

Donor Diffusion Dynamics in Silicon

R. N. Ghoshtagore

Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235

(Received 10 August 1970)

Arsenic, antimony, and bismuth have been diffused into (111) silicon from doped epitaxially deposited source layers in a flowing hydrogen atmosphere. Under intrinsic conditions, the dopant profiles show excellent Fickian behavior. The diffusion coefficients, obtained as a function of temperature, can be described by the following equations: $D_{As} = 6.55 \times 10^{-2} \times \exp(-3.44 \pm 0.04 \text{ eV}/kT \text{ cm}^2/\text{sec})$; $D_{Sb} = 2.14 \times 10^{-1} \exp(-3.65 \pm 0.05 \text{ eV}/kT \text{ cm}^2/\text{sec})$; and $D_{Bi} = 1.08 \exp(-3.85 \pm 0.06 \text{ eV}/kT \text{ cm}^2/\text{sec})$. These data, together with those of phosphorus reported earlier, are shown to be consistent with a point-defect mechanism that involves a closely coupled vacancy-impurity ensemble.

I. INTRODUCTION

The nature of the point defect predominantly responsible for substitutional diffusion in silicon, and its interaction with electrically active impurities has remained unresolved¹⁻⁵ for more than a decade, even after the accumulation of a vast wealth of experimental diffusion data. Experimentally, evidence in support of any particular mechanism has been sought^{6,7} from the diffusion characteristics of substitutional atoms under different conditions predicted by the theory.⁸⁻¹⁰ From the other end, nonequilibrium point defects have been generated and their characteristics studied.^{4,11-27} Theoretical investigations have included (a) the calculation of point-defect formation parameters^{3,28-31} and, consequently, direct diffusivities,^{2,10,28} (b) the correlation factors for impurity and self-diffusions in silicon,^{32,33} and (c) the comparative behavior of experimental diffusion parameters with some probable point-defect mechanism.^{1-3,34} As a result of all these investigations, considerable evidence in support of vacancy-controlled substitutional diffusion in silicon has developed.^{1,6,7,9,10,17,34} The exact species involved in the case of each impurity diffusion, however, has so far eluded positive identification. As a first step towards such a goal, a fresh attempt is made in the present report to obtain intrinsic donor diffusion data in silicon, free from all possible extrinsic effects and assumptions.³⁵ Subsequently, such data are analyzed to pinpoint the underlying point-defect mechanism.

II. EXPERIMENTAL

The details of the experimental technique, as used for boron and phosphorus diffusion in silicon, have been reported elsewhere.³⁵ Basically, the technique was to grow a doped 4–12- μ -thick epitaxial silicon (diffusant) source layer on (111) float-zoned silicon wafers of the proper resistivity type and level. The deposition reaction involved the hydrogen reduction of silicon tetrachloride at 1150–1250 °C

in an induction-heated reactor. Arsenic was introduced into the epitaxial layer by gas-phase doping with properly diluted arsine in hydrogen. Antimony was introduced by bubbling hydrogen through "electronic-grade" trimethyl antimony and mixing this saturated (trimethyl antimony) gas with the reactant gas stream (silicon tetrachloride in hydrogen) at the reactor entrance. Since trimethyl bismuth reacted with silicon tetrachloride, a bismuth-doped epitaxial silicon layer was grown by the pyrolysis of 0.2–0.3% silane (in hydrogen) at 1050–1150 °C. Even then the maximum concentration of bismuth was $< 3 \times 10^{16} \text{ cm}^{-3}$. Special care was taken to generate a δ -function-type impurity profile at the substrate-epi interface. The diffusion couples were finally covered with a 2000–2500-Å layer of amorphous silicon nitride at 800 °C (by the reaction of silane and ammonia) to serve as an outdiffusion barrier.

All the diffusion experiments were done under intrinsic conditions, i.e., the dopant concentrations were below the intrinsic carrier concentration of silicon at all diffusion temperatures. Such low dopant concentrations also insured noninterference from from such extrinsic effects as dislocation generation and motion, plastic deformation, and dopant precipitation. The diffusion annealings were performed in an induction furnace, on silicon nitride-coated graphite susceptor, in a flowing hydrogen atmosphere (40–50 liter/min). In addition, to inhibit the removal of the silicon nitride-coating by dissociation, just enough partial pressure of ammonia and silane (by manual adjustment) was maintained in the diffusion environment. The true temperature of a diffusion couple was determined from a chemically polished silicon wafer, placed next to it by a properly calibrated³⁵ optical pyrometer, to an accuracy of ± 5 °C or better. After annealing, the silicon nitride-coating was stripped off on 49% HF and the impurity profile determined on a 1°–3° bevelled angle by the automatic spreading-resistance technique.³⁶ The accuracy of the spreading-resis-

