communication).

[15] The isotopes were obtained from the Oak Ridge and Brookhaven National Laboratories on allocation from the U. S. Atomic Energy Commission.

[16] The finite concentration levels reached at large distances are believed due to residual copper from the sides and backs of the specimens.

[17] This is the equivalent of a straight-line plot on probability paper. See C. Wells, *Atom Movements* (Am. Soc. Metals, 1951), p. 33.

[18] The previously reported ΔH^* of 12 000 cal (reference 3) is too high, probably because of the limited number of determinations available at the time and the lack of sufficiently pure Ge (see IV).

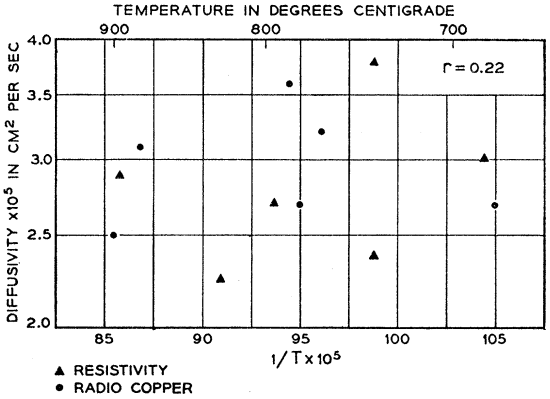

FIG. 4. Scatter diagram of diffusivity *versus* reciprocal of absolute temperature.

mentioned, from the penetration curves (Figs. 2 and 3). These have been included in Table I for both the resistance and radiotracer methods. Direct measurements have also been obtained by equilibrating specimens of germanium[19] at fixed temperatures in contact with copper. Both resistance and radiotracer methods have been employed in this manner as described below.

A. Procedures for Determination of Solubility

1. *Resistance Method*

High-resistivity *n*-type germanium specimens in the form of prisms (0.5×0.25×1.0 cm) were measured for resistivity by the four point probe method.[20] Copper was applied to the surface by displacement from a 0.5 percent by weight copper nitrate solution. Heat treatment was carried out in helium for times calculated sufficient to bring the specimens to above 99 percent saturation at each temperature. Resistivity was measured after treatment and the number of added holes calculated as in Sec. I(A).

2. *p-n Junction Method*

This method is a modification of method (1) above. A bar, 0.2×0.2×5.0 cm was cut from the central portion of a germanium single crystal grown to have a resistivity gradient from 0.1 ohm cm to 25.0 ohm cm from end to end.[17] The resistivity gradient in the bar was determined by the potential probe method as described in Sec. I(B)(1). The bar was then treated with copper as already described and heated at successively higher temperatures, starting at 500°C. From the location of the *p-n* junction and the original resistivity at the junction location, it is possible to determine the number of holes introduced, since at the junction the number of holes must just equal the electrons originally present. It is assumed none of the other impurities in the Ge are altered by the experiment. By heating until an equilibrium was established at a given temperature, approached from above and below, and determining the *p-n* boundary positions, solubility was determined as a function of temperature under the assumption that each copper atom supplies one hole to the filled band. An advantage of this method is that it enables solubilities to be determined below the eutectic temperature of Cu-Ge (650°C).[29]

3. *Radiotracer Method*

The method employed and the results have already been published.[6] These results are included in Fig. 5.

B. Solubility Results

Figure 5 shows a plot of all of the experimental data on solid solubility of copper in Ge as a function of temperature. The solid curve has been drawn favoring the determinations made by extrapolation of the curves of Fig. 2 and the previously published[6] radiotracer results which are believed to be the most accurate of the measurements.

As can be seen from Fig. 5, the direct resistivity methods give lower solubilities at temperatures in the range 700°–850°C. This is believed to be due to variations in resistivity near the surfaces of the specimens as a result of copper precipitation (see below). All of the measurements are in substantial agreement at the lower temperatures. Likewise, at the higher temperatures a definite solubility maximum is indicated at about 875°C.

The agreement between the radiotracer results and those obtained by extrapolation of the curves of Fig. 2, which are considered the most accurate of the resistivity results, provides evidence that each copper atom supplies substantially one conducting hole in germanium at room temperature. Other evidence for this is reported in references 5 and 6.

