

## Effect of Heavy Doping on the Self-Diffusion of Germanium\*†

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The germanium self-diffusion coefficients for intrinsic, heavily-doped *n*- and *p*-type germanium were measured at several temperatures. It was found that the self-diffusion coefficient is greater for heavily-doped *n*-type than for intrinsic germanium and that the self-diffusion coefficient for intrinsic germanium is greater than for heavily-doped *p*-type. If one assumes that a vacancy acts as an acceptor and that germanium self-diffusion goes by the vacancy mechanism, the observed changes in the value of the self-diffusion coefficient with doping are in the direction and of the order of magnitude of changes calculated from the shift in the Fermi level alone. It is concluded that germanium self-diffusion probably proceeds by the vacancy mechanism.

### INTRODUCTION

THESE experiments were performed in order to determine whether germanium self-diffusion occurs by the vacancy mechanism. If self-diffusion does occur by means of vacancies, the diffusion coefficient at a given temperature will be proportional to the concentration of vacancies. By changing the concentration of vacancies by a known amount, one would then be able to predict the variation in the self-diffusion coefficient. A method for varying the concentration of vacancies is suggested in the work of Reiss and Fuller if one further assumes that vacancies act as acceptors.<sup>1,2</sup> They<sup>2</sup> have been able to confirm the predictions of the former author,<sup>1</sup> namely that the solubility of a donor increases with increasing acceptor content and that the solubility of a donor decreases in the presence of another donor. Similarly, Reiss<sup>1</sup> predicts that an acceptor would be more soluble in a donor environment than in an acceptor environment. Consequently, if vacancies behave as acceptors, one would expect that at a given temperature the equilibrium concentration of vacancies in *n*-type germanium would be greater than in *p*-type germanium,<sup>3</sup> i.e., germanium self-diffusion should be greater in *n*-type than *p*-type germanium in the case of diffusion via vacancies.

Evidence indicating that vacancies act as acceptors is found in data obtained from irradiated germanium.<sup>4,5</sup> The interpretation that the acceptors brought about by thermally quenching germanium from high temperatures are, in part, vacancies is as yet questionable.<sup>6,7</sup>

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<sup>1</sup> H. Reiss, *J. Chem. Phys.* **21**, 1209 (1953).

<sup>2</sup> H. Reiss and C. S. Fuller, *J. Metals* **8**, 276 (1956).

<sup>3</sup> R. L. Longini and R. F. Greene, *Phys. Rev.* **102**, 992 (1956).

<sup>4</sup> H. Y. Fan and K. Lark-Horovitz, *Report of Bristol Conference on Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 232.

<sup>5</sup> Cleland, Crawford, and Holmes, *Phys. Rev.* **102**, 722 (1956).

<sup>6</sup> Blank, Geist, and Seiler, *Z. Naturforsch.* **9a**, 515 (1953).

<sup>7</sup> R. A. Logan, *Phys. Rev.* **101**, 1455 (1956).

### EXPERIMENTAL

The diffusivity of the tracer Ge<sup>71</sup> in intrinsic, heavily-doped *n*- and *p*-type, single crystal germanium was measured. In order to obtain significant changes in the concentration of vacancies, it is necessary to use heavily-doped germanium. About  $6 \times 10^{18}$  arsenic atoms/cm<sup>3</sup> were present in the *n*-type specimens, while the *p*-type specimens contained about  $5 \times 10^{19}$  and  $1 \times 10^{20}$  gallium atoms/cm<sup>3</sup>. The heavily-doped single crystals were prepared by W. W. Tyler of the G. E. Research Laboratory. At any particular temperature, three germanium specimens, one intrinsic, one *n*-type, and one *p*-type, were electroplated with neutron-irradiated germanium (from Oak Ridge), sealed in separate Vycor tubes containing argon at a pressure of about 30 cm of mercury, and then annealed in the same, constant temperature furnace for the same amount of time. Both sides of each specimen were simultaneously electroplated. Chromel-Alumel thermocouples were used to measure temperatures; the error in the temperature values is estimated to be from  $\pm 2$  to  $\pm 3^\circ\text{C}$ . Care had to be exercised in polishing the heavily-doped specimens prior to electroplating and annealing, for otherwise the germanium surfaces would become markedly eroded. Argon was added with the hope of it aiding in the prevention of this thermal etching by decreasing the rate of evaporation of the doping materials. The composition of the electroplating solution<sup>8</sup> was: 50 cc of H<sub>2</sub>O containing 0.52 g of irradiated GeO<sub>2</sub>, 0.86 g of KOH and 3.2 g of K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> · H<sub>2</sub>O. It was necessary to maintain this bath at about 85°C while electroplating. An advantage of this solution is that it will also dissolve, to a certain extent, the oxide coating of the germanium itself; this electroplating technique does have a disadvantage in that it is difficult to obtain uniformly deposited layers.

