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Diffusion of Donor and Acceptor Elements in Silicon

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(Received December 14, 1955)

The diffusion of the Group III (B, Al, Ga, In, and Tl) and Group V (P, As, Sb, and Bi) elements in silicon has been measured in the temperature range 1050–1350°C. A method based on change in conductivity through the penetration layer has been used for B and P. The p-n junction method has been used for the other elements. Aside from B and P, which have similar diffusional properties, the acceptor elements diffuse more rapidly than the donor elements. Diffusion coefficients are given by $D_{B,P} = 10.5 \exp - (85\,000/RT)$, $D_{Al} = 8.0 \exp - (80\,000/RT)$, $D_{Ga} = 3.6 \exp - (81\,000/RT)$, $D_{In,Tl} = 16.5 \exp - (90\,000/RT)$, $D_{As} = 0.32 \times \exp - (82\,000/RT)$, $D_{Sb} = 5.6 \exp - (91\,000/RT)$, $D_{Bi} = 1030 \exp - (107\,000/RT)$ with an average estimated error of about $\pm 40\%$. This corresponds to an error in the activation energies of about ± 5 kcal. Sources of error including the effects of impurities in the oxides are discussed. D_0 values in most cases conform to the predictions of Zener for substitutional diffusion.

THE measurement of p-n junction distances provides a convenient method for investigating diffusion in semiconductors.[1,2] Measurements of the diffusion of a number of donor and acceptor elements in germanium and of lithium in silicon have already been reported.[3,4]

In a previous publication[5] the authors also reported preliminary work on the diffusion of boron and phosphorus in Si from boron trichloride and from elemental phosphorus, respectively. These measurements have been repeated using the oxide of boron (B_2O_3) and phosphorus pentoxide (P_2O_5) as diffusion sources. A higher value for the activation energy for diffusion has been found which is in better agreement with the value reported by Dunlap et al.[6] The present work describes similar work on Si for the Group III acceptor and the Group V donors. Such information is particularly useful in the design of semiconductor devices.[7,8(a)]

Most of the results have been obtained by measuring the junction depths in two specimens of Si of known but different resistivities run under identical conditions of surface concentration.[1] However, special precautions are necessary to secure good results, and a new technique for precisely measuring the depths of such junctions had to be developed. In a few cases results by the above method have been supplemented by calculations based on known surface concentrations from chemical analyses. For boron and phosphorus an attempt was

made to determine the entire penetration curves by means of incremental conductivity measurements obtained by successive lappings of plane parallel specimens. This work will be discussed first.

DIFFUSION OF BORON AND PHOSPHORUS

Because it was desired to have as complete information as possible on the diffusion of boron (B) and of phosphorus (P) in Si, we decided to measure the sheet resistivity changes as a function of depth through the diffusion layer on plane parallel specimens. Figure 1 illustrates the principle of the method. There are shown four equally-spaced (0.0127 cm) conducting probes in contact with a diffusion layer of opposite type to the base Si so that a p-n junction is formed. Measurements of the potential E between probes 2 and 3 are taken for successive lappings (Δl) on W, parallel to the surface. It is assumed that the layer is sufficiently extensive to neglect end effects, that the current flow is laminar, that the p-n junction acts as an insulating plane, and that the successive layers removed are thin compared with W. All of these assumptions appear to be adequately met.

If a lapping (Fig. 1) of thickness $\delta l = l_2 - l_1$ is considered, its conductance parallel to the junction per cm², G_l is

$$G_l = G_2 - G_1$$

where G_2 and G_1 are the conductances in mhos per cm² before and after lapping. Introducing the factor 4.5 to correct for the geometry of the 4-point probe arrangement,*,[8(b)]

$$G_l = \frac{1}{4.5}\left(\frac{I_2}{E_2} - \frac{I_1}{E_1}\right) = n_l q \mu_l \delta l, \tag{1}$$

where n_l is the number of carriers per cm³ in the lapping increment of thickness δl, μ_l is the mobility of the carriers in this layer in cm²/v sec, and q is the

[1] Fuller, Theuerer, and van Roosbroeck, Phys. Rev. **85**, 678 (1952); Fuller, Struthers, Ditzenberger, and Wolfstirn, Phys. Rev. **93**, 1182 (1954).

[2] D. E. Brown and W. C. Dunlap, Jr., Phys. Rev. **87**, 616 (1952); W. C. Dunlap, Jr., Phys. Rev. **94**, 1531 (1954).

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

[4] C. S. Fuller and J. A. Ditzenberger, Phys. Rev. **91**, 193 (1953); C. S. Fuller and J. C. Severiens, Phys. Rev. **95**, 21 (1954).

[5] C. S. Fuller and J. A. Ditzenberger, J. Appl. Phys. **25**, 1439 (1954).

[6] Dunlap, Bohm, and Mahon, Phys. Rev. **96**, 822(A) (1954).

[7] G. L. Pearson and C. S. Fuller, Proc. Inst. Radio Engrs. **42**, (April, 1954); Chapin, Fuller, and Pearson, J. Appl. Phys. **25**, 676 (1954).

[8] (a) M. Tanenbaum and D. E. Thomas, Bell System Tech. J. **XXXV**, 1 (1956). (b) A. Uhlir, Bell System Tech. J. **XXXIV**, 105 (1955).

* The authors are indebted to A. Uhlir of these Laboratories who derived the correction factor for this case using the method of images. The factor holds for equally-spaced probes and assumes a probe spacing at least twice the layer thickness.
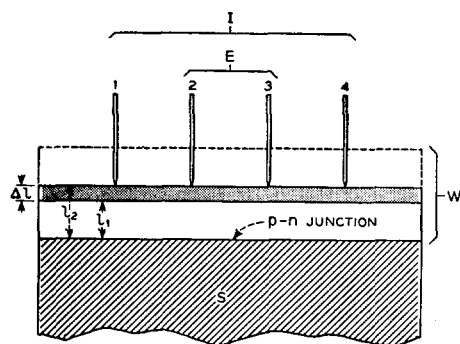
FIG. 1. Four-point probe arrangement for measuring sheet conductivity. Current is passed through points 1 and 4; potential difference is measured between points 2 and 3. The points are spaced 0.127 cm apart.

electronic charge in Coulombs. Thus, since the number of donor or acceptor atoms (ionization is essentially complete at room temperature) is equal to the number of carriers, electrons or holes respectively, the concentration per cm^2 of the diffusant, N, in a 2 micron lapping is

$$N = \frac{7.05 \times 10^{21}}{\mu_l} \Delta, \qquad (2)$$

where

$$\Delta = (I_2/E_2) - (I_1/E_1)$$

and μ_l is the mobility in the layer. The values of the latter have been taken as Hall mobilities from the work of Morin and Maita.[9] These data have been plotted in Fig. 2, the dashed portion being our extrapolation. No attempt has been made to correct these mobilities to drift mobilities since the ratio μ_H/μ_D changes over the entire impurity range in a complicated way. The error so introduced is believed to be less than $\pm 25\%$ except at impurity concentrations above 10^{19} where the error could be $\pm 50\%$. In the vicinity of the junction drift mobilities[10] were used.

