

# Physical Models of Boron Diffusion in Ultrathin Gate Oxides

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## ABSTRACT

Based on a network defect model for the diffusion of B in  $\text{SiO}_2$ , we propose that B diffuses via a peroxy linkage defect whose concentration in the oxide changes under different processing conditions. We show that as the gate oxide is scaled below 80 Å in thickness, additional chemical processes act to increase B diffusivity and decrease its activation energy, both as a function of the distance from the Si/SiO<sub>2</sub> interface. For a 15 Å oxide, the B diffusivity at 900°C would increase by a factor of 24 relative to diffusion in a 100 Å oxide. The role of nitridation of SiO<sub>2</sub> to create a barrier to B diffusion is modeled by assuming the N atoms compete with B for occupation of diffusion-defect sites. The model predicts that nitridation is ineffective in stopping B penetration when  $\text{BF}_3$  implants are used to dope the polysilicon gate, and similarly for B implants when the gate oxide thickness decreases below approximately 30 to 40 Å.

## Introduction

It has been recognized for over 20 years that  $p^+$  Si-gate technology for p-channel metal oxide semiconductor field-effect transistors (MOSFETs) can be hampered by the diffusion of B from the doped polysilicon gate through the underlying gate oxide and into the channel region.<sup>1-13</sup> Typically,  $p^+$  gates are doped by ion implanting either B or  $\text{BF}_2$  into patterned polysilicon during the source/drain doping step followed by diffusion and activation during the source/drain anneal. If the annealing conditions use too high a temperature or if the furnace ambient contains  $\text{H}_2$  or  $\text{H}_2\text{O}$ , B may penetrate the gate oxide<sup>14-17</sup> and cause a positive threshold voltage shift in the  $p^+$  gate MOSFETs. It has also been noted that  $\text{BF}_2$  implants made into the polysilicon gate cause enhanced B diffusion in oxide relative to B implants.<sup>7-9,18-20</sup>

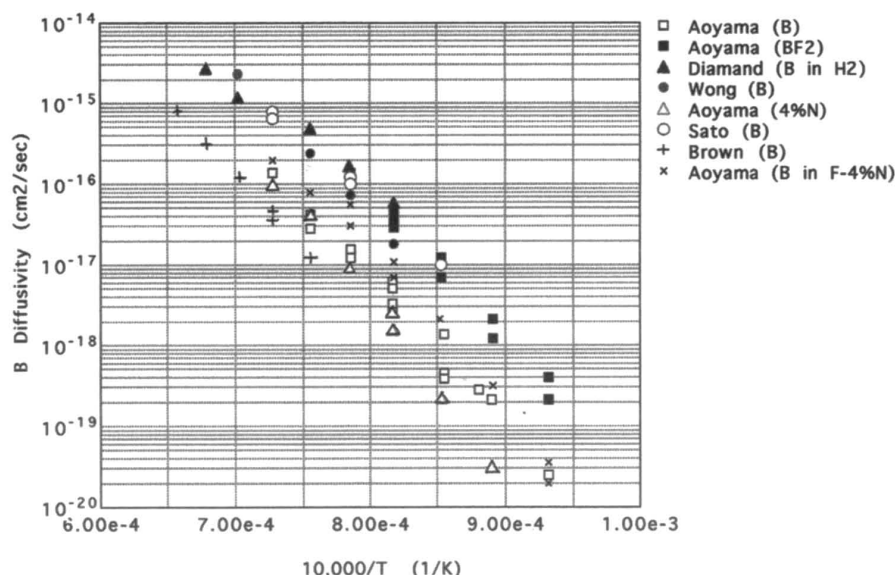
To date there have been numerous reports of B diffusion coefficients in  $\text{SiO}_2$  obtained under the various processing conditions. Many of these data are presented in Fig. 1, and they show a wide spread over the temperature range of 800 to 1200°C.<sup>1,15-18,20</sup> However, there has been very little effort to explain the basis for these data. Diamond and Oldham<sup>15</sup> attempted to explain the effect of hydrogen on B diffusion by proposing vacancy diffusion or interstitial-substitutional diffusion mechanisms, but no attempt was made to develop these models. Indeed, most of the effort in explaining impurity diffusion in oxides has been aimed at ionic diffusion in silica glasses in which the impurities fall

into the broad class of network modifiers.<sup>21,22</sup> These types of impurities diffuse in  $\text{SiO}_2$  as ions by deforming the network (elastic energy) and by breaking ionic bonds (electrostatic energy). Typical diffusion activation energies in silica fall in the range of 0.43 eV ( $\text{H}_2$ ) to 1.63 eV for  $\text{Mg}^{++}$ . Network former impurities such as B, P, and As, on the other hand, diffuse by reacting with the network itself at preferred locations or network defects by expending a certain amount of energy to be activated (migration) through the defect. In addition, the total activation energy of diffusion must include the energy required to form the preferred diffusion site (defect formation energy). Typical diffusion activation energies in  $\text{SiO}_2$  fall in the range of 3 eV (B in  $\text{H}_2$  ambient)<sup>15</sup> to 4.7 eV (As).<sup>23</sup> As a result, network formers diffuse very slowly at low temperatures.

