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Diffusion and segregation of ion-implanted boron in silicon in dry oxygen ambients

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The diffusion of ion-implanted boron in silicon has been studied in the temperature range 1050–1250°C. The diffusion drive-ins were carried out in oxygen and in various oxygen-nitrogen mixtures. Computer calculations were made to solve the diffusion equation under oxidizing conditions and to yield values of sheet resistance, junction depth, etc., for given values of the diffusion coefficient and the coefficient of segregation of boron between silicon and silicon dioxide. By iteration, values of diffusion coefficient and segregation coefficient were found which yielded values closest to the experimental sheet resistance and junction depth. It was found that boron diffusion in (100) silicon was significantly enhanced if the oxygen content in the annealing ambient was more than 10%. During drive-in in oxygen as much as 2/3 of the initially implanted boron could be lost to the oxide. The temperature dependence of the segregation coefficient and of the diffusion coefficient could be described by $m = 9.82 \exp(-0.29\ \text{eV}/kT)$, $D = 0.15 \exp(-3.19\,\text{eV}/kT)\ \text{cm}^2/\text{sec}$. These data have been discussed in light of the available data from previously reported investigations. A possible mechanism of diffusion in an oxidizing medium has been examined.

INTRODUCTION

In recent years, when strict control on device parameters is required, considerable interest has been shown in using ion implantation followed by a drive-in anneal for the formation of doped regions. In the case of boron implantation, the drive-in step is generally carried out in an oxidizing medium in order to prevent the continuous loss of boron to the ambient. It is, however, well known[1-16] that the thermal oxidation of silicon during such drive-ins causes a loss of boron to the oxide formed at the interface. This loss is controlled by the segregation coefficient, which is the ratio of the concentration of boron in the silicon and that in the oxide at the silicon-silicon dioxide interface.

It is also known[17-23] that the diffusion of boron in (100) oriented silicon is enhanced if the diffusion anneal has been carried out in an oxidizing ambient. While there is over-all good agreement on the values of the diffusion coefficient D of boron in silicon, there has been considerable controversy over the value of the segregation coefficient m. Most of these investigations have been carried out using a two-step diffusion which involves a predeposition of boron from a vapor (BBr_3 or BN) or solid (B_2O_3) phase followed by drive-in in the oxidizing ambients. The resulting surface concentrations were in the approximate range of 5×10^{17}–$10^{21}\ \text{cm}^{-3}$ and the diffusion depths were confined to 2–4 μm from the silicon-silicon dioxide interface. In spite of the various attempts made to obtain mathematical solutions of the diffusion equation under the boundary condition imposed by oxidizing ambients, the lack of agreement in m remains. One wonders if this lack of agreement could be attributed to the experimental conditions such as those mentioned above.

Ion implantation provides a very good means of accurately doping silicon at very low concentrations where D and m can be assumed to be independent of concentration. To date the only known experimental work using ion-implanted boron to investigate the segregation and the diffusion of boron in an oxidizing ambient (steam) is that of Prince and Schwettmann.[15] In the present investigation ion implantation has been used to obtain a surface doping of boron in the range of $10^{16}\ \text{cm}^{-3}$ subsequent to a diffusion drive-in of 15.5 h in dry oxygen or oxygen-nitrogen mixtures. In the investigated temperature range 1050–1250 °C, the diffusion depth and the sheet resistivity varied, respectively, between 3.2 to 18.5 μm and between 684 to 2036 $\Omega/\square$.

A computer program, developed by Misawa[14] to analyze impurity redistribution in silicon during oxidation, has been employed to generate diffusion profiles and calculate sheet resistivity, junction depth, etc., for each diffusion condition and for a given value of segregation coefficient m and diffusion coefficient D. By iteration the values of m and D are obtained which yielded sheet resistivity and junction depth equal to those obtained experimentally. In the following the method and the results are discussed at length.

MATHEMATICAL ANALYSIS

The model for boron diffusion in silicon in oxidizing ambients could be best described[3] by a double coordinate system as shown in Fig. 1. Here

the moving Si-SiO_2 boundary is defined by the X coordinate, the movement in the silicon is given by the Y coordinate and the moving oxide-gas interface is described by the Z coordinate. Thus, the impurity concentrations in the silicon and in the oxide are given by $C(Y, t)$ and $C(Z, t)$. At any time t, the silicon-silicon oxide interface will be given by $X = 0$, $Y = Y_0(t)$, and $Z = Z_0(t)$, where Y_0 is the thickness of silicon transformed into oxide of thickness Z_0 during this time, such that

$$Y_0(t) = \alpha Z_0(t) . \tag{1}$$

Here $\alpha = 0.45$ and can be easily calculated from the densities and molecular weights of silicon and silicon dioxide and assuming 100% dense oxide formation.

The boron distribution will be given by Fick's second diffusion equation

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial Z}\left(D_0 \frac{\partial C}{\partial Z}\right), \quad 0 < Z < Z_0 \text{ in the oxide} \tag{2}$$

and

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial Y}\left(D \frac{\partial C}{\partial Y}\right), \quad Y > Y_0 \text{ in the silicon ,} \tag{3}$$

where D_0 and D are the boron diffusion coefficients in oxide and silicon, respectively.

Boron is known to preferentially segregate in the oxide.[1-16] Thermodynamically, this preferential segregation is determined by a quantity called the segregation coefficient m which is the ratio of the concentration of boron in silicon and that in the oxide. Mathematically,

$$M = C(Y_0, t)/C(Z_0, t) . \tag{4}$$

Following the mathematics of the continuity of the impurity flux across the Si-SiO_2 interface and neglecting the diffusion in the oxide, one obtains an equation

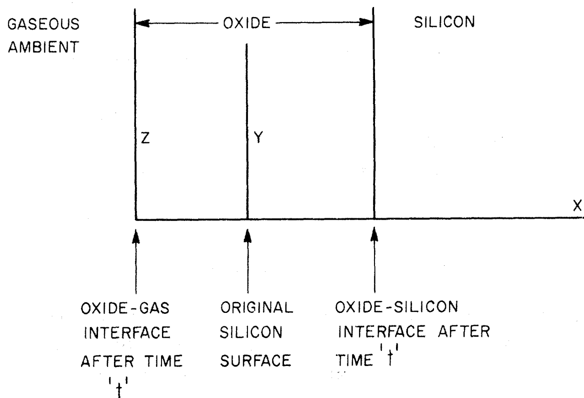

FIG. 1. Mathematical model for diffusion in silicon in oxidizing ambients.

$$C \frac{dZ_0}{dt}\left(\alpha - \frac{1}{m}\right) = -D \frac{\partial C}{\partial X} , \tag{5}$$

which forms one of the boundary conditions to solve the diffusion Eq. (3). In Eq. (5), dZ_0/dt is the oxidation rate of silicon, which can be obtained from the oxide thickness- (Z_0) vs-time (t) relationship[24]

$$Z_0^2 + A Z_0 = B(t + \tau) , \tag{6}$$

where A, B, and τ are oxidation constants. τ corresponds to a shift in the time coordinate which corrects for the presence of the initial oxide layer at $t = 0$. This quantity was found to be temperature dependent[24] and can be neglected at temperatures above 1000 °C and for larger diffusion drive-in times such as those used in the present investigation. Values of A and B were calculated for different temperatures of interest by use of the following equations due to Grove.[25] For dry oxidation

$$B = 1317 e^{-1.24 \text{ eV}/kT} \ \mu\text{m}^2/\text{h} \tag{7}$$

and

$$B/A = 1.032 \times 10^7 e^{-2.0 \text{ eV}/kT} \ \mu\text{m/h} . \tag{8}$$

Numerical values of A and B thus calculated are listed in Table I for various temperatures.

The problem of calculating the boron concentration profiles in silicon after a diffusion drive-in in an oxidizing ambient boils down to solving Eq. (3) for the boundary condition (5) and given an initial boron concentration distribution $C(Y,O)$. In the present investigation ion implanted boron was driven in. This initial boron distribution was assumed to be Gaussian[26] and given by the equation

$$N(X) = (N_D/C_1) \exp\{-[(X - R_P)/C_2]^2\} . \tag{9}$$

In the following, R_P, C_1, and C_2 were taken to be 0.15, 1, and 0.06 μm, respectively. N_D is the total ion implanted dose and X is the penetration in silicon.

TABLE I. Silicon dry-oxidation parameters.[a] $B = 1317 \exp(-1.24 \text{ eV}/kT)$ $\mu m^2/h$, $B/A = 1.032 \times 10^7 \exp(-2.0 \text{ eV}/kT)$ μm/h.

Temperature (°C)	B (μm^2/h)	A (μm)
1250	0.1040	0.041 74
1200	0.075 45	0.050 788
1150	0.053 54	0.062 68
1100	0.037 05	0.078 55
1050	0.024 93	0.1001

[a] Calculated by use of the following equations from Grove (Ref. 25).

Misawa[14] has developed a computer program to solve the diffusion equation by a numerical method. In this method, the partial differential equation of the diffusion was reduced to a set of ordinary differential equations by replacing space derivatives with differences. The set of equations was solved in the time domain by implicit integration. In these calculations both oxidation rate constants A and B and the boron diffusion constant D were assumed to be independent of boron concentration, which simplified the analysis considerably. Finally, the assumption was made that all boron atoms were ionized. The sheet resistivity was computed by use of the computed boron profile and Irvin's data.[27] In the present investigation use of Misawa's computer program[14] was made to obtain boron diffusion profiles in silicon and the sheet resistivity. Because of the limitation of the number of mesh points in computations and to get an accurate diffusion profile near the surface of silicon a two step solution was employed, the first one for the short diffusion drive-in time of 0.5 h and the next one for this initial condition and a final drive-in time which was 0.5 h less than the actual experimental time used. The required input data were the ion implanted dose, values of t, α, m, A, B, and D. The output data were the initial ion implanted profile for $t=0$, the boron diffusion profile after $t=0.5$ h and the final concentration profile after the complete drive-in. Also given were the calculated oxide thickness, sheet resistivity and total boron content remaining in silicon. Figures 2, 3, and 4 show typical calculated boron concentration profiles at $t=0$, $t=0.5$ h, and $t=15.5$ h for a 1200 °C drive-in, respectively. At the top of the figures, all the input and some output data are given. D, A, and B are given in $\mu m^2/h$, μm, and $\mu m^2/h$, respectively. Diffusion junction depths were obtained from these curves for the known initial doping of the silicon wafers. One can now compare the calculated and experimental sheet resistivity, junction depth and even oxide thickness to determine m and D.

