

Intrinsic Diffusion of Boron and Phosphorus in Silicon Free From Surface Effects

R. N. Ghoshtagore

Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235

(Received 6 August 1970)

Boron and phosphorus were diffused in either hydrogen or pure-argon atmosphere into float-zoned, epitaxial, and oxygen-doped (111) silicon from a 4–12- μ -thick epitaxial doped silicon surface layer. Under intrinsic conditions, the concentration profiles obtained show Fickian behavior at all surface and bulk concentration conditions. Between 1130 and 1405 °C, the intrinsic diffusivities can be described by $D_P = 7.4 \times 10^{-2} \exp[(3.30 \pm 0.03 \text{ eV})/kT] \text{ cm}^2/\text{sec}$. Compared with earlier studies using $\exp[-(3.30 \pm 0.03 \text{ eV})/kT] \text{ cm}^2/\text{sec}$ oxide diffusion sources, the diffusion coefficients of both boron and phosphorus are found to be considerably smaller. Moreover, above 1130 °C they are independent of surface concentration ($\leq 3 \times 10^{19} \text{ cm}^{-3}$), bulk conductivity type (*n* or *p*) and level (6×10^{13} – $8 \times 10^{18} \text{ cm}^{-3}$), surface face-to-bulk concentration ratio (~ 1 – 3.3×10^5), and oxygen concentration (to 10^{18} cm^{-3}). In the light of some related work, the present results are shown to indicate the true bulk-diffusion process in silicon.

I. INTRODUCTION

Since the pioneering work of Fuller and Ditzemberger^{1,2} on the diffusion of dopants in silicon, the high-temperature migration of boron and phosphorus in silicon has been the most widely investigated diffusion behavior in semiconductors. Most of these investigations have been performed by the eventual use of an oxide diffusion source^{2–16} on the silicon surface. The concentration-profile data obtained by either electrical^{1–16} and/or radioisotope^{8,10} methods have been analyzed for diffusion coefficients by assuming some type of theoretical behavior, depending on the experimental boundary conditions. The intrinsic diffusion coefficients of boron and phosphorus in silicon, thus obtained, have been shown to depend primarily on the resistivity type and level of the host crystal,^{5–8,10,17} surface concentration of the diffusant,^{6–8,10,13–16} and consequently the electric field set up,^{4,8} and the composition of the diffusion atmosphere.^{18,19} Some of the reasons postulated for non-Fickian boron and phosphorus distribution profiles in silicon are out-diffusion and evaporation,²⁰ multiple diffusing species,^{8,16} fast diffusion near the surface due to lattice strain,^{10,18,21} pipe diffusion, and/or precipitation along the imperfections created by diffusion,²² and compound formation (with or without precipitation) between the dopants and/or the host.²³

With the advent of some theoretical treatments, in recent years, on the mechanism of diffusion in silicon,^{24–27} based on a probable point defect, it has become imperative to reexamine the bulk-diffusion behavior in silicon by a method that does not make any assumption as to the effect of an experimental condition and the mathematical analysis of the concentration-profile data in calculating the diffusion coefficients. To obtain such data a novel experi-

mental technique has been used in the present study whereby both phase and crystallographic boundaries between the source and the host crystal have been eliminated and the effects of all silicon surface reactions^{28–30} on the dopant concentration profile have been avoided.

II. EXPERIMENTAL

All the diffusion data were obtained under intrinsic conditions, i. e., the dopant concentrations were not allowed to exceed the intrinsic carrier concentration in silicon at all diffusion temperatures. Moreover, at such low impurity concentrations ($\leq 2 \times 10^{19} \text{ cm}^{-3}$), no interference from dislocations, plastic deformation, precipitation, and compound formation on the resultant concentration profiles were expected.

The diffusion couples used in this study were made by growing a 4–12- μ -thick doped epitaxial silicon layer on (111), 1–2 $\frac{1}{4}$ -in.-diam, 15–18-mils-thick properly doped single-crystal silicon substrates by the hydrogen reduction of silicon tetrachloride at 1150–1250 °C. Most of the substrates used were float zoned and had low dislocation ($< 5 \times 10^2/\text{cm}^2$) and stacking fault ($< 10/\text{cm}^2$) contents. When the diffusion behavior in epitaxial silicon was investigated, a base layer (85–120 μ) of properly doped episilicon was grown on the substrates before putting on the source layer. All dopings were performed with dilute phosphine or diborane (in hydrogen). Special care was taken to generate as sharp an impurity profile as possible near the substrate-epitaxial source interface. To serve as an out-diffusion barrier, a layer of 2000–2500- Å amorphous silicon nitride was then chemically vapor deposited³¹ at 800 °C (by the reaction of SiH_4 and NH_3) on top of the epitaxially grown diffusion source. This entire structure is schematically

shown in Fig. 1. When phosphorus-32 was used to radiochemically determine³² the phosphorus concentration profile, the episilicon source layer was grown by liquid-phase doping of SiCl_4 with P-32 tagged PCl_3 .³³

The diffusion couple was then annealed in an induction furnace (on a silicon nitride-coated graphite susceptor) in a flowing hydrogen atmosphere (40–50 l/min) with just enough partial pressure of NH_3 and SiH_4 maintained (by manual adjustment) to control the removal of the silicon nitride coating by dissociation. The temperature was read by an optical pyrometer from a chemically polished silicon wafer placed next to the diffusion couple, with proper corrections applied for absorption by the quartz tube wall and the emissivity of silicon.³⁴ A major effort was directed toward the determination of the real temperature of the diffusion couple by calibrating the optical pyrometer against a NBS standard pyrometer, Beckmann "Coloratio" two-color pyrometer and the melting point of silicon; the reported temperatures are believed to be accurate within $\pm 5^\circ\text{C}$.

