Mathematical Modeling of Boron Diffusion from Boron Oxide Glass Film Sources

Mathematical models are developed to examine two alternative means of boron doping from boron-rich glass films. For the planar source diffusion system, in which boron diffusion and glass film growth occur simultaneously at high temperature (900-1,200°C), glass film growth rates and the degree of doping achieved are predicted. In most cases, the solubility limit of boron in silicon is attained at the silicon surface. It is found that depletion of the boron source wafers used in this process may be slowed considerably by their removal from the reactor after a short time. Model predictions for an alternative method, in which the glass film is pregrown at low temperature (300°C) and the diffusion subsequently performed at high temperature, demonstrate a strong dependence of the boron surface concentration on the initial boron content in the pregrown glass film, for concentrations of boron near the solubility limit. The conditions for which a masking film of SiO_2 is insufficient to prevent boron diffusion into silicon, known as mask failure, are also predicted by the models.

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Introduction

In the fabrication of microelectronic devices, it is frequently necessary to introduce small amounts of impurities to alter the semiconducting properties of silicon. In particular, it is often desired to reduce the resistivity of a thin surface layer of the silicon by introducing impurities from groups III and V of the periodic table, such as the group III element boron, and group V elements arsenic and phosphorus. These species, electron-rich in the case of P and As, and electron-deficient in the case of B, may act as positive and negative charge carriers in the silicon, thereby reducing the resistivity of the thin surface layer into which the impurities are introduced. For most applications, a small amount of the impurity, referred to as the dopant, is either implanted or diffused into a very thin layer at the surface of the silicon, after which the source of the dopant is removed. The dopant that has entered the silicon is then redistributed by exposing the silicon wafer to high temperature, usually for tens of minutes or hours, which is called the "drive-in" step.

During the first step, which is usually referred to as the "prediffusion" step, it is vital to control the total amount of impurities that enter the silicon wafer to maintain good reproducibility of the resistivity of the diffused layer after drive-in. In the case of ion implantation, one can virtually count the atoms that are implanted, an advantage that often outweighs the disadvantages that implantation causes extensive surface damage and requires single wafer processing.

The deposition of a dopant-rich glass source film onto the silicon wafer is another means whereby impurities are introduced into silicon, in which case the dopant enters the silicon wafer by diffusion. For this system, it is necessary to control the concentration of the dopant at the silicon surface to control the total amount of impurity that enters the silicon wafer. Although process reproducibility is somewhat poorer for deposited source films than for ion implantation, multiwafer processing is possible, which is a great advantage from the standpoint of process throughput. It is, therefore, of interest to examine the dependence of impurity concentration at the silicon surface on the system parameters to understand how variations in process parameters influence the degree of doping that is achieved. Towards this end, this paper considers two alternative means of diffusion from B_2O_3/SiO_2 glass source films. In the case of the planar source diffusion system, the diffusion of boron into the silicon occurs simultaneously with the growth of the glass source film. An alternative means, in which the glass source film is deposited at low temperature, requires a separate high temperature step for the diffusion of boron into the silicon to occur.

The boron nitride planar source diffusion system, introduced in 1965 by Goldsmith et al., has several advantages over conventional carrier gas systems used for doping silicon wafers. Some of the advantages of other planar dopant sources have been recently reviewed by Wheeler and Rapp (1985), and Robinson (1986). In particular, more uniform deposition of the dopant-rich glass film onto the silicon is observed with the planar source diffusion system than with conventional carrier gas systems (Goldsmith et al., 1965; Wheeler and Rapp, 1985; Robinson, 1986; Rupprecht and Stach, 1973; Monkowski and Stach, 1976; Jones, et al., 1976; Steslow et al., 1975).

Figure 1 shows the conventional stacked wafer configuration, in which reactant and carrier gas flow through the annular region between the edges of the wafers and the reactor wall. In this system, radial diffusion is necessary for deposition to occur across the wafer surface, and radial nonuniformity is a common problem, particularly for wafers 4 in. (102 mm) or greater in diameter. Also, depletion of reactants along the length of the reactor leads to wafer-to-wafer nonuniformity (Wheeler and Rapp, 1985; Robinson, 1986). In the planar source diffusion system, Figure 1, dopant source wafers are placed between silicon wafers, and reactant evolves within the interwafer regions. When the interwafer spacing is small, diffusion occurs primarily in the axial direction, with the result of radially uniform film growth. Also, evolution of the reactant at the site of each wafer is found to largely eliminate wafer-to-wafer nonuniformity (Rupprecht and Stach, 1973; Monkowski and Stach, 1976).

Although the improved uniformity of growth of the B_2O_3/SiO_2 glass film source appears to result from the proximity of the source wafers to the silicon wafers, and from the absence of a reactant in the carrier gas that could be depleted along the length of the reactor tube, it has been shown that the growth rates that are observed in practice for boron source wafers require the presence of water in the carrier gas (Rupprecht and Stach, 1973). The boron precursor for this system is B_2O_3, which is known to react with water to form its hydrated species, HBO_2 (Randall and Margrave, 1960):

$$B_2O_3 + H_2O \leftrightarrow 2HBO_2 \tag{1}$$

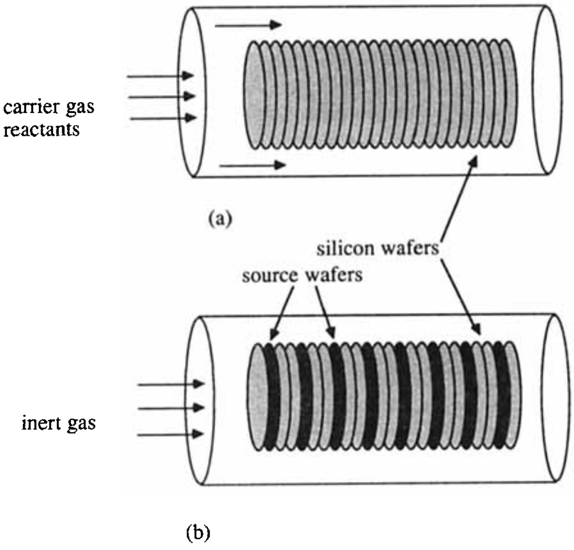

Figure 1. a) Carrier gas system; b) planar source diffusion system.

Spectroscopic observation has shown that the principle gas phase species present is HBO_2 (Rupprecht and Stach, 1973).

If water is present in the carrier gas and reacts with B_2O_3, the HBO_2 that is formed may subsequently deposit with the release of hydrogen. This overall reaction scheme would lead to the depletion of water both radially and along the length of the reactor, which are the characteristics of the carrier gas system and are not consistent with the excellent uniformity reported for the planar source diffusion system. A simple mass balance shows, in fact, that the amount of water entering the system, typically a few ppm, is inadequate to explain in this fashion the growth rates of 5–20 Å/min that are observed. The logical conclusion then is that the water behaves similarly to a catalyst, in which the overall reaction scheme allows for the regeneration of H_2O according to

$$2HBO_2 \rightarrow B_2O_{3,\text{glass}} + H_2O \tag{2}$$

The function of the water is to form a species, in this case HBO_2, whose vapor pressure is much higher than that of B_2O_3. In the absence of water, the concentration of B_2O_3 that can be achieved in the gas at the source surface is limited by its low vapor pressure. Transport of B_2O_3 from the source wafer to the silicon wafer is then limited by the small driving force that this low concentration provides. The presence of H_2O allows the formation of HBO_2, which can exist at much higher gas phase concentrations, and thus can provide an adequate supply of material to explain the observed growth rates (Monkowski and Stach, 1976; Rupprecht and Stach, 1973). If the forward and reverse reactions of Eq. 1 are sufficiently rapid that equilibrium is maintained in the gas phase, the presence of water in the carrier gas should not lead to the nonuniformity problems characteristic of carrier gas systems.