In this study our aim was to obtain values of D and m as a function of temperature and oxygen pressure. As is apparent from the above, one cannot uniquely determine both of them from the computer outputs. Therefore an iterative method was used to generate the plots of sheet resistivity as a function (a) of diffusion coefficient for given segregation coefficient m, (b) of segregation coefficient for given diffusion coefficient D, and (c) of the parabolic oxidation rate constant B for given m and D values. Figures 5–7 show these curves. Figure 7 was computed in order to calculate the diffusion coefficient for diffusion drive-ins carried out in ambients with different

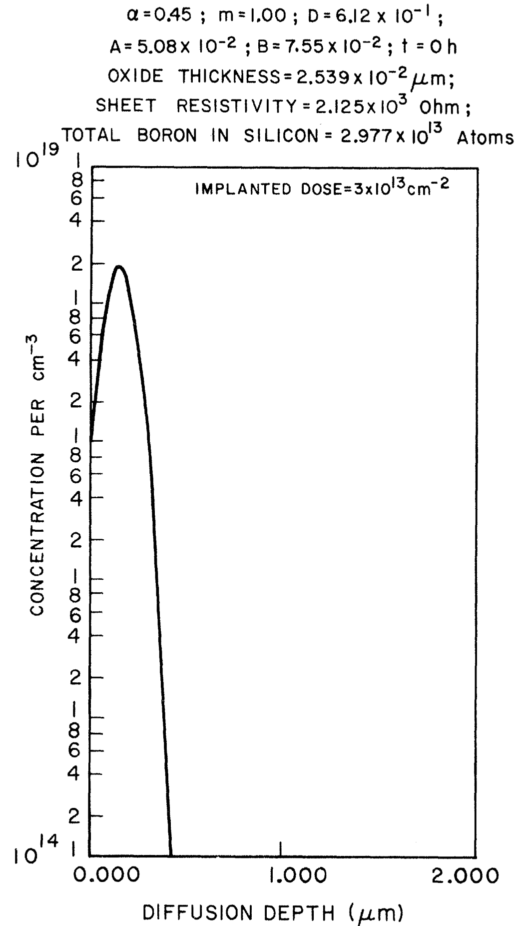

FIG. 2. Computed ion-implanted boron concentration profile for $t=0$.

oxygen contents. It is known[24] that the oxidation rate of silicon is very much dependent on the oxygen partial pressure. This dependency has been demonstrated to be reflected only in the parabolic rate constant B. A has been shown to be independent of the oxygen partial pressure. Values of 100 B/B_A in Fig. 7 directly give the oxygen content of the ambient gas in percent.

Curves similar to those shown in Figs. 2–7 were obtained for each temperature. First calculations were done for 1200 °C drive-in temperature. Based on these calculations, the range of the values of m was narrowed down for this temperature as well as for other temperatures. By use of such computation and comparison of these calculated values with those obtained experimentally, a set of values of D and m were assigned for a given experimental diffusion condition.

In order to compare and to ascertain the use-

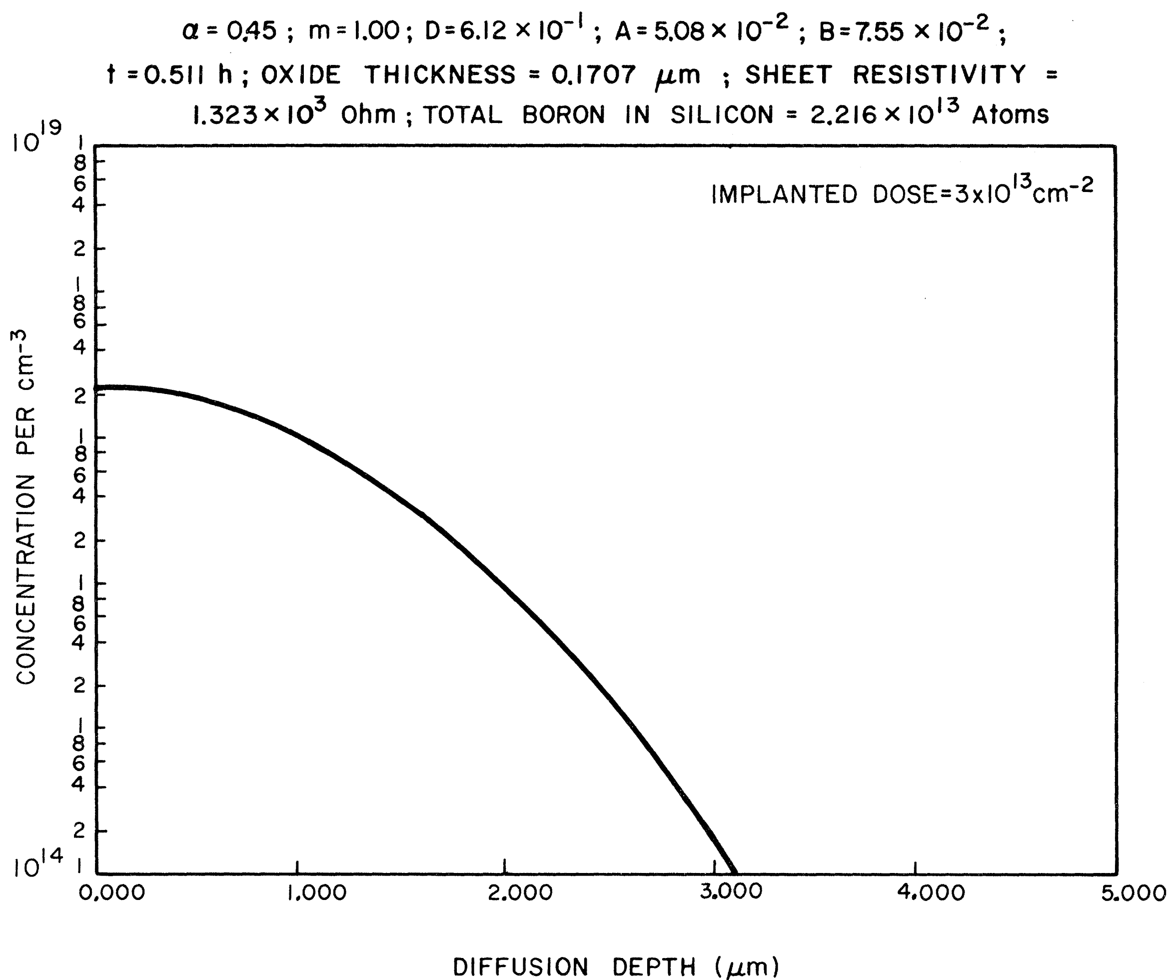

FIG. 3. Computed boron diffusion profile in 100% oxygen at 1200 °C for $t = 0.5$ h.

fulness of such elaborate calculations, the diffusion coefficient was also calculated assuming an ideal Gaussian or error function concentration profile. D was calculated by use of the equations

$$C_B = C_S e^{-X_j^2/4Dt} \tag{10}$$

and

$$C_B = C_S[1 - \operatorname{erf} X_j/2(Dt)^{1/2}] \ , \tag{11}$$

where C_B is the bulk doping of the n-type silicon used in this investigation, C_S is the surface concentration after diffusion anneal, obtained from sheet resistivity and junction depth data by use of Irvin's curve[27] for Gaussian or error function diffusion as applicable, X_j is the junction depth measured by angle lap and staining and t is the time of diffusion anneal.

As will be shown later a Gaussian diffusion profile appears to be closer to the computed profiles for boron diffusion in oxidizing ambients. For a fixed amount of ion implanted boron available and the long drive-in time of 15.5 h, one does expect a Gaussian-type diffusion, especially for those cases where 100% N_2 was used as the drive-in ambient.

EXPERIMENTAL

Arsenic-doped (100) silicon wafers were used in this study. Table II lists the source of these wafers together with their doping, etc. The wafers were degreased and cleaned by use of the standard process used in the device development laboratory. Boron was ion implanted at 50 keV in the desired dose. Only one ion energy was used since it is known[28] that for all practical purposes there is no effect of the ion energy on the resulting surface concentrations after a long drive-in