PROCEDURE AND RESULTS FOR BORON AND PHOSPHORUS

Specimens of single crystal† 10 ohm cm Si, 1 cm on a side and 0.5 cm thick were prepared by lapping flat to about $\pm 0.2\mu$ on the Bond lapping machine.[11(a)] p-type Si (boron-doped) was employed for the phosphorus diffusion and n-type Si (arsenic-doped) for the boron. All specimens were preheated 15 min at 1200°C in helium to minimize body resistivity changes‡

[9] F. J. Morin and J. P. Maita, Phys. Rev. 96, 28 (1954).
[10] M. B. Prince, Phys. Rev. 93, 1204 (1954).
† The authors are indebted to E. Buehler and R. Landgren of these Laboratories for supplying these crystals.
[11](a) W. L. Bond, Quartz Crystals, R. A. Heising, editor (D. Van Nostrand Company, Inc., New York, 1949). (b) C. L. Luke, Anal. Chem. 27, 1150 (1955); C. L. Luke and Mary E. Campbell, Anal. Chem. 25, 1588 (1953).
‡ Rotated crystals such as used in this work sometimes undergo resistivity changes at high temperatures because of heat treatment during growth.
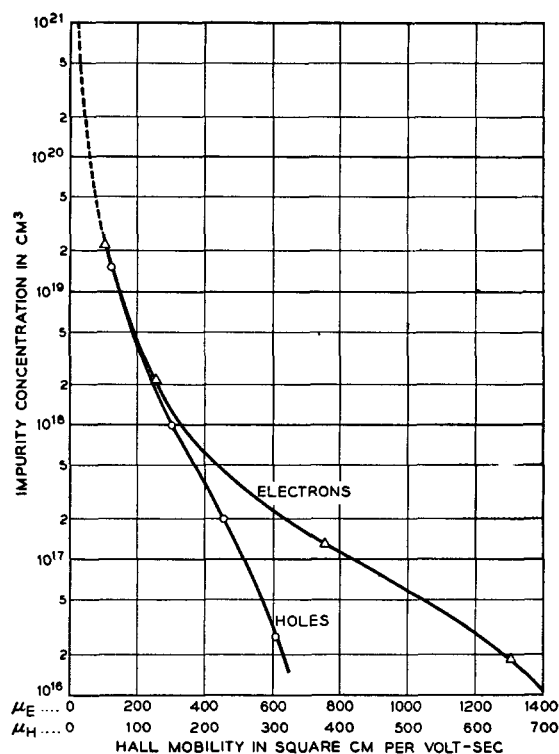
FIG. 2. Plot of Morin and Maita mobility data from Phys. Rev. 96, 28 (1954) showing authors' extrapolation.

during diffusion. After cleaning in nitric and hydrofluoric acids, applied separately, duplicate specimens were diffused in sealed quartz tubes using 1 mg portions of boric oxide in the boron diffusions and 0.5–1.0 mg of phosphorus pentoxide in the phosphorus diffusions. Diffusions were carried out at temperatures ranging from 950 to 1275°C for each element. Temperatures were measured with a Pt–Pt 10% Rh couple to ± 2°C.

Lapping of one face of each specimen was carried out with a suspension of aluminum oxide (No. 600) or with American optical No. 303.5 in water. The back faces were lubricated with light machine oil. The rate of lapping was kept very low (1μ per 15 min) in order to minimize damage to the surfaces. Specimens were interchanged regularly to insure planarity of lap. Four-point probe measurements were taken about every micron. Depths were measured on a Zeiss optimeter to $\pm 0.2\mu$. Lapping was continued until the junction was passed as shown by reversal of resistance versus distance curves.

Independent measurements of the junction distances were made by grinding the back faces of the specimens at an angle of 5° and, where differences with the lapped values were found, corrections for changes in thickness were made to allow for unavoidable grinding losses from the back faces during the lapping procedure. The magnitude of these corrections was at most about 10% of the total p-n boundary distances.

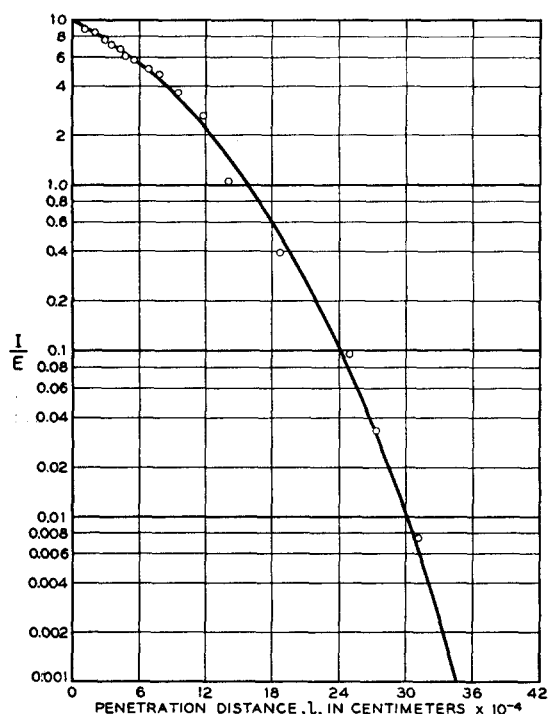The corrected penetration distances were plotted

FIG. 3. Plot of four-point probe conductance against distance in microns for a phosphorus diffusion of 18.5 hours at 1235°C (see Table II).