In the planar source diffusion system, high temperature (900–1,200°C) is necessary for enough B_2O_3 to volatilize from the source wafer to achieve film growth. The use of high temperature to achieve film growth results in the simultaneous diffusion of boron into the silicon. It is generally accepted that the growth of the glass film occurs via the oxidation of Si by B_2O_3 at the interface between the silicon and glass film, which results in the release of atomic boron at the glass-Si interface (Brown and Kennicott, 1971)

$$B_2O_3 + \tfrac{3}{2}\,Si \rightarrow \tfrac{3}{2}\,SiO_2 + 2B \tag{3}$$

Boron may then diffuse into the silicon as an impurity or remain in the glass film behind the interface, which itself advances into the silicon wafer as the oxidation proceeds. In most reported cases of boron doping with the planar source diffusion system, the formation of a third phase composed of boron and silicon is observed, which appears as a brownish stain that remains after the glass film is etched away (Rupprecht and Stach, 1973; Monkowski and Stach, 1976; Stach and Turley, 1974; Steslow et al., 1975). This thin SiB skin (typically 100–200-Å-thick) is not removed in any glass etch, and thus requires an additional etching step for removal (Brown and Kennicott, 1971). The formation of this phase occurs when the solubility of boron in silicon is exceeded at the glass-Si interface. A number of these investigators have attributed the excellent uniformity of doping to the formation of this phase, which maintains boron at its solubility limit at the silicon surface. If the boron concentration is pinned at its solubility limit, variations in the concentration of boron at the silicon surface are eliminated and process reproducibility is made simpler.

An alternative to this simultaneous film growth and boron diffusion is the low-temperature (300°C) growth of a B_2O_3/SiO_2 glass film from the gas-phase oxidation of silane and diborane, reported in 1968 by Fisher et al. At the low temperature of film growth, the oxidation of silicon by B_2O_3 at the glass-Si interface is negligible. A second high-temperature processing step is then necessary for oxidation and diffusion to proceed. The advantages of this sytem have been reported by Brown and Kennicott (1971). Although this system requires a separate processing step to deposit the glass film, it is possible to control the initial B_2O_3 concentration in the glass by proper choice of deposition conditions. Brown and Kennicott (1971) present results for the concentration of boron at the silicon surface, for various initial glass compositions and show that boron may be held below the solubility limit by proper choice of initial glass composition. The absence of a SiB phase eliminates the need for an additional process step to remove it. Brown and Kennicott (1971) also cite the additional advantage that fewer dislocations are introduced during diffusion, if boron is held at concentrations just below the solubility limit.

Several authors have previously attempted to model the two-phase diffusion of dopant atoms from a glass film into silicon, for the case of a pregrown glass source film (Sah et al., 1959; Allen et al., 1960; Horiuchi and Yamaguchi, 1962; Brown and Kennicott, 1971). In all cases, these authors have attempted to apply a solution found in Crank (1956) for mass transfer of a single species through a composite medium of a thin film on a semiinfinite substrate. This model, first proposed for P_2O_5/SiO_2 glass diffusions by Sah et al. (1959), fails to account for the generation term that arises when dopant atoms are released by the oxidation of silicon at the interface. The movement of the interface is also neglected in these treatments.

Mathematical models which account for reaction at the glass-Si interface and interface movement, for both the case of a pregrown glass source film and for the planar source diffusion system, are presented in this paper. The effect of a masking film of SiO_2 between the silicon and the glass film is also considered. The planar source diffusion model predicts that the boron concentration at the silicon surface can be maintained below the solubility limit by use of glass film growth rates that are lower than those typically employed for this system. The degree of doping, however, is highly sensitive to variations in the growth rate of the glass film under these circumstances. In the case of the pregrown glass source film, the model predicts that the concentration of boron at the silicon surface can be maintained below the solubility limit by control of the glass composition. It is shown that under these circumstances, however, the boron surface concentration is very sensitive to the composition of the glass film, except at concentrations much lower than the solubility limit of boron in silicon. The model is also used to consider the effect of radial thickness nonuniformity of the deposited film on the degree of doping that is achieved.

A comparison of the models presented here to the model proposed by Sah et al. (1959) reveals that, although the mathematical form of the solutions is similar, the dependence of the boron concentration at the silicon surface on physical parameters, such as the diffusion coefficients, is different. Although the Sah et al. (1959) model can be fitted to experimental data by proper choice of segregation and diffusion coefficients, physical parameters determined in this fashion might be incorrect, since the model basis is not totally consistent with the physics of the problem. It is shown that this model fails to consider diffusion of atomic boron into the glass film, where in fact most of the boron resides.

The models presented here assume that all diffusion coefficients in the glass film and the silicon are independent of concentration. At concentrations above the intrinsic carrier concentration, the diffusion coefficient for boron in silicon varies approximately linearly with the boron concentration (Fair, 1975; Kurtz and Yee, 1960). The diffusion coefficient for boron oxide in B_2O_3/SiO_2 glass films has been shown to depend strongly on boron oxide concentration for high concentrations (Brown and Kennicott, 1971). It is, therefore, likely that the models are not valid for high concentrations of either boron or boron oxide.

It is shown that the model for doping from a predeposited glass film agrees well with experimental data for boron surface concentration at very low concentrations. It is found that if the diffusion coefficients determined from a fit of the model to data at low concentrations are used, the model is in reasonable, but not total, agreement with experimental data for high surface concentrations of boron. If the diffusion coefficients at infinite dilution are replaced with concentration dependent diffusion coefficients, the results derived from the model are in excellent agreement with experimental results.

Planar Source Diffusion Model

Figure 2 defines a coordinate system that is stationary with respect to the glass-ambient interface. If we allow for the possibility of an initial film of SiO_2 on the silicon, the Si—SiO_2 interface is initially at a position X_o. As the film growth and diffusion proceeds, a SiB phase may precipitate at the glass-Si interface, Figure 2.

Data for glass film growth rates in the planar source diffusion system show an inverse $\sqrt{t}$ time dependence, characteristic of a diffusion-limited rate of oxidant reduction at the glass-Si interface (Deal, 1963). Thus, at all but short times the concentration of B_2O_3 at the glass-Si interface is very small. The possibility of this $\sqrt{t}$ dependence occurring due to a transport limitation within the boron source wafer itself is ruled out. Source wafers are used to dope hundreds of silicon wafers before they are discarded due to dopant depletion. If the growth rate decreases appreciably during a single doping cycle due to a transport limitation within the source wafer, the growth rate of subsequent doping cycles with the same source wafer should continue to decrease so rapidly, which does not occur. Each individual doping cycle, which may last 60–120 minutes, is simply too short for source depletion to cause this $\sqrt{t}$ dependence for film growth rates. Authors who have previously cited a diffusion-limited evolution of dopant from the source wafer as the reason for good batch to batch doping uniformity have done so on the basis of thermogravimetric analysis of source wafer depletion (Steslow et al., 1975; Monkowski and Stach, 1976; Rupprecht and Stach, 1973). TGA shows a $\sqrt{t}$ dependence for source weight loss over hundreds of hours of exposure to elevated temperatures and flow

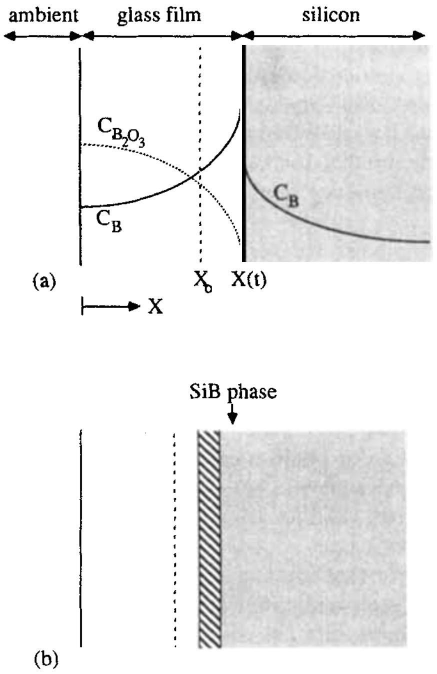

Figure 2. a) Coordinate system for models; b) silicon boron phase formation.

of an inert gas across the source wafer surface. TGA gives a useful estimate of source wafer lifetime but fails to represent deposition conditions, since the reported diffusion limitation for dopant evolution, which is observed by TGA, is artificially created by the gas flow which is imposed across the source surface.

