

calculated by both methods, however, agree fairly well. Table I and Fig. 1 show the results at different temperatures for the cold probe method. The straight line of Fig. 1, plotted by least squares, gives an activation energy of 51,000 calories. This value provides the following tentative diffusion equation which applies within experimental error to both arsenic and antimony,

$$D_{As} = D_{Sb} = 0.71 \exp(-51,000/RT) \text{ where } R = 1.98 \text{ calories.}$$

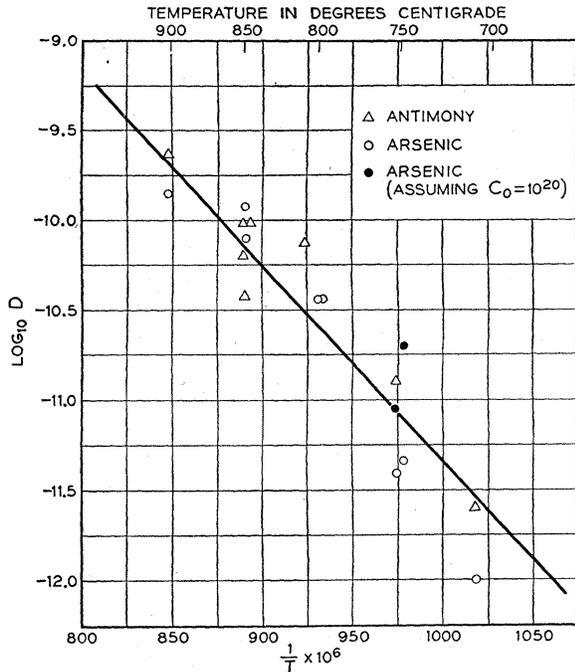


FIG. 1. Diffusion constants of antimony and arsenic as a function of temperature.

Because germanium when heated above 500°C tends toward *p*-type, all specimens were equilibrated at 500°C for 40 hours before measurement. Figure 2 shows plots of barrier distance (cold probe method) against square root of time for arsenic and antimony diffusions. The linear trend of these plots indicates that, for the surface concentrations employed, ideal behavior is approximated.

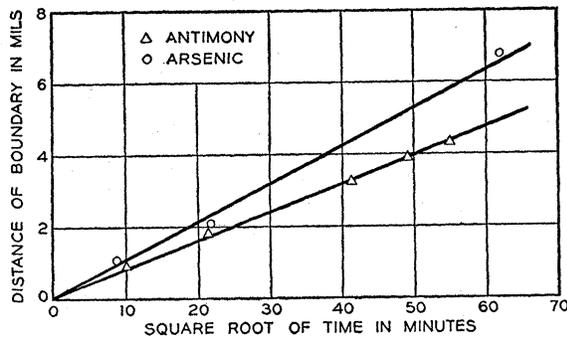


FIG. 2. Diffusion distance versus time for antimony and arsenic.

The diffusion constants for indium and zinc determined by this same method are 0.9×10^{-12} and 2.3×10^{-12} cm² per sec (775°C), 4.0×10^{-12} and 1.0×10^{-11} cm² per sec (845°C), respectively. The activation energies are approximately 50,000 calories for both elements.

The writer is indebted to W. Van Roosbroeck for formulations of Eqs. (1) and (2) and to J. A. Ditzberger for assistance with the experimental work.

* Work very similar to that described here has just been reported by W. C. Dunlap, Jr. [Bull. Am. Phys. Soc. 27, No. 1, 40 (1952)]. See the accompanying Letter by McAfee, Shockley, and Sparks, Phys. Rev., this issue. ¹ Teal, Sparks, and Buehler, Phys. Rev. 81, 637 (1951).

Measurement of Diffusion in Semiconductors by a Capacitance Method

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SHOCKLEY¹ has derived a relationship between the capacitance of a *p-n* junction biased in the reverse direction and the gradient a of the difference between the concentrations of donors and acceptors in the transition region. If one of the impurities is present uniformly throughout, a junction can be made by introducing a larger concentration of the opposite type impurity into one end of the sample. In such a junction a will be just the gradient of the nonuniform impurity. At high