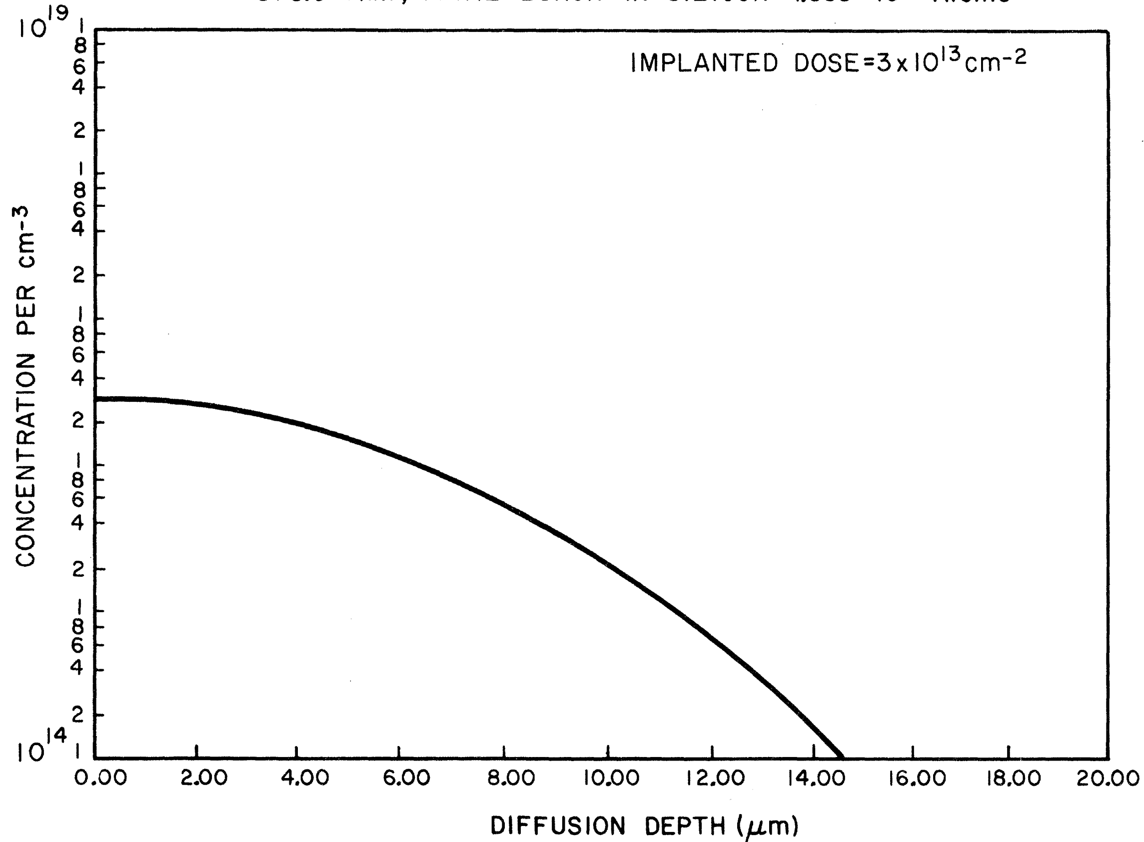

FIG. 4. Computed boron diffusion profile in 100% oxygen at 1200 °C for t = 15.5 h.

of 15.5 h. Ion-implanted wafers were given a 100 : 1 water : HF rinse for 1 min, followed by 2-min deionized water rinse and spin drying. These slices were then annealed for diffusion drive-in at the desired temperature in the range of 1050-1250 °C for a selected time period and in the selected oxygen-nitrogen gas mixture. Diffusion drive-ins were carried out in 100% N_2, 99% N_2–1% O_2, 90% N_2–10% O_2, and in 100% O_2. All these and subsequently described gas concentrations are given as the percent of total volume of gases flowing in. In cases where anneals were made in 100% N_2, a chemical-vapor-deposition undoped capping oxide ~3000 Å thick was deposited on the surface of the ion-implanted wafer prior to drive-in. This was done to prevent depletion of boron from the bare silicon surface at these high temperatures. The total gas flow rate was always 2000 ± 100 cm^3/min through the furnace tube of ≈76–80-mm i. d. The variation in flow rate of the gases has been shown[25] not to affect the oxidation rates of silicon which in turn could affect the diffusion. Thus, no attempt was made to achieve better accuracies in the gas flow rates.

After the diffusion anneal, the oxide layer on the surface was etched off in buffered hydrogen fluoride and the surface cleaned with deionized water and spin dried. The sheet resistance was measured at the center of the wafers by use of the four-point probe technique. In the large volume of the data collected it was found that measured sheet resistivity after a given experimental treatment varied by less than 5% from wafer to wafer in a given run. The variation was, however, observed to be as much as 10% from run to run, especially in those cases where lower doping levels of boron were used. Better accuracies were observed for samples annealed in 100% oxygen

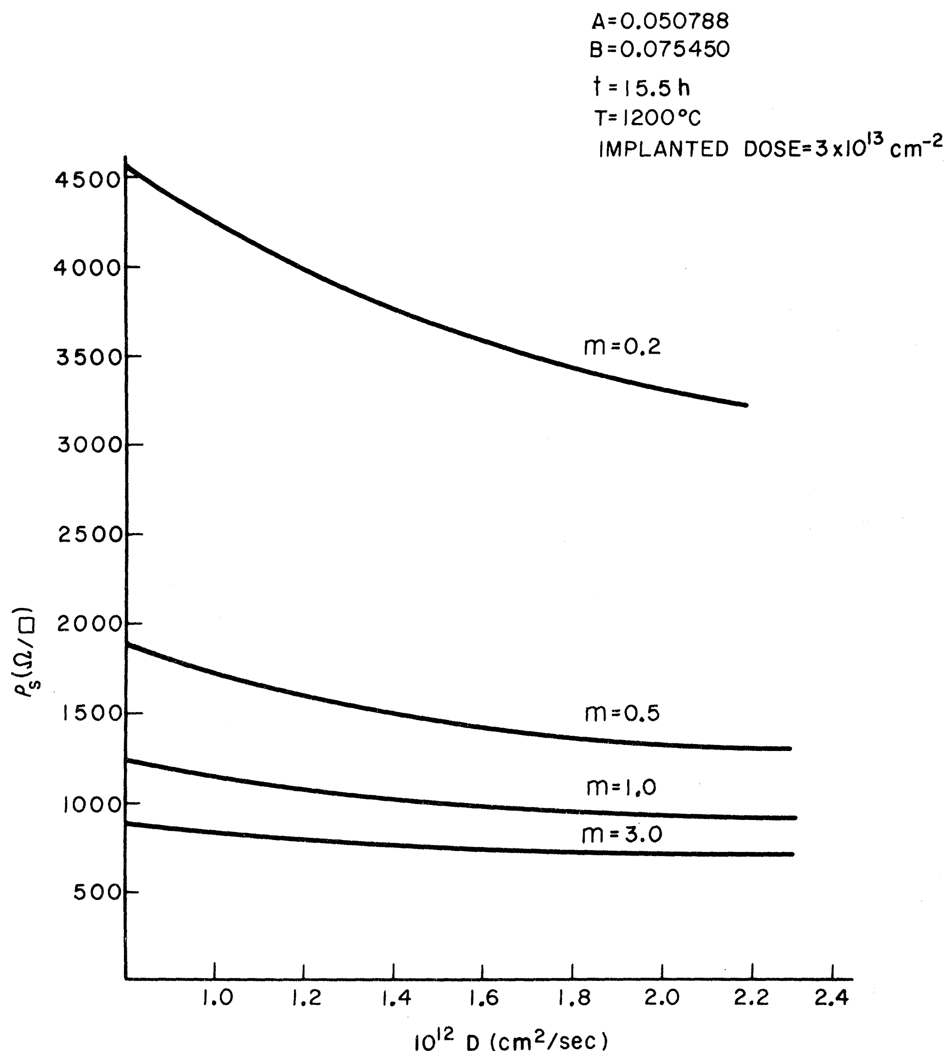

FIG. 5. Computed sheet resistivity as a function of diffusion coefficient for various m values in 100% oxygen ambient (at 1200 °C/15.5 h).

than those annealed in 10 or 1% oxygen ambients.

The *p-n* junction depth was measured by angle lapping and staining and are accurate within 0.27 μm of the given value. Thus, the accuracy of the reported values depended upon the junction depth itself. In a few cases the thickness of the oxide formed during drive-in was measured by Talystep.

RESULTS

Typical experimental results are shown in Figs. 8–11, where the measured sheet resistivities have been plotted, respectively, as a function of the drive-in temperature, ion implanted dose, the drive-in time, and the oxygen partial pressure in the drive-in ambient. The oxygen partial pressure dependence was investigated only at 1150 and 1200 °C since at lower temperatures the resulting sheet resistance was considerably higher and junction depth lower thus increasing the error in these measurements.

Table III lists the experimental results and the calculated diffusion coefficients by use of Eqs. (10) and (11). Also listed are the surface concentration values thus obtained.

Table IV lists the values of diffusion coefficients and segregation coefficients obtained by use of the computed curves similar to those shown as Figs. 5–7 and the experimental value of sheet resistivities. As mentioned earlier the measured sheet resistivity varied from run to run and from wafer to wafer. Such variations place a limit on the