With the assumption of a diffusion limited rate of B_2O_3 reduction at the glass-Si interface, and constant diffusion coefficient the governing equations for B_2O_3 diffusion and film growth are written

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} \tag{4}$$

$$C_1 = 0 \quad \text{at } t = 0 \tag{5}$$

$$C_1 = C_{1,o} \quad \text{at } x = 0 \tag{6}$$

$$C_1 = 0 \quad \text{at } x = X(t) \tag{7}$$

$$N\frac{dX}{dt} = -D_1 \frac{\partial C_1}{\partial x} \quad \text{at } x = X(t) \tag{8}$$

where N is given by

$$N = \frac{2}{3}\frac{\rho_{\text{glass}}}{M_{\text{SiO}_2}} \tag{9}$$

The factor of ⅔ arises from the stoichiometry of Eq. 3. The solution to Eqs. 4–8 is given by Crank (1956) as

$$\frac{C_1}{C_{1,o}} = 1 - \frac{\operatorname{erf}(x/2\sqrt{D_1 t})}{\operatorname{erf}(\alpha)} \tag{10}$$

$$X(t) = 2\alpha\sqrt{D_1 t} \tag{11}$$

where α is determined from

$$\frac{C_{1,o}}{N} = \sqrt{\pi}\,\alpha \exp(\alpha^2) \operatorname{erf}(\alpha) \tag{12}$$

For $C_{1,o}/N \ll 1$, Eq. 12 simplifies to

$$\alpha = \left(\frac{C_{1,o}}{2N}\right)^{1/2} \tag{13}$$

In the derivation of Eqs. 10–12, it is assumed that no film is present initially.

It is possible to calculate source wafer depletion by use of Eq. 10, according to

$$\frac{dC_s}{dt} = \frac{D_1}{d}\frac{\partial C_1}{\partial x}\bigg|_{x=0} = -\frac{\alpha N}{d}\left(\frac{D_1}{t}\right)^{1/2} \tag{14}$$

where d is half the thickness of a source wafer. Although α depends on C_s, the change in C_s over one doping cycle is so small that α may be taken constant in the integration of Eq. 14, with the result that after n doping cycles the source wafer concentration is given by

$$\frac{C_{s,n}}{C_{s,o}} = \prod_{j=1}^{n}\left[1 - \frac{2\alpha_j N\sqrt{D_1 t_j}}{d}\right] = \prod_{j=1}^{n}\left[1 - \frac{NX_j}{d}\right] \tag{15}$$

where the subscript j refers to the conditions of the jth doping cycle. If the glass source film thickness is maintained the same over all n doping cycles, then the depletion is given by

$$\frac{C_{s,n}}{C_{s,o}} = \left[1 - \frac{NX_o}{d}\right]^n \doteq 1 - \frac{nNX_o}{d} \tag{16}$$

If the time required to deposit a film of thickness X_o changes very slowly with source depletion over the usable lifetime of a source wafer, as reported (Owens-Illinois, 1986), the depletion given by Eq. 16 depends nearly linearly on the age of a source wafer.

To apply Eqs. 10–12, it is necessary to determine $C_{1,o}$, the concentration of B_2O_3 at the glass-ambient interface. In general, $C_{1,o}$ is determined by the relative resistances to mass transfer in the source wafer, the gas phase, and the glass film. Although the transport of B_2O_3 through the film is the rate-limiting step for growth, transport through the other two phases requires that gradients exist in these phases. If transport through the film requires a significant gradient, as it does, a significant gradient is likely to occur within the source wafer itself, since both phases are expected to have diffusion coefficients of similar magnitude. Source wafer manufacturers recommend that source wafers are "seasoned," by exposure to high temperature and an inert ambient. Otherwise, batch to batch uniformity of doping is poor during an initial period of time comparable to the recommended "seasoning" time, due to excessive evolution of B_2O_3. After the surface of the source wafer is depleted of B_2O_3, transport resistance within the source slows the rate of evolution, and batch to batch uniformity is improved. Also, experimental results show that the amount of boron that is incorporated into the silicon depends on the interwafer distance and on the choice of inert gas, which suggests that significant transport resistance is present in the gas phase as well. The topics of transport in the source wafer and the gas phase, as well as wafer seasoning, are of importance in the modeling of the planar source diffusion system, and are the subjects of future work. For the purposes of the present discussion, however, $C_{1,o}$ is treated as an unknown, to be determined from experimental data. Since growth rate data are the only available data for the planar source diffusion system, $C_{1,o}$ and D_1 cannot be uniquely determined by use of Eq. 11. A unique determination of these parameters is unnecessary, however, to estimate the concentration of boron at the silicon surface, as will be shown.

The growth of the glass film results in the release of atomic boron at the glass-Si interface, which may then diffuse into the silicon, or may remain in the glass film. From Eq. 10, the rate at which boron is released is given by

$$q(t) = -2D_1 \frac{\partial C_1}{\partial x}\bigg|_{x=X(t)} = 2\alpha N (D_1/t)^{1/2} \qquad (17)$$

If no initial film is present on the silicon, we expect that for short time, when the glass film is still quite thin, the boron concentration within the film will be nearly constant. It is known that if the concentration of boron at the silicon surface is held constant and the diffusion coefficient is not a function of composition, the solution to the diffusion equation is given by the error function. In this case, the rate at which boron diffuses into the silicon decreases inversely proportional to $\sqrt{t}$. We note from Eqs. 11 and 17, however, that the rate of film growth and the rate of boron generation at the silicon surface both exhibit this same $\sqrt{t}$ dependence. It is suggested, therefore, that, as growth proceeds, the fraction of boron that is left in the glass film behind the advancing interface and the fraction that diffuses forward into the silicon remain constant with time. The result is that the concentration of boron remains constant with time throughout the glass film. Thus, to model the diffusion of boron, we need only to solve the diffusion equation in the silicon.

If we assume that the diffusion coefficient of boron in silicon, D_2, is independent of concentration, the diffusion equation is written

$$\frac{\partial C_2}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2} \qquad (18)$$

with boundary and initial conditions

$$C_2 = 0 \quad \text{at } t = 0 \qquad (19)$$

$$C_2 = 0 \quad \text{at } x = \infty \qquad (20)$$

Conservation of boron at the interface requires that

$$-D_2 \frac{\partial C_2}{\partial x} + bC_2 \frac{dX}{dt} - C_3 \frac{dX}{dt} = q(t) \quad \text{at } x = X(t) \qquad (21)$$

The concentration of boron in the glass, C_3, is related to the boron concentration at the silicon surface by

$$C_3 = mC_2 \quad \text{at } x = X(t) \qquad (22)$$

where m is the segregation coefficient, defined by Eq. 22. The second and third terms of Eq. 21 account for the boron that is lost from the silicon to the glass as the interface advances into the silicon. The factor b relates the thickness of silicon that is consumed to the thickness of glass that is produced and is given by

$$b = \frac{\rho_{\text{glass}} M_{\text{Si}}}{\rho_{\text{Si}} M_{\text{SiO}_2}} \qquad (23)$$

Equations 11 and 17 are substituted into Eq. 21, which gives

$$-D_2 \frac{\partial C_2}{\partial x} = \frac{2\alpha N D_1^{1/2}}{t^{1/2}} \left(1 - \frac{C_2(m-b)}{2N^{1/2}}\right) \quad \text{at } x = X(t) \qquad (24)$$

The set of Eqs. 18–20 and 24, are solved by means of the Laplace Transform (Carslaw and Jaeger, 1959; Crank, 1956). The solution is given by

$$\frac{C_2}{C_{2,X}} = \operatorname{erfc}\left(\frac{x - X}{2\sqrt{D_2 t}}\right) \qquad (25)$$

where the surface concentration of boron in silicon is found from

$$C_{2,X} = \left(\frac{(D_2/D_1)^{1/2}}{2\pi^{1/2}\alpha N} + \frac{(m-b)}{2N}\right)^{-1} \qquad (26)$$

Equation 26 has three unknown parameters which require estimation: D_1, m and α. We note, however, that D_1 and α appear as the combination $\alpha D_1^{1/2}$, which can be uniquely determined from a fit of Eq. 11 to growth rate data.