In this paper we develop a physical basis for the diffusion of network former atoms in  $\text{SiO}_2$  and, in particular, B in the presence of F,  $\text{H}_2$ , and N. We rely on published molecular dynamics (MD) calculations as well as published thermochemical data to postulate the most likely diffusion defects in the oxide network and their formation enthalpies. In addition, we determine the most likely reaction of B, P, and As with these diffusion defects and determine the migration enthalpies. From random walk theory it is possible then to calculate the diffusion coefficients. We find that as the gate oxide decreases below 80 Å, the effect of chemical processes at the Si-SiO<sub>2</sub> interface act to cause a noticeable increase in B diffusivity and a corresponding decrease in the diffusion activation energy, both occurring as a function of the distance from the Si-SiO<sub>2</sub> interface.

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Fig. 1. Reported data for B diffusion in  $\text{SiO}_2$  under different annealing conditions showing a large spread in values depending upon the processing conditions. Data from Ref. 1, 15-18, 20.

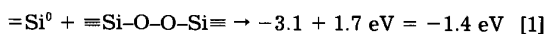


Finally, the effect of nitridation on controlling B penetration in thin oxides is described in terms of the competition between N and B at preferred diffusion defect sites.

### Diffusion Defects in SiO<sub>2</sub>

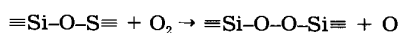
Defects in SiO<sub>2</sub> have been extensively studied and reviewed.<sup>24-26</sup> The three primary research methods used are (i) electron spin resonance, which only detects electrically active defects, (ii) molecular structure calculations, and (iii) charge injection into oxides or radiation of oxides with UV light or with charged particles. From this work, detailed microscopic models have emerged for three fundamental defects: the E' center, which is an oxygen vacancy with a hole trapped on one of the Si atoms nearest the vacancy: O<sub>3</sub>=Si...<sup>+</sup>Si=O<sub>3</sub>,<sup>27,28</sup> the nonbridging oxygen hole center (NBOHC), which is a trapped hole on a singly coordinated O<sup>2-</sup> ion: O<sub>3</sub>=Si-O...H-O-Si=O<sub>3</sub>,<sup>29,30</sup> and the peroxy radical, which is a trapped hole on a singly coordinated O<sup>2-</sup> ion: O<sub>3</sub>=Si-O-O...Si=O<sub>3</sub>.<sup>29,30</sup> We propose that the precursors to the NBOHC and the peroxy radical both can act as preferred diffusion defects for network formers in SiO<sub>2</sub>.

Edwards and Fowler<sup>31</sup> studied the peroxy-radical defect and used molecular-orbital calculations to determine the peroxy precursor or peroxy linkage structure shown in Fig. 2 from which the peroxy radical is created. The peroxy linkage defect (PLD) is characterized by a large Si-Si separation of approximately 5 Å, and such peroxy linkages are reported to be quite stable. It is believed that PLDs could be abundant in vitreous SiO<sub>2</sub> due to the appreciable straggling of the Si-Si distances in the material.<sup>32</sup> Griscom and Friebele<sup>30</sup> assumed the existence of bridging peroxy linkages in their model for peroxy radical formation. Dianov *et al.*<sup>33</sup> studied several possible reactions that would form the twofold coordinated silicon atom, =Si<sup>0</sup>, and concluded that the most probable channel of reaction is described by Eq. 1

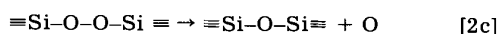


Equation 1 is based on molecular cluster calculations and shows that the reaction producing the PLD is energetically favorable relative to other possible reaction channels described in Ref. 33.

As silicon dioxide growth commences, PLDs can be formed throughout the thickness of the oxide by the dissolution reaction of gaseous O<sub>2</sub> into SiO<sub>2</sub>



$$\Delta H_f = -0.7 \text{ eV} \quad [2b]$$



Reaction 2c shows that some or most of the formed PLDs will be transformed back into =Si-O-Si= until some equilibrium concentration of PLDs is achieved at the oxidation temperature with a reaction enthalpy of  $\Delta H_f = -0.7$  eV, based on thermochemical data and molecular dynamic calculations. The O that is formed represents a parallel flux of oxidant in addition to O<sub>2</sub>.

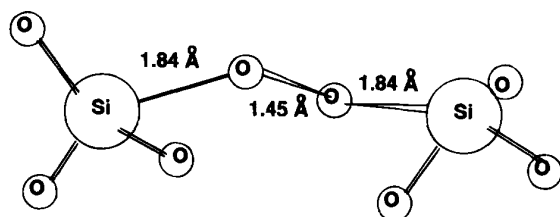
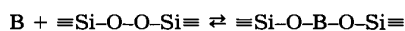


Fig. 2. Schematic representation of calculated atomic positions for the peroxy precursor with initial Si-Si separation of 5.2 Å. After Ref. 31.

As a result, network former element diffusion in SiO<sub>2</sub> is believed to be an activated process where atoms, I, interact with a PLD, first being activated from a low energy interstitial position to form an O-I-O bridging molecule, followed by I migration to the next interstice by breaking O-I-O bonds. The PLD acts, therefore, as a low energy doorway between interstices in the SiO<sub>2</sub> network. This activation process is illustrated in Fig. 3 for the diffusion of atomic B. Boron sits in a low energy interstitial site near a PLD whose formation enthalpy is  $\Delta H_f$ . Then B is activated through the PLD to the next low energy interstitial site with migration energy,  $\Delta H_m$ .