Assuming that at  $t=0$  we have plated onto our specimen a uniform Ge<sup>71</sup> layer having a thickness  $d$  and concentration  $C_0$  and that no Ge<sup>71</sup> is either leaving or entering the surface ( $X=0$ ), then the concentration at

<sup>8</sup> Letaw, Portnoy, and Slifkin, *Phys. Rev.* **102**, 636 (1956).

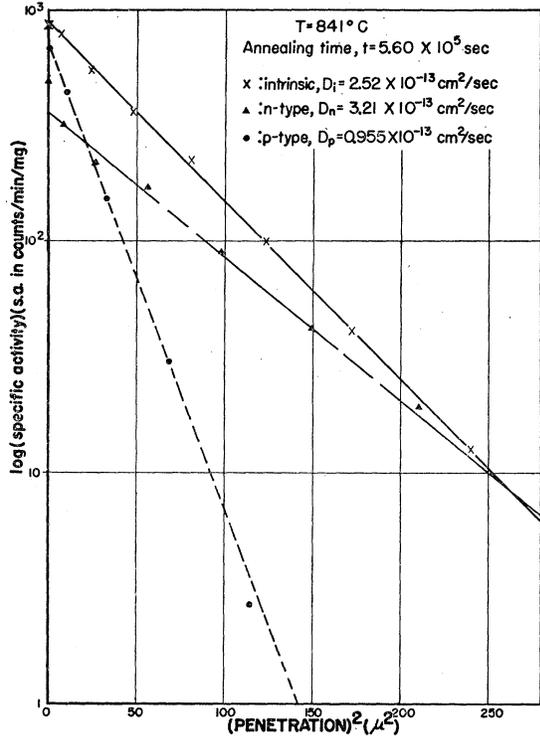


FIG. 1. A penetration plot of the data taken at 841°C. These data were obtained from one side of each type of germanium specimen. Since it is assumed that the specific activity (concentration) varies as  $\exp(-X^2/4Dt)$ , the diffusion coefficients are inversely proportional to the absolute value of the slope of the straight lines.

a time  $t$  is given by<sup>9</sup>

$$C(X,t) = \frac{C_0}{\pi^{3/2}} \left[ \int_0^{u+\delta} \exp(-v^2) dv - \int_0^{u-\delta} \exp(-v^2) dv \right], \quad (1)$$

where  $X$  = distance from the surface,  $D$  = diffusion coefficient,  $u = X/2(Dt)^{1/2}$ , and  $\delta = d/2(Dt)^{1/2}$ . For  $\delta \ll 1$ , Eq. (1) becomes the familiar

$$C(X,t) = [C_0 d / (\pi Dt)^{1/2}] \exp(-X^2/4Dt). \quad (2)$$

Equation (2) was used in the determination of all of our diffusion coefficients.

Sections, each having a thickness of the order of 1  $\mu$  and a weight of the order of a milligram, were taken from the surfaces of the annealed specimens by using a precision grinding machine.<sup>10</sup> Weight determinations having a precision of  $\pm 0.01$  mg were performed on a semimicrobalance. As  $\text{Ge}^{71}$  decays by electron-capture, Tracerlab Geiger-Mueller tubes particularly sensitive to x-rays were used in assaying; the magnitudes of the specific activities generally extended over approxi-

<sup>9</sup> W. Jost, *Diffusion* (Academic Press, Inc., New York, 1952), p. 23.