If $C_{2,X}$ predicted by Eq. 26 exceeds the solubility limit of boron in silicon, C_b, Eq. 25 applies with $C_{2,X}$ replaced by C_b. Since D_2 is a function of the concentration of boron in silicon under these circumstances, the actual concentration profile of boron in silicon differs from the prediction of Eq. 25 (Fair, 1975). Equation 25 is still useful, however, to estimate the total quantity of boron that enters the silicon, which in general is of greater concern than details of the concentration profile. It is subsequently shown that, if D_2 is taken to be its value at $C_{2,X}$, the total quantity of boron that is predicted by Eq. 25 to enter the silicon is nearly identical to that predicted if we account for the variation of D_2 with C_2 in the solution of Eq. 18, even though the concentration profile that is predicted differs markedly from the error function profile in this case.

In most cases for the planar source diffusion system, the growth rate of the glass film is such that boron rapidly exceeds its solubility limit at the glass-Si interface, in which case a boron rich SiB phase forms. The presence of this phase insures sufficiently rapid delivery of boron to the silicon to maintain boron at its solubility limit at the silicon surface (Rupprecht and Stach, 1973). Since excess boron is present in the glass, doping of the silicon from the glass film will continue after the source wafers are removed, if the silicon wafers continue to be exposed to high temperature. If the silicon wafers are exposed to the source wafers for a time t' at a temperature T_o, the total amount of boron that remains within the glass film at t' is found from

$$Q_{g,o} = \int_0^{t'} \left(D_2 \frac{\partial C_2}{\partial x} \bigg|_{x=X} - 2D_1 \frac{\partial C_1}{\partial x} \bigg|_{x=0} \right) \mathrm{dt} = 2NX_o - 2C_{b,0} \left(\frac{D_{2,0} t'}{\pi} \right)^{1/2} \quad (27)$$

where the subscript 0 denotes values at the temperature T_o. If at time t' the source wafers are removed, but the silicon wafers continue to be exposed to a temperature T_1, excess boron within the glass film will continue to diffuse into the silicon. To estimate the depletion of the glass film under these circumstances, Eq. 18 is solved subject to the boundary conditions

$$C_2 = C_{b,0} \operatorname{erfc} \left(\frac{x}{2\sqrt{D_{2,0} t'}} \right) \quad \text{at } t = 0 \quad (28)$$

$$C_2 = C_{b,1} \quad \text{at } x = 0 \quad (29)$$

If $C_{b,0} = C_{b,1}$, the solution is given by

$$C_2 = C_{b,1} \operatorname{erfc} \left(\frac{x}{2\sqrt{D_{2,1}(t + t'')}} \right) \quad (30)$$

where

$$t'' = \frac{D_{2,0} t'}{D_{2,1}} \quad (31)$$

In the case that $C_{b,0} \neq C_{b,1}$, a zeroth-order correction is given by Eq. 30 with t'' replaced by

$$t'' = \frac{D_{2,0}}{D_{2,1}} \left(\frac{C_{b,0}}{C_{b,1}} \right)^2 t' \quad (32)$$

The rate of depletion of the glass film is then given by

$$\frac{dQ_g}{dt} = D_{2,1} \frac{\partial C_2}{\partial x} \bigg|_{x=0} = -C_{b,1} \left[\frac{D_{2,1}}{\pi (t + t'')} \right]^{1/2} \quad (33)$$

which when integrated gives

$$Q_g = 2NX_o - 2C_{b,0} \left(\frac{D_{2,0} t'}{\pi} \right)^{1/2} (1 + t/t'')^{1/2} \quad (34)$$

Equation 34 no longer applies when the concentration of boron at the silicon surface falls below the solubility limit.

Equation 34 may be used to find the maximum time t^* that the wafer may be exposed to temperature T_1 before the boron at the silicon surface begins to fall below the solubility limit. We find that

$$t^* = \frac{\pi Q_s^2 C_{b,0}^2 D_{2,0}}{4 C_{b,1}^4 D_{2,1}^2} \left(\frac{C_{b,1}^2 D_{2,1}}{C_{b,0}^2 D_{2,0}} - \frac{C_{b,1}^2 D_{2,1}}{\pi \alpha^2 D_{1,0} (2N - mC_{b,1})^2} \right) \quad (35)$$

where Q_s is the total amount of boron that has entered the silicon at t^*. Q_s is given by

$$Q_s = X_o (2N - mC_{b,1}) \quad (36)$$

and the time necessary to expose the silicon wafer to the source wafer to achieve this level of doping is given by

$$t' = \frac{Q_s^2}{4 \alpha_o^2 D_{1,0} (2N - mC_{b,1})^2} \quad (37)$$

The second term in brackets in Eq. 35 is typically much smaller than the first term, in which case Eq. 35 reduces to

$$t^* = \frac{\pi Q_s^2}{4 C_{b,1}^2 D_{2,1}} \quad (38)$$

The second term in brackets in Eq. 35 gives the ratio of the degree of depletion of the source wafer to its depletion were it not removed at time t'. Since this term is usually much less than one, a considerable extension of the source wafer lifetime is possible by removal of the source wafers from the reactor after a brief exposure to the silicon wafers.

Pregrown Glass Film Diffusion Model

The model for diffusion from pregrown B_2O_3/SiO_2 glass films is also developed with reference to Figure 2. In this case, X_o is the initial thickness of the glass film that has been deposited at low temperature. To model the diffusion and reduction of B_2O_3, Eq. 4 is solved subject to the boundary and initial conditions

$$C_1 = C_{1,o} \quad \text{at } t = 0 \quad (39)$$

$$\frac{\partial C_1}{\partial x} = 0 \quad \text{at } x = 0 \quad (40)$$

$$C_1 = 0 \quad \text{at } x = X(t) \quad (41)$$

where the interface position is determined from Eq. 8, with the initial condition

$$X = X_o \quad \text{at } t = 0 \quad (42)$$

Equations 4 and 39–41 are solved by means of the Laplace transform. The solution is given by

$$\frac{C_1}{C_{1,o}} = 1 - \sum_{n=0}^{\infty} (-1)^n \left[\operatorname{erfc} \left(\frac{X(2n+1) - x}{2\sqrt{D_1 t}} \right) + \operatorname{erfc} \left(\frac{X(2n+1) + x}{2\sqrt{D_1 t}} \right) \right] \quad (43)$$

The rate of film growth is determined from Eqs. 8 and 43, and is given by

$$N \frac{dX}{dt} = \frac{D_1^{1/2} C_{1,o}}{\sqrt{\pi t}} \sum_{n=0}^{\infty} (-1)^n \left[e^{-n^2 X^2 / D_1 t} - e^{-(n+1)^2 X^2 / D_1 t} \right] \quad (44)$$

Under typical processing conditions, $X_o / 2\sqrt{D_1 t} > 0.7$, and only the leading term ($n = 0$) of Eq. 44 is significant. Integration then gives

$$X = X_o + \frac{2 C_{1,o}}{N} \left[\frac{D_1 t}{\pi} \right]^{1/2} \quad (45)$$

Under these conditions, the rate of boron generation is given by

$$q = 2C_{1,o}\sqrt{D_1/\pi t} \tag{46}$$

which has the same $\sqrt{t}$ dependence as Eq. 17.

To model the diffusion of boron, Eqs. 18–20 are used for the silicon, and equations for diffusion of boron in the glass film are given by

$$\frac{\partial C_3}{\partial t} = D_3\frac{\partial^2 C_3}{\partial x^2} \tag{47}$$

$$C_3 = 0 \quad \text{at } t = 0 \tag{48}$$

$$\frac{\partial C_3}{\partial x} = 0 \quad \text{at } x = 0 \tag{49}$$

Conservation of boron at the interface requires that

$$-D_2\frac{\partial C_2}{\partial x} + D_3\frac{\partial C_3}{\partial x} - bC_2\frac{dX}{dt} + mC_2\frac{dX}{dt} = q(t) \quad \text{at } x = X(t) \tag{50}$$

Substitution of Eqs. 45 and 46 into 50 then gives

$$D_3\frac{\partial C_3}{\partial x} - D_2\frac{\partial C_2}{\partial x} = 2C_{1,o}(D_1/\pi t)^{1/2}\left[1 - \frac{m-b}{2N}C_2\right] \quad \text{at } x = X(t) \tag{51}$$