tance data has already been demonstrated.³⁵

III. RESULTS

Under the boundary condition of diffusion from a finite layer with a reflecting boundary into a semi-infinite body, the concentration profile of the diffusant, at a constant temperature, is described by the equation³⁷

$$N(x, t) = \frac{1}{2}N_0 \left(\operatorname{erf}(h-x)/2(Dt)^{1/2} + \operatorname{erf}(h+x)/2(Dt)^{1/2} \right), \quad (1)$$

where N_0 is the initial uniform dopant concentration in the epitaxial diffusion source of thickness h and the other symbols have usual meanings. Equation (1) is distinct from the familiar Gaussian distribution in x (under thin-film boundary condition) only if $t < h^2/D$ and $x > Dt/h$.³⁸ In this study, at all diffusion temperatures, h and t were set such that these conditions of compliance with Eq. (1) were adequately met.

The spreading-resistance data obtained from the diffused samples (as a function of depth from the surface) were computed to produce impurity-concentration profiles.³⁶ They were then fitted with calculated theoretical profiles [from Eq. (1)] to an accuracy of $\pm 0.05 \mu$ in $2(Dt)^{1/2} \geq 2.00 \mu$ and to $\pm 0.10 \mu$ in $1.40 \mu \leq 2(Dt)^{1/2} < 2.00 \mu$. Typical fitted arsenic, antimony, and bismuth profiles are shown in Figs. 1–3. They all show excellent Fickian behavior.

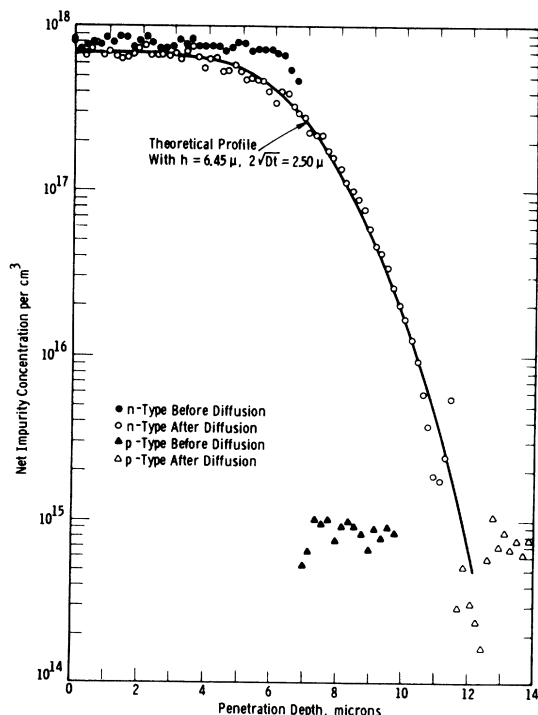


FIG. 1. Concentration profile of arsenic in boron-doped epitaxial silicon. $T = (1390 \pm 5)^\circ\text{C}$, $t = 7.2 \times 10^3$ sec.

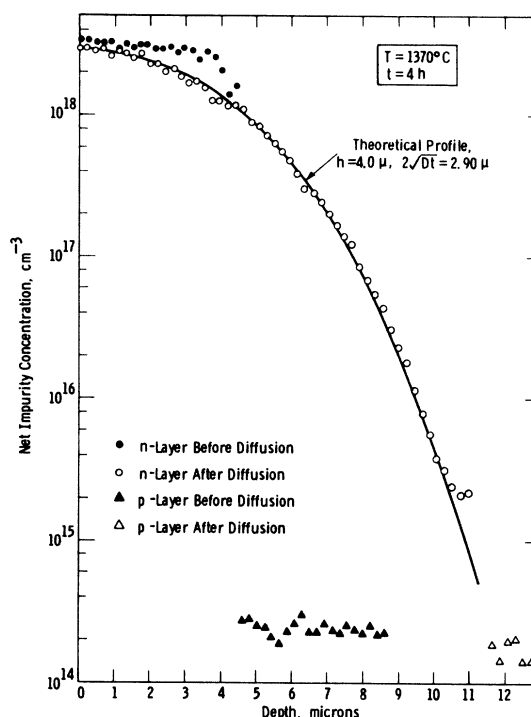


FIG. 2. Concentration profile of antimony in boron-doped float-zoned silicon.