Evidence for atomic diffusion in oxide has been given by Inoue *et al.*<sup>34</sup> Both atomic B and oxidized B were observed by Auger electron spectroscopy (AES) in BN-diffused polysilicon on SiO<sub>2</sub> structures in an oxidizing ambient. It can be seen in Fig. 4 that the B in the oxide below the polysilicon is elemental B.



$$\Delta H_f = -2.96 \text{ eV} \quad [3]$$

Now, from Fig. 5 the activation energy for solid-state B diffusion,  $E_A$ , in thick, pure SiO<sub>2</sub> annealed in N or Ar is 3.56 eV,<sup>1,16,35</sup> where

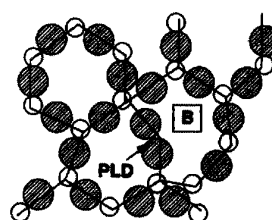
$$E_A = \Delta H_f + \Delta H_m \quad [4]$$

and  $\Delta H_m$  is the energy required to activate (migrate) B through the PLD and  $\Delta H_f$  is the PLD formation energy. If we assume that a B atom is activated for diffusion when it breaks free from its bridging position, then  $\Delta H_m$  is just the reaction energy given in Eq. 3. Thus, the PLD formation energy,  $\Delta H_f$ , should be  $3.56 - 2.96 \text{ eV} = 0.6 \text{ eV}$ . A similar analysis has been performed using thermochemical data on heats of formation at 1200 K for PO<sub>2</sub>, AsO<sub>2</sub>, and GaO<sub>2</sub>. These results are shown in Table I. Also shown are measured activation energies for the diffusion in oxide,  $E_A$ , of B, As,<sup>23</sup> P,<sup>36</sup> and Ga.<sup>37</sup> It can be seen that the values for  $\Delta H_f$  are consistently around 0.6 eV for all four diffusers. Thus the peroxy linkage defect requires approximately a 0.6 eV formation energy which agrees well with the reaction energy of Eq. 2b.

### Diffusion Theory in SiO<sub>2</sub>

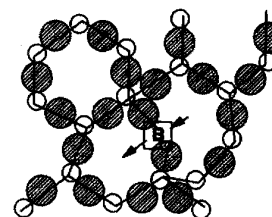
In the random-walk treatment of diffusion, the diffusion coefficient has the form<sup>38</sup>

$$D = \gamma \lambda^2 \Gamma \quad [5]$$



### Energetics

$\Delta H_f$  - PLD defect formation



$\Delta H_m$  - B activation thru PLD

Fig. 3. Intrinsic B atomic diffusion in pure SiO<sub>2</sub> via the peroxy linkage defect. The total diffusion activation energy is the sum of the PLD formation energy,  $\Delta H_f$ , plus the B activation energy required to break bonds with the PLD,  $\Delta H_m$ .

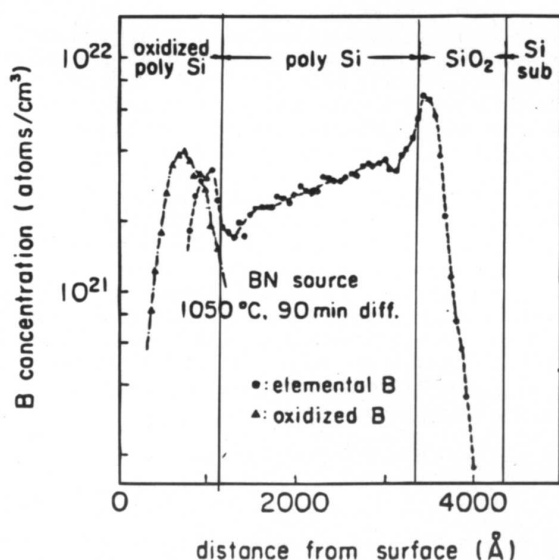


Fig. 4. Depth profiles of B diffused into the poly Si-SiO<sub>2</sub>-Si structure, showing the elemental and oxidized B distributions. The B in the SiO<sub>2</sub> under the poly is elemental. After Ref. 34.

where  $\gamma$  is a geometric constant (1/6),  $\bar{\lambda}^2$  is the average square of the jump lengths, and  $\Gamma$  is the average number of jumps per second and is given by

$$\Gamma = X_{\text{PLD}} X_{\text{act}} \nu \quad [6]$$

where  $X_{\text{PLD}}$  is the molecular fraction of PLDs in the oxide which is also the probability that a PLD defect is adjacent to a diffusant atom in the oxide network and is determined by statistical thermodynamics to be

$$X_{\text{PLD}} = [\text{PLD}]/[\text{SiO}_2] = \exp(\Delta S_f/k) \exp(-\Delta H_f/kT) \quad [7]$$

where  $\Delta S_f$  is the entropy of formation of the PLD and  $\Delta H_f$  is the enthalpy of formation (assumed to be 0.6 eV). The product of the vibration frequency,  $\nu$ , of an atom in equilibrium at a bridging site on a peroxy linkage defect and the atom fraction of atoms activated from that site,  $X_{\text{act}}$ , is the jump frequency,  $\omega$

$$\begin{aligned} \omega &= X_{\text{act}} \nu \\ &= \exp(\Delta S_m/k) \exp(\Delta H_m/kT) \nu \end{aligned} \quad [8]$$

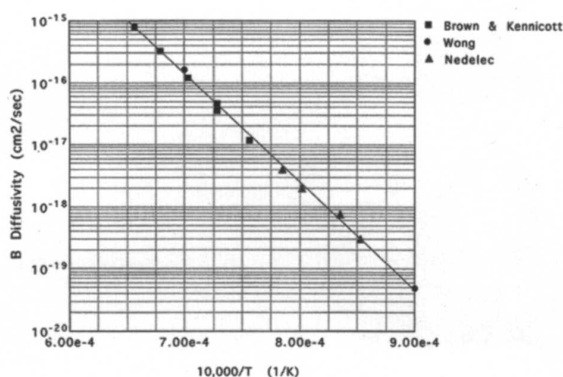


Fig. 5. B diffusion coefficient vs. temperature in pure SiO<sub>2</sub> of thickness >100 Å. These data represent intrinsic solid-state diffusion in SiO<sub>2</sub>. After Ref. 1, 16, 35.

