

FIG. 1. Typical curves used to calculate the total cross section of ions of 400-volts energy in argon. The readings indicated by triangles were taken as the pressure was increased, and then the readings indicated by circles were taken as the pressure was reduced.

These pressures were measured on an ionization gauge calibrated for each gas. A weak magnetic field applied across the ion beam swept out stray electrons.

Considerable scattering of the measured cross sections was observed, which was partially a result of variations in emission from the cathode during a particular run. This variation can be seen in Fig. 2. The gases used should not react chemically with the cathode and did not appear to affect the ion yield. The temperature of the cathode was measured by means of a thermocouple but was found not to vary appreciably with the gas pressure or variations in the heater current. Therefore the variation in emission was not mainly caused by variation in the temperature of the cathode or gas pressure.

The types of collisions that are expected are elastic collisions, de-ionization of the iodine ion by a neutral molecule, and inelastic collisions. Charge transfer is not possible, as the gases used do not form negative ions. De-ionization of a negative ion produces a neutral atom which will not be detected. The energy selection of the spectrometer prevents all ions slowed down by more than one volt from reaching the plate. Therefore, all ionizing and nearly all inelastic collisions are included in the measured cross section. Elastic collisions prevent the ions from reaching the plate if the decrease in the velocity along the axis of the tube corresponds to more than one volt. For ions of 20 volts energy this corresponds to scattering of more than 6° and for ions of 400 volts, more than 1.4° from conservation of energy and momentum.

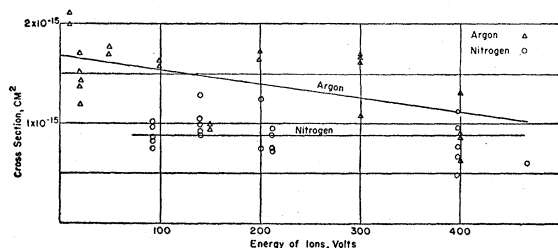


FIG. 2. The measured cross sections for collisions of negative iodine ions in argon and nitrogen.

The average value of the measured cross section in nitrogen was 9×10^{-16} cm². The measured cross section was constant within the accuracy of the measurements from 100 to 400 volts. The average value of the measured cross section in argon was 14×10^{-16} cm². The measured cross section appeared to decrease slightly from 10 to 400 volts, and the decrease was on the borderline of experimental error. The accuracy of both averages is estimated to be $\pm 3 \times 10^{-16}$ cm².

¹ For example, R. B. Kennard, Phys. Rev. 31, 423 (1928); A. J. Dempster, Phil. Mag. 3, 115 (1927); G. P. Thomson, Phil. Mag. 2, 1076 (1926); C. Ramsauer and O. Beek, Ann. Physik 87, 1 (1928); J. S. Thompson, Phys. Rev. 35, 1196 (1930).

² W. H. Bennett, J. Appl. Phys. 21, 143 (1950).

Diffusion of Donor and Acceptor Elements into Germanium*

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WHEN donor or acceptor elements diffuse into *p*-type or *n*-type germanium, respectively, *pn* barriers are formed. By determining the distance of these barriers for two specimens of different but known original conductivities, the diffusion constant, *D*, as well as the surface concentration, *C*₀, can be determined from

$$\frac{\sigma_1}{q\mu} = C_0 \operatorname{erfc} \left[\frac{x_1}{2(Dt)^{1/2}} \right], \quad \frac{\sigma_2}{q\mu} = C_0 \operatorname{erfc} \left[\frac{x_2}{2(Dt)^{1/2}} \right], \quad (1)$$

where σ_1, σ_2 are the original conductivities in ohm⁻¹ cm⁻¹; *q*=elementary charge, 1.6×10^{-19} coulombs; μ =carrier mobility, 3600 cm²/volt sec for *n* type, 1700 cm²/volt sec for *p*-type; *erfc*=error function complement,

$$1 - \frac{2}{\sqrt{\pi}} \int_{-x/2(Dt)^{1/2}}^0 \exp(-\beta^2) d\beta;$$

*x*₁, *x*₂=corresponding diffusion distances of barriers in cm; *D*=diffusion constant in cm²/sec; *t*=time in seconds, and *C*₀=the surface concentration in cm⁻³, assumed to be constant and the same for both specimens.

In Eq. (1) the quantity $\sigma/q\mu$ is the concentration of the carriers in the original germanium. This at the boundary is equal to the concentration of diffusing atoms if we assume each atom supplies one electron to the conduction band or one hole to the filled band.

Thus, in a given experiment, Eq. (1) allows *D* to be calculated from the ratio of the conductivities (*p* or *n*) of two specimens exposed to the same surface concentration of donor or acceptor element, respectively, from the relation

$$\operatorname{erfc} \left[\frac{x_1}{2(Dt)^{1/2}} \right] / \operatorname{erfc} \left[\frac{x_2}{2(Dt)^{1/2}} \right] = \frac{\sigma_1}{\sigma_2}. \quad (2)$$

When *D* is known, *C*₀ is obtainable from (1).

Specimens of single crystal *p*-type germanium containing gallium have been subjected to both arsenic and antimony diffusion. Similar specimens of *n*-type germanium have been diffused with indium. The barrier positions were determined by means of a "cold" tungsten probe employing contact rectification as an indicator and by means of a "hot" tungsten probe connected to a galvanometer to measure the sign of the thermoelectric voltage. The hot probe method in most instances gave somewhat lower values for the barrier distances. Values of *D*

TABLE I. Data for antimony and arsenic diffusion into germanium.