against the corresponding readings of I/E on a semi-logarithmic scale and the best smooth curves drawn. The results are shown for phosphorus at 1235°C in Fig. 3. The quantity Δ of Eq. (2) was determined by
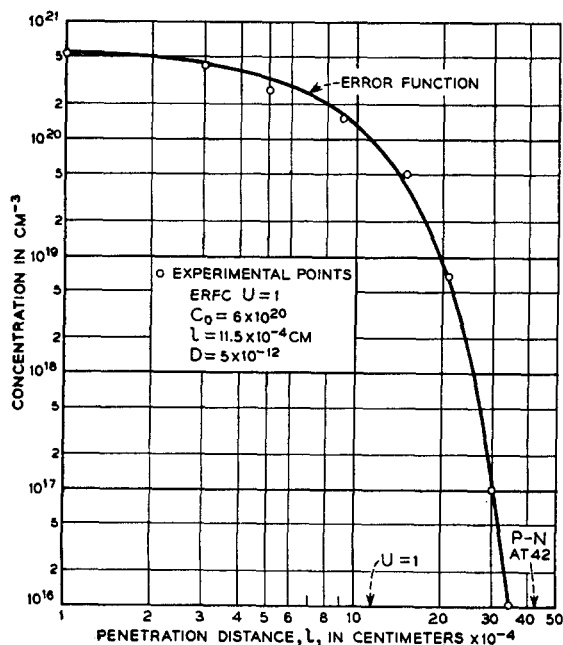

FIG. 4. Log-log plot of erfc u against u (solid line) showing also the experimentally determined concentration *versus* penetration distance data (open circles) for phosphorus from Fig. 3 using $C_0 = 6 \times 10^{20}$.

subtracting the ordinates at even micron penetration depths. In this way, average concentrations, N, in atoms per cm², at each odd micron distance were determined from Eq. (2) in terms of μ_l, the mobility, for each 2μ layer.

To obtain the best values of the diffusion coefficient and surface concentration in any given run the following approximation procedure§ was employed: a plot of erfc‖ u against u on log-log paper was fitted to the measured p-n junction depth on the horizontal axis and to the surface concentration, as determined from chemical analysis (see below) on the vertical axis. These were also plotted on log-log paper of the same scale as the erfc u *versus* u plot. Concentrations of the diffusant were read for arbitrary penetration distances from this plot. The mobilities corresponding to these concentrations and distances were then read from Morin and Maita's mobilities plotted against impurity concentration of their specimens¶ (Fig. 2). These mobilities were used to calculate observed concentrations from Eq. (2) using the values of Δ corresponding to the distances chosen. This curve was then fitted to the erfc u *versus* u curve shifting vertically and horizontally to secure the best fit with all of the data. Usually one such fitting was sufficiently accurate. However, if the values of μ_l changed more than about $\pm5\%$ for the new concentrations a second fitting was carried out.

From the curves of best fit, penetration distances, l, corresponding to abscissa distance $u=1$ were read for each temperature, and D, the diffusion constant, determined from

$$D = l^2/4t. \tag{3}$$

Likewise, values of C_0, the surface concentration, were determined from the ordinate value erfc $u=1$.

To conserve space, the method of fitting the experimental data to the error integral curve is shown (in Fig. 4) only for one temperature, namely, for phosphorus at 1235°C. The measurements for the other temperatures were treated in the same manner, as were also those for boron. For the same reason, the bulky conductance data taken during the lapping procedure have not been reproduced here.

C_0 values from the chemical analysis of diffused specimens were calculated as follows: the integrated area under the penetration curves is given by

$$N_s = 2(Dt)^{\frac{1}{2}} \int_0^\infty C_0 \, \text{erfc}\beta d\beta, \tag{4}$$

where N_s is the total impurity content per cm² of diffusion surface as determined by chemical anal-

ysis,[**],[11(b)] D is the diffusion constant in cm²/sec, t is the time in sec, C_0 is the surface concentration in cm⁻³ and β is defined as $x/\sqrt{Dt}$. D is taken from the previous work[5] and, since t is known, C_0 can be calculated. The expression (4) can be written

$$C_0 = N_s/1.13(Dt)^{\frac{1}{2}} \qquad (5)$$

for this calculation, where N_s is the number of atoms of diffusant per cm². These results are given in Table I. The results of the diffusion measurements for B and P are summarized in Table II. Two specimens were run at each temperature and the values given are the averages of the two. The values of C_0 in Table I differ

TEMPERATURE IN DEGREES CENTIGRADE

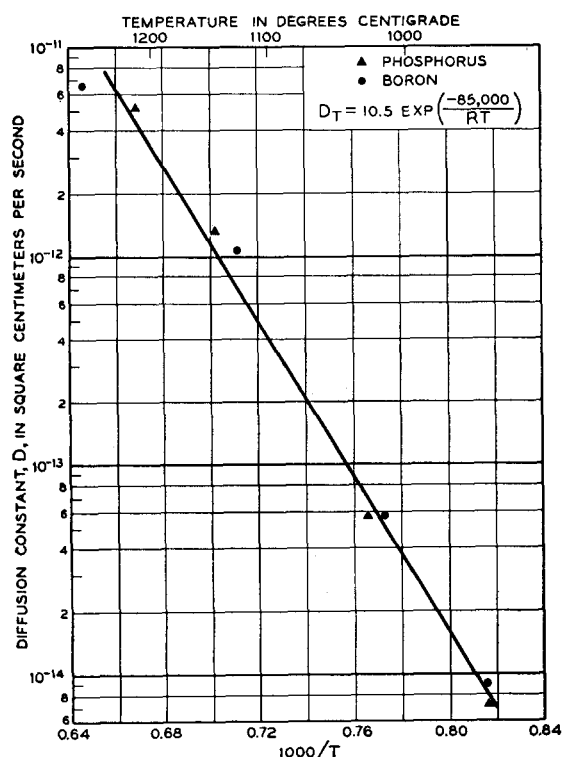$$D_T = 10.5 \; \text{EXP}\left(\frac{-85,000}{RT}\right)$$

FIG. 5. Diffusion coefficients for boron and phosphorus plotted against reciprocal of absolute temperature.

from those of Table II because of the curve fitting done to secure the data of Table II. A discussion of the rather large variations is given later.

A plot of the diffusion constants for B and P against reciprocal of absolute temperature is given in Fig. 5. We do not feel the precision warrants differentiating between the boron and phosphorus results and so have drawn only one curve through all of the points. The corresponding equation is

$$D = 10.5 \exp\left(\frac{-85000}{RT}\right), \qquad (6)$$

** The analyses were made by dissolving the diffused portions of specimens of known area and determining the amount of impurity by a spectrophotometric method. See reference 11(b).