III. DISCUSSION OF ERRORS

Because of the extremely high rate of diffusion of copper in Ge and its very low solubility (less than 3 atoms per million of Ge at the maximum), precise determinations of these quantities are difficult. Further complications arise from the presence of temperature gradients at the start and finish of the heating periods, from the possibility of precipitation from the supersaturated solution during the quench, from previous contamination of the germanium with copper, and from surface reactions which may influence rate.[21] The presence of inhomogeneities in resistivity can also influence the results obtained by the methods depending on resistance measurement, especially at lower temperature where low copper concentrations prevail. A

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[19] The authors are indebted to E. Buehler for the single crystals from which these specimens were prepared.

[20] L. B. Valdes, Proc. Inst. Radio Engrs. 42, 420 (1954).

[21] The presence of oxygen or nitrogen in the gas atmosphere has been found to reduce the diffusion rate.

discussion of the influence of these factors upon the reliability of the determinations is therefore in order.

The method[13] of correcting for the temperature rise upon insertion of the specimens in the furnace is recognized as not being entirely adequate. Surface concentration changes occurring during the heat-up period will also effect the results. These errors will lower the values of the diffusivity at the higher temperatures relative to those at the lower temperatures. The effects, however, do not exceed 10 percent of the diffusivity values reported.

Tests have shown that the errors arising from precipitation are small provided quenching is sufficiently fast.[22] Because of the maximum in the solubility curve at about 875°C, there is the possibility that the solubilities determined above 875°C will show solubilities which are too high. Small variations may likewise occur in the diffusion because of changes in surface solubility near this temperature.

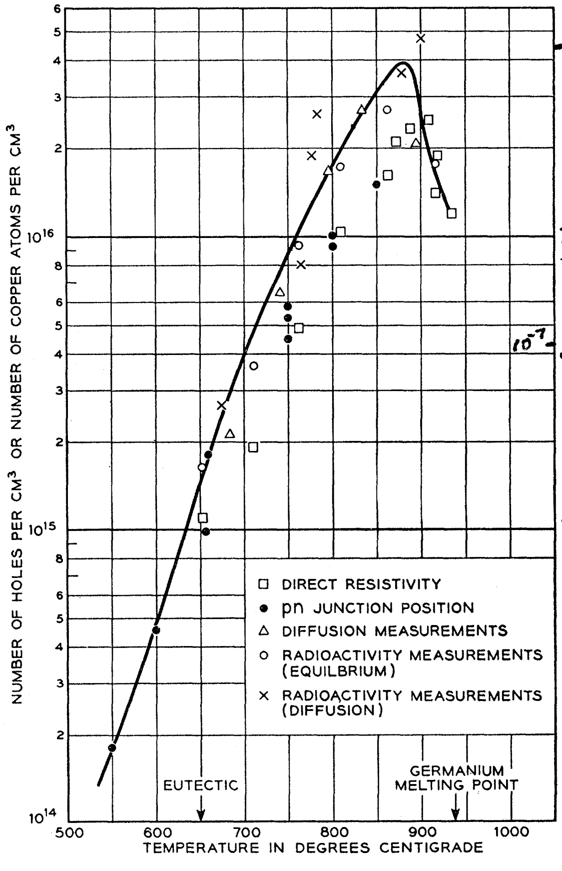

FIG. 5. Plot of number of conducting holes or number of copper atoms per cm³ against temperature.

Errors from copper contamination, while present, are small except at the lower temperatures where the effect is to give apparently higher diffusivities than actual. At the lowest temperature (686°C) this may amount to as much as 10 percent error in D. Such contamination should not, however, influence appreciably the solubility results.

Errors caused by random inhomogeneities in the resistivity of the germanium contribute to the scatter of the data. These errors are, however, relatively small compared to those mentioned above except possibly at the lowest temperatures.

Likewise the random errors in the measurement of resistivity (±2) percent, time (±1 percent), distance (±0.5 percent), radio count (±1–10 percent), mobility (±5 percent) are less important than the errors incidental to heat-treatment mentioned above. The over-all probable error in the determination of D is therefore largely determined by the latter and is estimated to be about ±10 percent. The same applies to the best determinations of C_0.

IV. PRECIPITATION OF COPPER IN GERMANIUM

Although the high diffusivity of copper established by the work reported in the paragraphs above accounts well for the observed conversion of n-type germanium to p-type upon heat treatment, it is not immediately evident how the other features[2] of thermal conversion can be explained. For example, it is well known that heat treatment at 500°C of thermally converted Ge will result in a change back to its original resistivity.