After diffusion annealing, the silicon nitride coating was stripped off in 49% HF and the impurity profile determined on a 1–3° bevelled angle by the spreading resistance technique.³⁵ In the samples where P-32 was used as the phosphorus dopant the concentration profile was determined, in addition, by the radiochemical technique.

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 equation³⁶

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

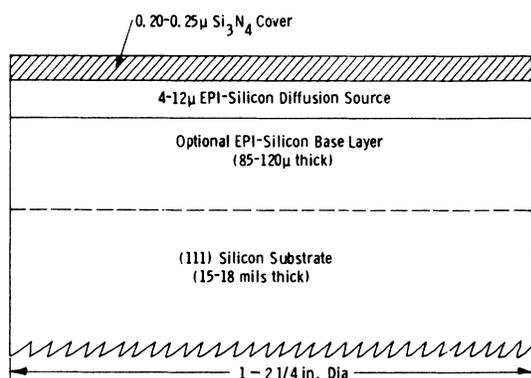


FIG. 1. Schematic diagram of the diffusion couple used in this study.

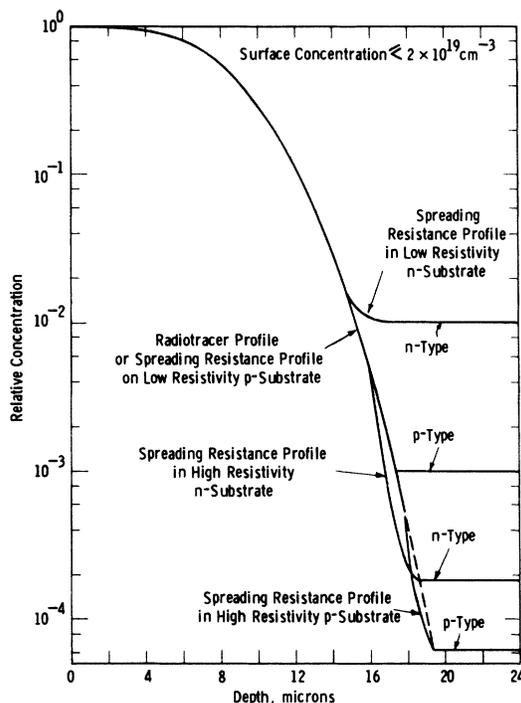


FIG. 2. Diagrammatic comparison of the phosphorus concentration profiles in silicon obtained by two different methods.

where N_0 is the initial uniform dopant concentration in the epitaxial diffusion source of thickness h and the other symbols have their usual meanings. Equation (1) is distinct from the familiar Gaussian distribution in x (under thin-film boundary conditions) only if $t < h^2/D$ and $x > Dt/h$.³⁷ In this study, care was taken to set h and t such that these conditions of compliance with Eq. (1) are fulfilled.

The spreading resistance data (obtained from the diffused samples as a function of depth from the surface) were computed to produce impurity concentration profiles using Irvin's curves³⁸ and proper junction correction factors.³⁵ With P-32 deep diffusions (6–12 μ), the spreading-resistance profiles were directly compared with the radiochemically determined phosphorus profiles (in the same sample) in the concentration range $\sim 3 \times 10^{15} - \sim 7 \times 10^{16}$ cm^{-3} . These results are summarized in Fig. 2.

In the p -type substrates the spreading-resistance phosphorus profiles completely coincided with the radiotracer profiles for the source-to-bulk concentration ratios of $\gtrsim 10^3$, whereas those with this ratio $\gg 10^3$ showed some negative deviation within $1-1\frac{1}{2}$ μ of the $p-n$ junction. In the n -type substrates, the spreading-resistance phosphorus profiles also showed negative deviation with $\frac{1}{2}-2$ μ of the junction for the source-to-bulk concentration ratios of $\gtrsim 2 \times 10^2$. But, when the n -type substrate

dopant concentration was within two orders of magnitude of the source dopant concentration, the spreading-resistance profile showed a positive deviation extending as much as 3–4 μ . The surface concentrations, however, were within $\pm 10\%$ on all p -type and $\pm 50\%$ on all n -type substrates. Though these deviations from the actual phosphorus concentration profiles could be adjusted by using proper junction correction factors, they were used directly (80–90% of the profiles represented correct concentrations) to obtain diffusion coefficients. Moreover, in all spreading-resistance profiles, the junction could be correctly defined by extrapolation of the initial part of the profile [following Eq. (1)] to the average bulk impurity concentration.