The solution to Eqs. 18–20, 47–49, and 51 is given by

$$\frac{C_2}{C_{2,X}} = \frac{1}{\Phi}\sum_{n=0}^{\infty}\beta^n\left[\operatorname{erfc}\left(\frac{k(x-X)+2nX}{2\sqrt{D_3 t}}\right) + \operatorname{erfc}\left(\frac{k(x-X)+2(n+1)X}{2\sqrt{D_3 t}}\right)\right] \tag{52}$$

where β and k are defined by

$$k = (D_3/D_2)^{1/2} \qquad \beta = \frac{km-1}{km+1} \tag{53}$$

The concentration of boron at the silicon surface is found from

$$C_{2,x} = \frac{\Phi}{\dfrac{m-b}{2N}\Phi + \dfrac{D_2^{1/2} + mD_3^{1/2}}{2C_{1,o}D_1^{1/2}}} \tag{54}$$

where Φ is given by

$$\Phi = 1 + (\beta + 1)\sum_{n=0}^{\infty}\beta^n\operatorname{erfc}\left(\frac{(n+1)X}{\sqrt{D_3 t}}\right) \tag{55}$$

In the case that $X_o/2\sqrt{D_3 t} < 0.7$, the second term makes a significant contribution to Eq. 55, with the result that Φ, and therefore $C_{2,X}$, changes with time. It will be shown that this change is relatively slow, however, occurring over many hours for typical processing conditions. Thus the approximation that $C_{2,X}$ remain constant, invoked in the derivation of Eq. 52, should be valid except at very long diffusion times.

Mask Failure

It is oftentimes desirable to selectively dope certain areas of the silicon wafer in the fabrication of electronic devices. A common practice is the use of a masking film, typically SiO_2, which is deposited and etched to expose only the areas which are to be doped. It is useful to predict the condition of mask failure, by which it is meant that the oxide film is of insufficient thickness to prevent significant diffusion of boron into the underlying silicon.

In general, the diffusion coefficient of B_2O_3 is much smaller in SiO_2 than in B_2O_3/SiO_2 glass films (Brown and Kennicott, 1971). In this case, the transport of B_2O_3 to the Si–SiO_2 interface is limited by its diffusion through the oxide mask. We assume, therefore, that diffusion within the glass film is sufficiently rapid to maintain a constant concentration of B_2O_3 at the glass–SiO_2 interface, for both the case of a pregrown glass film, and for the planar source diffusion system. Thus, Eq. 4 is solved subject to the boundary and initial conditions

$$C_1 = 0 \quad \text{at } t = 0 \tag{56}$$

$$C_1 = C_{1,o} \quad \text{at } x = 0 \tag{57}$$

$$C_1 = 0 \quad \text{at } x = X(t) \tag{58}$$

The same solution procedure that was used to derive Eq. 43 is applied to Eqs. 4 and 56–58, with the result that

$$\frac{C_1}{C_{1,o}} = \sum_{n=0}^{\infty}\left[\operatorname{erfc}\left(\frac{2nX + x}{2\sqrt{D_1 t}}\right) - \operatorname{erfc}\left(\frac{2(n+1)X - x}{2\sqrt{D_1 t}}\right)\right] \tag{59}$$

The generation of boron at the interface is given by

$$q = 4C_{1,o}\sqrt{D_1/\pi t}\sum_{n=0}^{\infty}e^{-(2n+1)^2X^2/4D_1 t} \tag{60}$$

Under most circumstances $X_o/2\sqrt{D_1 t} > 0.7$, and only the leading term of Eq. 60 is important, so that

$$q = 4C_{1,o}\sqrt{D_1/\pi t}\,e^{-X^2/4D_1 t} \tag{61}$$

The model equations for the diffusion of boron are identical to those solved for the case of a pregrown glass film, except that Eq. 61 is used in place of Eq. 46. The solution is found to be

$$\frac{C_2}{C_{2,X}} = \frac{1}{\Phi}\sum_{n=0}^{\infty}\beta^n\left[\operatorname{erfc}\left(\frac{k(x-X)+(2n+k')X}{2\sqrt{D_3 t}}\right) + \operatorname{erfc}\left(\frac{k(x-X)+(2(n+1)+k')X}{2\sqrt{D_3 t}}\right)\right] \tag{62}$$

where

$$k' = (D_3/D_1)^{1/2} \tag{63}$$

The concentration of boron at the silicon surface, $C_{2,X}$, is given by Eq. 54, with Eq. 55 replaced by

$$\Phi = \operatorname{erfc}\left(\frac{X}{2\sqrt{D_1 t}}\right) + (\beta + 1)\sum_{n-0}^{\infty} \beta^n \operatorname{erfc}\left(\frac{(2(n+1) + k')X}{2\sqrt{D_3 t}}\right) \quad (64)$$

The use of Eq. 54, and the leading term approximations for Eqs. 62 and 64, gives a relation between the junction depth and the oxide mask thickness, according to

$$X_J = (1 - (D_2/D_1)^{1/2})X_o + 2\sqrt{D_2 t}\,\arg \cdot \left[\operatorname{erfc}\left(\frac{C_J(D_2^{1/2} + mD_3^{1/2})}{2C_{1,o}D_1^{1/2}}\right)\right] \quad (65)$$

where C_J is the background concentration of dopant, and X_J is the junction depth, namely the position in the silicon at which the boron concentration is C_J.

Equations 62 and 65 are similar in form to the model of Sah et al. (1959), presented as Eqs. 2 and 3 in the paper by Brown and Kennicott (1971). The model of Sah et al. differs from ours in that it neglects the production of boron at the glass-Si interface. Instead of relating the concentration of boron at the glass-Si interface to its rate of chemical production, these authors relate the boron concentration on the silicon side of the interface to the B_2O_3 concentration on the glass side of the interface by a "segregation" coefficient. Thus, the diffusion equation is solved only for two species, B_2O_3 in the glass, and boron in the silicon. The diffusion of boron in the glass is neglected altogether, therefore, a diffusion coefficient for boron in the glass (D_3) does not appear in their model.

Comparison of Theory to Experiment

In order to estimate the diffusion coefficients D_1, D_2 and D_3 at infinite dilution, the model for mask failure is compared to data from Horiuchi and Yamaguchi (1962). These authors were particularly careful to take data at very low concentrations of boron oxide and boron. A fit of Eq. 54, with Φ given by Eq. 64, is compared in Figure 3a to data taken at 1,150°C for boron surface concentration as a function of mask thickness and oxidation time. Figure 3b shows a similar comparison to data taken at 1,200°C and 1,250°C. Figure 4 shows the diffusion coefficients that are determined from Figures 3a and 3b vs. $1/T$. Table 1 gives preexponential factors and activation energies from a fit of the results of Figure 4. To determine all three diffusion coefficients, the slope and intercept of a plot of X_J vs. X_o, given by Eq. 65 and reported experimentally by Horiuchi and Yamaguchi (1962), are used along with the best fit of Eq. 54 to data in Figures 3a and 3b. The values used for the slope and intercept of Eq. 65 are given in Table 2.

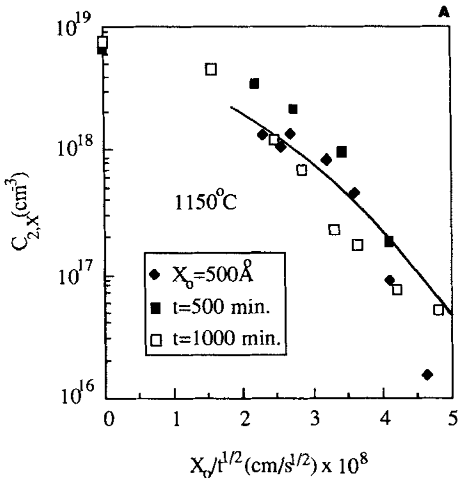

Figure 3a. Boron concentration at silicon surface vs. mask thickness and time of exposure.

Data of Horiuchi and Yamaguchi (1962), taken at 1,150°C, are compared to a fit of Eqs. 54 and 64.