TABLE I. Surface concentration of B and P as obtained by chemical analysis.[a]

$T°C$	Diffusion time (secs) 10^{-4}	N_s cm⁻² ×10^{-16}	C_0 ×10^{-20} cm⁻³ calculated from (5)
Boron			
980	62.00	128	100
1045	60.00	250	93
1110	33.50	85	20
1165	52.50	36	40
1230	2.61	98	23
1345	0.42	183	41
Phosphorus			
1000	58.00	9.8	6.0
1040	58.70	65.0	23.0
1105	23.20	336.0	104.0
1140	6.03	1200.0	500.0
1225	2.52	1268.0	285.0
1275	1.08	307.0	64.0
1335	0.24	41.6	8.7

[a] The authors are indebted to C. L. Luke and Miss M. E. Campbell for these analyses.

where the activation energy of diffusion is 85 000 cal. This value is appreciably higher than that given previously[5] and in good agreement with recent value for boron reported by Dunlap and co-workers,[6] namely, 3.5 ev or 81 000 cal.

DIFFUSION OF THE OTHER GROUP III AND GROUP V ELEMENTS

The method employed has already been described.[3] It consists in determining the p-n junction depths x_1 and x_2 in Si specimens of resistivities ρ_1 and ρ_2 diffused together under identical conditions. n-type Si is chosen for acceptor diffusants and p-type Si for donor. Since the surface concentrations are the same, the equation

$$\frac{\rho_1\mu_1}{\rho_2\mu_2} = \frac{\text{erfc}[x_2/2(Dt)^{\frac{1}{2}}]}{\text{erfc}[x_1/2(Dt)^{\frac{1}{2}}]} \qquad (7)$$

holds, where μ_1 and μ_2 are the drift mobilities[10] in cm²/v sec, D is the diffusion coefficient in cm²/sec, and t is the time in sec. Values of μ are available from Fig. 2. Equation (7) is solved for D by the method of approximation. C_0 values for the conditions of the experiment

TABLE II. Summary of results on boron and phosphorus.

$T°C$	Time sec ×10^{-3}	D cm² sec⁻¹	C_0 ×10^{-20} cm⁻³	Junction depth (cm ×10^4)
Boron				
950	1730	8.7×10^{-15}	80	8
1020	1100	5.7×10^{-14}	80	19
1122	229	1.1×10^{-12}	100	37.5
1275	61	6.4×10^{-12}	10	42
Phosphorus				
950	1730	7.7×10^{-15}	25	7
1030	1100	5.7×10^{-14}	30	17
1148	229	1.3×10^{-12}	90	39
1235	66.6	5.0×10^{-12}	6	42

are then calculated from

$$C_x = C_0 \, \text{erfc}[x/2(Dt)^{\frac{1}{2}}]^{\frac{1}{2}} \qquad (8)$$

for each specimen from the known values of erfc and the values of C_x as given by

$$C_x = 1/\rho\mu q, \qquad (9)$$

where ρ is the body resistivity in ohm cm, μ the mobility in cm^2/v sec, and $q = 1.60 \times 10^{-19}$ coulombs. C_x is the number of atoms of diffusant per cm^3 at the p-n junction located x cm from the diffusion plane.

PROCEDURE FOR GROUP III AND GROUP V ELEMENTS

Single crystal Si, both n-type (doped with As) and p-type (doped with B), was employed. Rectangular wafers $1.0 \times 0.5 \times 0.15$ cm were cut from the crystals parallel to (100).†† These were lapped plane with fine carborundum powder suspended in water as previously described. The surfaces of the specimens were next prepared for diffusion by etching to a mirror polish in a mixture of concentrated HF and concentrated HNO$_3$, the proportions being adjusted to give the desired etching rate. Such surfaces are necessary in order to obtain the desired accuracy in the depth measurements (see below).

The diffusions were carried out in the same manner as described above for B and P except that somewhat less diffusant was employed (200–500 micrograms per

(a)

(b)

FIG. 6. (a) Cross-sectional view of jig used for grinding 5° angles on specimens. (b) Cross-sectional and top views of ground specimen showing positions where optimeter readings are made to determine angle of grinding; d is width of diffusion layer.

†† No effects of crystallographic direction upon diffusion have been noted within the error of these experiments.

tube of two specimens). Also as before, the oxides of the elements were used as diffusant sources. The ambient in the tubes was air at 0.001-mm Hg pressure. Temperatures, times, and heating procedure were similar to those already described for B and P.

SELECTION OF DIFFUSANT OXIDES

Oxides of the elements were employed as diffusion sources‡‡ inasmuch as previous experience with most of the elements led to severe surface erosion of the specimens. No such attack occurs under oxidizing conditions provided large excesses of the diffusants are avoided. However, it is very important, because of the small quantities which are effective, that the highest purity oxides be used. For this reason we have gone to considerable trouble to secure as pure materials as possible. This is of particular importance for the donors arsenic (As), antimony (Sb), and bismuth (Bi), since they diffuse more slowly than the acceptors. Thus, in the p-n junction method acceptor impurities in the donor oxides can lead to spurious junction positions. Donor impurities on the other hand do not appreciably influence the junction positions for aluminum (Al),
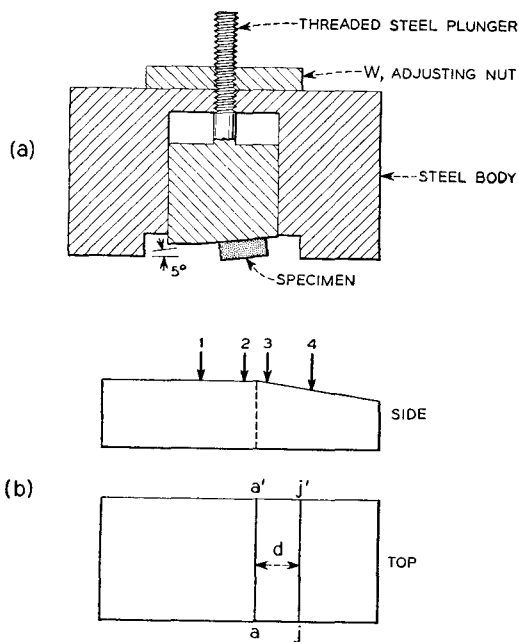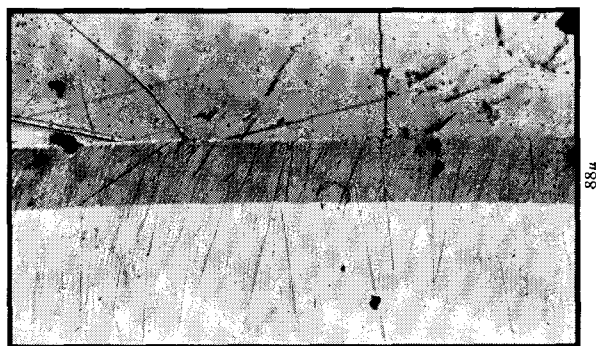

(a)

(b)

FIG. 7. Photograph of stained diffusion regions (a) p-layer in Ga diffused specimen; (b) n-layer in Sb diffused specimen.