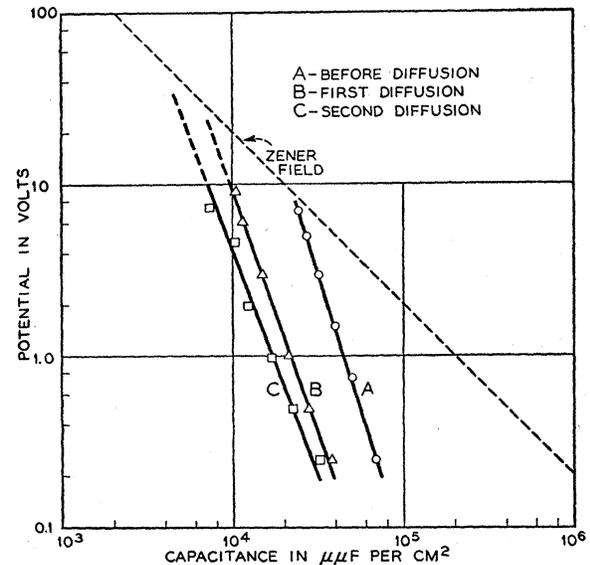


FIG. 1. Change in capacitance of a *p-n* junction with heat treatment. A dielectric constant of 16 is assumed for germanium.

temperatures the nonuniformly distributed impurity will diffuse into the material. Measurement of the capacitance of the junction before and after one or more heat treatments thus determines the change of the gradient of one impurity. From this and a knowledge of the limiting concentrations of donors and acceptors immediately adjacent to the transition region, a diffusion constant may be calculated for the nonuniform impurity by solution of the diffusion equation.

Experiments have been performed with single crystals of germanium in which gallium was the uniformly distributed acceptor, and arsenic was the nonuniform donor. The capacitance data for one junction are shown in Fig. 1, and the deduced concentrations of these two impurities in the region of the junction are shown in Fig. 2. Ten similar junctions were studied at temperatures between 600 and 925°C. Heat treatments were about 50 hours each. The calculated diffusion constant for arsenic in

germanium at 800°C, where several measurements were taken, fell between 1×10^{-13} and 5×10^{-12} cm²/sec. This value is several orders of magnitude smaller than that reported by Fuller in the accompanying letter and by Dunlap.² The activation energy for the process, which is calculated from the temperature dependence of the diffusion rate, is about 3.0 electron volts.

The limiting concentrations were calculated from conductivity measurements made locally on each side of the junction. The calculation employs the mobility of holes and electrons, and we have used Hall effect data obtained from Pearson and Debye³ which include most of the range of impurity concentration in the junctions studied.

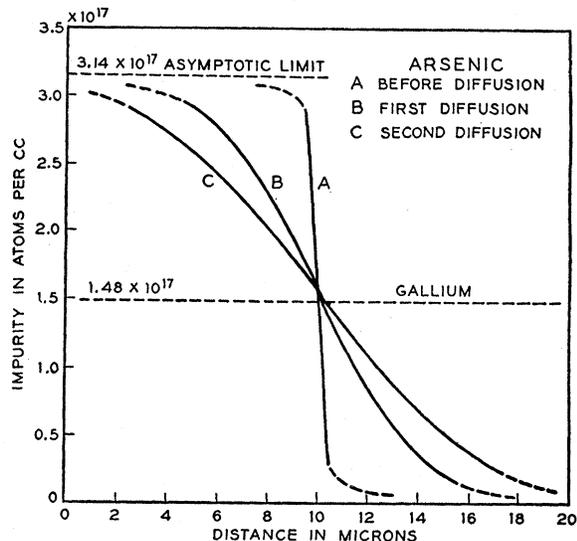


FIG. 2. Impurity concentration gradients in the region of the *p-n* junction as deduced from Fig. 1.

For all junctions the capacitance was found to be proportional to the inverse cube root of the bias voltage. This relationship is expected for junctions in which the gradient is constant across the transition region.¹ For one junction it was possible to observe a sharp Zener break⁴ in the current-voltage curve at each step throughout the heat treatments. The concentration gradients obtained from the critical Zener voltages agreed to within 20 percent with those obtained from the capacitance measurements.

There are two features of the technique which make it particularly suitable for measurement of diffusion. First, it permits the significant measurement of very small diffusion distances and very low concentrations of impurities. Second, and perhaps more important, diffusion may be studied from a gradient which is established in the crystal at the time it is grown. In the usual techniques for measurement of diffusion in solids, the impurity atoms are introduced at the surface. Their concentration here is difficult to determine since it may be influenced by adsorption and chemical reactions. If the surface concentration builds up sufficiently, it may reach a composition which will melt at the temperature under investigation. In the method described here there is no reservoir of the impurity and no mechanism for its concentration to increase beyond that built into the crystal when it is grown.