With these characteristics of the calculated spreading-resistance impurity profiles calibrated, all the boron and phosphorus diffusion profiles could be well fitted with standard theoretical profiles calculated from Eq. (1). Good fitting was achieved to an accuracy of $\pm 0.05 \mu$ in $2(Dt)^{1/2} \geq 2.00 \mu$ and of $\pm 0.10 \mu$ in $1.40 \mu \leq 2(Dt)^{1/2} < 2.00 \mu$. Typical fitted phosphorus and boron concentration profiles are shown in Figs. 3 and 4, respectively. The validity of the spreading-resistance profile is evident in Fig. 3, where the radiochemically determined phosphorus profile of the same sample is also included. The intrinsic diffusivities of boron and phosphorus in (111) silicon, obtained from such

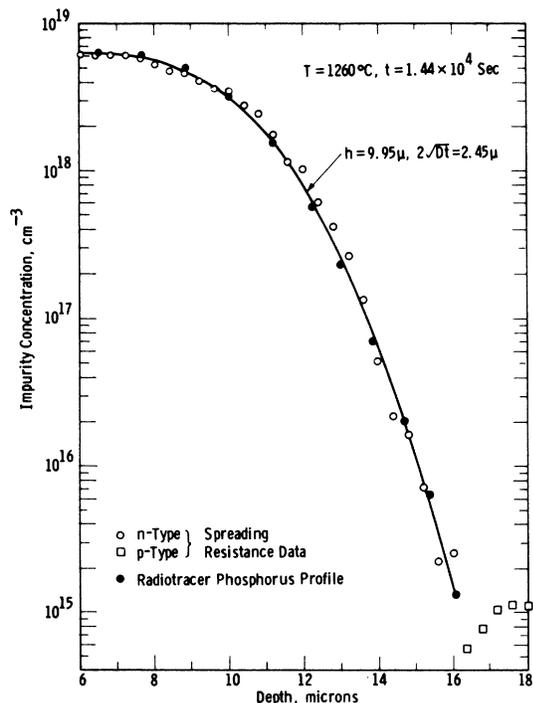


FIG. 3. Typical phosphorus concentration profile in p -type silicon.

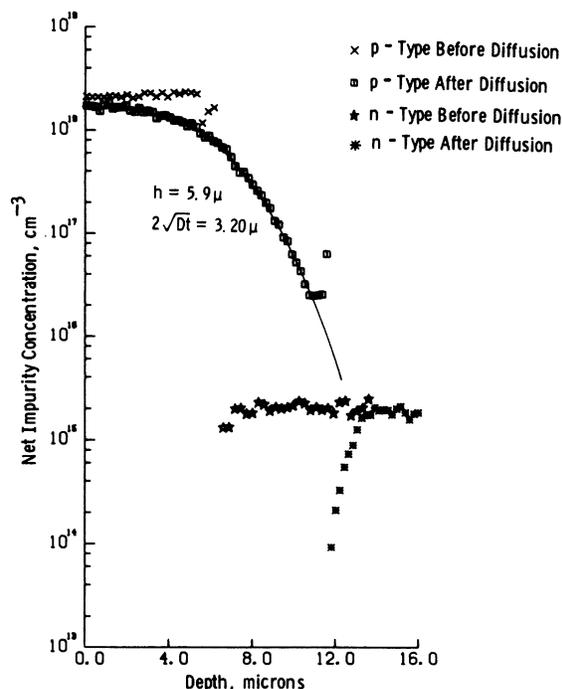


FIG. 4. Concentration profiles of boron in n -type silicon obtained from spreading resistance data; $T = 1342^\circ\text{C}$, $t = 10^4$ sec.

profiles, are shown in Figs. 5 and 6, plotted as a function of inverse absolute temperature. For the purpose of clarity, only about 60% of the data points could be shown. Between 1130 and 1405 $^\circ\text{C}$, they are described by the least-square equations

$$D_B = 2.1 \times 10^{-3} \exp[-(2.85 \pm 0.05 \text{ eV})/kT] \text{ cm}^2/\text{sec} \quad (2)$$

$$D_P = 7.4 \times 10^{-2} \exp[-(3.30 \pm 0.03 \text{ eV})/kT] \text{ cm}^2/\text{sec} \quad (3)$$

To improve the accuracy of Eqs. (2) and (3), enough data were taken such that the addition of one point did not change the activation energy by more than $\sim 0.1\%$.

Above 1130 $^\circ\text{C}$, boron and phosphorus intrinsic diffusivities in (111) silicon were studied at different surface or source concentrations, bulk boron or phosphorus impurity levels, and, consequently, at different surface-to-bulk concentration ratios. Some of these data are included in Figs. 5 and 6. Figure 7 shows the diffusivity of phosphorus in (111) silicon at two different temperatures as a function of the source concentration with different indicated bulk boron or phosphorus concentrations. Figure 8 shows similar data for boron in (111) silicon. As is evident, within the range of experimental error, and in the range of surface concentrations between $\sim 3 \times 10^{16}$ and $\sim 3 \times 10^{19} \text{ cm}^{-3}$ and bulk concentrations between $\sim 6 \times 10^{13}$ and $\sim 8 \times 10^{18} \text{ cm}^{-3}$ (either boron or phosphorus), the diffusivities of

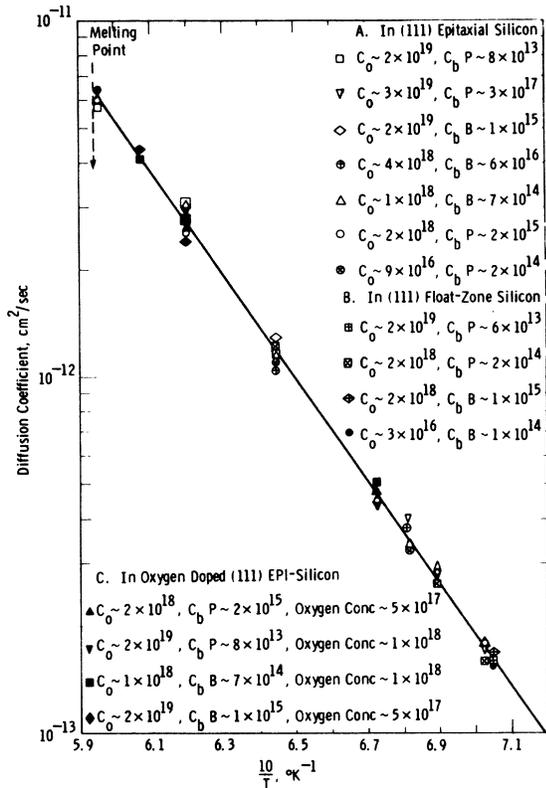


FIG. 5. Temperature dependence of boron diffusivity in (111) silicon. C_0 =source conc., C_bP or C_bB =phosphorus or boron bulk conc.