‡‡ Except for Al which was used as the metallic element.

TABLE III. Summary of results.

	$T(°C)$	ρ_1 (ohm cm)	ρ_2 (ohm cm)	μ_1 (cm²/ volt sec)	μ_2 (cm²/ volt sec)	x_1 (cm $\times 10^3$)	x_2 (cm $\times 10^3$)	t(hr)	D (cm²/sec)	C_0 (cm⁻³)
					Aluminum					
1	1375	1.74	20.5	1125	1500	10.0	13.6	7.0	1.9×10^{-10}	3×10^{16}
2	1375	0.35[a]	5.5[a]	700	1375	2.64	7.29	2.67	4.4×10^{-10}	7×10^{16}
3	1380	0.60	8.04	825	1490	2.92	4.98	1.17	1.7×10^{-10}	4×10^{17}
4	1310	0.66	5.76	840	1405	2.31	3.99	3.0	1.2×10^{-10}	5×10^{16}
5	1300	1.83	34.0	1125	1500	6.25	10.3	16.0	4.9×10^{-11}	5×10^{16}
6	1255	0.59	6.48	850	1450	2.03	4.67	18.0	3.0×10^{-11}	4×10^{16}
7[b]	1250	1.97	99.0	1150	1500	8.15	13.1	71.0	2.7×10^{-11}	1×10^{17}
8	1250	0.63	34.7	830	1500	5.64	12.4	64.0	3.3×10^{-11}	9×10^{16}
9[b]	1195	0.58	8.65	825	1450	0.686	6.00	91.0	1.2×10^{-11}	2×10^{16}
10[b]	1190	1.87	42.0	1125	1500	2.62	7.62	96.0	1.3×10^{-11}	1×10^{16}
11	1130	0.58	4.69	825	1350	0.323	1.57	64.0	1.4×10^{-12}	2×10^{16}
12[b]	1085	3.75	91.0	1300	1600	1.42	2.31	234.0	4.3×10^{-13}	3×10^{16}
					Gallium					
1	1360	0.571	6.47	810	1415	3.16	3.97	2.42	5.40×10^{-11}	1.4×10^{19}
2	1320	0.538	8.26	790	1450	4.07	4.93	4.75	3.55×10^{-11}	6.7×10^{19}
3	1255	0.573	6.29	810	1405	5.58	6.72	22.5	1.7×10^{-11}	1.5×10^{19}
4	1170	0.493	7.54	775	1435	5.49	6.55	136.5	2.0×10^{-12}	2.1×10^{20}
5	1105	0.584	4.88	815	1360	2.93	3.43	146.0	6.15×10^{-13}	5.8×10^{19}
					Indium					
1	1360	0.606	8.76	825	1460	1.51	1.98	2.42	1.55×10^{-11}	3.5×10^{18}
2	1320	0.588	5.52	820	1380	1.53	2.14	4.75	7×10^{-12}	6.7×10^{19}
3	1255	0.562	6.02	805	1395	1.54	2.32	22.5	3.7×10^{-12}	2.8×10^{17}
4	1170	0.592	6.10	815	1400	1.59	2.30	136.5	5.2×10^{-13}	5.5×10^{17}
5	1105	0.588	6.15	820	1400	0.944	1.22	142.0	1.1×10^{-13}	4.3×10^{18}
					Thallium					
1	1360	0.572	7.64	810	1440	0.975	1.71	2.42	2.03×10^{-11}	1.3×10^{17}
2	1320	0.581	5.35	815	1375	1.20	1.86	4.75	1.2×10^{-11}	2.3×10^{17}
3	1255	0.579	10.4	815	1475	1.18	2.22	22.5	3.6×10^{-12}	1.2×10^{17}
4	1170	0.604	5.58	825	1380	0.994	1.84	136.5	5×10^{-13}	9.0×10^{16}
5	1105	0.580	6.17	815	1400	0.594	0.888	142.0	8×10^{-14}	3.7×10^{17}
					Arsenic					
	1380	0.845	31.0	382	500	0.896	1.24	2.5	5.55×10^{-12}	4.5×10^{18}
	1305		17.3				0.879	4.25	1.72×10^{-12c}	
	1250	0.806	17.9	388	500	0.640	0.945	16.0	7.65×10^{-13}	5.9×10^{17}
	1220		19.5				1.33	64.0	3.9×10^{-13c}	
	1200	0.770	31.0	376	500	0.590	0.910	42.75	2.45×10^{-13}	5.8×10^{17}
	1190		23.3				0.797	43.0	4.1×10^{-13c}	
	1095		16.4				0.453	103.0	2.9×10^{-14c}	
	1095		44.8				0.366	71	2.8×10^{-14c}	
					Antimony					
	1380	0.663	15.1	368	500	1.48	1.69	2.5	6.0×10^{-12}	2.7×10^{21}
	1305		14.7				1.18	4.25	1.5×10^{-12c}	
	1250	0.856	17.8	385	500	0.96	1.27	16.0	8.5×10^{-13}	9.2×10^{21}
	1200	0.850	28.8	383	500	0.99	1.24	42.75	2.5×10^{-13}	5.7×10^{19}
	1190		18.7				0.790	43.0	1.05×10^{-13c}	
	1095	0.853	18.4	383	500	0.290	0.413	103.0	1.9×10^{-14}	1.4×10^{18}
					Bismuth					
	1380	0.860	19.5	383	500	0.98	1.47	2.5	1.05×10^{-11}	8.9×10^{17}
	1305	0.856	13.7	382	500	0.54	0.81	4.25	2.2×10^{-12}	5.4×10^{17}
	1250	0.840	13.8	382	500	0.45	0.77	16.0	6.3×10^{-13}	2.2×10^{17}
	1220	0.904	25.7	385	500	0.802	1.12	64.0	2.0×10^{-13}	2.4×10^{18}
	1220	0.900	72.1	385	500	0.410	0.910	42.75	2.9×10^{-13}	1.0×10^{17}

[a] Measured prior to diffusion anneal.
[b] Unavoidable n-layers on surface.
[c] These values for D have been calculated from C_0 and ρ_2 as described in the text.

gallium (Ga), indium (In), and thallium (Tl).§§ Both types of impurities, however, would greatly influence the surface conductivity method and probably account for failures with it for elements other than P and B for which the solubility is high enough to show little

§§ n-type skins from donor impurities have been observed particularly in Al diffusions. There is no evidence, however, that these have influenced the results.

influence of the other elements. In no case was more than 0.01% by weight of a significant impurity present and in most instances no such impurities were detected by spectrographic analysis beyond faint traces.