This is now easily understood on the basis of the solubility results shown in Fig. 5. The solubility of copper rapidly decreases below 875°C so that, if equilibrium conditions prevail, nearly all of the copper should be precipitated at sufficiently low temperatures. Evidence that such precipitation does in fact occur is obtainable from resistivity measurements. These show that once a specimen of germanium is saturated with copper at high temperature and reconverted by heating at 500°C in the usual way, subsequent conversions proceed almost homogeneously throughout the specimen. Determinations of the rate of movement of p-n junctions, likewise, show that in previously converted and annealed specimens of germanium, the conversion proceeds at a much higher rate at the same temperature that it does in the original germanium. The high diffusivities previously reported[3] are now believed due to the presence of some precipitated copper in the Ge employed.

The proof of the precipitation of copper, however, is provided by the use of radioactive copper. Germanium saturated with radiocopper at 900°C was annealed at 520°C for 17 hours, after which time the specimen was cut in two and radioautographs taken of the interior surfaces. Figure 6 shows the results. It is evident that the copper is no longer as uniformly distributed, as is shown by the mottled appearance of the annealed as

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[22] A possibility of a small error entering because of other acceptors or defects being retained by very rapid quenching [see R. A. Logan, Phys. Rev. 91, 757 (1953)] exists. Tests on copper-free specimens of the Ge employed showed, however, less than 10^{14} carriers retained.

compared to the unannealed specimens. This is especially evident at the surfaces. Quantitative measurements of activity in fact show that except near the surface, precipitation occurs throughout the specimen. That the surface is an especially good locus for nucleation is shown not only by the radioactivity measurements, but also by the early observation[2] of thin *n*-type layers on heat converted specimens of germanium which were slowly cooled.

The reversal of conductivity type and the return of the heat-converted germanium to its original resistivity, which occurs on annealing is therefore made understandable by the precipitation of copper.

V. DISCUSSION—MECHANISM OF DIFFUSION

The characteristic features about the diffusion of copper into germanium are its extremely high diffusivity, approaching that of liquid diffusions, and its relatively low activation energy of diffusion. One is tempted on this basis to postulate an interstitial mechanism for this diffusion.[23] Wert and Zener[24] have examined the case for interstitial diffusion generally, and have shown that for many diffusions, supposedly interstitial, ΔS^* for diffusion is positive. They give the following expression for D_0:

$$D_0=\lambda a_0^2\nu\exp(\Delta S^*/R), \tag{4}$$

in which λ is a constant depending on lattice geometry, a_0 is the lattice constant for Ge, ν = vibration frequency, ΔS^* is the entropy of diffusion, and $R=1.99$ calories. They further have indicated how $\Delta S^*/R$ may be determined in terms of ΔH^* for diffusion from a knowledge of the temperature coefficient of the shear modulus, μ, of the solvent including the magnitude of this modulus, μ_0, at absolute zero:

$$\Delta S^*=-\Delta H^*(1/\mu_0)(d\mu/dT). \tag{5}$$

Here μ_0 is the extrapolated modulus, and ΔH^* is the activation energy for diffusion. The temperature coefficient of the rigidity modulus, has been determined for germanium as a function of temperature.[25] From the high-temperature slope of the curves for the shear modulus in the (110) plane,[26] $d\mu/d=-0.00060\times10^{11}$ dynes/cm^2/°C and the extrapolated value of the modulus, $\mu_0=4.2\times10^{11}$ dynes/cm^2. According to Eq. (4), where $\lambda=\frac{1}{8}$ for the germanium lattice,[27] $a_0=5.62\times10^{-8}$ cm, and ν, taken as the average lattice vibration frequency, is 0.45×10^{12} sec^{-1}, one obtains

$$\log D_0=-3.75+0.000031\Delta H^*. \tag{6}$$

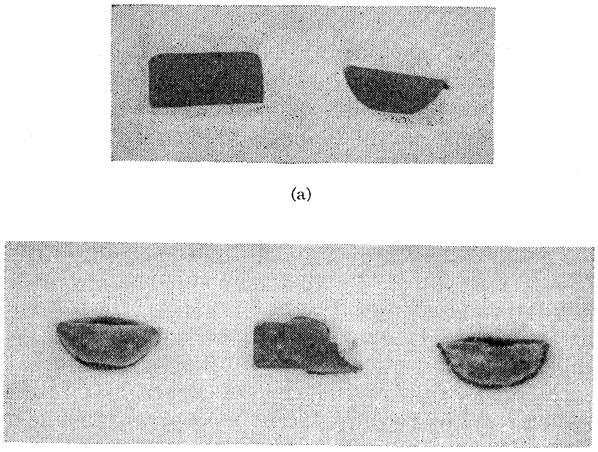
The average experimental value for D is 2.8×10^{-5} cm^2/sec at 1073°K. By substituting these values in the general diffusion equation, using D_0 from (4), ΔH^* comes out to be 4100 cal for copper in Ge. This value is in agreement with the results reported here and suggests the equation,

$$D=0.00019\exp(-4100/RT), \tag{7}$$

may apply in the temperature range 700°–900°C.