<i>T</i> (°C)	(Time) ¹ (sec) ²	$\frac{\sigma_1}{q\mu}$ (ohm ⁻¹ cm ⁻¹)	$\frac{\sigma_2}{q\mu}$ (ohm ⁻¹ cm ⁻¹)	<i>x</i> ₁ (cm)	<i>x</i> ₂ (cm)	<i>D</i> × 10 ¹⁰ cm ² /sec	<i>C</i> ₀ (cm ⁻³)
Antimony							
710	778	14.5	1.12	0.0038	0.0045	0.03	2.0×10^{20}
755	761	11.1	0.50	0.0084	0.0123	0.13	3.2×10^{19}
810	564	32.3	1.08	0.0152	0.0229	0.76	1.8×10^{18}
850	922	52.6	1.25	0.0350	0.0399	0.37	1.0×10^{22}
850	704	52.6	1.25	0.0186	0.0265	0.51	2.9×10^{19}
850	481	13.5	1.30	0.0166	0.0217	0.96	4.4×10^{18}
850	481	13.5	1.30	0.0180	0.0227	0.96	7.0×10^{18}
905	408	32.3	1.08	0.0154	0.0263	2.3	7.2×10^{17}
Arsenic							
710	778	13.5	1.12	0.0064	0.0075	0.01	1.0×10^{20}
750	831	11.1	1.30	0.0127	0.0138	0.05	1.0×10^{20a}
755	761	11.1	0.50	0.0150	0.0164	(0.09) ^a 0.04	1.0×10^{20a}
800	613	16.7	5.6	0.0112	0.0133	0.36	3.0×10^{18}
800	487	16.7	8.3	0.0038	0.0052	0.36	3.0×10^{17}
850	701	76.9	12.5	0.0183	0.0350	1.2	1.5×10^{18}
850	920	76.9	12.5	0.0169	0.0355	0.79	2.2×10^{18}
905	701	14.3	1.08	0.0222	0.0333	1.4	1.0×10^{18}

^a These values of *D* are calculated assuming *C*₀ = 1.0×10^{20} .

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,

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

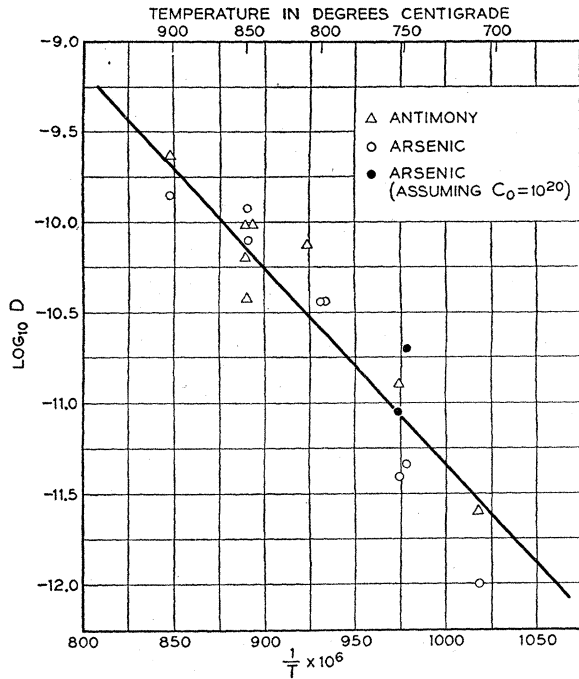


FIG. 1. Diffusion constants of antimony and arsenic as a function of temperature.

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.

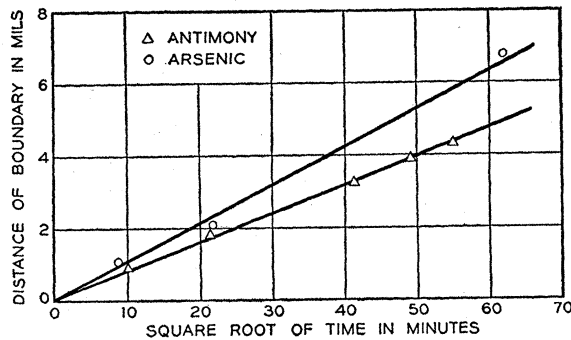


FIG. 2. Diffusion distance versus time for antimony and arsenic.

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

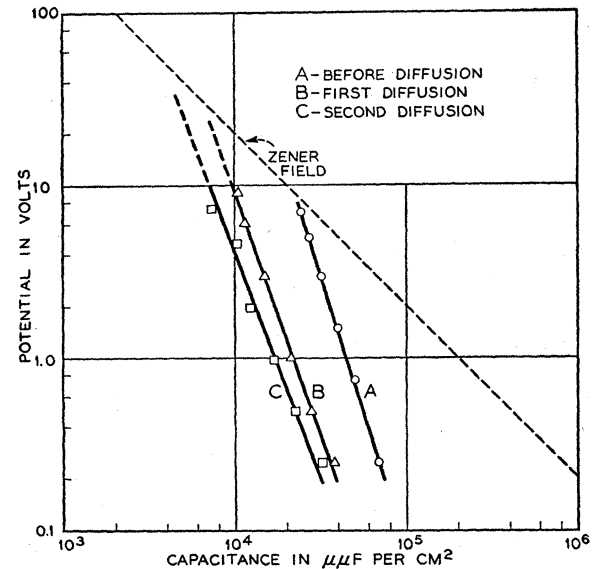


FIG. 1. Change in capacitance of a *p-n* junction with heat treatment. A dielectric constant of 16 is assumed for germanium.

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