The calculated intrinsic diffusivities of arsenic, antimony, and bismuth, obtained from such fitted profiles, are shown in Figs. 4–6 as a function of inverse absolute temperature. Between 1167 and 1394 °C, arsenic intrinsic diffusivity in (111) silicon can be described by the least-squares fitted equation

$$D_{As} = 6.55 \times 10^{-2} \exp(-3.44 \pm 0.04 \text{ eV}/kT) \text{ cm}^2/\text{sec}. \quad (2)$$

Between 1190 and 1405 °C, antimony intrinsic diffusivity in (111) silicon can be described by the least-squares fitted equation

$$D_{Sb} = 2.14 \times 10^{-1} \exp(-3.65 \pm 0.05 \text{ eV}/kT) \text{ cm}^2/\text{sec}, \quad (3)$$

and between 1190 and 1394 °C, bismuth intrinsic diffusivity in (111) silicon is represented by the least-squares fitted equation

$$D_{Bi} = 1.08 \exp(-3.85 \pm 0.06 \text{ eV}/kT) \text{ cm}^2/\text{sec}. \quad (4)$$

For the purpose of clarity, only about half of the diffusion data, at most temperatures, could be shown in Fig. 4.

During the present study, only the diffusivity of arsenic was studied in the entire range of surface concentrations from $2 \times 10^{17} \text{ cm}^{-3}$ to $1.5 \times 10^{19} \text{ cm}^{-3}$ and bulk concentrations of 2.5×10^{13} to 1×10^{17} arsenic and 1×10^{14} to 1×10^{17} boron. Figure 7 shows some of these data at two temperatures. Within the range of experimental error, they are seen to be concen-

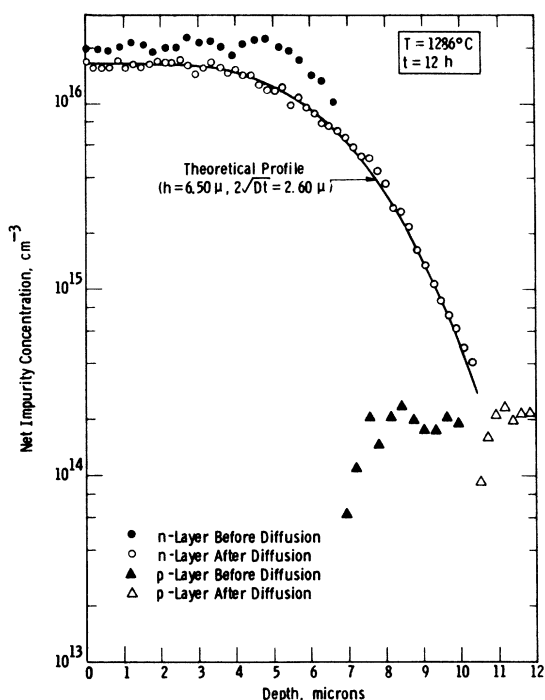


FIG. 3. Concentration profile of bismuth in boron-doped float-zoned silicon.

tration independent. Concentration-dependence studies for antimony and bismuth diffusion were possible only to a limited extent because of the source-dopant concentration limitation imposed by the epitaxial growth technique used. Some of these data are included in Figs. 5 and 6. Thus, in the intrinsic range, all the donors (P, As, Sb, and Bi) have concentration- and impurity- (dopant-) type-independent diffusivities in silicon. Consequently, no need for isoconcentration diffusion studies was felt. Such information, obtained earlier for phosphorus in silicon,³⁵ did not provide any further insight into the mechanism of the process.

IV. DISCUSSION

A. Comparison with Literature Data

Available information on the diffusivity of arsenic, antimony, and bismuth in silicon is compiled in Table I. As in the case of boron and phosphorus diffusion in silicon,³⁵ even the "intrinsic" diffusion parameters are found to vary over a very wide range. Except the measurements of Raju *et al.*⁴⁵ and Masters and Fairfield⁷ for arsenic in silicon, and the data of Nakanuma and Yamagishi⁴⁶ for antimony in silicon, they were all determined with oxide diffusion sources. Consequently, all these data probably have included the extrinsic effects connected with the redox reaction at the surface of silicon.^{49,50} Even though Raju *et al.*⁴⁵ and Masters and Fairfield⁷ obtained their data under "non-