Another argument favoring an interstitial diffusion mechanism is furnished by the fact that elements which there is good reason to believe go into Ge substitutionally show very low diffusivities and high activation energies for diffusion in Ge. For example, at 800°C antimony has a diffusion constant[28] roughly 10^{-6} times that for copper. The corresponding activation energy is about a factor of 12 times that for copper.

Attempts to determine the diffusivity of copper in germanium at temperatures below 650°C indicate a much lower diffusion rate. However, since a eutectic between Cu and Ge occurs at this temperature,[29] the low values may be a consequence of lack of equilibrium conditions. Esaki[30] has recently published diffusion constants due to "thermal acceptors" in this temperature range. He finds a much higher activation energy (35 000 cal) than that reported here. Diffusion limited by a surface reaction may possibly explain the difference between Esaki's and our results assuming they both have the same origin. In any event, there is considerable doubt that Eq. (7) applies below 650°C.[31]



(a)

(b)

FIG. 6. Radioautographs of copper in Ge.

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[23] C. Wagner, Z. phys. Chem. **B38**, 325 (1937).

[24] C. A. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949); C. Zener, J. Appl. Phys. **22**, 373 (1951).

[25] Bond, Mason, McSkimin, Olsen, and Teal, Phys. Rev. **78**, 176 (1950); H. J. McSkimin, J. Appl. Phys. **24**, 988 (1953). M. E. Fine, J. Appl. Phys. **24**, 338 (1953).

[26] This is the shearing plane for an interstitial jump.

[27] λ in Eq. (4) follows from the random walk expression $1/6(\Delta x)^2\nu$, where Δx is jump distance and ν is jump frequency, taking into account the number, $n=4$, of alternate paths and the fact that $\Delta x=\sqrt{3}a_0/4$.

[28] D. E. Brown and W. C. Dunlap, Jr., Phys. Rev. **87**, 616 (1952); C. S. Fuller, Phys. Rev. **86**, 136 (1952).

[29] M. Hansen, *Der Aufbau der Zweistofflegierungen* (Springer, Berlin, 1936), p. 565.

[30] Leo Esaki, Phys. Rev. **89**, 1026 (1953).

[31] As C. Goldberg, Phys. Rev. **88**, 920 (1952), has indicated, Eq. 7 and that previously published (reference 3) do not appear

The nature of the copper particle which diffuses is of interest. If copper of itself is the acceptor, one might expect, analogously to other acceptors in Ge, that it would be present as a negative ion. However, the diameter of such a negative copper ion would appear to be too large $(>1.5A)$ to permit interstitial diffusion, since the interstitial space (Fig. 7) is just sufficient to accommodate a Ge atom (1.22A).[32]

No firm explanation of this apparent discrepancy can be given until more is known about the behavior of copper in Ge. Since there are indications of a trapping level[33] as well as an acceptor level for copper,[34] the true state of the dissolved atom may be complicated. Furthermore, little is known of the effect of temperature on the ionization processes of copper under these circumstances. It is for example, conceivable that copper may diffuse at high temperatures as Cu^+ or Cu^0, and assume the role of acceptor only at lower temperatures. Evidence for this has recently been obtained through experiments on the diffusion of copper in a dc field.[35] It is found that copper behaves as a positive ion at temperatures 850°–900°C and there is evidence that little or no migration occurs at 700°C.

Another point of interest is the reversal in the solid solubility of copper in Ge as shown in Fig. 5. Such behavior in solid systems is rather rare and at first might suggest nonideal solution behavior of copper. Recently Thurmond[36] has shown that the above solubility behavior ("retrograde solubility") follows normally from thermodynamic treatment of the copper-germanium system. We are led to conclude therefore that copper in Ge behaves as a Henry's-law dilute solution.