No significant differences were observed between oxides of different stoichiometry. However, the presence of water was found to reduce the C_0 values significantly in the case of As_2O_3.
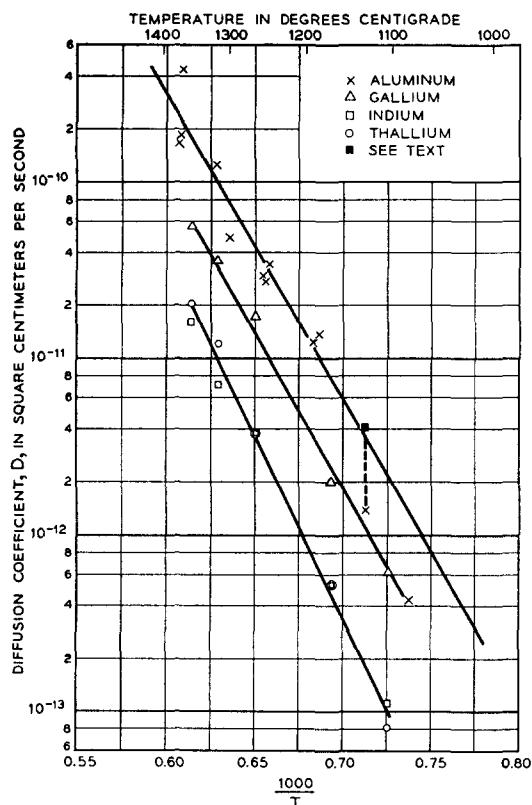
FIG. 8. Diffusion coefficients for Al, Ga, In, and Tl plotted against reciprocal of absolute temperature.

p-n JUNCTION DEPTH MEASUREMENT

Errors in p-n junction depths greatly affect the accuracy of the diffusion coefficients calculated from Eq. (7). In order to secure accurate measurements, therefore, we have developed a staining procedure which permits an optical measurement of this distance. The procedure is as described in the following.

The specimen to be measured is mounted by means of a thermoplastic adhesive to the plunger of a heavy jig shown in Fig. 6. The surface of the plunger is milled to an angle of approximately 5° to the horizontal, and by careful lapping of the specimen a regular area is ground away. Without removing the specimen from its support, it is wet (by means of a plastic or wooden rod) with a small drop of conc. HF acid containing a trace of HNO₃.‖‖ If conditions are right the p-regions of the lapped area turn dark, sharply defining the p-n junction.¶¶ Figure 7 illustrates such a stained specimen. When the proper shade is obtained, the specimen is rinsed with water and dried. The stain is permanent.

‖‖ The best mixtures lie between 0.5 and 0.1% by volume of conc. (70%) HNO₃ in conc. (48%) HF.

¶¶ The mechanism of this reaction is not understood. The formation of the dark stain does not involve appreciable etching and appears to be the result of the formation of SiO on the p-type regions by preferential oxidation. Checks with a rectifying probe verify the p-n junction position as determined by this "staining" method.

By means of a traveling microscope fitted with a vertical illuminator, the width of the p or n diffusion layer is accurately measurable. The next step is to measure the exact angle through the diffusion layer. This is done by means of a Zeiss optimeter mounted over a leveled micrometer table in such a way that the change in elevation from the horizontal can be precisely measured at four points of known spacing, two on either side of the edge marking the ground area. The angle is easily calculated from

$$\theta = \tan^{-1}[(m_2 - m_1)/1 + (m_1 m_2)], \quad (10)$$

where m_1 and m_2 are the slopes of the lines on either side of the edge. The depth is given by

$$x = d/\sin\theta,$$

where d is the horizontal distance in centimeters across the stained surface. Junction depths of one mil are measurable to at least ± 0.05 mils by this technique.

RESULTS OF p-n JUNCTION METHOD

Table III tabulates the results on the Al, Ga, In, Tl, As, Sb, and Bi diffusions obtained by the method described above. Figures 8 and 9 show the plots of D versus $1/T$ for these elements. The slopes provide the activation energies and lead to the equations:

$$D_{Al} = 8.0 \exp(-80\,000/RT) \quad (11)$$

$$D_{Ga} = 3.6 \exp(-81\,000/RT) \quad (12)$$

$$D_{In, Tl} = 16.5 \exp(-90\,000/RT) \quad (13)$$

$$D_{As} = 0.32 \exp(-82\,000/RT) \quad (14)$$

$$D_{Sb} = 5.6 \exp(-91\,000/RT) \quad (15)$$

$$D_{Bi} = 1030 \exp(-107\,000/RT). \quad (16)$$

The accuracy of the results is not sufficient to distinguish between values for In and Tl which are represented by the same equation.

The surface concentrations given in Table III apply only to the conditions of these experiments. Variation from run to run because of different amounts of diffusant or of water vapor occurs, so that the figures have only limited significance. The values in most cases are well below the equilibrium alloy values. Reasons for this are discussed later.

ERRORS

It is very difficult to evaluate the effect of all errors upon the final values of D and ΔH. For example, it is impossible to know what effect traces of impurities (particularly of acceptor impurities) have upon the p-n junction depth determinations. If we ignore such influences, we have in the p-n junction method to consider errors in the p-n junction depth, errors in the specimen resistivity, and errors in mobilities of the carriers. The latter two factors influence the concentra-

tion determinations. Since the mobilities enter as a ratio in Eq. (7), their effect is rather small. We estimate the probable error in concentration at the junction in the range employed in these experiments to be $\pm 7\%$. The concentration ratio is subject to twice this variation or $\pm 14\%$. The relatively small average error of $\pm 3\%$ in p-n junction depth can lead to a maximum error in the erfc ratio of about $\pm 40\%$. The total probable error in D can thus be as high as $\pm 50\%$. We believe the average error is closer to $\pm 40\%$. Considering the temperature range covered this means a probable error in ΔH of about 5%.