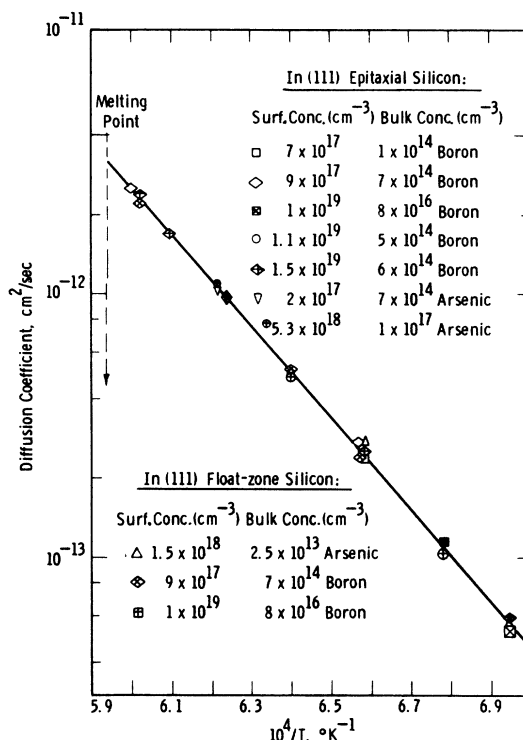


FIG. 4. Temperature dependence of arsenic diffusivity in intrinsic (111) silicon.

oxidizing" conditions, enough oxygen partial pressure was maintained (at the diffusion temperature) by the quartz enclosure to produce a partial effect of the surface redox reaction. Moreover, even

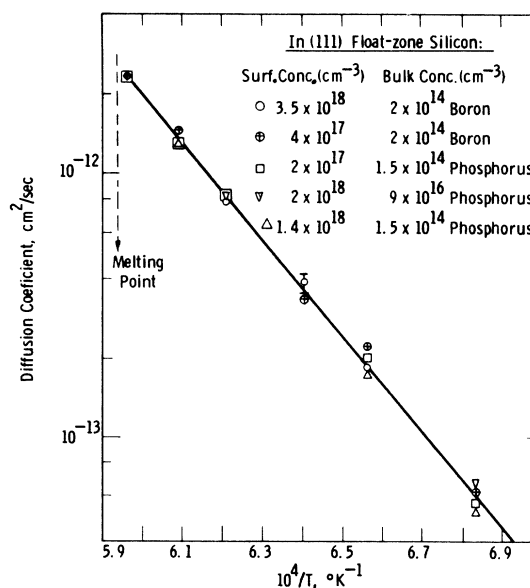


FIG. 5. Temperature dependence of antimony diffusivity in intrinsic (111) silicon.

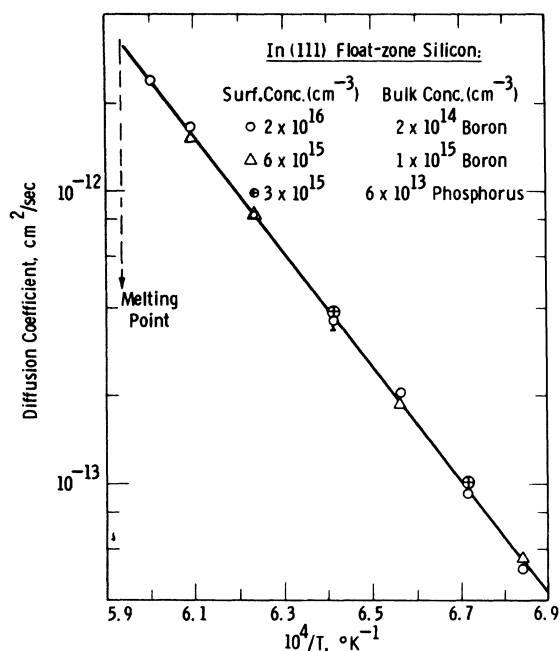


FIG. 6. Temperature dependence of bismuth diffusivity in intrinsic (111) silicon.

in strictly nonoxidizing atmosphere, the free surface is known to produce some unknown extrinsic effect on the calculated diffusivity values.⁵⁰ Nakamura and Yamagishi, on the other hand, have too sketchy an information on antimony diffusion in silicon to warrant any detailed analysis.

The present results indirectly appear to be in disagreement with the conclusions of Grove *et al.*⁵¹ and Joyce *et al.*⁵² on the dopant profiles produced by epitaxy. While no single tenable explanation can be offered for the disagreement, several can be cited:

(a) Since both these groups of workers depended on the differential-capacitance method⁵³ to obtain impurity distribution profiles within the epitaxial silicon layer, the ability of such a method in providing the true impurity profile may be rather suspect. Moreover, the diode fabrication heat treatment performed may not have negligible effect on the impurity profile.

(b) The comment made by Joyce *et al.* on the arsenic diffusivity data of Bhola and Mayer⁵⁴ by the capacitance-voltage method may be applicable to both these sets of work, i. e., the diffusivity values can be changed over several factors and still include the experimental data equally satisfactorily.

(c) Both these groups of workers primarily concentrated on the tail of the rather sharp concentration profiles to show the validity of the diffusion coefficients used; whereas, with a slight adjustment of the substrate-film interface position, the same data could be made to fit the diffusion data obtained

in this study. A case in support of this contention may be the much higher phosphorus diffusivity value (than provided by the literature) Joyce *et al.* had to assume for a theoretical fit of their phosphorus profile.