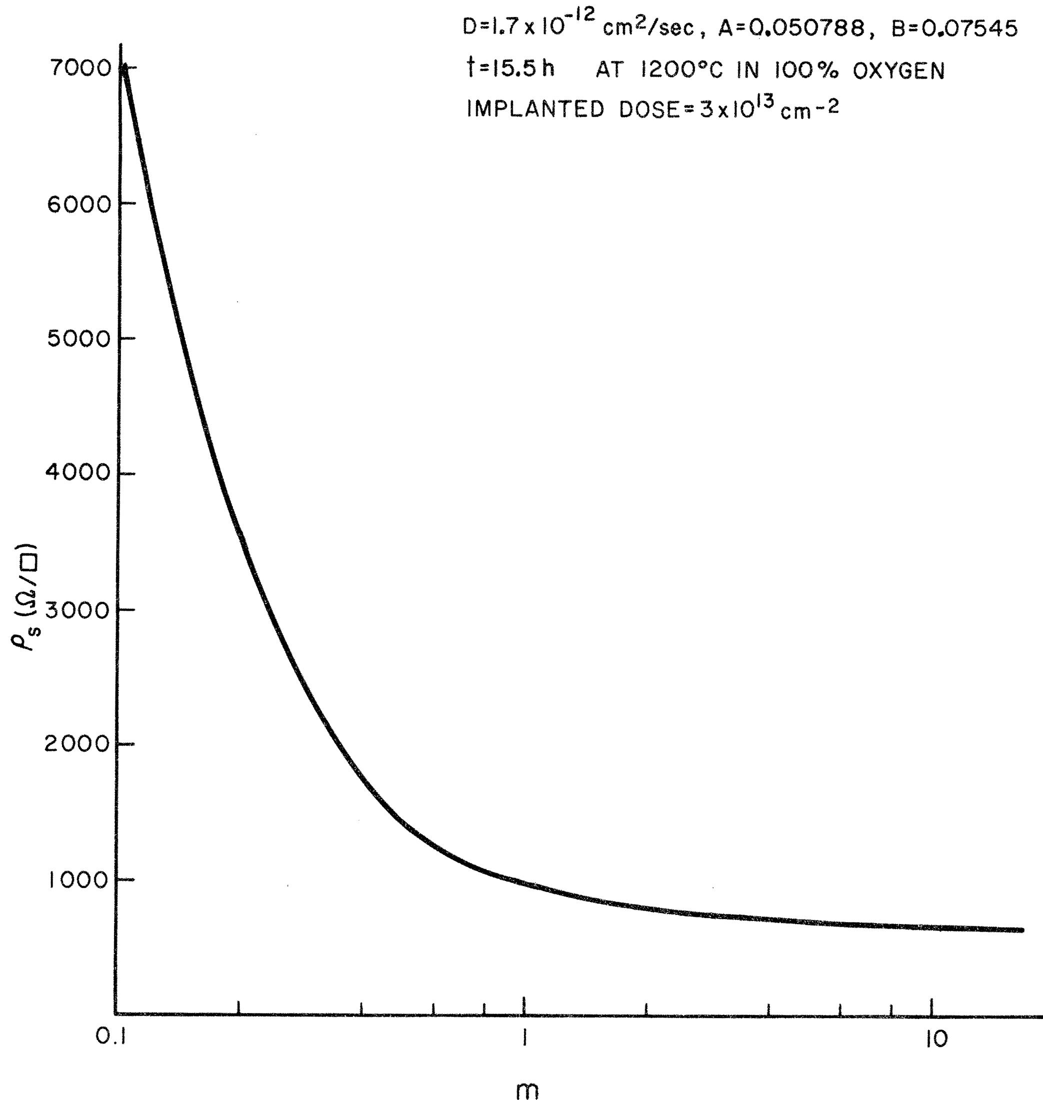

FIG. 6. Computed sheet resistivity as a function of m for a given D in 100% oxygen ambient (at 1200 °C/15.5 h).

choice of correct value of the sheet resistance for comparison with the calculated value. In Table IV the chosen m values lie in the range 0.75–1.05 for the temperature range 1050–1250 °C. As can be seen from Figs. 5 and 6 in this range there is very little variation in sheet resistance with respect to variation in m for a given D value or with respect to variation in D for a given m value. For example at 1200 °C, for the chosen value of $D = 1.7\times10^{-12}$ cm^2/sec and for diffusion in 100% O_2, the sheet resistivity values of 999.4, 979.8, and 960.6 Ω/□ were obtained for $m = 1.05$, 1.00, and 0.95, respectively. The measured average value of ρ_S was 980 Ω/□, justifying the chosen value of $m = 1.0$ for 1200 °C. Considering, however, the individual measurements of ρ_S one can choose any value between 1.1 and 0.9 for m at 1200 °C. Thus, an inaccuracy of ~10% has been estimated in the m and D values listed in Table IV. The observed narrow variation in experimental ρ_S values excludes the choice of wider range of m or D values for a given temperature.

In order to compute D values for the diffusion anneals carried out in 10% O_2–90% N_2 or 1% O_2–99% N_2 ambients, one must use oxidation constants for these oxygen partial pressures.[24] In Fig. 7 the dependence of sheet resistance on the values of the parabolic rate constant B has been

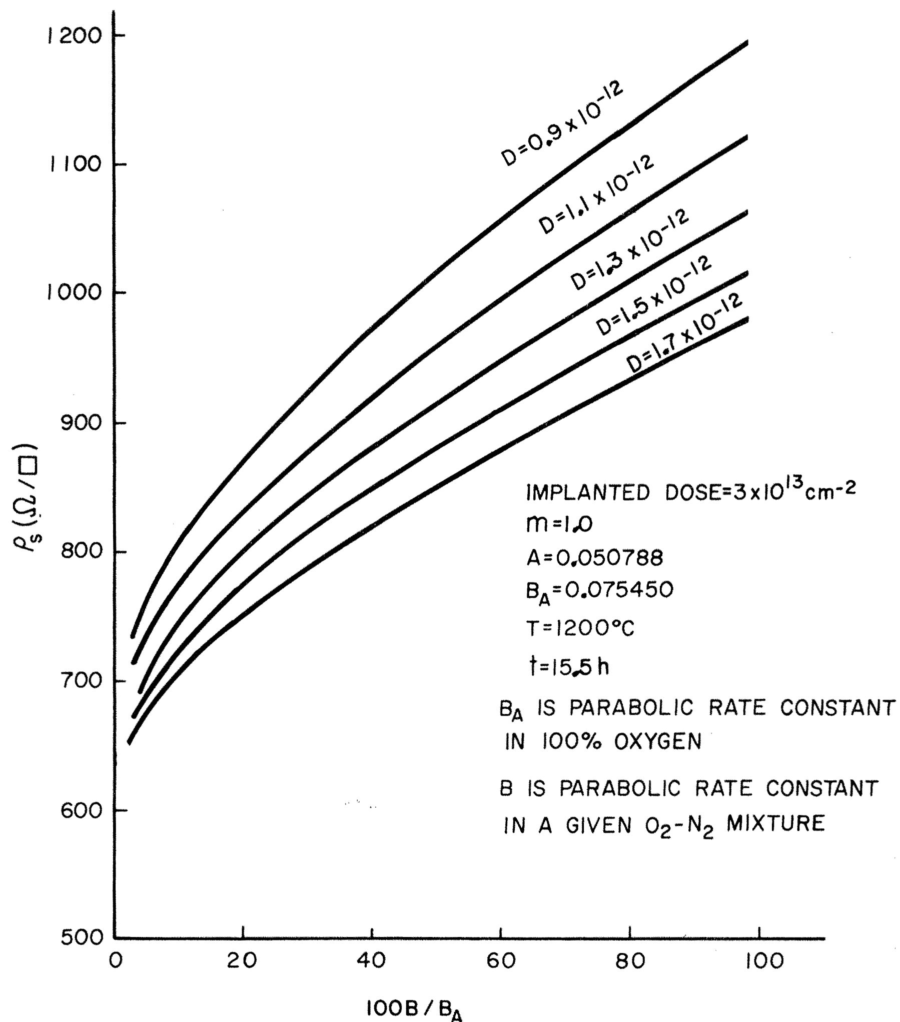

FIG. 7. Computed sheet resistivity as a function of the parabolic rate constant B for different D values and $m=1$ (at 1200 °C/15.5 h).

TABLE II. Silicon used in these investigations. All wafers polished on one side.

Crystal identification	Type (dopant)	Resistivity (Ω cm)	Wafer diameter (cm)	Thickness (μm)
WE[a] 390 571	n (As)	~5–7	3.8	~250
REC[b] 940 100	n (As)	~3–4	5.1	~400–500

[a] WE is Western Electric.
[b] REC is Recticon.

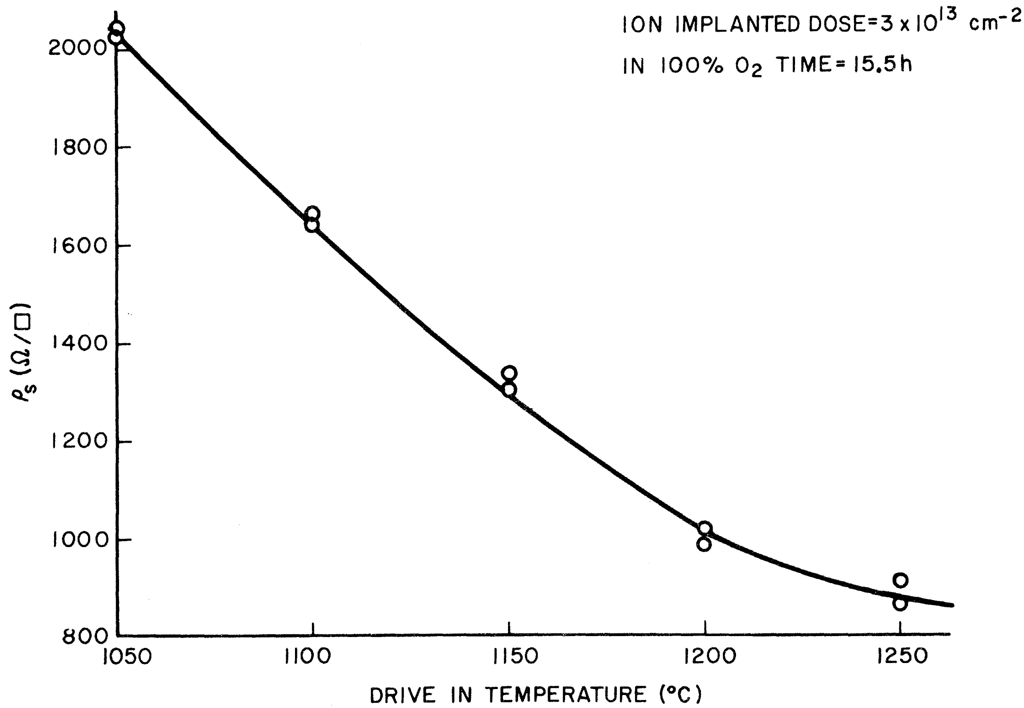

FIG. 8. Experimental sheet resistivity as a function of drive-in temperature for drive-in carried out in 100% oxygen for 15.5 h.

shown for several D values. Consider the drive-in carried out in 10% O_2–90% N_2. For this case Fig. 12 was reconstructed from Fig. 7 to show the variation of sheet resistivity with diffusion coefficient. For an experimental value of sheet resistivity $= 870\ \Omega/\square$, this yields $D = 6.3 \times 10^{-13}$ cm^2/sec at 1200 °C. The arbitrary assumption has been made here that $m(=1)$ is independent of oxygen partial pressure.

Calculations similar to the above were made for diffusion anneals carried out in 1% O_2—99% N_2 and those in 100% N_2. As seen from Table IV there does not appear to be any significant change in D values as one goes down from 10% O_2 to 1% O_2 or to 0% O_2.