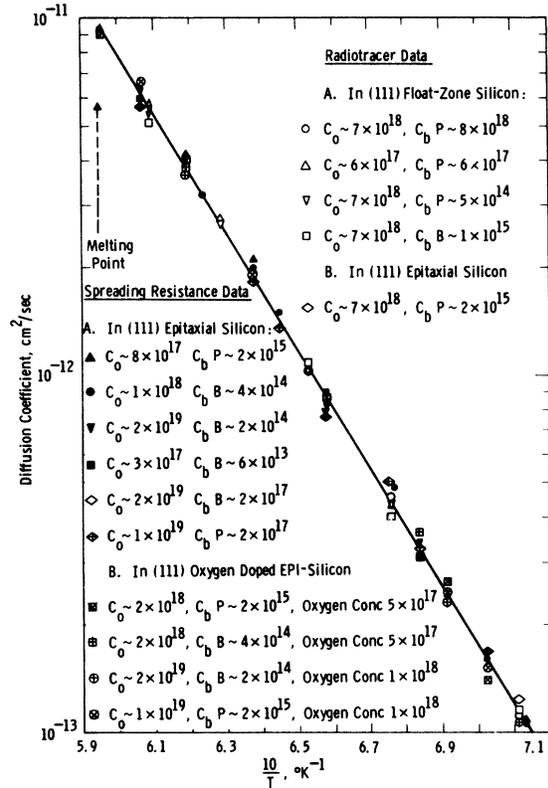


FIG. 6. Temperature dependence of phosphorus diffusivity in (111) silicon. C_0 =source conc., C_bP or C_bB =phosphorus or boron bulk conc.

both boron and phosphorus are independent of both the impurity type and level. Some isoconcentration phosphorus diffusions were also made and shown in Figs. 6 and 7. Although no such study was possible for boron, the evidence obtained at lower concentrations (Fig. 8) made its significance doubtful.

Figure 9 shows two radiotracer phosphorus profiles obtained under the same annealing conditions, one on *p*-type and the other on *n*-type silicon. Within the range of experimental accuracy, they are seen to be indistinguishable. This has also been found to be the case at other concentrations and temperatures (Fig. 6). The situation is seen to be similar for boron (Fig. 5). Thus, the so-called "electrical field effect"^{4,39} on the diffusivity of both phosphorus and boron in silicon, if present, is unrecognizable in the range of concentrations, temperatures, and penetrations used in this study. Again, the concentration-dependence studies (in various forms) of both boron and phosphorus diffusivities in silicon, as reported above, can be converted to generate diffusion coefficients independent of surface-to-bulk concentration ratios (in the range $\sim 1-3.3 \times 10^5$).

As shown in Figs. 5 and 6, boron and phosphorus diffusivities were also determined in epitaxially grown silicon. The epitaxial materials, grown by the hydrogen reduction of silicon tetrachloride at 1150–1250 °C and at growth rates of 1.0–1.4 μ /min, were in the resistivity range 0.007–200 Ω cm, and were doped either *n* type (phosphorus) or *p* type

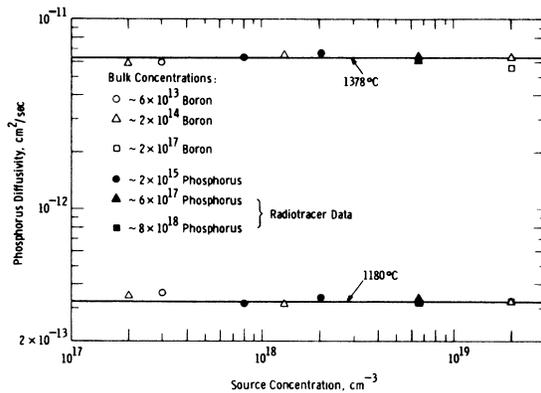


FIG. 7. Phosphorus diffusivity in silicon as functions of the surface and bulk conductivity type and level.

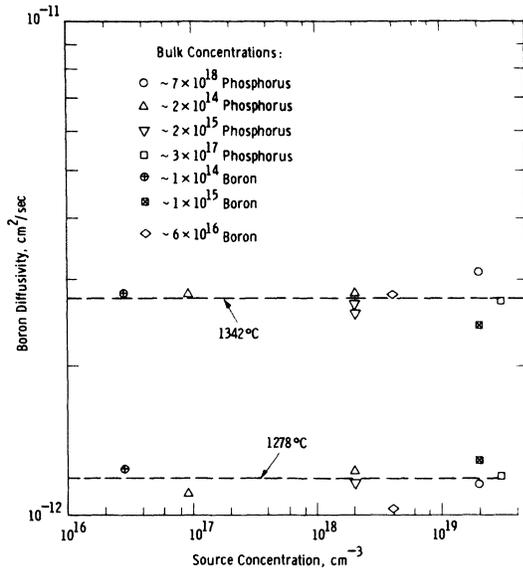


FIG. 8. Diffusivity of boron in silicon as functions of the surface and bulk conductivity type and level.