(d) The accuracy of the diffusion coefficient obtained from the as-produced impurity profile (by epitaxy) has been found to be unacceptably poor during the course of the present work. Moreover, the only published data by Grove *et al.* on the effect of additional heat treatment on the impurity profile (by thermal oxidation) conceivably includes the extrinsic effect connected with surface oxidation.^{49,50} Also, to be able to validate the epitaxial profiles with a theoretical impurity diffusion coefficient (to a reasonable certainty and accuracy), more complete and detailed profiles are needed.

B. Dynamics of Donor Diffusion Process

The kinetics of the donor diffusion process in silicon, which is controlled by point-defect migration, must be reflected in the experimental preexponential factors and activation energies as given in Eqs. (2)–(4). Because of the overwhelming support of the lattice vacancy control for such a process and the availability of considerable theoretical understanding, the results of this study will first be examined in that light.

1. Activation Energy of Diffusion

The most reliable indicator for the point defect predominantly responsible for any solid-state diffusion process is the activation energy of diffusion. For any system this, in fact, is the sum of two energies: the energy of formation of the thermally produced point defect and the activation energy of migration of this defect through the lattice causing the observed diffusion. Both of these fundamental parameters, and consequently their sum, are quite

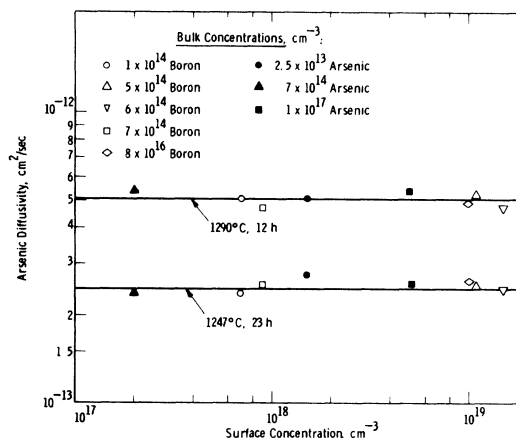


FIG. 7. Concentration dependence of arsenic diffusivity in (111) silicon.

TABLE I. Reported diffusion parameters for As, Sb, and Bi in silicon.

Ref.	Surface concentration (cm ⁻³)	Base concentration (cm ⁻³)	Temp. range (°C)	Activation energy (eV)	Frequency factor (cm ² /sec)
Arsenic					
39	5.8–45 × 10 ¹⁷	3–230 × 10 ¹⁴ (B)	1095–1380	3.55	0.32
43	10 ¹⁷ –10 ¹⁹	6 × 10 ¹⁶ (B)	1100–1350	4.24	68.6
44	1.5 × 10 ¹⁹	3.5–13 × 10 ¹⁴ (B)	1164–1280	5.20	8.3 × 10 ⁴
45	0.7–7 × 10 ¹⁸	...	1125–1312	3.88	2.564
7	7.1–220 × 10 ¹⁹	7.1–220 × 10 ¹⁹ (As)	850–1150	4.20	60
This work	2–150 × 10 ¹⁷	2.5 × 10 ¹³ –1 × 10 ¹⁷ (As) 1 × 10 ¹⁴ –1 × 10 ¹⁷ (B)	1167–1394	3.44	6.55 × 10 ⁻²
Antimony					
39	1.4 × 10 ¹⁸ – 9.2 × 10 ²¹	4.6–270 × 10 ¹⁴ (B)	1095–1380	3.95	5.6
40	...	5 Ω cm	940–1300	2.86	0.112
41	10 ¹⁹ –10 ²⁰	2.5 × 10 ¹³ (P?)	1190–1398	3.98	12.9
42	1–13 × 10 ¹⁸	1.5–17.1 × 10 ¹⁵ (B?)	1200–1300	~4.2	14.3
46	3.9–13 × 10 ¹⁸	4.4–34 × 10 ¹⁴ (B)	~1150–1250	4.4	3.63 × 10 ²
47	1 × 10 ²⁰	1 × 10 ¹⁴ (B?)	~1125–1290	~6.6	~6.3 × 10 ⁹
48	~1200	5.85	2 × 10 ⁷
This work	2–35 × 10 ¹⁷	2 × 10 ¹⁴ (B) 1.5 × 10 ¹⁴ –9 × 10 ¹⁶ (P)	1190–1405	3.65	0.214
Bismuth					
39	1–24 × 10 ¹⁷	1.9–200 × 10 ¹⁴ (B)	1220–1380	4.64	1.03 × 10 ³
This work	3–20 × 10 ¹⁵	2–10 × 10 ¹⁴ (B) 6 × 10 ¹³ (P)	1190–1394	3.85	1.08

different for different point defects.