Table I. Estimation of diffusion defect formation enthalpy from diffusion activation energies and heats of O-O formation.

| Impurity (I) | $E_A$ in N <sub>2</sub> (eV) | $\Delta H_m$ (eV)       | $\frac{\Delta H_f}{(E_A - \Delta H_m)}$ (eV) |
|--------------|------------------------------|-------------------------|----------------------------------------------|
| B            | 3.56                         | 2.95 <sup>a</sup>       | 0.61                                         |
| Ga           | 4.17                         | 3.6 (est.) <sup>b</sup> | 0.57                                         |
| P            | 4.44 ± 0.23                  | 3.99 <sup>a</sup>       | 0.45 ± 0.23                                  |
| As           | 4.7                          | 4.11 <sup>b</sup>       | 0.6                                          |

<sup>a</sup> At 1200 K.

<sup>b</sup> At 298 K.

where  $\Delta S_m$  and  $\Delta H_m$  are the entropy and enthalpy of atomic migration, respectively. From this analysis we conclude that since

$$D = D_0 \exp(-E_A/kT) \quad [9]$$

with  $E_A$  given by Eq. 4, then  $D_0$  is expressed as

$$D_0 = \gamma \bar{\lambda}^2 \nu \exp[(\Delta S_m + \Delta S_f)/k] \quad [10]$$

For B diffusion in pure, thick SiO<sub>2</sub>,  $D_0 = 3.63 \times 10^{-4}$  cm<sup>2</sup>/s. Using  $\bar{\lambda} = 5.5$  Å (molecular diffusion in fused silica) and  $\nu = 5 \times 10^{12}$  Hz,<sup>38</sup> then

$$(\Delta S_m + \Delta S_f)/k = -0.105 \quad [11]$$

Using Eq. 2b and 7, it is possible to estimate  $\Delta S_f$ . During oxidation it is known that Si-self interstitials are injected from the oxidizing Si/SiO<sub>2</sub> interface into the Si. Hu<sup>39</sup> estimated that oxidation is usually incomplete to the extent that approximately one silicon atom in 1000 is not incorporated into the oxide network. Equation 2b describes the formation of PLDs which are defects in the network where Si-O bonds are absent. An alternative reaction illustrates the formation of excess  $\equiv\text{Si}^0$  when PLDs are created

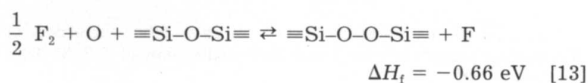


Note that the enthalpy of Eq. 12 is the same as that in Eq. 2b. The formation of excess  $\equiv\text{Si}^0$  in SiO<sub>2</sub> may be the process whereby excess Si-self interstitials become injected into the Si substrate, since the  $\equiv\text{Si}^0$  are available to be partitioned into the Si at a higher probability. In Eq. 12, the concentration of excess  $\equiv\text{Si}^0$  is equal to the concentration of PLDs formed. From Eq. 7,  $X_{\text{PLD}}/\exp(\Delta S_f/k) = 3 \times 10^{-3}$  at 1200 K. If it is assumed that each excess  $\equiv\text{Si}^0$  is injected into the Si and their atomic fraction is  $10^{-3}$ , then  $\Delta S_f \approx -1.1 k$  and  $\Delta S_m \approx 1 k$ . Negative entropies are common in silicate glasses as the size of the diffusing species increases.<sup>38</sup>

### Boron Diffusion in SiO<sub>2</sub>

The goals of this section are to understand the effects responsible for the observed spread in B diffusion coefficients shown in Fig. 1 and to calculate the B diffusivity with the appropriate concentration dependencies built into the expression. The effects of hydrogen and fluorine are considered. In the sections following this one the effects of oxide thickness and nitridation are presented.

**Fluorine effect.**—Fluorine is introduced into SiO<sub>2</sub> by BF<sub>2</sub> implants into either a polysilicon gate over oxide or into the oxide itself. The effects of F dose on B diffusion in pure SiO<sub>2</sub> has been studied extensively by Aoyama *et al.*<sup>20</sup> whose data show that B diffusivity increases approximately with the (F dose)<sup>1/2</sup>. Using the peroxy linkage defect as the basis for B diffusion, it is proposed that F introduced into SiO<sub>2</sub> creates additional PLDs which then enhance B diffusion according to the following reaction