Since the values of D for the B and P diffusions were obtained by fitting the conductivity data as well as the p-n junction measurements and the chemically determined surface concentrations, we believe these results are somewhat more accurate than for the other elements.

Other possible sources of error are (1) the possibility of a Kirkendall effect[12] which would throw the measurements in error because of change of the surface as a plane of reference, and (2) the possibility that the assumption of constant surface concentration is not met. We have investigated (1) by means of optimeter measurements. It was already known that a glass-like layer builds up on the silicon surface during diffusion. This is, however, readily removed in HF so that over-all measurements were made before and after diffusion at 1200°C treating with HF before each measurement.
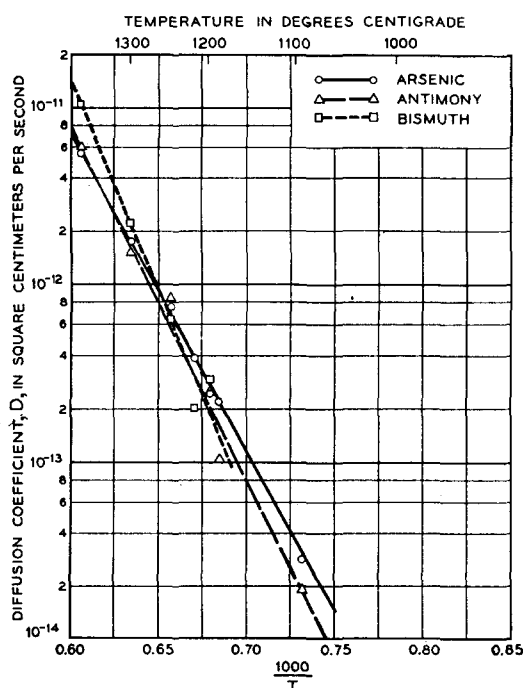

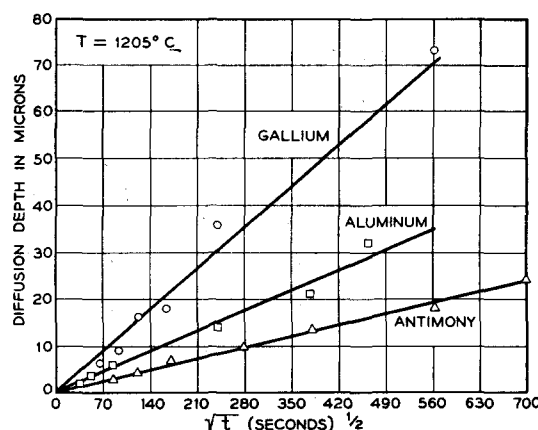FIG. 9. Diffusion coefficients of As, Sb, and Bi plotted against reciprocal of absolute temperature.

FIG. 10. Plots of penetration distances against square root of times for Al, Ga, and Sb diffusions at 1200°C.

The change in dimension found under these conditions was less than 0.5μ. We believe therefore that no dimensional changes in the diffusion direction beyond experimental error occur during diffusion. We have not investigated dimensional changes perpendicular to the diffusion direction but these seem very unlikely in view of Balluffi and Seigle's[13] findings.

In order to test whether the assumption of constant surface concentration was met, tests were conducted using Ga, Al, and Sb in which the junction distances were followed as a function of heating time. These results are shown in Fig. 10. It is evident that for times of diffusion up to about 40 hours essentially linear plots are obtained for Sb, Al, and Ga diffusions at 1205°C. Since the diffusion times employed in this work are (except for a few cases) within the linear ranges of Fig. 10, we believe that little error has arisen from this source. However, it has been noted that the lower temperature (longer time) diffusions often give points which fall below the log D versus $1/T$ plots based on higher temperature (shorter time) determinations. This would suggest a loss of oxide diffusant or the buildup of a resistant surface film on the specimens, for the longer diffusion times. It should be noted that the individual measurements in Fig. 9 are subject to greater error than the two-specimen runs since variations in C_0 from run to run, may occur because of differences in the amount of diffusant present.

Low values for D have also been observed when the diffusion distances are very small. This suggests that the doping element, B in the donor cases and As for the acceptors, may be lost by outward diffusion and thus alter the concentration at the p-n boundary. That this may occur is suggested by a recalculation of the next to last point (1130°C) of the Al curve of Fig. 8 for which the diffusion distance was only 0.323×10^{-3} cm. Assuming zero concentration of As doping at the surface, we have calculated the concentration at this

[12] A. D. Smigelskas and E. O. Kirkendall, Trans. Am. Inst. Mining Met. Engrs. 171, 130 (1947).

[13] R. W. Balluffi and L. L. Seigle, J. Appl. Phys. 25, 607 (1954); R. W. Balluffi, ibid. 23, 1407 (1952).

distance using

$$C_x = C_1 \operatorname{erf}[x/2(Dt)^{\frac{1}{2}}], \qquad (17)$$

where D, is the diffusion coefficient for As taken from Fig. 9, C_1 is the uniform As doping, and erf is the error integral. Recalculation of D for Al on this basis gives the point shown as a solid square in Fig. 8 which agrees better with the other (deeper) diffusion runs.

The line for Al was in fact drawn taking this correction into account. The last point (at 1089°C) has likewise been disregarded. The justification for this is the trend toward low D-values for long diffusion times (in this case 234 hours) as found in the runs of Fig. 8.

The probability of error in translating resistivity measurements directly into concentrations is important at room temperature only for In and Tl, for which the ionization energies are appreciable (0.14 and 0.22 ev, respectively). However, inasmuch as strongly n-type specimens have been used, these corrections are negligible.

The loss of B by outward diffusion also may be a factor in the As, Sb, and Bi diffusions as shown by the fact that the p-n junction method sometimes fails for low diffusion depths. These cases are noted in Table III by the superscript "a." They result in the difference in depth in the high and low resistance specimens being too small and leading to very inaccurate D-values. For these cases, we have calculated D from Eq. (8) taking the values of C_0 from runs giving the greater depths of diffusion which are apparently free from this difficulty. The values of x from the deeper (higher resistivity) specimens are employed in these calculations.