The authors have carried out similar work on silicon to that described above for germanium. Preliminary results[6] indicate Cu to be an acceptor in Si. However, as yet the magnitude of the resistivity changes has not allowed determinations of D or C_0 to be made by this method. On the other hand, the radiotracer method shows that $D_{900^\circ\mathrm{C}}$ is of the same order as that for Cu in Ge (5×10^{-5} cm^2/sec) and C_0 is roughly ten times that observed for Ge at 850°C.[34] We hope to publish details of this work in a later paper.

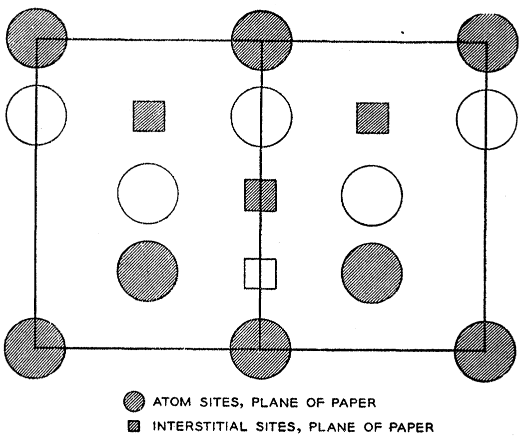

FIG. 7. Projection of atom and interstitial sites of diamond lattice on (110) plane.

SUMMARY

1. The diffusivity of Cu in Ge has been determined in the temperature range 700°–900°C by two independent methods, one based on electrical resistivity and the other on copper radioactivity. Both methods agree within the limit of error, for a value of $D=2.8\pm0.3\times10^{-5}$ cm^2/sec in this temperature interval. From the elastic constants for Ge and the theory of Wert and Zener an activation energy of 4100 cal per mol is derived leading to the relation

$$D=0.00019\exp(-4100/RT).$$

2. The solid solubility of copper in Ge as a function of temperature has also been determined by both electrical and radioactive methods. The best results support the conclusion that one copper atom contributes one conducting hole at room temperature.[37]

3. The role the precipitation of Cu plays in the reversible resistivity changes observed during the "thermal conversion" of Ge is discussed.

4. It is pointed out that the acceptor properties of Cu in Ge are in disagreement with the diffusional properties. It is suggested that the anomaly may be resolved by assuming a different state of ionization for copper at room temperature and at the temperature of diffusion.

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to account for the slow process observed at lower temperatures (560°C). However, it must be pointed out that the solubility of Cu at this temperature is very low and so far, no determinations have been made at these temperatures.

[32] C. Herring has suggested to the authors that the Cu atom and its accepted electron may behave as separate entities.

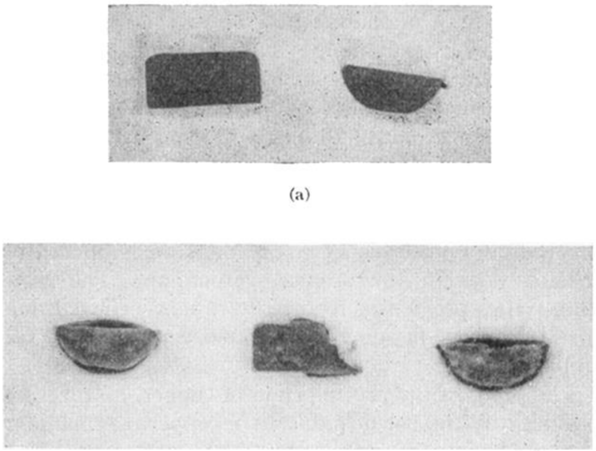
[33] Burton, Hull, Morin, and Severiens, *Symposium on Impurity Phenomena* (Schnectady, New York, 1953); J. Phys. Chem. **57**, 853 (1953).

[34] An energy level for copper ionization of 0.04 ev has been reported. F. J. Morin and J. P. Maita, Phys. Rev. **90**, 337 (1953); W. DeSorbo and W. C. Dunlap, Jr., Phys. Rev. **83**, 879 (1951). G. L. Pearson in W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 227.

[35] J. C. Severiens and C. S. Fuller, Phys. Rev. **92**, 1322 (1953).

[36] C. D. Thurmond and J. D. Struthers, Symposium on Impurity Phenomena, Schenectady, New York (1953); J. Phys. Chem. **57**, 831 (1953). Retrograde solubility of Cu in Si was observed in this work.

[37] Some recent work indicates that the second level (see reference 34) may contribute to the conductivity in strongly n-type Ge.



(a)

(b)

FIG. 6. Radioautographs of copper in Ge.