Figures 3a and 3b show good agreement of the model with data at low concentrations. The diffusion coefficient for boron in silicon obtained from the data agrees well with values reported in the literature and correlated by Fair (1975), Figure 4. From Eq. 54 and the diffusion coefficients obtained in Figure 4, it is found that about 15% of the boron released at the glass-Si interface diffuses into the glass film rather than the silicon. The D_1 obtained in Figure 4 is somewhat higher than that given by Horiuchi and Yamaguchi (1962). Although the values for D_1 and D_2 are quite similar to those obtained from the model of Sah et al. (1959), the interpretation of the segregation coefficient m is quite different. A value of 3 for m was used in Eq. 54, which is reasonable for boron segregation at an Si–SiO_2 interface (Ghandi, 1983). Since most of the boron enters the silicon, the surface concentration predicted by Eq. 54 is relatively insensitive to the choice of m, for values less than about 5. Horiuchi and Yamaguchi report a value of 10^{-2} or less for m. Their definition of m does not give a true segregation coefficient, however, since it relates the concentration of boron at the interface to the concentration of boron oxide. Physical interpretation of this coefficient is difficult.

Figure 5 shows boron concentration at the silicon surface, as a function of the initial concentration of boron in a deposited B_2O_3/SiO_2 glass film. The results of Figure 5 are obtained from sheet resistance and junction depth data of Brown and Kennicott (1971). Since the concentration of boron in silicon is well

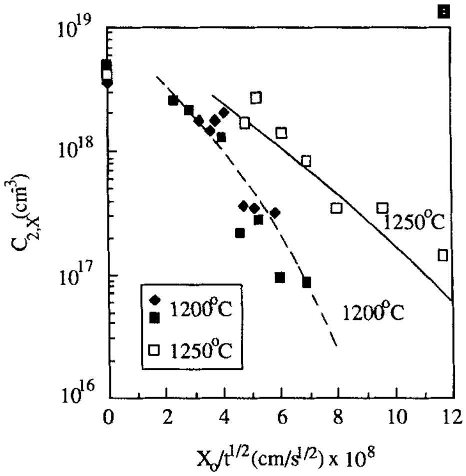

Figure 3b. Same as Figure 3a for data taken at 1,200 and 1,250°C.

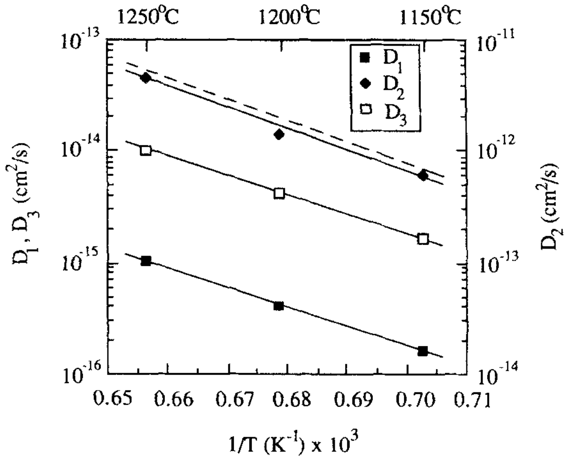

Figure 4. Diffusion coefficients vs. 1/*T*.
They were determined from Figure 3 and a fit of the slope and intercept of Eq. 65 to values reported by Horiuchi and Yamaguchi (1962), which are given in Table 2. Preexponential factors and activation energies determined from the solid curves are given in Table 1. Dashed curve is from Fair (1975).

above the intrinsic carrier concentration, use of Eq. 25 to determine $C_{2,X}$ from X_j and R_s [sheet resistance; see Irvin (1962) or Fair (1975) for the relationship between sheet resistance and concentration profile] may not be accurate. For cases in which the boron concentration exceeds the intrinsic carrier concentration, Fair has shown that D_2 is well correlated by

$$D_2 = \frac{D_{2,i} C_2}{n_i} \tag{66}$$

where $D_{2,i}$ is the intrinsic diffusion coefficient and n_i is the intrinsic carrier concentration. An approximate solution for the concentration profile of boron in silicon is given by Fair (1975), from which results for the surface concentration and junction depth are given by

$$X_j = 2.45 \left[\frac{C_{2,X} D_{2,i} t}{n_i} \right]^{1/2} \tag{67}$$

$$C_{2,X} = \frac{2.78 \times 10^{17}}{R_s X_j} \tag{68}$$

The data shown in Figure 5 are obtained by Eqs. 67 and 68 from junction depth and sheet resistance data, with $D_{2,i}$ given by D_2 obtained from Figure 4. The curve shown in Figure 5 is the prediction of Eq. 54, with Φ given by Eq. 55, and diffusion coefficients obtained from Figure 4. The curve shown is for results at 1,050°C, and is only slightly shifted for results at 1,000°C and 1,100°C. Although the diffusion coefficients are obtained at low concentrations, the prediction of Eq. 54 agrees fairly well with data taken at high concentrations. Since only ratios of the diffusion coefficients appear in Eq. 54, we expect that, if all the diffusion coefficients increase with increasing concentration, some cancellation of error should occur when diffusion coefficients obtained at low concentrations are used.

Table 1. Diffusion Coefficients Obtained from Model Fit to Data

$D = A_o e^{-E_a/RT}$	A_o(cm²/s)	E_a(J/mol)
D_1	2.03×10^{-4}	3.32×10^5
D_2	1.20×10^1	3.66×10^5
D_3	1.18×10^{-3}	3.25×10^5

Table 2. Slope and Intercept of X_j vs. X_o (Eq. 65)

T(°C)	Slope	Intercept (cm)
1,150	60.6	3.3×10^{-6}
1,200	58.8	5.0×10^{-6}
1,250	66.6	8.8×10^{-6}

From Horiuchi and Yamaguchi (1962).

Equation 54 is obtained by equating the production of boron at the glass-Si interface to its rate of diffusion into the silicon and the glass film. Since at high concentrations the diffusion coefficient of boron is greater than its value at infinite dilution, the model underestimates the total amount of boron to enter the silicon when $D_{2,i}$ is used in Eq. 54. A high surface concentration of boron is obtained when the concentration of B_2O_3 in the glass is high. At high concentrations, however, these glasses are known to undergo a transition from a mixture that is part liquid and part crystal to a mixture that is solely a liquid (Charles and Wagstaff, 1968; Rockett and Foster, 1965). The viscosity of this liquid decreases rapidly at high concentrations at B_2O_3, which suggests a corresponding increase in the diffusion coefficients in the glass. Therefore, if D_1 and D_3 obtained from data at infinite dilution are used, the rate at which boron is produced at the interface is also underestimated by Eq. 54. Since it is unlikely that the concentration dependence of the diffusion coefficients in the glass is identical to the concentration dependence of D_2, the cancellation of error will not be exact, however.

From results derived by Fair (1975) for diffusions at high concentration, the total quantity of boron to enter the silicon is

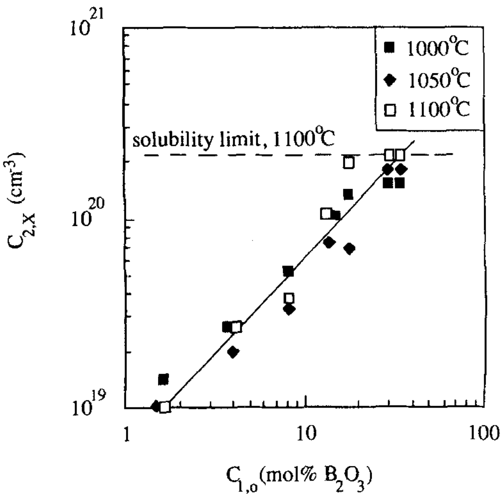

Figure 5. Boron concentration vs. glass composition.
Data of Brown and Kennicott (1971) are compared to a fit of Eqs. 54 and 55, with the diffusion coefficients obtained from Figure 4.

given by

$$Q_s = 0.98\left[\frac{C_{2,X}^3 D_{2,i} t}{n_i}\right]^{1/2} \tag{69}$$

The total quantity of boron to enter the silicon given by Eq. 52 is

$$Q_s = 1.13\left[\frac{C_{2,X}^3 D_{2,i} t}{n_i}\right]^{1/2} \tag{70}$$

where the D_2 is taken to be its value at the silicon surface, given by Eq. 66 with $C_{2,X}$ in place of C_2. Equation 52, with D_2 taken to be its value at $C_{2,X}$, overestimates by 15% the amount of boron that enters the silicon. The dependence of Q_s on system parameters is identical in both Eq. 69 and 70, however, which suggests that to a good degree of approximation, Eq. 54 can be used with a D_2 taken to be its value at the surface concentration of boron.