Calculations similar to those described above were made for 1150 °C drive-in anneals as well. All these values are also listed in Table IV. A comparison of D values listed in Table IV which are believed to represent true diffusivities for diffusion of boron in silicon under oxidizing ambients, can be made with those listed in Table III obtained by use of Eqs. (10) or (11). It is apparent that D values obtained by the use of a Gaussian diffusion solution (10) are very similar to those obtained from exact computer solution of Eq. (3) under boundary condition (5). The D values obtained by use of the error function solution (11) are about 20–40% larger. Figure 13 shows an experimental diffusion profile constructed by serial etching and sheet resistivity-junction depth measurements and by use of Irvin's curve[27] for Gaussian diffusion. Also shown is the computed diffusion profile with $D = 1.7 \times 10^{-12}$ cm^2/sec and $m = 1.0$ at 1200 °C for 100% oxygen ambient diffusion. Experimental points are on the lower concentration side, but are fairly close to the computed curve. These results thus indicate that a Gaussian distribution would be closer to the true distribution of the boron atoms after a long drive-in of the implanted boron. During these boron diffusion anneals in oxygen ambients, there occurs a loss of boron to oxide. In the computation thus made, a calculation of the total amount of boron remaining in silicon was also made. Figure 14 shows a plot of amount of boron remaining in silicon versus the annealing temperature in 100% O_2. It is seen that there is considerable loss of boron during such annealings. One can lose almost 50% of the implanted boron at 1200 °C. Similar calculations show that the loss is considerably less when annealed in 10% O_2, being only 23% at 1200 °C. Less boron is lost after high-temperature drive-in than after low-temperature drive-in. This can be at-

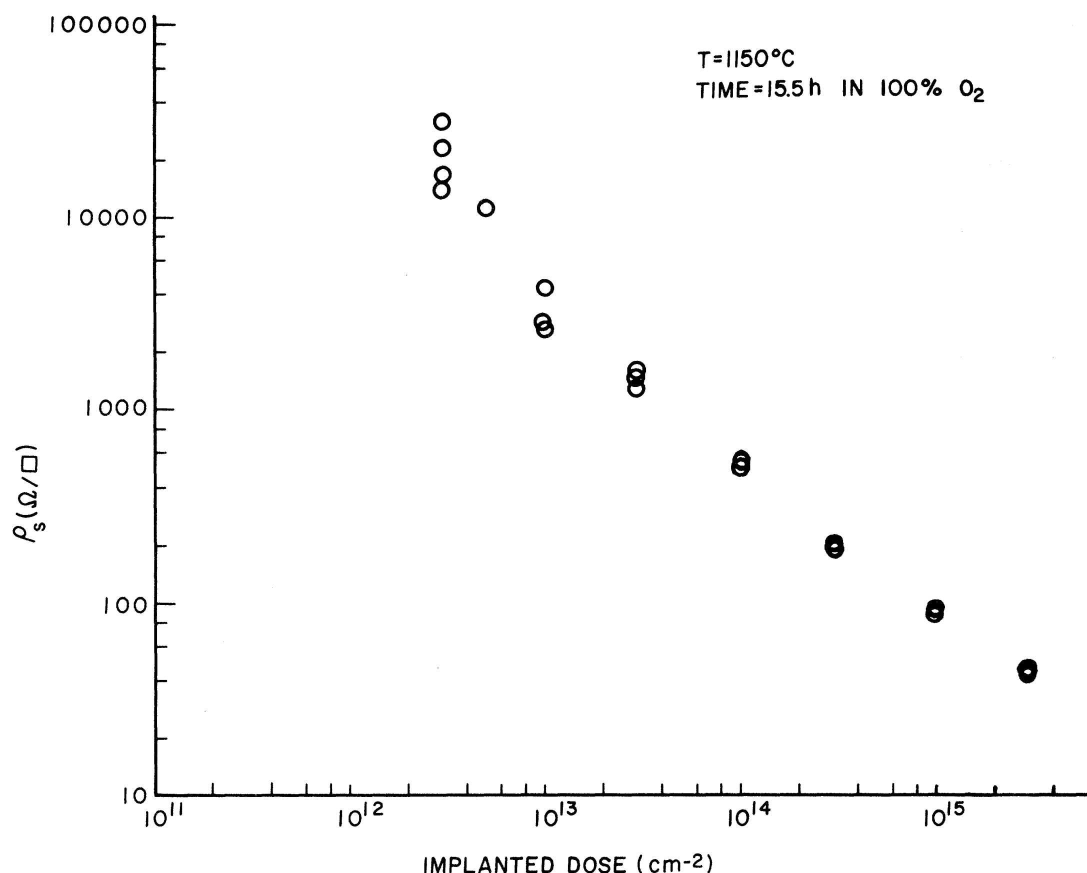

FIG. 9. Experimental sheet resistivity as a function of ion implanted boron dose after drive-in at 1150 °C for 15.5 h (in 100% oxygen).

tributed to the fact that the higher the temperature the higher are the segregation coefficient and the diffusion coefficient in silicon (diffusion in oxide is still very small).

Finally, Figs. 15 and 16 show the temperature dependence of m and D in a typical Arrhenius-type plot for the diffusion anneals carried out in 100% oxygen. The error bars in Fig. 15 give the expected range of m for each temperature. The temperature dependence of these can be described by the following (obtained by use of the least-squares method):

$$m = 9.82\, e^{-0.29 \text{ eV}/kT} ,$$

$$D = 0.15\, e^{-3.19 \text{ eV}/kT} \text{ cm}^2/\text{sec} .$$

DISCUSSION

Several authors in the past have reported the results of their investigation of diffusion of boron in silicon in oxidizing ambients. Their results and various relevant experimental conditions are compared in Table V together with the findings of the present investigation. It is apparent from these results that there is considerable discrepancy in the reported values of segregation coefficients. Experimental conditions of the investigations differ considerably. There are two distinct differences between the present experimental conditions and those of others: (i) until now, the experimental diffusion profiles were confined to a narrow region near the oxide-silicon interface and (ii) the surface concentrations were generally higher up to about four orders of magnitude, than those obtained in the present investigation.

In the present investigation the study of boron diffusion in silicon in oxidizing ambients were carried out as a part of the program to form p regions for n channel complementary-metal-oxide semiconductor (CMOS) based devices for which a surface doping of the order of 10^{16} cm^{-3} was required. We have, thus, investigated boron diffusion from an ion implanted source which was found to provide a good control[28] on the doping levels and

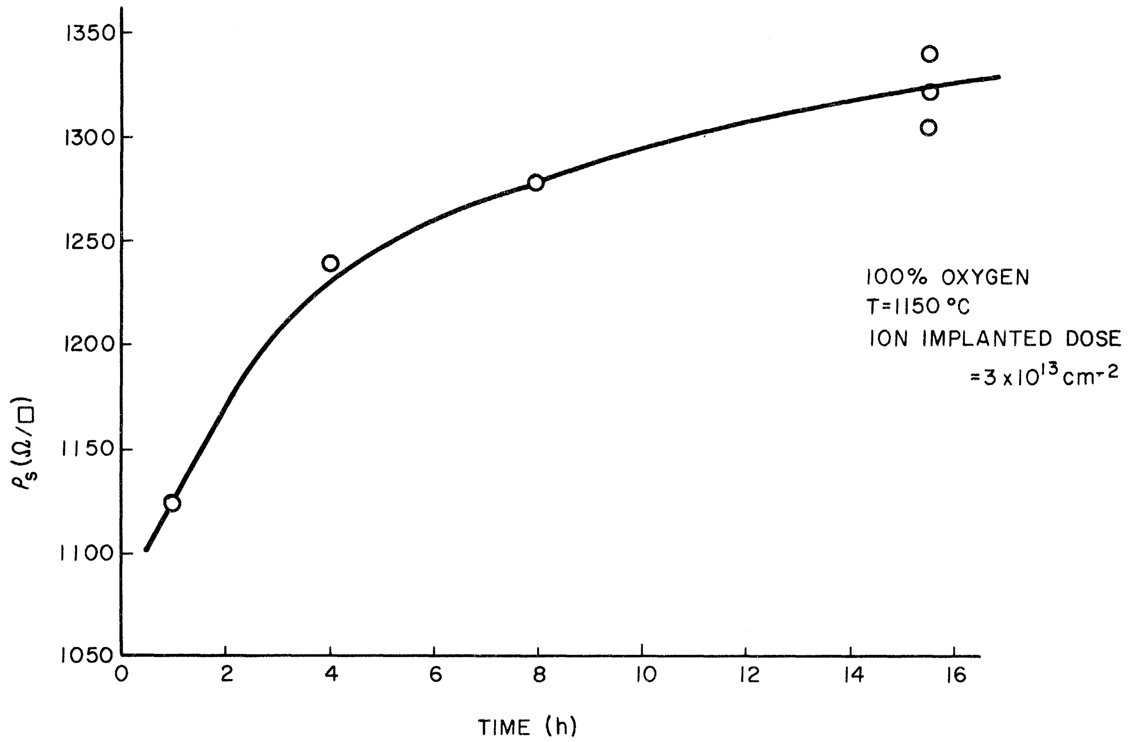

FIG. 10. Experimental sheet resistivity as a function of the drive-in time at 1150 °C in 100% oxygen.