(boron). Typically they had $\sim 10^2$ dislocations and < 10 stacking faults per cm^2 . The diffusivities of both boron and phosphorus were found to be unaltered in this material compared to those in float-zoned silicon (Figs. 5 and 6). A natural extension of the use of this epitaxial silicon as the bulk material was to saturate it with oxygen to different concentrations and study the effect of dissolved oxygen on the boron and phosphorus diffusion in silicon. The epitaxially grown wafers were annealed in oxygen in a resistance heated furnace to more than 99% saturation [$(Dt)^{1/2}/L \geq 1.5$, where $2L$ is the wafer thickness] with oxygen,⁴⁰ the thermal oxide etched off in dilute HF and the epitaxial silicon source layer and Si_3N_4 cover layer grown as before. The oxygen concentrations in bulk silicon thus prepared were in the range $5\text{--}10 \times 10^{17} \text{ cm}^{-3}$. The diffusion coefficients of boron and phosphorus obtained from these diffusion couples were, however, no different from those obtained from either float-zoned or epitaxial (111) silicon. Some of these data are shown in Figs. 5 and 6. Finally, the replacement of ultrapure hydrogen by ultrapure argon (during diffusion annealing) did not affect either boron or phosphorus diffusivity in silicon.

IV. DISCUSSION

Boron and phosphorus diffusion in single-crystal silicon have previously been studied intensively as functions of temperature, surface concentration, and bulk impurity type and level (Tables I and II). Until the present work, the general experimental philosophy was to use oxide dopant sources on the free surface of silicon and obtain diffusion coef-

ficients from the dopant profiles, either assumed (the solution of the diffusion equation under proper boundary conditions) between the experimental surface concentration and the p - n junction or determined from the change of electrical properties of silicon (conductivity, capacitance, etc.) as a function of diffusion depth. In all these studies the dopant was transported into silicon by the solid-state reduction of the dopant oxide by elemental silicon at the surface. Boundary motion, compound formation (between dopants and/or silicon), precipitation (dopant and/or the compound), and dislocation generation and motion were always associated with such experimental techniques. Moreover, some hitherto undetected surface effects²⁸⁻³⁰ were also included. Consequently, considerable difficulty was experienced (particularly at high impurity concentrations) in fitting the experimental concentration profiles with the proper solution of the diffusion equation. Thus, it is no surprise that such a variety of diffusion characteristics of both boron and phosphorus in silicon are available in the literature (Tables I and II). This is true even in the case of "intrinsic" silicon.

Sanders and Dobson²⁸ have shown that under oxidizing conditions the vacancy concentration near the silicon surface is different from that of the interior. Lane²⁹ made a similar conclusion from a study of the Si-SiO₂ interface states. Recently, Ghoshtagore³⁰ obtained different phosphorus dif-

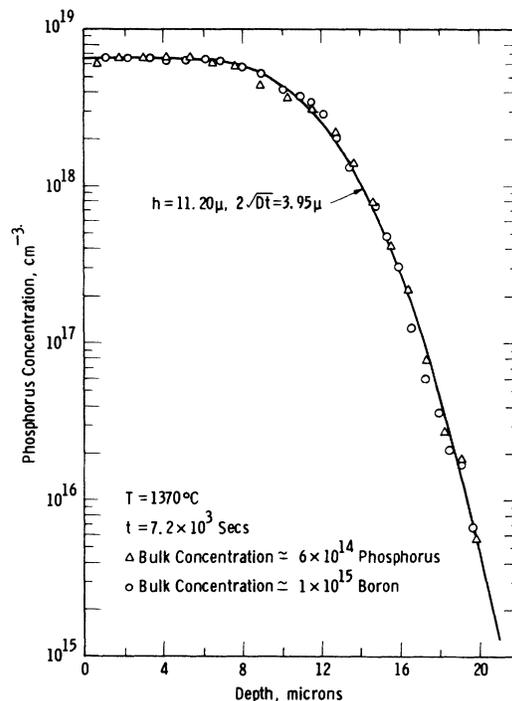


FIG. 9. Phosphorus concentration profiles in both p - and n -type silicon under identical annealing conditions.

TABLE I. Some reported diffusion parameters for boron in silicon.

Ref.	Surface conc. (cm ⁻³)	Bulk impurity conc. (cm ⁻³)	Temp. range (°C)	Activation energy (eV/atom)	Preexponential factor (cm ² /sec)
1	$< 3-6 \times 10^{20}$	$5-50 \times 10^{14}$ (As?)	1000-1300°	2.52	1×10^{-3}
2	$1-10 \times 10^{21}$	5×10^{14} (As)	950-1275°	3.68	10.5
3	$2-5 \times 10^{20}$	2.5×10^{14} (P?)	~ 1150-1350°	3.68	17.1
4	$1.6-61 \times 10^{17}$... (Sb)	1050-1350°	3.51	~ 5
5	$3-20 \times 10^{20}$	$2 \times 10^{13}-8 \times 10^{19}$ (P?)	1050-1350°	3.68	16
6	$2-4 \times 10^{19}$	2×10^{15} (P?)	...	~ 3.7	~ 5
10	$< 2 \times 10^{19}$	9×10^{14} (P)	1100-1300°	~ 3.5	~ 5
	$> 2 \times 10^{19}$	$9-115 \times 10^{14}$ (P)	1050-1300°	~ 3.7	~ 15
	$> 2 \times 10^{19}$	1.4×10^{19} (P)	1100-1250°	~ 3.7	~ 40
11	$< 5 \times 10^{21}$	~ 5×10^{15} (P?)	1025-1200°	3.52	2.02
12	$10^{15}-10^{17}$	1.5×10^{14} (P)	1100-1270°	4.25	0.15
13	$< 10^{18}$	10^{15} (P?)	700-1150°	1.67	6×10^{-7}
14	3.5×10^{19}	<i>n</i> type	1000-1280°	~ 3.7	~ 19
15	$4-8 \times 10^{19}$	2×10^{14} (P?)	1100-1250°	3.7	5.1
This work	$\leq 3 \times 10^{19}$	$6 \times 10^{13}-3 \times 10^{17}$ (B or P)	1150-1405°	2.85	2.1×10^{-3}