In Eq. 13 the role of F is to break a Si–O bond so that reaction with O is possible. The heat of formation of this reaction is very similar to that which is found in Eq. 2b and 12, implying a consistency in the enthalpies for forming PLDs. Thus when F is present, the resulting total PLD molecular fraction in SiO<sub>2</sub> is given by the following expression

$$X_{\text{PLD}}(\text{tot}) = X_{\text{PLD}} + X_{\text{PLD}}(\text{F})$$

$$\approx \exp(-0.6 \text{ eV}/kT) \{ \exp(\Delta S_{\text{f}}/k) + K' [\text{F}_2]^{1/2} \} [14]$$

where we have used  $\Delta H_f = -0.6$  eV from Table I rather than the  $-0.7$  or  $-0.66$  eV from Eq. 2b and 13, respectively,  $X_{\text{PLD}}$  is the intrinsic PLD fraction (Eq. 12),  $X_{\text{PLD}}(\text{F})$  is the PLD fraction created by Eq. 13,  $[\text{F}_2]$  is the molecular  $\text{F}_2$  concentration and  $K'$  is an equilibrium constant obtained from Eq. 13. It is more convenient to express  $[\text{F}_2]$  in terms of  $\text{F}_2$  dose  $\phi_{\text{F}_2}$  (atom/cm<sup>2</sup>). Thus, the B diffusion coefficient in  $\text{SiO}_2$  from a  $\text{BF}_3$  implanted polysilicon source can be found from Eq. 9 and 14 with  $D_0$  obtained from a best fit to B diffusion coefficient data. For example, for an oxide thickness equal to 60 Å and with no F present, a least squares fit to the data of Aoyama *et al.*<sup>20</sup> yields a prefactor such that the total diffusivity becomes<sup>40</sup>

$$D_{(\text{BF}_2)} = D_{\text{B}} + D_{(\text{F})} \\ = 1.1 \times 10^{-3} [\exp(-3.56 \text{ eV}/kT) \{0.33 + 2.5 \times 10^{-7} \Phi_{\text{F}_e}^{1/2}\}] \quad [15]$$

where  $D_B$  is the diffusivity of B in pure  $\text{SiO}_2$ , and  $D_{(B)}$  is the diffusivity of B in the presence of F. The units are  $\text{cm}^2/\text{s}$ . Equation 15 reduces to the case of B diffusion in pure  $\text{SiO}_2$  when  $\phi_{F_2} = 0$ . A comparison between the experimental data of Aoyama *et al.*<sup>20</sup> and calculations using Eq. 15 is shown in Fig. 6 with reasonably good agreement. It can be seen that the influence of F on B diffusivity is predicted at F doses as low as  $1 \times 10^{12}$  ion/ $\text{cm}^2$ . It will be shown later that the B diffusivity depends on oxide thickness, so Eq. 15 is only valid for diffusion in a 60 Å oxide. In these data a F dose of  $1 \times 10^{16}/\text{cm}^2$  is assumed equal to the F content in a BF<sub>3</sub> dose of  $5 \times 10^{15}/\text{cm}^2$ .

Computer simulations are shown in Fig. 7 of B diffusion in polysilicon/oxide/Si for three  $\text{BF}_3$  implants into 1600 Å of polysilicon over 60 Å of oxide. We used the simulator ZOMBIE<sup>41</sup> to solve the diffusion-segregation equation at 900°C for 30 min with  $D_{(\text{BF}_3)}$  given by Eq. 15. <sup>42</sup> A segregation coefficient of  $m = 0.5$  was assumed at the poly/SiO<sub>2</sub> interface and the Si-SiO<sub>2</sub> interface. The higher implant dose creates a significantly larger penetration of the oxide by B due to the higher F concentration present.

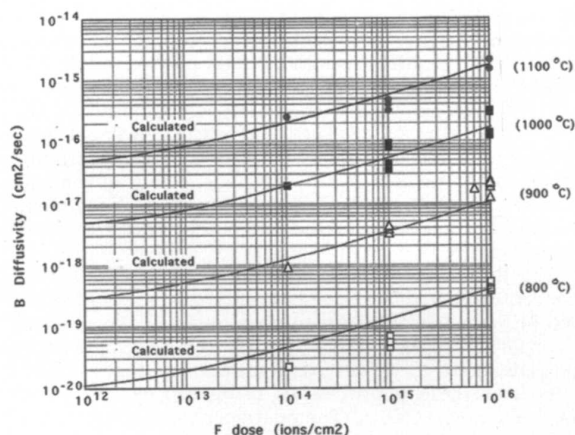


Fig. 6. Calculated B diffusivity vs. F dose in SiO<sub>2</sub> at four temperatures compared with measured data of Ref. 20. Boron diffusivity exhibits a square root dependence on F concentration. After Ref. 40.

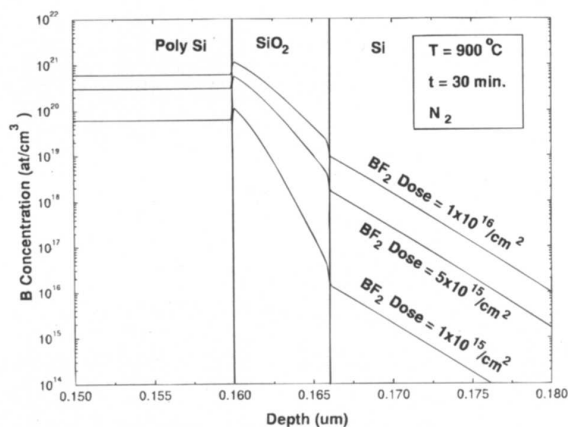
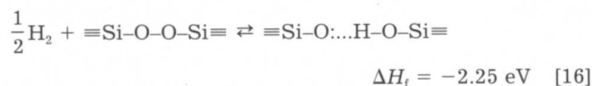


Fig. 7. Solutions to the diffusion-segregation equation for B for the case of  $\text{BF}_3$  implanted into poly-Si on  $\text{SiO}_2$  on Si and annealed at  $900^\circ\text{C}$  for 30 min. B penetration through the gate oxide occurs easily under these conditions. After Ref. 42.