<sup>10</sup> Letaw, Slifkin, and Portnoy, *Rev. Sci. Instr.* **25**, 865 (1954).

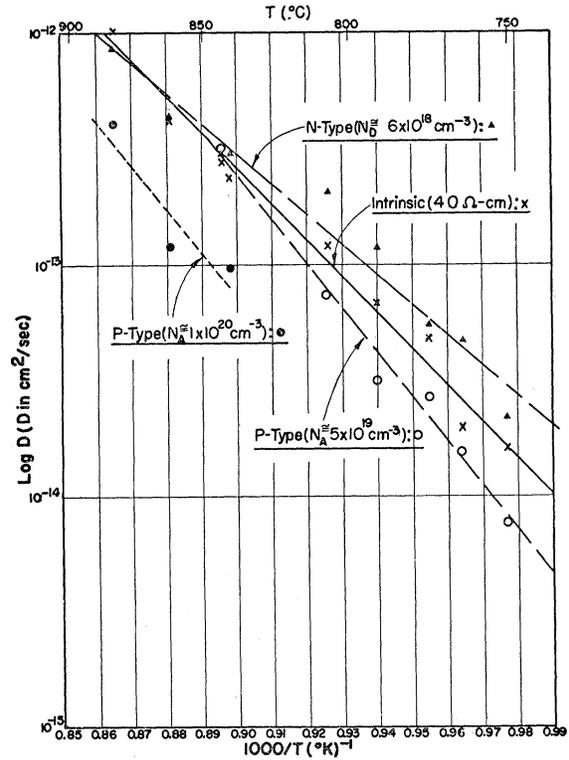


FIG. 2. The observed germanium diffusion coefficient,  $D$ , at various temperatures and for different dopings. From the shift in the Fermi at 800°C:  $D/D_i = 1.4$  for  $N_D = 6 \times 10^{18}/\text{cm}^3$  and  $D/D_i = 0.17$  for  $N_A = 5 \times 10^{19}/\text{cm}^3$ . These ratios do not differ by more than 20% from those at 800°C over the temperature range in question (gradually decreasing with increasing temperature in the former case and gradually increasing with increasing temperature in the latter case).

mately three cycles, the lowest specific activities being as low as a few counts/min/mg above background. Each section was counted until the statistical error was at most  $\pm 2\%$ . From a plot of the logarithm of the specific activity vs the square of the penetration, the diffusion coefficient is obtained from the slope of the straight line. Figure 1 is a plot of typical data.

The logarithm of the diffusion coefficient vs a multiple of the reciprocal of the absolute temperature is plotted in Fig. 2. Probably an important contribution to the scatter of the data is inherent in the use of Eq. (2) for determining the diffusion coefficients. Equation (2) was arrived at under the assumption that  $d/2(Dt)^{1/2} \ll 1$ , but owing to the low specific activity of the irradiated germanium and the smallness of the diffusion coefficients it was difficult to maintain rigidly this inequality; consequently the diffusion coefficients obtained in this way were sensitive to the thickness of the electroplated layer and are generally too high. It is difficult to determine the error introduced by nonuniformity in the thickness of the electroplated layer for the case where  $d \sim (Dt)^{1/2}$ . In the case where  $d \ll (Dt)^{1/2}$ , it has been shown that no error is introduced by nonuniformity provided the diffusion coefficient is determined by the above

method (Fig. 1).<sup>11</sup> If surface diffusion were much greater than bulk diffusion, the error introduced by non-uniformity in the electroplated layer thickness would, of course, be small.