A simple vacancy in silicon is known to be an electron acceptor and is extremely unstable in the lattice.¹⁵ Consequently, its identification by quenching from high temperatures has either been unsuccessful⁵⁵ or anomalous.^{25,26} On the other hand, theoretical calculations of the vacancy formation energy in silicon have been in fair to very good agreement with each other,^{3,28–30} with a mean value of 2.35 eV per vacancy. Again, since a reasonable concentration of the vacancy-related defect is required to provide the observed diffusive fluxes, such simple vacancies are required to be stabilized by interaction with other thermal or nonthermal defects in the lattice. One such type of simple vacancy-related defect is the impurity-vacancy pair, irradiation produced, and studied by EPR^{4,17} and thermal annealing^{18,20,23} for all the normal donors in silicon. Such defects are characterized by rather large binding energies (1.04–1.64 eV)²³ compared to kT at diffusion temperatures. They must partially dissociate, however, to migrate through

the lattice by reorientation.^{4,17,23} Consequently, such a complex formation increases both the local vacancy lifetime (and concentration), and the effective activation energy of vacancy motion in silicon. If this higher migration energy of the vacancy (around the impurity atom) is considered operative in the donor-diffusion-process dynamics and if the final step of direct exchange of the impurity with the adjacent vacancy is assumed non-rate-determining, then the experimental activation energies for diffusion can be compared with that required by this model. This is shown in Table II where the agreement is seen to be excellent for all the donors.

2. Preexponential Factor

From the random-walk theory of diffusion, the preexponential factor of the Arrhenius Eqs. (2)–(4) for any impurity I in the diamond lattice is given by

$$D_0^I = \frac{1}{6} a^2 f \nu e^{\Delta S_D^I / k}, \quad (5)$$

TABLE II. Comparison of experimental activation energies with that for the impurity-vacancy pair migration (all energies are in eV).

Donor element	Activation energy of impurity-vacancy pair motion (E_{iv}^m)	Cal. activation energy of diffusion by pair migration $E = E_v^f + E_{iv}^m$ ($E_v^f = 2.35$ eV)	Experimental activation energy of diffusion
Phosphorus	0.94	3.29	3.30 ± 0.03
Arsenic	1.07	3.42	3.44 ± 0.04
Antimony	1.28	3.63	3.65 ± 0.05
Bismuth	1.46	3.81	3.85 ± 0.06

where a is the lattice parameter, ν is the Debye frequency, f is the correlation factor, k is the Boltzmann constant, and ΔS_D is the entropy of diffusion. ΔS_D is the sum of the entropy of defect formation (ΔS_f) and the activation entropy of defect migration (ΔS_m). For silicon, $a = 5.43$ Å, $\nu = 1.38 \times 10^{13}$ sec⁻¹, and to a first approximation (for all the normal donors) $f \approx 5 \times 10^{-3}$.³⁵ Therefore, from Eq. (5), $\Delta S_D^P/k = 7.98$; $\Delta S_D^{As}/k = 7.85$; $\Delta S_D^{Sb}/k = 9.02$; and $\Delta S_D^{Bi}/k = 10.65$.

Of all the parameters in Eq. (5), the entropy of diffusion is the one least understood. Attempts to calculate ΔS_D from the first principles have offered only order of magnitude values.⁵⁶ Dienes⁵⁷ and Zener⁵⁸ have successfully developed semiempirical relationships to calculate ΔS_D in metals. Application of their theory to silicon, however, only offers about one-third of the observed ΔS_D values. But Zener's fundamental criteria, that the entropy of activation is positive and increases with the energy of activation, are found to be valid in silicon. Also, Dienes's empirical observation that $D_0 = Ce^{E/RT_m}$, where C is a constant for a particular host lattice of melting point T_m and E is the activation energy of diffusion, is found to hold ($C_{Si} \approx 3.8 \times 10^{-12}$ cm²/sec) reasonably.

No attempt, empirical or otherwise, to calculate D_0 for the case where the diffusing species is an impurity-vacancy pair, has been reported in the literature. Experimental data in some such cases,⁵⁹ however, indicate ΔS_D values of the same order as obtained in this study. Hirata *et al.*²³ have recently

TABLE III. Entropy of donor-vacancy pair diffusion in silicon.