We wish to acknowledge the assistance of Mr. R. M. Mikulyak in growing the crystals and of Miss C. J. Peffer in taking many of the measurements. Mr. W. van Roosbroeck obtained the particular solutions of the diffusion equation.

¹ W. Shockley, Bell System Tech. J. **28**, 335 (1949).

² W. C. Dunlap, Jr., Bull. Am. Phys. Soc. **27**, No. 1 (1952).

³ G. L. Pearson and P. P. Debye, private communication.

⁴ McAfee, Ryder, Shockley, and Sparks, Phys. Rev. **83**, 650 (1951).

Pressure Broadening of Absorption Lines*

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SPITZER¹ has shown that the familiar Lorentz formula for the absorption coefficient

$$k(\nu) = (S\alpha/\pi)[(\nu - \nu_0)^2 + \alpha^2]^{-1} \quad (1)$$

is valid when $|\nu - \nu_0| < 3M^{-1}$, where α is the half-width of the line, ν is expressed in wave numbers, S is the total intensity of the line, $M = 27.8(c/\nu)^{6/5}b^{1/5}$, and b is the constant in the frequency perturbation $\nu_p(t) = b\nu^{-6}$. Although the following calculations can be easily extended to perturbations varying as r^{-n} , we give only the results for Van der Waals forces.

Holstein² has shown that $k(\nu)$ derived from statistical theories is valid at moderate pressures and for nondegenerate levels when $|\nu - \nu_0| > 3M^{-1}$. In this range of frequencies the Lindholm³ equations are valid in the wings of the line

$$k(\nu) = (0.933)(M^2S\alpha/\pi)[M(\nu_0 - \nu)]^{-3/2} \quad (2a)$$

and

$$k(\nu) = (0.638)(M^2S\alpha/\pi)[M(\nu - \nu_0)]^{-7/3}. \quad (2b)$$

In the usual case Eqs. (2a, b) apply to the red and violet wings, respectively. Instead of the discontinuous rectangular pulses used by Lindholm, Holstein,⁴ using an inverse power frequency perturbation, obtains Eq. (2a) for the red wing and

$$k(\nu) = (16.6)(M^2S\alpha/\pi)(\nu - \nu_0)^{-7/3} \times \exp\{-(0.474)[M(\nu - \nu_0)]^{5/6}\} \quad (2c)$$

for the violet wing. All of the calculations reported here have been made using both Eqs. (2b) and (2c). Although the latter equation is based on more reasonable physical assumptions, we find that the difference in the results calculated from these two equations does not differ by more than a few percent within the range of validity of the statistical theory. This is because the absorption from the red wing dominates the violet. Since Lindholm's equations are easier to integrate and give the same answers as Holstein's, we report below only on calculations made with Eqs. (2a, b).

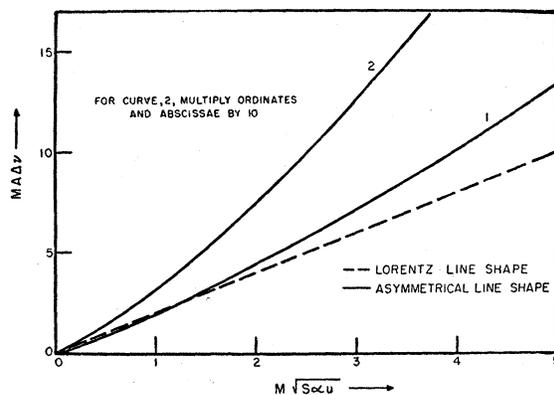


FIG. 1. Absorption of a single line as a function of $M(Sau)^{1/2}$ [Eqs. (3) and (4)]. The dashed and solid lines show the absorption with the Lorentz and asymmetrical line shapes, respectively. Both the ordinates and abscissae of curve 2 should be multiplied by ten.

The fractional absorption, A , by a single line is given by the familiar square root law

$$A\Delta\nu = 2(Sau)^{1/2}, \quad (3)$$

when the radiation is completely absorbed at the center of the line, where u is the optical thickness of the absorbing gas. If $k(\nu) \sim |\nu - \nu_0|^{-n}$ in the wings of the line, by the usual derivation $A \sim (Sau)^{1/n}$. For $n=2$, this agrees with Eq. (3). If $k(\nu)$ is given