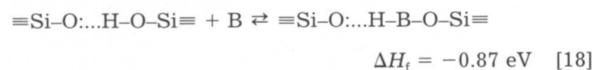
*H<sub>2</sub> effect.*—It has been reported<sup>14-17</sup> that B diffusivity is larger in oxides annealed in wet O<sub>2</sub> or when H<sub>2</sub> is intentionally present in the furnace ambient during B diffusion. A [H<sub>2</sub>]<sup>1/2</sup> concentration dependence of B diffusion and a 3 eV activation energy were reported by Shacham-Diamand and Oldham.<sup>15</sup> To explain these observations, numerous possible reactions were considered between hydrogen and the SiO<sub>2</sub>. One reaction that explains both the H<sub>2</sub> concentration effect and the lowered activation energy involves a possible precursor to the NBOHC defect



This reaction describes the interaction of hydrogen with a PLD to form a hydrogen-related-defect (HRD). The molecular fraction of HRDs relative to PLDs is given as

$$X_{\text{HRD}} = K_H \exp(-2.25 \text{ eV}/kT)[\text{H}_2]^{1/2} \quad [17]$$

It is energetically possible for B to interact with the HRD according to this reaction



Thus the total activation energy for B diffusion is the sum of the reaction energies for Eq. 16 and 18, which is 3.12 eV. Using the empirical result of  $E_A = 3$  eV as well as the diffusion coefficient data in Ref. 15, the diffusion of B in a hydrogen ambient (no F present) becomes<sup>40</sup>

$$D(\text{H}_2) = D_{\text{B}} + D(\text{HRD})$$

$$= 3.63 \times 10^{-4} [\exp(-3.56 \text{ eV}/kT)]$$

$$+ 2.65 \times 10^{-5} \exp(-3.0 \text{ eV}/kT) [\text{H}_2]^{1/2} \quad [19]$$

where  $D(\text{HRD})$  is the component of B diffusion via the HRD defect,  $[\text{H}_2]$  is the percentage of  $\text{H}_2$  in the furnace and  $D_{(\text{H}_2)}$  is in units of  $\text{cm}^2/\text{s}$ . As the percentage of hydrogen increases, then  $D(\text{HRD})$  becomes large compared to  $D_{\text{B}}$ . A comparison between calculations based on Eq. 19 and the concentration data in Ref. 15 is shown in Fig. 8. From this figure it can be seen that a very small percentage of  $\text{H}_2$  in the annealing ambient can increase B diffusion in the oxide. Indeed it has been shown that the diffusivity of B in oxide increases by a factor of two during wet oxidation.<sup>14</sup> At  $1150^\circ\text{C}$  this corresponds approximately to 65 ppm of  $\text{H}_2$  molecules in the gas mixture.

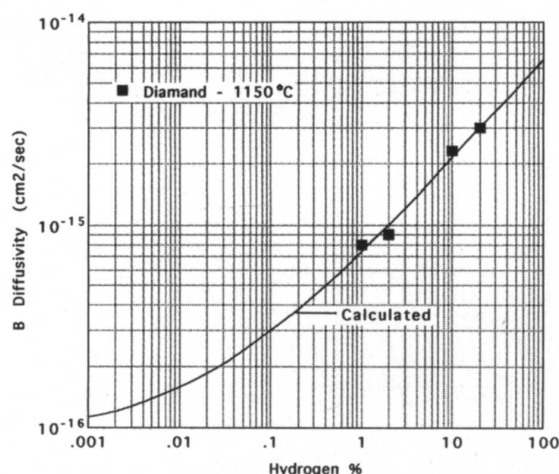


Fig. 8. Comparison between the data of Ref. 15 showing the  $H_2$  effect on B diffusion in  $SiO_2$  and calculations based on Eq. 19. It can be seen that a very small amount of  $H_2$  in the furnace can enhance B diffusivity, which is the case for wet oxidation.

### B Diffusion in Thin Oxides

Recent data suggest that there may be an increase in B diffusivity in  $SiO_2$  as the thickness of the oxide decreases below 80 Å.<sup>43</sup> The thin oxide diffusion effect is illustrated in Fig. 9 where experimental B diffusion coefficient data are plotted for temperatures of 900,<sup>19,20,35</sup> 950,<sup>20,35</sup> and 1000°C<sup>20,35</sup> vs. oxide thickness. These data show that B diffusivity increases as the  $t_{ox}$  decreases. The curves shown in Fig. 9 are calculated based upon the model presented below.

During oxidation of Si it has been proposed that SiO is formed at the Si-SiO<sub>2</sub> interface as a by-product of an intermediate SiO\* absorbed at the Si surface.<sup>44</sup> The SiO species is metastable since partial decomposition into Si and O atoms occurs at elevated temperatures as SiO diffuses away from the interface. The lowest enthalpy decomposition reaction involves SiO and SiO<sub>2</sub> in which a PLD is formed

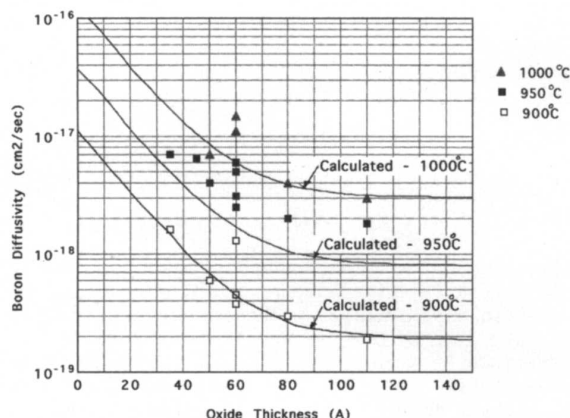
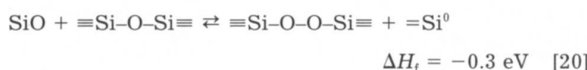


Fig. 9. Measured and calculated B diffusivity in pure  $SiO_2$  from B implants into poly-Si over  $SiO_2$  as a function of temperature and oxide thickness. Data are from Ref. 19, 20, and 35. A strong thickness dependence on B diffusivity is observed.