Defect species	Entropy of diffusion	Entropy of migration	Entropy of formation
Phosphorus-vacancy	7.98k	~ 0	7.98k 7.5k ^a
Arsenic-vacancy	7.85k	~ 0	7.85k
Antimony-vacancy	9.02k	4.5k	4.52k
Bismuth-vacancy	10.65k	8.5k	2.15k

^aSee text for details.

determined ΔS_m values for all the donor-vacancy pairs from their annealing characteristics. Their interpretation of the EPR data of Watkins *et al.*^{4,17} also produced comparable results. They are $\Delta S_m^{P-v} \approx \Delta S_m^{As-v} \approx 0$, $\Delta S_m^{Sb-v} = 4.5k$, and $\Delta S_m^{Bi-v} = 8.5k$. That leaves 7.98k, 7.85k, 4.52k, and 2.15k for ΔS_f of phosphorus-vacancy, arsenic-vacancy, antimony-vacancy, and bismuth-vacancy pair formation, respectively. Swalin²⁸ estimated $\Delta S_f^v = 2.2k$, and the low-temperature solubility data⁶⁰ provides 5.3k for the entropy of solution of P in silicon. Now, if the vibrational and configurational contributions to the ΔS_f of the impurity-vacancy pair formation is neglected, $\Delta S_f^{P-v} \approx 7.5k$. Considering the uncertainty of some of the parameters used to derive ΔS_D values from Eq. (5), the agreement in the case of phosphorus is considered good. Finally, it should be noted that the preceding analysis provides the expected decreasing ΔS_f and increasing ΔS_m with increasing binding energies of the donor-vacancy complexes in silicon (Table III).

V. CONCLUSIONS

The intrinsic bulk diffusion characteristics of all the regular donors in silicon have been determined for the first time. The available literature data for donor diffusion in silicon appears to have unsuspectingly included some extrinsic effects due to both the free surface and the solid-state redox reactions on it. The demonstrated ability of such extrinsic literature values to explain epitaxial doping profiles in silicon is believed to be adjustable. The present diffusion data are shown to be properly explained by a closely coupled impurity-vacancy ensemble as the dominant migrating species.

¹R. N. Ghoshtagore, Phys. Status Solidi **20**, K89 (1967).

²A. Seeger and K. P. Chik, Phys. Status Solidi **29**, 455 (1968).

³A. Seeger and M. L. Swanson, in *Lattice Defects in Semiconductors*, edited by R. R. Hasiguti (Pennsylvania State U. P., University Park, 1968), pp. 93-130.

⁴E. L. Elkin and G. D. Watkins, Phys. Rev. **174**, 881 (1968).

⁵A. Seeger, Comments Solid State Phys. **2**, 55 (1969).

⁶M. F. Millea, J. Phys. Chem. Solids **27**, 315 (1966).

⁷B. J. Masters and J. M. Fairfield, J. Appl. Phys.

40, 2390 (1969).

⁸R. L. Longini and R. F. Greene, Phys. Rev. **102**, 992 (1956).

⁹S. M. Hu and S. Schmidt, J. Appl. Phys. **39**, 4272 (1968).

¹⁰S. M. Hu, Phys. Rev. **180**, 773 (1969).

¹¹G. D. Watkins and J. W. Corbett, Phys. Rev. **121**, 1001 (1961).

¹²J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, Phys. Rev. **121**, 1015 (1961).

¹³G. D. Watkins and J. W. Corbett, Discussions Fara-

day Soc. 31, 86 (1961).

¹⁴P. Baruch, C. Constantin, J. C. Pfister, and R. Saintespruit, *Discussions Faraday Soc.* 31, 76 (1961).

¹⁵G. D. Watkins, *J. Phys. Soc. Japan Suppl. II* 18, 22 (1963).

¹⁶H. Saito and M. Hirata, *Japan. J. Appl. Phys.* 2, 678 (1963).

¹⁷G. D. Watkins and J. W. Corbett, *Phys. Rev.* 134, A1359 (1964).

¹⁸G. D. Watkins and J. W. Corbett, *Phys. Rev.* 138, A543 (1965).

¹⁹H. Djerassi, J. Merlo-Flores, and J. Messier, *J. Appl. Phys.* 37, 4510 (1966).

²⁰M. Hirata, M. Hirata, H. Saito, and J. E. Crawford, Jr., *J. Appl. Phys.* 38, 2433 (1967).

²¹L. J. Cheng and J. Lori, *Phys. Rev.* 171, 856 (1968).

²²J. C. Price and A. E. Kiss, *IEEE Trans. Nucl. Sci.* 15, 3 (1968).

²³M. Hirata, M. Hirata, and H. Saito, *J. Phys. Soc. Japan* 27, 405 (1969).

²⁴V. M. Gusev and V. V. Titov, *Fiz. Zekh. Poluprov.* 3, 3 (1969) [*Soviet Phys. Semicond.* 3, 1 (1969)].