fusivities in silicon under different surface conditions. Although all these studies clearly indicate pronounced effects of both the free surface and the redox reactions on it on the equilibrium vacancy concentration near the surface of silicon, their detailed nature is not known at present.

The present experimental philosophy was designed to circumvent these problems and extrinsic effects. The results have contradicted earlier reports on the concentration dependence of both boron and phosphorus diffusivities in silicon. The simple vacancy in silicon is an electron acceptor with very high mobility.⁴¹ But, as long as the impurity concentration (donor or acceptor) does not exceed the intrinsic carrier concentration at the diffusion temperature, the effect of the donor or acceptor impurities in changing the Fermi level⁴² (and hence

the local vacancy concentration) will be negligible. Also, the internal electric field due either to faster diffusing carriers or the *p-n* junction should be nonexistent under such conditions.³⁹ This is what the present study has observed.

The present work has further established the equivalence of 1150-1250 °C grown, SiCl₄ and H₂ reaction produced epitaxial silicon with float-zoned melt-grown single crystals to the extent of point defect concentrations. Although both these types of silicon crystals are known to contain equivalent amounts of carbon,⁴³ epitaxial silicon (grown in hydrogen atmosphere at high temperatures) is considered to contain the lowest amount of dissolved oxygen ($\ll 10^{15}$ cm⁻³). Even when this oxygen content was increased to $\sim 10^{18}$ cm⁻³, no effect of the oxygen content on the diffusivities of boron and

TABLE II. Some reported diffusion parameters for phosphorus in silicon.

Ref.	Surface conc. (cm ⁻³)	Bulk impurity conc. (cm ⁻³)	Temp. Range (°C)	Activation energy (eV/atom)	Preexponential factor (cm ² /sec)
1	$\leq 3-6 \times 10^{20}$	$1.3-16 \times 10^{15}$ (B)	1000-1300°	2.52	1×10^{-3}
2	$6-90 \times 10^{20}$	1.3×10^{15} (B)	950-1235°	3.68	10.5
7	3×10^{18}	5×10^{14} (B)	1200-1320°	3.7	~ 4.8
	3×10^{19}	5×10^{14} (B)	1200-1320°	3.4	~ 0.6
	3×10^{20}	5×10^{14} (B)	1200-1320°	3.0	5×10^{-2}
	1.1×10^{21}	5×10^{14} (B)	1200-1320°	2.6	3×10^{-3}
	3×10^{18}	1×10^{17} (B)	1200-1320°	3.4	~ 0.7
	3×10^{19}	1×10^{17} (B)	1200-1320°	3.3	~ 0.44
	3×10^{20}	1×10^{17} (B)	1200-1320°	2.9	3×10^{-2}
	9.5×10^{20}	1×10^{17} (B)	1200-1320°	2.4	8.7×10^{-4}
	$2-8 \times 10^{18}$	1×10^{16} (B)	1100-1250°	3.7	~ 6
	~ 10^{21}	$1-40 \times 10^{16}$ (B)	1100-1250°	2.28	3.2×10^{-5}
~ 10^{21}	4.2×10^{19} (B)	1150-1200°	2.0	6×10^{-5}	
~ 10^{21}	3.8×10^{20} (B)	1100-1250°	2.0	2.4×10^{-4}	
16	$6-12 \times 10^{19}$	1.6×10^{16} (B)	820-1100°	3.77	49.3
	$6-12 \times 10^{19}$	1.6×10^{16} (B)	820-1100°	2.0	2.5×10^{-5}
This work	$\leq 2 \times 10^{19}$	$6 \times 10^{13}-8 \times 10^{18}$ (B or P)	1130-1405°	3.30	7.4×10^{-2}

phosphorus in silicon could be observed. This probably indicates that the concentration of thermal vacancies (at diffusion temperatures) is virtually unaltered even by the maximum possible concentration of interstitial oxygen.

In general, substitutional impurity diffusion in solids is faster than self-diffusion, although they might both proceed by the vacancy mechanism. Usually, it is believed to be so because of higher vacancy concentration in the immediate neighborhood of the impurity atom. If an extreme case of such a vacancy-impurity ensemble like the E center⁴⁴ (phosphorus-vacancy pair) is considered²⁴ as the defect dominating phosphorus diffusion in silicon, the diffusion parameters obtained in this work can be analyzed. The activation energy of phosphorus diffusion is seen to be in excellent agreement with the sum of the calculated monovacancy formation energy (2.35 eV)^{25,45} and the activation energy of diffusion of the E center (0.94 eV).^{44,46-48} However, the agreement is only reasonable with the recent experimental data of Boltaks and Budarina⁴⁹ for the energy of vacancy formation and of Swanson⁵⁰ for that of motion.