The excess Si is free to react with the  $SiO_2$  or become partitioned into the Si substrate as excess self-interstitials. The fraction of PLDs formed relative to  $SiO_2$  is  $X_{PLD(SiO)}$

$$X_{PLD(SiO)} = K_S \exp(-0.3 \text{ eV}/kT) X_{SiO} \quad [21]$$

This expression shows that the molecular fraction of PLD defects formed according to Eq. 20 is directly proportional to the fraction of SiO in the oxide. And  $X_{SiO}$  is believed to be highest near the Si-SiO<sub>2</sub> interface.<sup>44</sup> Thus, we will assume the following things as the basis for a model (i) SiO is formed at the interface during oxidation, (ii) as a gas SiO either reacts with O to form  $SiO_2$  or it diffuses away from the interface, (iii) the diffusing SiO can react with the network to form peroxy linkage defects, and (iv) the distribution of excess PLDs follows the distribution of SiO according to Eq. 21.

This model predicts that there will be position-dependent diffusion of Si dopant atoms whose diffusion in  $SiO_2$  is mediated by the concentration of PLDs. The formation energy of PLDs near the Si-SiO<sub>2</sub> interface is  $\Delta H_f = -0.3 \text{ eV}$  compared to 0.6 eV in the bulk oxide. This implies that there would be significantly more PLDs at the interface under equilibrium conditions than in the bulk.

The B diffusion activation energy near the Si-SiO<sub>2</sub> interface would be reduced by 0.3 eV to  $2.96 + 0.3 \text{ eV} = 3.26 \text{ eV}$ . Thus, the total B diffusivity would be,  $D_T$ , including effects of F and H, would be

$$D_T = D_B + D_{(F)} + D_{(HRD)} + D_{(SiO)} \quad [22]$$

where  $D_{(SiO)} = D_{o(SiO)} \exp(-3.26 \text{ eV}/kT) X_{SiO}$ , and  $D_{o(SiO)}$  is a prefactor for the B diffusion coefficient at the interface. For simplicity, the SiO concentration is assumed to decay exponentially from the interface with a characteristic decay length,  $\lambda_c$ , according to  $\exp(-t_{ox}/\lambda_c)$ , where  $t_{ox}$  is the distance from the Si-SiO<sub>2</sub> interface. The parameter  $\lambda_c$  represents the thickness of the diffuse Si-SiO<sub>2</sub> interface region. Recent measurements<sup>45,46</sup> using medium energy ion scattering (MEIS) analysis have yielded a compositionally graded interface region thickness of 10 to 15 Å which is Si-rich. For first-order diffusion coefficient calculations we will assume that  $t_{ox}$  is equal to the thickness of the oxide. This assumption is somewhat crude, but it is required since the only B diffusivity data available in thin oxides is data that are averaged across  $t_{ox}$ .

By fitting the prefactor  $D_{o(SiO)}$  to the Arrhenius data in Fig. 10 for  $t_{ox} = 110 \text{ Å}$ , the following result is obtained for  $D_{(SiO)}$

$$D_{(SiO)} = 9.7 \times 10^{-4} \exp(-3.26 \text{ eV}/kT) \exp(-t_{ox}/\lambda_c) \text{ cm}^2/\text{s} \quad [23]$$

with  $\lambda_c = 16 \text{ Å}$ , in excellent agreement with the MEIS measurements of Gusev *et al.*<sup>46</sup> Examination of Eq. 22 and 23 shows that as the oxide thickness decreases, so will the activation energy for B diffusion until it approaches 3.26 eV. This result is seen in the data plotted in Fig. 10<sup>20,35</sup> where Arrhenius data for several oxide thicknesses are plotted. Also shown are calculated curves based on  $D_T = D_B + D_{(SiO)}$  using Eq. 23. The trend toward lower activation energy is believed to be associated with PLD formation when SiO is present at the interface. Good agreement is shown between measured data and the calculated curves. Computer simulations of the thin oxide effect are presented in Ref. 47.

The thin oxide effect is not observed when significant concentrations of F are present in the oxide. Data are plotted in Fig. 11 for B diffusivity vs. oxide thickness at 800,<sup>16,18,20</sup> 900,<sup>18,20</sup> and 950°C<sup>18,20</sup> for  $5 \times 10^{15} \text{ BF}_3$  implants into polysilicon over oxide. Also shown are the calculated curves at these temperatures using the expressions for  $D_T = D_B + D_{(F)} + D_{(SiO)}$ . The relatively weak effect of oxide thickness that is observed in Fig. 11 results from the dominance of  $D_{(F)}$  over the other contributions to B diffusivity. We see later that the reaction of F with the  $SiO_2$  network to produce PLDs also dominates over nitridation of oxide for reducing B penetration in MOSFETs.