²⁵B. I. Boltaks and S. I. Budarina, *Fiz. Tverd. Tela* 11, 418 (1969) [*Soviet Phys. Solid State* 11, 330 (1969)].

²⁶M. L. Swanson, *Phys. Status Solidi* 33, 721 (1969).

²⁷E. Davoust-Saltiel and P. Baruch, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris, France*, 1964 (Dunod, Paris, 1965), Vol. 3, pp. 275-280.

²⁸R. A. Swalin, *J. Phys. Chem. Solids* 18, 290 (1961).

²⁹K. H. Bennemann, *Phys. Rev.* 137, A1497 (1965).

³⁰See A. Scholz and A. Seeger in Ref. 27, p. 315.

³¹See R. R. Hasiguti in Ref. 3, pp. 131-137.

³²J. R. Manning, *Phys. Rev.* 116, 819 (1959).

³³S. M. Hu, *Phys. Rev.* 177, 1334 (1969).

³⁴J. M. Fairfield and B. J. Masters, *J. Appl. Phys.* 38, 3148 (1967).

³⁵R. N. Ghoshtagore, this issue, *Phys. Rev. B* 3, 389 (1971).

³⁶R. G. Mazur and D. H. Dickey, *J. Electrochem. Soc.* 113, 255 (1966); P. A. Schumann, Jr. and E. E. Gardner, *ibid.* 116, 87 (1969).

³⁷B. I. Boltaks, in *Diffusion in Semiconductors* (Academic, New York, 1963), p. 102.

³⁸A. M. Smith, in *Fundamentals of Silicon Integrated Device Technology*, edited by R. M. Burger and R. P. Donovan (Prentice-Hall, Englewood Cliffs, N.J., 1967),

Vol. 1, pp. 194-196.

³⁹C. S. Fuller and J. A. Ditzenberger, *J. Appl. Phys.* 27, 544 (1956).

⁴⁰D. A. Petrov, Yu M. Shashkov, and I. P. Akimchenko, *Vopr. Met. i Fiz. Poluprov. Akad. Nauk SSSR* 1957, 130 (1957).

⁴¹J. J. Rohan, N. E. Pickering, and J. Kennedy, *J. Electrochem. Soc.* 106, 705 (1959).

⁴²D. Drimer, P. Taranu, A. Hafner, L. Vescan, and L. Nemoda, *Acad. Rep. Populare Romine, Filiala Iasi, Studii Cercetari Stiint., Fiz. Stiinte Tehn.* 13, 39 (1960).

⁴³W. J. Armstrong, *J. Electrochem. Soc.* 109, 1065 (1962).

⁴⁴Y. W. Hseuh, *Electrochem. Technol.* 6, 361 (1968).

⁴⁵P. S. Raju, N. R. K. Rao, and E. V. K. Rao, *Indian J. Pure Appl. Phys.* 2, 353 (1964).

⁴⁶S. Nakanuma and S. Yamagishi, *J. Electrochem. Soc. Japan* 36, 3 (1968).

⁴⁷M. O. Thurston and J. Tsai, Ohio State University Research Foundation, Report No. 1233-4Q, 1962 (unpublished).

⁴⁸F. L. Gittler, in *Proceedings of the Electrochemical Society Meeting, May, 1967, Extended Abstracts No. 94* (unpublished).

⁴⁹I. R. Sanders and P. S. Dobson, *Phil. Mag.* 20, 881 (1969).

⁵⁰R. N. Ghoshtagore, *Phys. Rev. Letters* 25, 856 (1970).

⁵¹A. S. Grove, A. Roder, and C. T. Sah, *J. Appl. Phys.* 36, 802 (1965).

⁵²B. A. Joyce, J. C. Weaver, and D. J. Maule, *J. Electrochem. Soc.* 112, 1100 (1965).

⁵³J. Hilibrand and R. D. Gold, *RCA Rev.* 21, 245 (1960).

⁵⁴S. R. Bhola and A. Mayer, *RCA Rev.* 24, 511 (1963).

⁵⁵W. H. Shepherd, *J. Phys. Chem. Solids* 23, 161 (1962).

⁵⁶H. B. Huntington, G. A. Shirm, and E. S. Wajda, *Phys. Rev.* 99, 1085 (1955).

⁵⁷G. J. Dienes, *J. Appl. Phys.* 21, 1189 (1950).

⁵⁸C. Zener, *J. Appl. Phys.* 22, 372 (1951); in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley et al. (Wiley, New York, 1952), pp. 289-314.

⁵⁹G. M. Hood, *Phil. Mag.* 21, 305 (1970).

⁶⁰N. Kh. Abrokosov, V. M. Glazov, and C. -Y. Lin, *Russ. J. Inorg. Chem.* 7, 429 (1962).