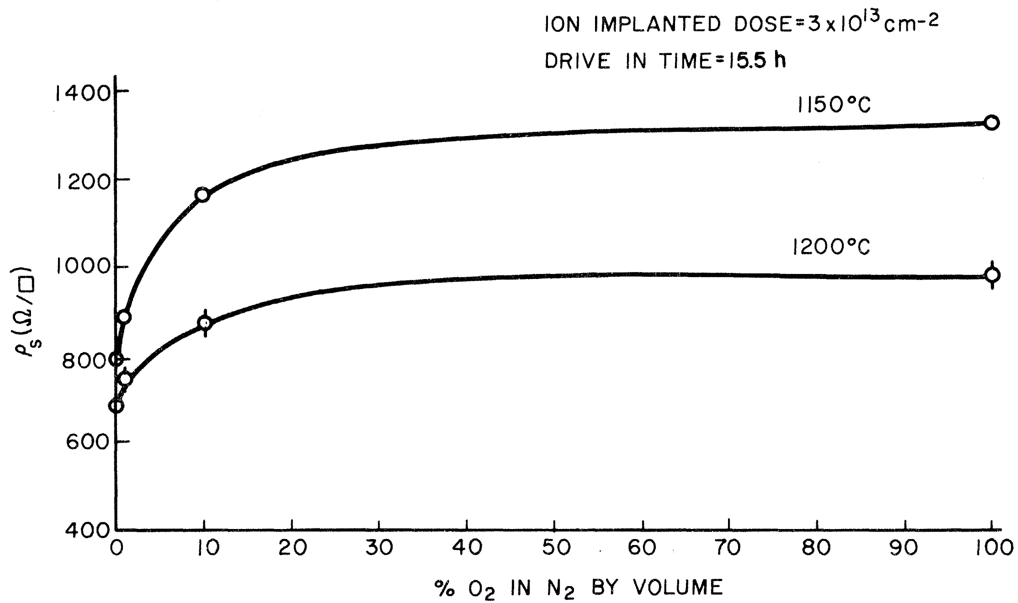

FIG. 11. Experimental sheet resistivity as a function of the oxygen content in the drive-in ambient (15.5 h) and temperature.

TABLE III. Calculation of approximate diffusion coefficient of B in (100) Si.

Temperature (°C)	Ion implanted dose (cm^{-2})	Oxygen partial pressure (%)	ρ_S [a] (Ω/□)	J_n [a] (μm)	Gaussian diffusion C_S (cm^{-3})	Gaussian diffusion D (cm^2/sec)	Error Function diffusion C_S (cm^{-3})	Error Function diffusion D (cm^2/sec)
1250	3×10^{13}	100	880	18.51	1.9×10^{16}	5.26×10^{-12}	2.7×10^{16}	7.06×10^{-12}
1200			981	12.15	3.2×10^{16}	1.91×10^{-12}	4.4×10^{16}	2.55×10^{-12}
1150			1322	7.30	4.2×10^{16}	6.61×10^{-13}	6.0×10^{16}	8.93×10^{-13}
1100			1657	4.32	6.8×10^{16}	1.98×10^{-13}	10.0×10^{16}	2.52×10^{-13}
1050			2036	3.24	7.8×10^{16}	1.08×10^{-13}	11.3×10^{16}	1.37×10^{-13}
1200	3×10^{13}	100	981	12.15	3.2×10^{16}	1.91×10^{-12}	4.4×10^{16}	2.55×10^{-12}
		10	870	11.34	4.2×10^{16}	1.54×10^{-12}	6.0×10^{16}	2.01×10^{-12}
		1	745	8.37	8.4×10^{16}	7.08×10^{-13}	12.5×10^{16}	8.93×10^{-13}
		0	684	8.64	9.4×10^{16}	7.36×10^{-13}	13.8×10^{16}	9.28×10^{-13}
1150		100	1322	7.30	4.2×10^{16}	6.61×10^{-13}	6.0×10^{16}	8.93×10^{-13}
		10	1170	7.02	5.5×10^{16}	5.51×10^{-13}	8.0×10^{16}	7.08×10^{-13}
		1	887	6.75	9.2×10^{16}	4.51×10^{-13}	13.7×10^{16}	5.68×10^{-13}
		0	795	7.02	10.3×10^{16}	4.76×10^{-13}	15.0×10^{16}	6.82×10^{-13}

[a] Experimental results.

thus on the threshold voltages. The drive-in time was always 15.5 h except for a few runs made to determine the relationship of the sheet resistivity–versus–drive-in time (Fig. 10). The resulting surface concentrations were in the range 2.2–10.3×10^{16} for the temperature range of 1050–1250 °C.

The use of large drive-in times and low boron concentrations provide several advantages: (a) Diffusion may be assumed to take place rather ideally with a concentration independent D, which is not valid at higher concentrations.[29] (b) Ionization of implanted boron may be assumed to be complete, thus sheet resistivity measurements will be more meaningful in evaluating the surface concentration values. (c) The segregation coefficient is a thermodynamic quantity, which is, therefore, expected to be ideal only at very low concentrations where the various interactions between segregating species themselves

TABLE IV. Diffusion and segregation coefficients for boron diffusion in dry-oxygen ambients.

Temperature (°C)	Oxygen partial pressure (%)	Experimental ρ_S (Ω/□)	Experimental J_n (μm)	Experimental Oxide thickness (Å)	Computed ρ_S (Ω/□)	Computed J_n (μm)	Computed Oxide thickness (Å)	Computed C_S (cm^{-3})	m	D (cm^2/sec)
1250	100	880	18.51	12 100	875	15.0	12 490	2.2×10^{16}	1.05	3.1×10^{-12}
1200		981	12.15	10 000	979	11.4	10 580	3.0×10^{16}	1.0	1.7×10^{-12}
1150		1322	7.30	8600	1324	6.8	8840	4.1×10^{16}	0.95	5.2×10^{-13}
1100		1657	4.32	7000	1707	4.3	7260	5.5×10^{16}	0.85	2.0×10^{-13}
1050		2036	3.24	5500	2045	3.1	5753	6.5×10^{16}	0.75	9.0×10^{-14}
1200	100	981	12.15	10 000	979	11.4	10 580	3.0×10^{16}	1.0	1.7×10^{-12}
	10	870	11.34	3100	870	7.5	3200	6.8×10^{16}	1.0	6.3×10^{-13}
	1	745	8.37	···	755	7.2	···	8.4×10^{16}	1.0	6.4×10^{-13}
	0	684	8.64	···	693	8.1	···	9.4×10^{16}	1.0	6.4×10^{-13}
1150	100	1322	7.30	8600	1324	6.8	8840	4.1×10^{16}	0.95	5.2×10^{-13}
	10	1170	7.02	1800	1170	6.1	1850	8.5×10^{16}	0.95	3.7×10^{-13}
	1	887	6.75	···	900	6.4	···	9.2×10^{16}	0.95	4.1×10^{-13}
	0	795	7.02	···	790	6.6	···	10.3×10^{16}	0.95	4.0×10^{-13}

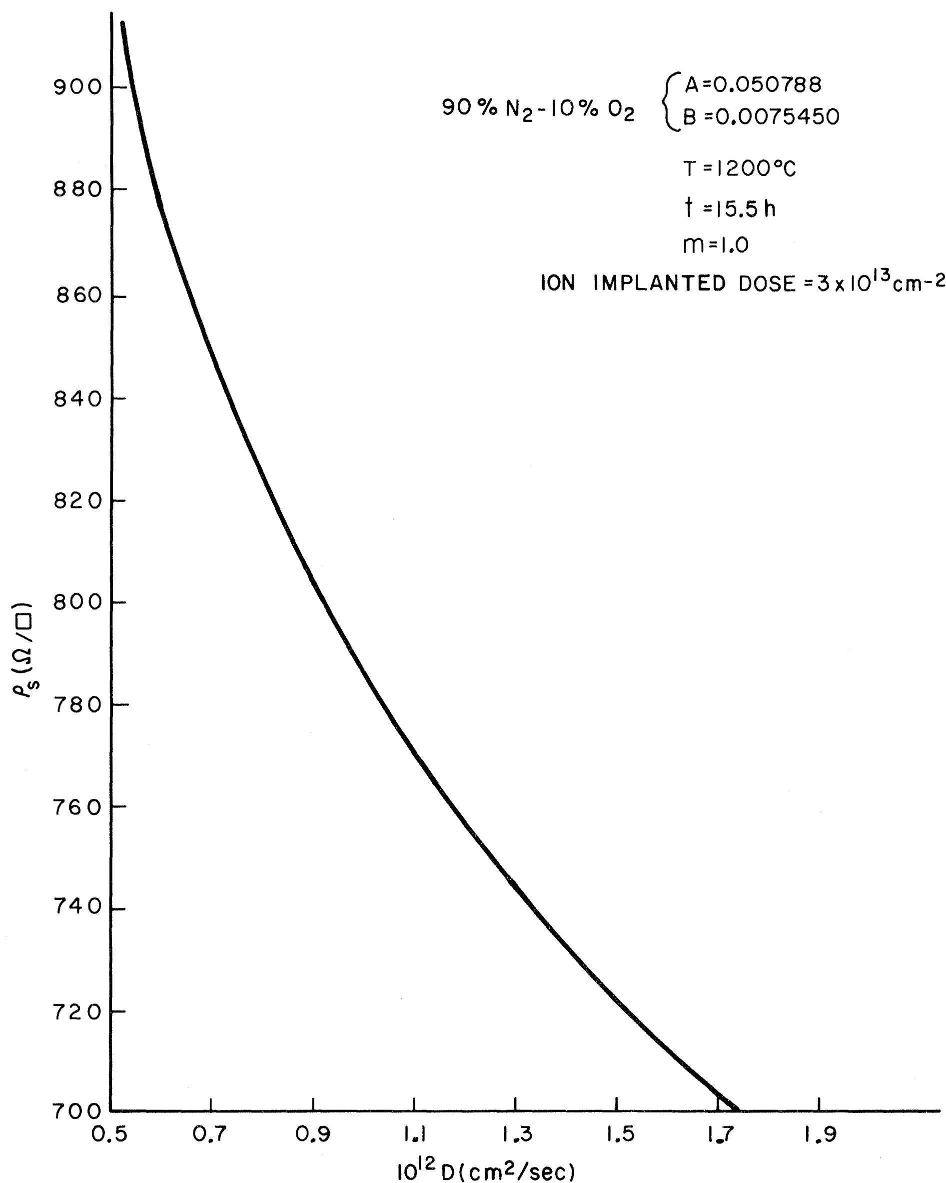

FIG. 12. Computed sheet resistivity as a function of diffusion coefficient, for drive-in at 1200 °C/15.5 h, carried out in 10% oxygen–90% nitrogen ($m = 1$).

and with solvent species are minimal. (d) Lattice strain effects, which are shown by Thai[30,31] to be very important at boron concentrations of 10^{20}–10^{21} atoms/cm^3, can be neglected.