In the absence of any theoretical basis of D_0 for diffusion by a complex defect mechanism, the present data will be examined for a simple vacancy mechanism. The frequency factor of Eq. (3) can be described by⁴⁵

$$D_0 = \frac{1}{8} f a^2 \nu e^{\Delta S_D / k} \text{ cm}^2 / \text{sec} , \quad (4)$$

where a is the lattice parameter and ν is the Debye frequency of silicon. ΔS_D is the entropy of diffusion in silicon, k is the Boltzmann factor and f is the correlation factor for phosphorus diffusion. Using Swalin's⁴⁵ estimated values, Eq. (4) can be reduced to

$$D_0 \approx 18f \text{ cm}^2 / \text{sec} . \quad (5)$$

Hu's⁵¹ calculated correlation factor can now be used in Eq. (5) to calculate D_0 . For $\alpha \approx 1$ and $\beta = 10$,⁵² Hu's data shows $f \approx 5 \times 10^{-3}$. Now from Eq. (5), $D_0 \approx 9 \times 10^{-2} \text{ cm}^2 / \text{sec}$. Thus, Eq. (3) can be well described by the proposed model.

No such information is available on the possible controlling defect in the diffusion of boron in silicon. Nonetheless, some interesting conjectures can be made from Eq. (2), if the defect responsible for boron diffusion is assumed to be similar to the E center. In such a case, the migration energy of a monovacancy-boron ensemble through the silicon lattice is expected to be $\sim 0.5 \text{ eV}$ and the correlation factor for boron diffusion $\sim 10^{-4}$. It should be noted that the activation energy of migration of this defect is very near to that of free vacancy⁴¹ in p -type silicon.

V. CONCLUSIONS

Intrinsic diffusivities of boron and phosphorus in silicon, obtained for the first time, show much lower values between 1130–1405 °C than previously believed. They are also unaffected by impurities like boron (to $3 \times 10^{19} \text{ cm}^{-3}$), phosphorus (to $2 \times 10^{19} \text{ cm}^{-3}$), and oxygen (to 10^{18} cm^{-3}) in silicon. The known properties of the phosphorus-monovacancy complex diffusion through the silicon lattice correctly explains the present phosphorus diffusion data. If a similar defect is responsible for boron diffusion in silicon, some of its properties can be deduced from the present study. Even though all the previous diffusion study in silicon appears to have included some surface effects, their detailed nature remains unknown.

ACKNOWLEDGMENTS

The author is grateful to Dr. J. E. Johnson for continued encouragement and to J. R. McKee and R. J. Pfeil for experimental assistance.

¹C. S. Fuller and J. A. Ditzenberger, *J. Appl. Phys.* **25**, 1439 (1954).

²C. S. Fuller and J. A. Ditzenberger, *J. Appl. Phys.* **27**, 544 (1956).

³J. Yamaguchi, S. Horiuchi, and K. Matsumura, *J. Phys. Soc. Japan* **15**, 1541 (1960).

⁴A. D. Kurtz and R. Yee, *J. Appl. Phys.* **31**, 303 (1960).

⁵E. L. Williams, *J. Electrochem. Soc.* **108**, 795 (1961).

⁶M. O. Thurston and J. Tsai, Ohio State University Research Foundation Report No. 1233-4Q, Columbus, Ohio, 1962 (unpublished).

⁷I. M. Mackintosh, *J. Electrochem. Soc.* **109**, 392 (1962).

⁸S. Maekawa, *J. Phys. Soc. Japan* **17**, 1592 (1962).

⁹S. Horiuchi and J. Yamaguchi, *J. Appl. Phys.* (Japan) **1**, 314 (1962).

¹⁰S. Maekawa and T. Oshida, *J. Phys. Soc. Japan* **19**, 253 (1964).

¹¹T. Kato and Y. Nishi, *J. Appl. Phys.* (Japan) **3**, 377 (1964).

¹²K. Nagano, S. Iwauchi, and T. Tanaka, *J. Appl. Phys.* (Japan) **7**, 1361 (1968).

¹³G. L. Vick and K. M. Whittle, *J. Electrochem. Soc.* **116**, 1142 (1969).

¹⁴M. L. Barry and P. Olofsen, *J. Electrochem. Soc.* **116**, 854 (1969).

¹⁵M. Okamura, *J. Appl. Phys.* (Japan) **8**, 1440 (1969).

¹⁶J. C. C. Tsai, *Proc. IEEE* **57**, 1499 (1969); D. W. Yarbrough, U. S. Army Electronics Command Technical Report No. ECOM-3016, Fort Monmouth, N. J., 1968 (unpublished).

¹⁷M. F. Millea, *J. Phys. Chem. Solids* **27**, 315 (1966).

¹⁸K. H. Nicholas, *Solid-State Electron.* **9**, 35 (1966).

¹⁹See, for example, M. S. R. Heynes, *Electrochem. Technol.* **5**, 25 (1967); M. C. Duffy, D. W. Foy, and W. J. Armstrong, *ibid.* **5**, 29 (1967); T. Nakamura, *NEC Res. & Dev. Japan* **1968**, 93 (1968); K. M. Whittle and G. L. Vick, *J. Electrochem. Soc.* **116**, 645 (1969); A.