DISCUSSION OF RESULTS

(1) Surface Concentrations

Although the determinations of C_0 for B and P, both by the chemical as well as by the graphical method (which likewise takes account of the chemical results), are not very precise, they show that both boron and phosphorus have solubilities in silicon which approach 10^{22} atoms per cm³. This suggests that perhaps borides or phosphides of silicon may be formed under the conditions of diffusion. It is dangerous, however, on the basis of the results of Tables I or II to attempt to deduce a trend of solutility with temperature although there is some evidence of a maximum in the solubility for phosphorus near 1150—1200°C. Also, it should be emphasized that the results from chemical analysis of necessity involve different specimens from those on which the conductivity method was used. This no doubt accounts for some of the differences between the results in Tables I and II. For example, there is definite indication in Table II that saturation is not reached in the 1235°C run for phosphorus.

The p-n junction distance determined by the rectification probe as well as by the staining method were in general about 1 to 2μ greater than those arrived at

using the fit to the conductivity data. That this is probably caused by a condition at the surface is suggested by the examination of the boron specimen run at 1275°C. In this case it proved necessary to shift the curve 4μ off of the p-n junction distance to obtain the best fit with the conductivity data. Furthermore, microscopic observation showed a fine wrinkled appearance of the surface, suggesting rupture of the surface during diffusion. This would be expected to lead to the deeper p-n junction. Similar observations have been made by Balluffi[13] who reported polygonization in vapor-solid Cu-Ni couples.

The values of the surface concentrations for the other elements show considerable variations among themselves. In general they are lower than those for B and P discussed above, a fact which might be expected on the basis of the distribution coefficients.[14] However, in the diffusion from the oxide the conditions at the surface appear to be determined, not by the alloy equilibrium between the diffusing element and silicon but rather by an equilibrium with a reaction phase. We believe this phase consists of the oxides of the diffusant and silicon and postulate a reaction at the surface which may be written, choosing antimony as an example,

$$2\,Sb_2O_3 + 3\,Si \rightleftarrows 4\,Sb + 3\,SiO_2$$
$$Sb\ (\text{reaction phase}) \rightleftarrows Sb\ (\text{silicon}), \qquad (18)$$
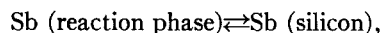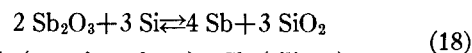
in which antimony or antimony ion is regarded as distributed between the two phases. We may write

$$C_0 = kC_r, \qquad (19)$$

where k is a distribution coefficient, C_0 the solubility at the Si surface, and C_r that in the reaction phase. We assume C_r to be constant with time in the reaction phase by virtue of the high diffusivity generally shown by ions in such media. It is reasonable therefore to expect Eq. (8) to hold for this situation, and as already mentioned, this is confirmed experimentally if the diffusions are not prolonged (Fig. 10).***

That there may be some relationship between the distribution coefficients for the elements in Si and the constants of Eq. (19) is indicated by the decrease in C_0 values with the atomic weight of the diffusing element in the oxide. Thus, Tl and Bi show only about 10^{-4} the solutilities shown by B and P.

(2) Activation Energies

The observed activation energies range from 80 kcal for Ga to 107 kcal for Bi. Although the estimated error is rather large (± 5 kcal) the trend to higher energies for the heavier donor and acceptor atoms appears to be real. The magnitude of the energy is in agreement with a substitutional mechanism for diffusion and

14 J. A. Burton, Physica 11, 845 (1954).
*** It is possible that loss of donor or of acceptor oxides to the quartz containers occurs after prolonged heating of 150 hours or more.

suggests an activation for self-diffusion in silicon of approximately 110 kcal, since in the diamond lattice the diffusing atom and the vacancy have no common nearest neighbor.[15]

(3) The D_0 Values

As is well known, the values of D_0 in the general diffusion equation

$$D = D_0 \exp(-\Delta H/RT) \qquad (20)$$

are highly sensitive to small variations in ΔH. For example, increasing the value of ΔH for Ga by 10% changes the value of D_0 by a factor of over 14. It is evident therefore that the D_0 values given in Eqs. (6) and (11) to (16) cannot be treated very quantitatively. The values given are justified to the exactness indicated only by the fact that they reproduce, for the values of ΔH there given, the curves through the experimental data. It is of interest to note, however, that the values do conform in general to those predicted by the Zener theory.[15] Zener deduced that in the equation for D_0 for substitutional diffusion in an f.c.c. lattice, given approximately by

$$D_0 \doteq a^2 \nu e^{\Delta S/R}, \qquad (21)$$

where a is the lattice constant (5.42 A for Si), ν the vibration frequency (1.3×10^{13} for Si), ΔS the entropy for diffusion is provided by

$$\Delta S \doteq -(\Delta H/\mu_0)d\mu/dT. \qquad (22)$$

In (22) $d\mu/dT$ is the temperature coefficient of the shear modulus for motion in the plane perpendicular to the diffusion jump and μ_0 is the value of this modulus at $T = 0$. If the average value for $d\mu/dT$ and μ_0 (obtained by extrapolation) from reference 16 are substituted in

(22), and the value of ΔS so obtained is substituted in (21), D_0 is found to fall in the range of 0.8 cm²/sec. This, in view of the earlier discussion, is in satisfactory agreement with the values of D_0 reported. here That different values of D_0 should be observed seems reasonable inasmuch as different impurities in the silicon lattice should affect the values of $d\mu/dT$ and ν.

CONCLUSION

The work described above was undertaken primarily to secure basic information on the diffusional properties of Group III and Group IV elements in pure silicon for use in the design of semiconducting devices from silicon. Several applications of diffusion techniques to the production of such devices have already been described.[7,8(a),17,18] It is the authors' hope that the results given here will be of use to those interested in research and development in this rapidly expanding field of technology. Finally, the many advantages of semiconductors, such as silicon, as media in which to investigate such fundamental phenomena as diffusion, solubility, and ionic interaction in the solid state should be re-emphasized.[2,19] We hope that the present work will serve as another example of how semiconductors can be of use in the investigation of diffusion and will stimulate work in this field.

[15] C. Zener, J. Appl. Phys. 22, 372 (1951).
[16] H. J. McSkimin, J. Appl. Phys. 24, 988 (1953).

[17] C. A. Lee, Bell System Tech. J. XXXV, 23 (1956).
[18] M. B. Prince, J. Appl. Phys. 26, 534 (1955).
[19] H. Reiss, J. Chem. Phys. 21, 1209 (1953).

Announcement

The Ninth International Congress of Applied Mechanics will be held at the University of Brussels, September 5 to 13, 1956. Section 1 will be on fluid dynamics and aerodynamics; section 2 will be on the mechanics of solids. Information may be obtained from the Secretariat of the Congress, Université Libre de Bruxelles, 50, Avenue F.-D. Roosevelt, Bruxelles, Belgium.