It is, therefore, believed that the m and D values obtained in the present investigations will be closer to their true values within the specified experimental and computational errors. As can be seen from Table IV, the chosen values of D and m yield values of sheet resistivities and junction depths within 1% and 10% of the experimental values, respectively.

DIFFUSION COEFFICIENTS

Diffusion coefficients obtained in this investigation (Table V) agree fortuitously very well with those reported by Colby and Katz[32] and are within a factor of 2 of those reported by others. There is an over-all remarkable agreement. A few conclusions are very much in line here.

(i) The diffusivities listed in Table IV are similar but smaller than those obtained assuming simple Gaussian type diffusion in silicon (Table III). Thus, the Gaussian diffusion can be fairly

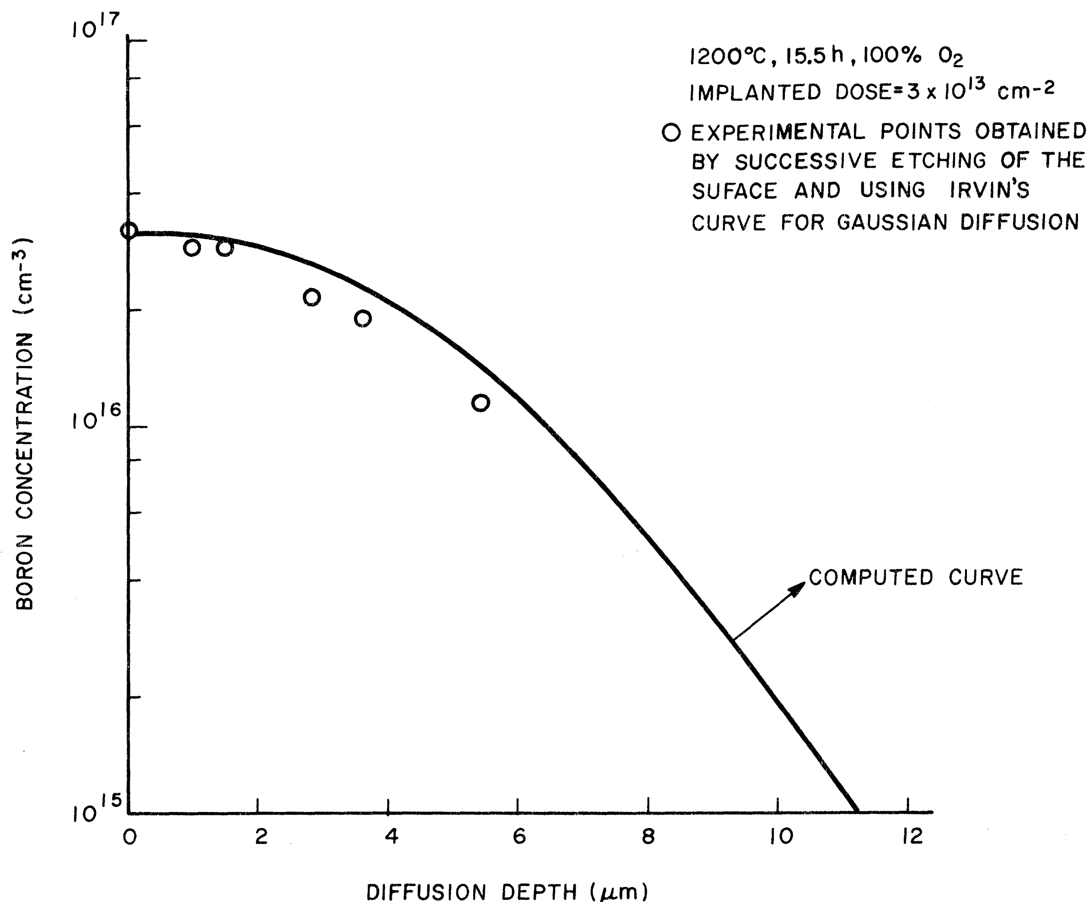

FIG. 13. Comparison of the experimental boron diffusion profile and the computed profile for boron diffusion at 1200 °C/15.5 h in 100% oxygen ($m = 1$).

good approximation for quick calculations. This is also reflected in the very little differences noticed in the computed C_S values (Table IV) and those obtained by assuming Gaussian distribution (Table III). The error-function-type distribution resulted in much higher D and C_S values (Table III).

(ii) Diffusion occurs faster in oxidizing ambients and it is dependent on the oxygen partial pressure (p_{O_2}) in the annealing ambient. There is no or very little dependence on p_{O_2} below 10% O_2 in the ambient. This dependence on p_{O_2} is more predominant at 1200 °C where $D_{100\%\,O_2} : D_{10\%\,O_2} = 2.7$ than 1150 °C, where the same ratio is only 1.41.

Several authors have reported enhancement of diffusion of boron in silicon in oxidizing ambients.[17-23,32] Recently, Hu[22] has coupled the formation of stacking faults in silicon during oxidation with the enhancement of boron diffusion under similar circumstances. It is assumed that due to incomplete oxidation of silicon at the Si-SiO_2 interface, an inward flux of silicon self interstitials will cause diffusion enhancement. Some interstitials are held responsible for nucleating stacking fault embryos at certain strain centers in the bulk and at the surface. If it is assumed that the creation of these self interstitials, which are responsible for enhanced diffusion and stacking fault generation, is highly temperature dependent, then the observed enhancements at 1200 and 1150 °C can be explained. Temperature dependence of these enhancement factors yields an activation energy of 2.3 eV which is very similar to the activation energy (2.1 ± 0.2 eV) obtained by Sanders and Dobson[33] from the study of the annealing (shrinkage) of the stacking faults created during thermal oxidation

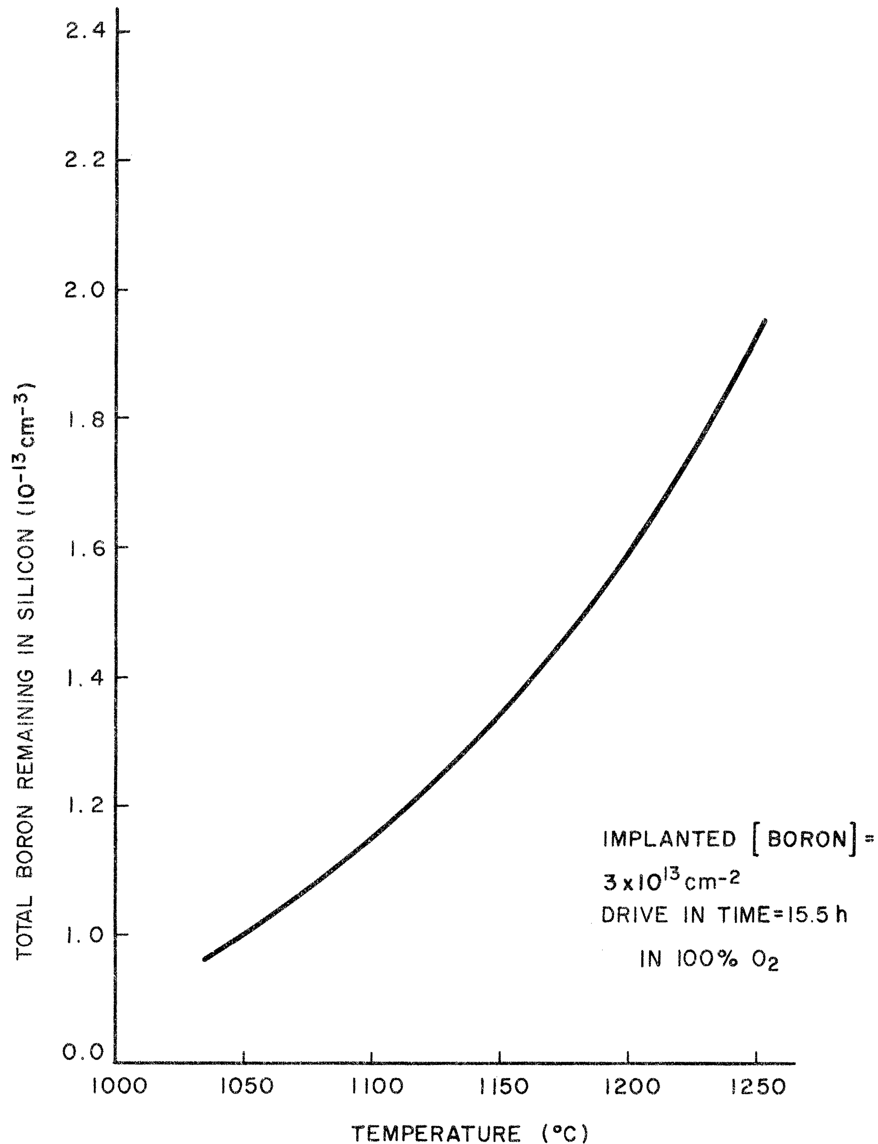

FIG. 14. Computed total amount of boron remaining in silicon after 15.5 h drive-in in 100% oxygen as a function of temperature.

of silicon. These results, thus, very well support Hu's model[22] of defect generation and diffusion enhancement. Further investigation to examine this model, which involves the study of the stacking faults and other defects in the boron diffused silicon wafers of the present investigation, is being carried out and the results will be reported in the near future.