- G. Nassibian and G. Whiting, *Solid-State Electron.* **8**, 843 (1965); E. Kooi, *J. Electrochem. Soc.* **111**, 1383 (1964).
- ²⁰B. I. Boltaks and N. N. Matveeva, *Fiz. Tverd. Tela* **4**, 609 (1962)[*Soviet Phys. Solid State* **4**, 444 (1962)].
- ²¹N. D. Thai, *Solid-State Electron.* **13**, 165 (1970); P. E. Bakeman, Jr., and J. M. Borrego, *J. Electrochem. Soc.* **117**, 688 (1970).
- ²²See, for example, M. L. Joshi and S. Dash, *IBM J. Res. Develop.* **10**, 446 (1966), K. H. Nicholas, *Philips Tech. Rev.* **28**, 149 (1967); S. Prussin, *J. Appl. Phys.* **32**, 1876 (1961); G. H. Schwutke and H. J. Quesser, *ibid.* **33**, 1540 (1962); J. E. Lawrence, *ibid.* **37**, 4106 (1966).
- ²³See, for example, P. F. Schmidt and R. Stickler, *J. Electrochem. Soc.* **111**, 1188 (1964); T. W. O'Keefe, P. F. Schmidt, and R. Stickler, *ibid.* **112**, 878 (1965); B. G. Cohen, in the *Proceedings of the IEEE Solid State Devices Research Conference*, Evanston, Ill., 1966 (unpublished); S. Zaromb, *IBM J. Res. Develop.* **1**, 57 (1957).
- ²⁴R. N. Ghoshtagore, *Phys. Status Solidi* **20**, K89 (1969).
- ²⁵A. 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.
- ²⁶A. Seeger and K. P. Chik, *Phys. Status Solidi*, **29** 455 (1968).
- ²⁷S. M. Hu, *Phys. Rev.* **180**, 773 (1969).
- ²⁸I. R. Sanders and P. S. Dobson, *Phil. Mag.* **20**, 881 (1969).
- ²⁹C. H. Lane, *IEEE Trans. Electron. Devices* **ED-15**, 998 (1968).
- ³⁰R. N. Ghoshtagore, *Phys. Rev. Letters* **25**, 856 (1970).
- ³¹R. N. Ghoshtagore, *J. Appl. Phys.* **40**, 4374 (1969).
- ³²R. N. Ghoshtagore, *Appl. Phys. Letters* **17**, 137 (1970).
- ³³H. C. Theuerer, *J. Electrochem. Soc.* **108**, 649 (1961).
- ³⁴F. G. Allen, *J. Appl. Phys.* **28**, 1510 (1957).
- ³⁵R. G. Mazur and D. H. Dickey, *J. Electrochem. Soc.* **113**, 255 (1966); P. A. Schumann, Jr. and E. E. Gardner, *ibid.* **116**, 87 (1969).
- ³⁶B. I. Boltaks, in *Diffusion in Semiconductors* (Academic, New York, 1963), p. 102.
- ³⁷A. 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. I, pp. 194-196.
- ³⁸J. C. Irvin, *Bell System Tech. J.* **41**, 387 (1962).
- ³⁹S. Zaromb, *IBM J. Res. & Develop.* **1**, 57 (1957); F. M. Smits, *Proc. IRE* **46**, 1049 (1968); W. Shockley, *J. Appl. Phys.* **32**, 1402 (1961).
- ⁴⁰R. A. Logan and A. J. Peters, *J. Appl. Phys.* **30**, 1627 (1959); H. J. Hrostowski and R. H. Kaiser, *J. Phys. Chem. Solids* **9**, 214 (1959).
- ⁴¹G. D. Watkins and J. W. Corbett, *Discussions Faraday Soc.* **31**, 86 (1961); G. D. Watkins, *J. Phys. Soc. Japan, Suppl.* **18**, 22 (1963).
- ⁴²R. L. Longini and R. F. Greene, *Phys. Rev.* **102**, 992 (1956); M. W. Valenta and C. Ramasasty, *ibid.* **106**, 73 (1957); R. N. Ghoshtagore and R. L. Coble, *ibid.* **143**, 623 (1966).
- ⁴³P. Rai-Choudhury, A. J. Noreika, and M. L. Theodore, *J. Electrochem. Soc.* **116**, 97 (1969).
- ⁴⁴G. D. Watkins and J. W. Corbett, *Phys. Rev.* **134**, A1359 (1964).
- ⁴⁵R. A. Swalin, *J. Phys. Chem. Solids* **18**, 290 (1961).
- ⁴⁶M. Hirata, M. Hirata, H. Saito, and J. E. Crawford, Jr., *J. Appl. Phys.* **38**, 2433 (1967).
- ⁴⁷M. Hirata, M. Hirata, and H. Saito, *J. Phys. Soc. Japan* **27**, 405 (1969).
- ⁴⁸E. Davoust-Saltiel and P. Baruch, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris*, 1964 (Dunod, Paris, 1965), Vol. 3, pp. 275-280.
- ⁴⁹B. I. Boltaks and S. I. Budarina, *Fiz. Tverd. Tela* **11**, 418 (1969)[*Soviet Phys. Solid State* **11**, 330 (1969)].
- ⁵⁰M. L. Swanson, *Phys. Status Solidi* **33**, 721 (1969).
- ⁵¹S. M. Hu, *Phys. Rev.* **177**, 1334 (1969).
- ⁵²Following Watkins and Corbett (Ref. 44) $\omega_1 \approx \omega_B$. Also, the binding energy of 0.6 eV to be overcome by the vacancy to separate to the next-next-nearest-neighbor position can be split equally between the two consecutive jumps (as a first-order approximation) leading to $E_b \approx 0.6$ eV (~ 0.3 eV for the migration energy of an isolated vacancy and ~ 0.3 eV for the binding energy). Consequently, between 1130 and 1405°C, $\beta = E_b/2kT \approx 8 - 12$.