In the first term in the denominator of Eq. 54 is neglected, then $C_{2,X}$ is given by

$$C_{2,X} = \frac{2C_{1,0}D_1^{1/2}}{D_1^{1/2} + mD_3^{1/2}} \tag{71}$$

If the boron that diffuses into the glass is neglected and D_2 is replaced by Eq. 66, from Eq. 71 we find

$$C_{2,X} = \left[\frac{4n_iD_1}{D_{2,i}}\right]^{1/3} C_{1,o}^{2/3} \tag{72}$$

Figures 6 shows the data of Figure 5 replotted and compared to Eq. 72, which is shown by the dashed curves. A considerable improvement is obtained if we assume that D_1 follows a power law according to

$$D_1 = D_{1,\infty}[1 + (C_{1,o}/C)^4] \tag{73}$$

where $D_{1,\infty}$ is taken to be D_1 at infinite dilution, obtained from Figure 4. The solid curves in Figure 6 are given by Eq. 72 with D_1 given by Eq. 73. The constant C is determined from a fit of Eq. 72 to the data in Figure 6. The agreement with the data is good.

The results shown in Figure 6 indicate that the concentration of boron at the silicon surface can be maintained below its solubility limit by use of a small initial concentration of B_2O_3 in the glass film. For concentrations below about 10 mol % B_2O_3 the surface concentration depends on $C_{1,o}$ to the 2/3 power. Above 10 mol % B_2O_3 the dependence of $C_{2,X}$ on $C_{1,o}$ is very strong, and the surface concentration of boron rises rapidly to its solubility limit. It is concluded, therefore, that reproducibility of doping is best attained from diffusions at surface concentrations roughly an order of magnitude below the solubility limit. Such a low surface concentration then restricts the degree of doping that can be achieved, which may be undesirable when heavy doping of the silicon is desired.

Brown and Kennicott (1971) also present results for mask failure, but at much higher concentrations than the experiments of Horiuchi and Yamaguchi (1962), in which case the diffusion coefficients at infinite dilution may not appropriate for model calculation. Data for X_j vs. X_o are shown in Figure 7. The broken

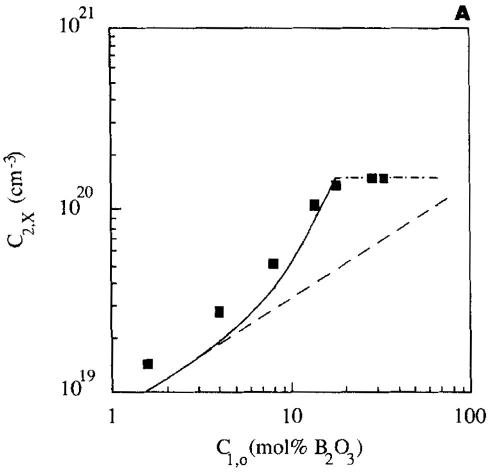

Figure 6a. Data from Figure 5, taken at 1,000°C, compared to prediction of Eq. 72.

Dashed curve is given by Eq. 72, with D_1 obtained from Figure 4, and solid curve is Eq. 72, with D_1 given by Eq. 73.

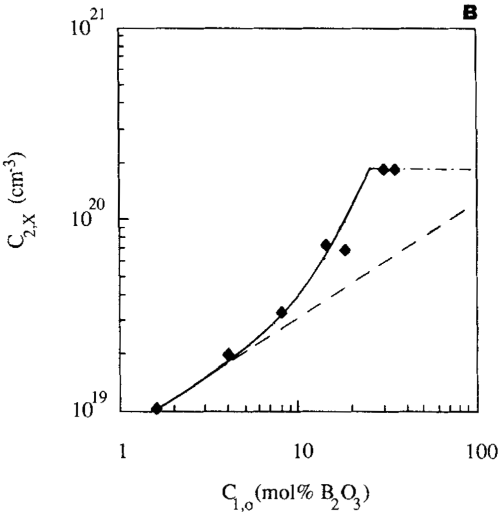

Figure 6b. Same as Figure 6a for data taken at 1,050°C.

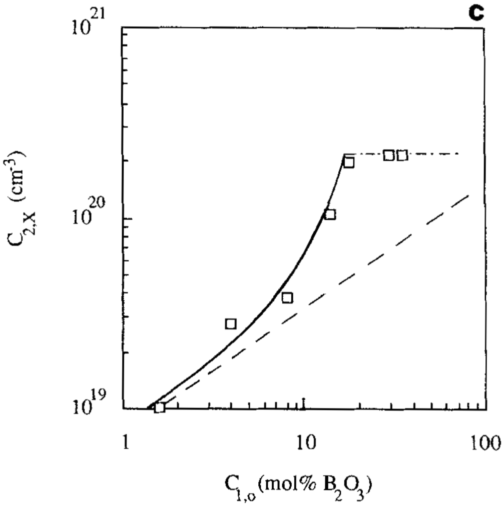

Figure 6c. Same as Figure 6a for data taken at 1,100°C.

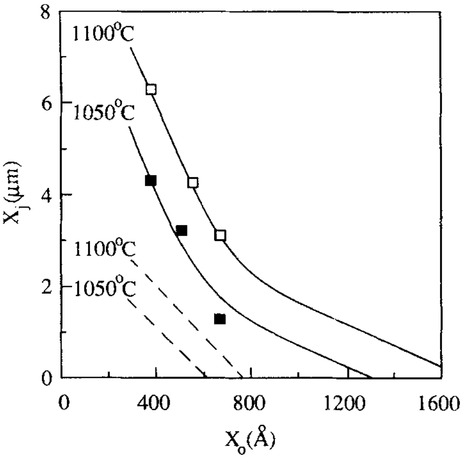

Figure 7. Junction depth vs. oxide mask thickness.
Data of Brown and Kennicott (1971). Dashed curves are Eq. 65 with diffusion coefficients obtained from Figure 4, and solid curves are Eq. 65 with diffusion coefficients given by Eq. 66 and 73.

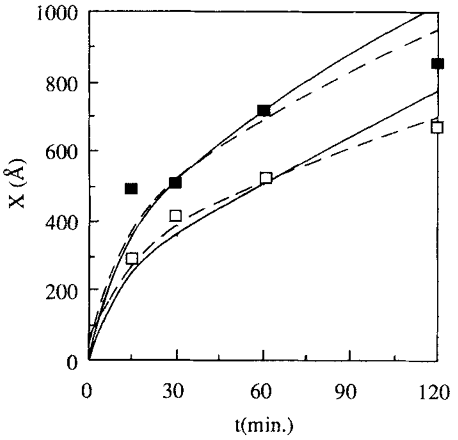

Figure 8. Glass film growth rates for planar source diffusion system (Owens-Illinois, 1986). Solid curves are a fit of Eq. 11, and dashed curves are a fit of Eq. 11 assuming an initial film 50 Å thick.

curves are given by Eq. 65, with diffusion coefficients taken to be their values at infinite dilution. In this case, the model predicts the data badly. The solid curves are given by Eq. 65, with D_1 and D_2 given by Eq. 66 and 73. The agreement is excellent. The results of Figure 7 emphasize the care that must be taken when using junction depth data to predict mask failure. Since Eq. 65, with the diffusion coefficients taken to be constant, predicts linear behavior, previous authors have linearly extrapolated such data to find the condition of mask failure. Brown and Kennicott (1971), from an extrapolation of the data in Figure 7, report mask failure for oxide thicknesses of 770 and 950 Å at 1,050 and 1,110°C, respectively. Instead, model results indicate that considerably thicker oxides, 1,300 and 1,700 Å, are necessary to prevent junction formation at these temperatures.

Brown and Kennicott (1971) state that the surface concentration of boron is independent of diffusion time and glass film thickness for the conditions of their experiment. The implication is that good control of the thickness or uniformity of the deposited film is not necessary to achieve reproducible diffusions. In all cases, for their experimental conditions, we estimate values for the dimensionless diffusion time, $\sqrt{D_3 t}/X_o$, that are much less than one. Under these circumstances the change of the surface concentration predicted by Eq. 55 is negligible, which indicates that the surface concentration is insensitive to variations in the thickness of the deposited film.