(iii) There is considerable loss of boron during the diffusion anneals in oxidizing ambient as shown in Fig. 14. These losses are considerably smaller than those reported by Huang and Welliver[7] from their studies of boron diffusion in a wet oxygen ambient. These authors have chosen a value of $m = 0.11$ to fit their experimental results which can easily explain the large boron losses calculated by them. It may be pointed out at this point that our values of remaining total boron in silicon are very well confirmed from the threshold measurements made on the CMOS devices where n-

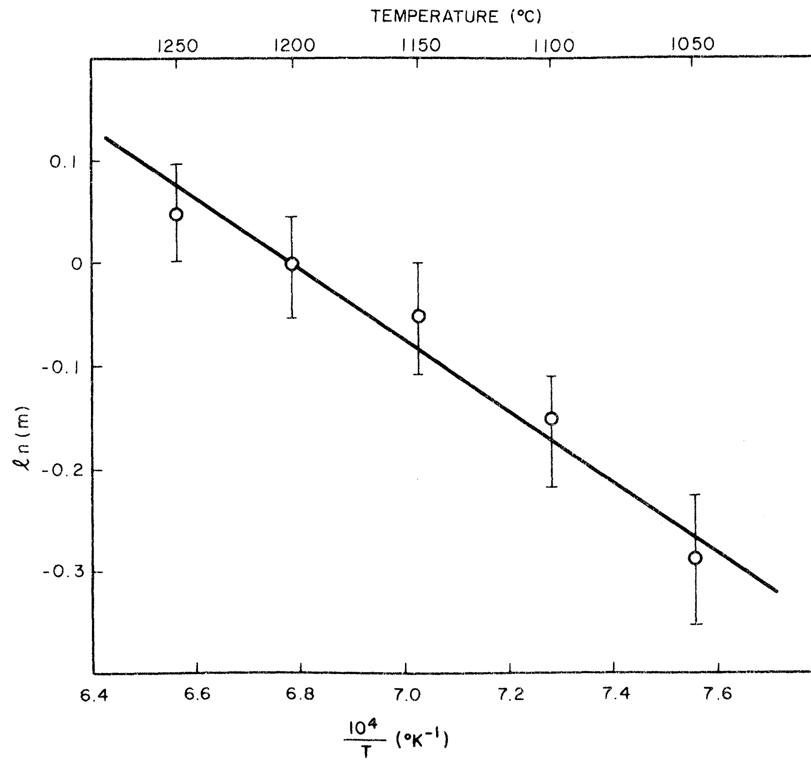

FIG. 15. Temperature dependence of the segregation coefficient m.

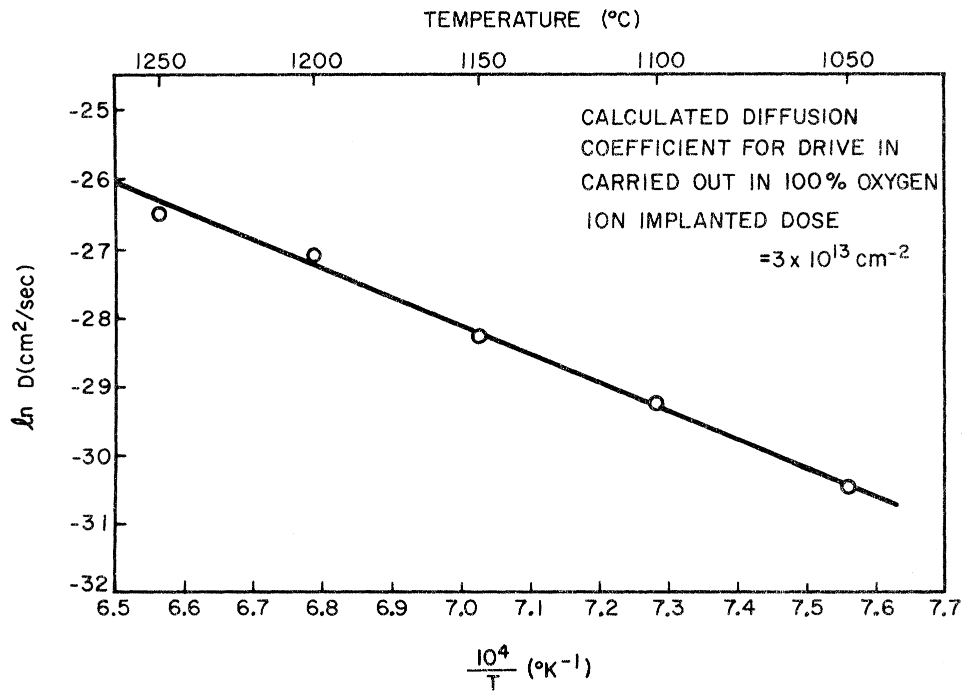

FIG. 16. Temperature dependence of the diffusion coefficient D.

TABLE V. Comparison of diffusion and segregation coefficient values.

Diffusion source	Temperature range (°C)	Drive-in ambient	Diffusion time (h)	Resulting C_S (cm^{-3})	D_0 (cm^2/sec)	Q (eV)	D (cm^2/sec) at 1200 °C	m	Reference
Out diffusion of B-doped Si	1200–1250	Steam or dry O_2	2–16	2×10^{16}	···	···	1.0×10^{-12}	0.32	3
B_2O_3	1120–1230	Dry O_2	<1	$<5\times10^{21}$	2.02	3.52	1.9×10^{-12}	0.1	4
BN	1100–1250	Wet O_2	0.5, 2	$>3\times10^{17}$	···	···	1.9×10^{-12}	0.1	7
BBr_3	1100	Dry O_2	1–64	10^{18}–3×10^{20}	···	···	a	0.25	11–13
B-doped glass	1000–1280	Dry N_2	1–16	3×10^{19}	···	···	1.0×10^{-12}	0.06	16
Ion implanted	1000–1200	Steam	0.25–3	$>3\times10^{17}$	0.0322	3.02	1.5×10^{-12}	$4.29\times10^3 e^{-1.135\ eV/kT}$ (0.1 to 0.66)	15
Ion implanted	1100	Dry O_2	0.5	2.5×10^{16}	···	···	···	1.0	10
Ion implanted	1050–1250	Dry O_2	15.5	$<10^{17}$	0.15	3.19	1.7×10^{-12}	$9.82e^{-0.29\ eV/kT}$ (0.75 to 1.0)	Present
Ion implanted	1000–1200	Dry O_2	5–20	$\sim2\times10^{19}$	0.19	3.22	1.9×10^{-12}	$33.3e^{-0.52\ eV/kT}$ (0.27 to 0.51)	31

[a] D was reported only at 1100 °C to be 4.4×10^{-13} cm^2/sec.

channel insulated gate field effect transistors (IGFETs) were made on *p* tubs created using above diffusion conditions.

SEGREGATION COEFFICIENT

The segregation coefficients obtained in this investigation do not agree very well with those obtained by other investigators except for the single unpublished result of Weber.[10] Prince and Schwettmann's[15] value of $m = 0.66$ at 1200 °C can be compared to $m = 1$ obtained in the present investigation. The temperature dependence of m as given in terms of the activation energy of 1.135 eV by Prince and Schwettmann[15] is much larger than that observed in this investigation (activation energy ≈0.3 eV). Recently, Colby and Katz have reported values of m and its temperature dependence by determining the boron concentration in the oxide and in silicon by use of the ion microprobe. They obtain an activation energy of 0.52 and a value of $m = 0.51 \pm 0.23$ at 1200 °C. In the absence of any obvious explanation the discrepancy in the m values (Table V) can be attributed to the variation in experimental conditions particularly the concentration and the drive-in times and to some extent to the differences in the mathematical formulation and solution of the diffusion equation.

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[1]M. M. Atalla and E. Tannenbaum, Bell. Syst. Tech. J. 39, 933 (1960).
[2]F. Leuenberger, J. Appl. Phys. 33, 2911 (1962).
[3]A. S. Grove, O. Leistiko, Jr., and C. T. Sah, J. Appl. Phys. 35, 2695 (1964).
[4]T. Kato and Y. Nishi, Jpn. J. Appl. Phys. 3, 377 (1964).
[5]K. J. S. Cave, Solid State Electron. 8, 991 (1965).
[6]W. H. Chen and W. S. Chen, J. Electrochem. Soc. 114, 1297 (1967).
[7]J. S. T. Huang and L. C. Welliver, J. Electrochem. Soc. 117, 1577 (1970).
[8]P. R. Wilson, Solid State Electron. 15, 961 (1972).
[9]R. H. Krambeck, J. Electrochem. Soc. 121, 588 (1974).
[10]G. R. Weber (unpublished work).
[11]G. Masetti, S. Solmi, and G. Soncini, Solid State Commun. 12, 1299 (1973).
[12]G. Masetti, P. Negrini, S. Solmi, and G. Soncini, Alta Frequenza XLII, 346 (1973).
[13]G. Masetti, P. Negrini, and S. Solmi, Alta Frequenza XLII, 626 (1973).
[14]T. Misawa (unpublished).
[15]J. L. Prince and F. N. Schwettmann, J. Electrochem. Soc. 121, 705 (1974).
[16]M. L. Barry and P. Olofsen, J. Electrochem. Soc. 116, 854 (1969).
[17]G. N. Wills, Solid State Electron. 12, 133 (1969).
[18]K. E. Bean and P. S. Gleim, Proc. IEEE 57, 1469 (1969).
[19]T. C. Chan and C. C. Mai, Proc. IEEE 58, 588 (1970).
[20]M. Okamura, Jpn. J. Appl. Phys. 9, 849 (1970).
[21]W. G. Allen and K. V. Anand, Solid State Electron. 14, 397 (1971).
[22]S. M. Hu, J. Appl. Phys. 45, 1567 (1974).
[23]R. B. Fair (unpublished).
[24]B. E. Deal and A. S. Grove, J. Appl. Phys. 36, 3770 (1965).
[25]A. S. Grove, *Physics and Technology of Semiconductor Devices* (Wiley, New York, 1967).
[26]T. E. Seidel, *Proceedings of the Second International Conference on Ion Implantation in Semiconductors Garmisch-Partenkirchen, West Germany* (*Springer*, New York, 1971), p. 47.
[27]J. C. Irvin, Bell Syst. Tech. J. 41, 387 (1962).
[28]S. P. Murarka (unpublished).
[29]S. M. Hu, in *Atomic Diffusion in Semiconductors*, edited by D. Shaw (Plenum, New York, 1973), Chap. 5.
[30]N. D. Thai, Solid State Electron. 13, 165 (1970).
[31]R. K. Jain and R. Van Overstraeten, J. Appl. Phys. 44, 2437 (1973).
[32]J. W. Colby and L. E. Katz (unpublished).
[33]I. R. Sanders and P. S. Dobson, Philos. Mag. 20, 881 (1969).