In order to investigate the possibility of the heavy-doping producing appreciable strain in the germanium lattice, thereby influencing the concentration of vacancies, determinations of the lattice parameter were made. X-ray measurements made at the G. E. Research Laboratory revealed only small changes in the lattice constant and in the same direction for both the heavily-doped *n*- and *p*-type germanium (about a 0.02% decrease).<sup>12</sup>

### INTERPRETATION AND DISCUSSION

An expression for the ratio  $D/D_i$ , where  $D$  is the self-diffusion coefficient for either *n*- or *p*-type germanium, can be arrived at by determining the change in the concentration of vacancies from the shift, due to doping, of the Fermi level. The concentration of neutral vacancies is maintained at an equilibrium value appropriate to the temperature, while the concentration of charged vacancies depends on both the temperature and position of the Fermi level. If vacancies act as acceptors, the concentration of charged vacancies,  $[v^-]$ , is given by

$$[v^-] = [v] / \{1 + \exp[(E_{vac} - E_F)/kT]\}, \quad (3)$$

where  $E_{vac}$  and  $E_F$  are the vacancy and Fermi levels, respectively, and  $[v]$  is the total concentration of vacancies (charged and neutral). Using (3) and the assumption that, to a first approximation, the concentration of neutral vacancies is independent of doping, we obtain

$$\frac{D}{D_i} = \frac{[v]}{[v]_i} = \frac{1 + \exp[(E_F - E_{vac})/kT]}{1 + \exp[(E_{Fi} - E_{vac})/kT]}, \quad (4)$$

where  $[v]_i$  is the total concentration of vacancies and  $E_{Fi}$  is the Fermi level in intrinsic germanium. For a low-lying acceptor level ( $E_F - E_{vac} \gg kT$ ), (4) becomes

$$D/D_i = \exp[(E_F - E_{Fi})/kT] = n/n_i, \quad (5)$$

where  $n$  and  $n_i$  are the electron concentrations in doped and intrinsic germanium, respectively. Calculations of  $D/D_i$  were made by using Morin and Maita's<sup>13</sup> data for  $n_i^2$  and the condition for charge neutrality.

In Fig. 2, the *n*-type data agree fairly well with those predicted by Eq. (5). However, the *p*-type data are somewhat higher than would be expected from (5).

A possible cause for the discrepancy may be the evaporation of gallium from the surfaces of the *p*-type specimens. Spectrographic estimations showed that the evaporation of gallium was appreciable at 895°C, the concentration of gallium decreasing by about a factor of four in a region extending about  $(Dt)^{1/2}$  from the surface. It was not possible to estimate spectrographically whether evaporation of arsenic occurred; still one would not expect the evaporation of arsenic to be as great as that of gallium, since it has been found that gallium goes readily into the Vycor walls at these temperatures. Possibly the convergence at higher temperatures of the doped germanium self-diffusion coefficients towards the values for intrinsic germanium could be attributed to the evaporation of doping materials. Another explanation for the *p*-type disagreement could be that the acceptor level is not far below the mid-gap position. In this case it would be necessary to use Eq. (4) instead of (5). Equation (4) would give significantly greater values for  $D_p/D_i$  ( $D_p$  being the *p*-type germanium self-diffusion coefficient) than (5), if the Fermi level were nearer to  $E_{vac}$ , without significantly altering  $D_n/D_i$  ( $D_n$  being the *n*-type diffusion coefficient). Nevertheless, it is concluded that these data indicate that germanium self-diffusion probably occurs via vacancies.

Extending the theory of the vacancy mechanism to the case of the diffusion of donors and acceptors into germanium, one might expect to account for the fact that donors and acceptors have diffusion coefficients greater than corresponding ones for germanium self-diffusion by association effects,<sup>14</sup> i.e., vacancies may be associated with the diffusing donor and acceptor atoms. Preliminary data taken with antimony by one of the authors (M.W.V.) tend to confirm that diffusion occurs by means of vacancies. Further experimental work along these latter lines is now in progress.

### ACKNOWLEDGMENTS

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<sup>11</sup> D. S. Tannhauser, J. Appl. Phys. 27, 662 (1956).

<sup>12</sup> These results on the lattice constant measurements were given to us by W. W. Tyler.

<sup>13</sup> F. J. Morin and J. P. Maita, Phys. Rev. 94, 1525 (1954).

<sup>14</sup> Reiss, Fuller, and Morin, Bell System Tech. J. 35, 535 (1956).