In the case of the planar source diffusion system, the absence of an oxidant other than boron oxide invariably leads to glass films with a high concentration of boron oxide, in which case diffusion coefficients which are used in the model should account for concentration dependence. We have already noted, however, that determination of D_1 is unnecessary when glass film growth rate data are available. The solid curves of Figure 8 are a fit of Eq. 11 to growth rate data (Owens-Illinois, 1986). A better fit of the data, shown by the dashed curves in the figure, can be obtained by assuming the presence of an initial film 50 Å thick. Equation 11 neglects the presence of a native oxide film, usually about 50 Å thick (Ghandi, 1983). The model also neglects the presence of a SiB phase, known to be present in the case of these data, and assumes that the growth rate is transport limited over the entire growth period. Given the error present in the experimental data, however, a more elaborate model does not appear to be necessary.

The values for $\alpha D_1^{1/2}$ determined from Figure 8 are 3.9×10^{-8} cm/s$^{1/2}$ at 925°C, and 5.4×10^{-8} cm/s$^{1/2}$ at 1,050°C. Although it is not possible to determine α and D_1 independently, a lower limit for D_1 can be estimated if we assume that the mole fraction of B_2O_3 is 1 at the glass-ambient interface, which gives values of 4.3×10^{-15} cm^2/s at 925°C, and 8.1×10^{-15} cm^2/s at 1,050°C. These values are two orders of magnitude higher than the values at infinite dilution obtained from Figure 4, which is consistent with the high boron oxide concentration in the glass film.

Figure 9 shows the concentration of boron at the silicon surface plotted as a function of the reciprocal of the dimensionless diffusion time, for various values of the segregation coefficient m. For m between 1 and 10, the surface concentration is only slightly affected by the actual value chosen. The model predicts that the solubility limit of 2×10^{20} atoms/cm^3 (Vick and Whittle, 1969) is exceeded at the silicon surface for the values of

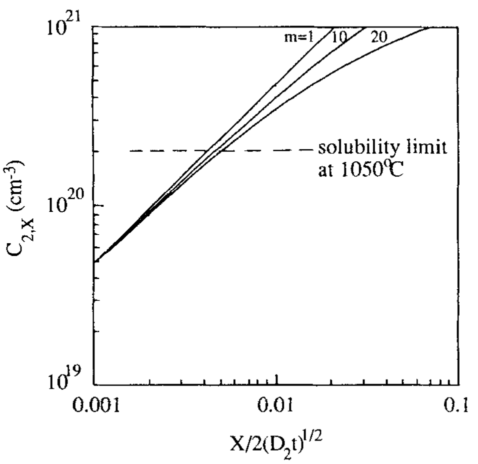

Figure 9. Boron concentration at silicon surface as a function of glass film growth rate for planar source diffusion system.

$\alpha D_1^{1/2}$ found from Figure 8, which is consistent with the observation of SiB phase formation for these experiments.

The planar source diffusion model predicts, as shown in Figure 9, that a surface concentration of boron below the solubility limit may be possible if $\alpha\sqrt{D_1/D_2}$ can be reduced by an order of magnitude below the values found from Figure 8. By reducing the growth rate, therefore, it is possible to prevent SiB phase formation. Genser (1987) reports that for a 100 Å film grown in 15 minutes at 950°C, no SiB phase is observed. If a 50 Å native oxide is assumed, this growth rate is a factor of five smaller than the rates shown in Figure 8. In this case the model predicts that boron still exceeds its solubility limit at the silicon surface, but the result of no SiB formation is consistent with the lower growth rate, especially in light of the considerable uncertainty of the data.

Several alternatives for manipulating the surface concentration of boron are apparent from the model for planar source diffusion. By manipulating the growth rate of the glass film, the rate of release of boron at the glass-Si interface can be controlled. The growth rate can be reduced by manufacturing source wafers with a lower concentration of B_2O_3, which would result in a shorter source lifetime. The growth rate can also be reduced by reducing the moisture content of the gas. In the complete absence of water the growth rate is reduced by an order of magnitude or more, due to the much lower vapor pressure of B_2O_3 than HBO_2. The growth rate under these circumstances is very sensitive to trace amounts of water (≤ 1 ppm) ordinarily found in electronic grade gases, however, which leads to considerable difficulty in maintaining run-to-run uniformity (Monkowski, 1987). It is preferred in industry, therefore, to blend in controlled quantities of water vapor in order to enhance process reproducibility.

A different approach to maintaining boron at or just below the solubility limit is to dilute the film with SiO_2, which can be accomplished by either oxidizing the wafer prior to deposition of the glass film, or by depositing the glass film in an oxidizing ambient, as is currently recommended by source wafer manufacturers. The presence of an oxidizing ambient is not considered in the model; the same principles used to develop the model, however, are easily extended to account for the presence of an additional oxidant in the glass film. The introduction of oxygen into the carrier gas, however, introduces the problems of gas phase transport and depletion that are typical of carrier gas systems, a treatment of which is beyond the scope of the present work.

If it is not critical that the surface concentration of boron be maintained below the solubility limit, then it may be possible to considerably extend source wafer lifetime by removal of the source wafers after a brief exposure to the silicon wafers. If an SiB phase forms during this exposure, then such a phase may act as a reservoir of boron from which the silicon may continue to be doped. For the conditions determined from Figure 8, we calculate from Eqs. 37 and 38 that an exposure of less than one minute is sufficient to provide enough boron in the glass film to continue doping the silicon for an hour at the same temperature. Since the model assumes steady state in the gas phase, an estimate of this timescale is not likely to be accurate, yet from the growth rate data of Figure 8 it is clear that an exposure of much less than an hour provides more than enough boron to continue doping the silicon for an hour, from which we conclude that a substantial extension of the source wafer lifetime may be possible.

Summary

Mathematical models have been developed for two alternative diffusion systems for boron doping from boron-rich glass films. Model results for the case of a pregrown glass source film show that the surface concentration of boron is extremely sensitive to the composition of the glass film, for boron concentrations near the solubility limit, but is insensitive to variations in the thickness of the deposited glass film. In the case of the planar source diffusion system it is shown that the surface concentration depends strongly on the growth rate of the glass film. It is found that source wafer depletion may be considerably reduced by the removal of the source wafers from the reactor after a short time of exposure to the silicon. Model results predict junction depths and mask failure conditions for the case of an SiO_2 mask. The condition of mask failure is found to differ considerably from that predicted by models which assume concentration independent diffusion coefficients. Although the models were developed for specific examples of boron doping, other dopants, such as phosphorus, are introduced by very similar means. It is expected, therefore, that similar models may be easily developed for other such dopant systems.

Notation

b = thickness of silicon consumed/thickness of glass produced, Eq. 23
C = Eq. 72, mol/cm^3
C_1 = concentration of B_2O_3 in glass film, mol/cm^3
C_2 = concentration of boron in silicon, mol/cm^3
C_3 = concentration of boron in glass film, mol/cm^3
$C_{s,n}$ = average concentration after n doping cycles of B_2O_3 in planar source wafer, mol/cm^3
$C_{i,o}$ = initial concentration of species i, mol/cm^3
$C_{2,X}$ = concentration of boron at silicon surface, mol/cm^3
C_b = solubility limit of boron in silicon, mol/cm^3
C_J = concentration of boron at junction depth X_J, mol/cm^3
d = half thickness of planar source wafer, cm
D_i = diffusion coefficient of species i, cm^2/s
$D_{2,i}$ = intrinsic diffusion coefficient of boron in silicon, cm^2/s
$D_{1,\infty}$ = diffusion coefficient at infinite dilution, cm^2/s
k = Eq. 53
k' = Eq. 63
m = segregation coefficient for boron at glass-Si interface
M = molecular weight, gm/mol
N = Eq. 9
R_s = sheet resistance, ohm/square
q = rate of boron generation at glass-Si interface, mol/cm$^2\cdot$s
Q_g = total boron in glass, Eq. 34, mol/cm^2
Q_s = total boron in silicon, Eq. 36, mol/cm^2
t = time, s
t_d = length of diffusion cycle, s
T = temperature, °C
x = position in glass film or silicon, cm
X = glass film thickness, cm
X_o = initial glass film or mask film thickness, cm
X_J = junction depth, cm

Greek letters

α = Eq. 12
β = Eq. 53
ρ = density, g/cm^3
Φ = Eq. 55

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