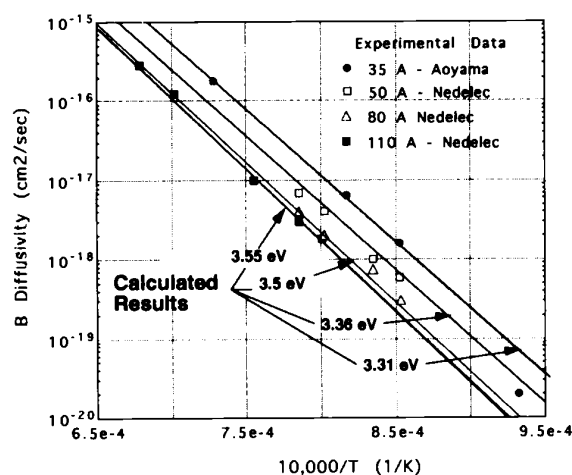


Fig. 10. Measured and calculated B diffusivity in pure SiO<sub>2</sub> vs. 1/T for oxide thicknesses ranging from 110 to 35 Å. A decrease in B diffusion activation energy is predicted from Eq. 22 and 23 and is observed experimentally using data from Ref. 20, 35.

In summary, it has been found that B diffusivity increases as oxide thickness decreases. The Si-rich region near the Si-SiO<sub>2</sub> interface (10 to 15 Å thick), where B diffusivity is relatively high, becomes a larger and larger fraction of the total oxide thickness as  $t_{ox}$  decreases below 80 Å. Indeed, it has been found experimentally that B diffusion in Si-rich (oxygen-deficient) oxides is significantly greater than in oxides prepared in high oxygen concentrations.<sup>48</sup> According to the model, the B diffusivity at 900°C in a 22 Å oxide would be ten times larger than in a 125 Å oxide.

Finally, the total B diffusion coefficient in SiO<sub>2</sub>, from Eq. 22, is summarized below, including the effects of F, H, and oxide thickness

$$D_T = A \left[ \exp(-3.56 \text{ eV}/kT)(B + C\phi_{F_2}^{1/2}) + G \exp(-3.26 \text{ eV}) \exp(-t_{ox}/\lambda_c) + E \exp(-3.0 \text{ eV}/kT)[H_2]^{1/2} \right] \quad [24]$$

where  $A = 1.1 \times 10^{-3} \text{ cm}^2/\text{s}$ ,  $B = 0.33$ ,  $C = 2.5 \times 10^{-7} \text{ cm}$ ,  $G = 0.88$ ,  $E = 2.65 \times 10^{-5} \text{ cm}^2/\text{s}$ ,  $\phi_{F_2} = F_2 \text{ dose (atom/cm}^2)$ ,  $[H_2]$  = percent H<sub>2</sub> in furnace ambient,  $\exp(-t_{ox}/\lambda_c)$  = SiO

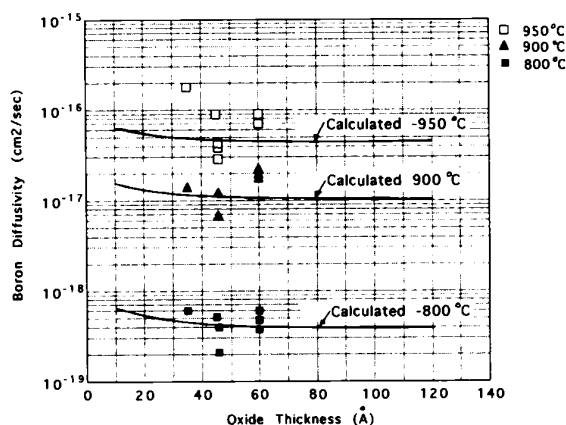


Fig. 11. Measured and calculated B diffusivity in pure SiO<sub>2</sub> from  $5 \times 10^{15} \text{ BF}_3/\text{cm}^2$  implants into poly-Si over SiO<sub>2</sub> as a function of temperature and oxide thickness. Data are from Ref. 16, 18, and 20. Very little thickness dependence on B diffusivity is observed when large concentrations of F are present.

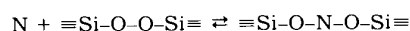
concentration distribution, and  $\lambda_c$  = characteristic SiO decay length = 16 Å.

## B Diffusion in Nitrided Oxides

Nitrided oxide films have been undergoing evaluation as thin gate dielectrics for use in fabricating MOSFETs. There have been reported improvements over pure SiO<sub>2</sub> in electrical properties as well as in reduced B diffusion from p-doped polysilicon gates into the underlying channel region during high temperature annealing.<sup>49-51</sup> Early films were produced by thermal nitridation of SiO<sub>2</sub> in ammonia (NH<sub>3</sub>), but improved films have been obtained by growing in N<sub>2</sub>O<sup>52,53</sup> or NO.<sup>54</sup>

For purposes of modeling the reduced B diffusion through nitrided oxide films, we will assume first that N is uniformly distributed throughout the film. There is support for this assumption from the work of Morimoto *et al.*<sup>51</sup> who measured N concentration profiles in 100 Å films using energy dispersive x-ray spectroscopy (EDX) with a spatial resolution of several angstroms. This result contrasts with reports from others who more typically have found an N pileup at the Si/nitrided oxide interface using SIMS<sup>49</sup> or AES<sup>50,51</sup> for such measurements. However, these latter techniques have spatial resolutions that are several times larger than EDX. Nevertheless, to accommodate non-uniform N distributions at the Si/SiO<sub>2</sub> interface, we also assume that the region of the oxide that is most highly doped will act to diffusion-limit the penetration of B.

It has been found by Yount and Lenahan<sup>55</sup> that the dominant electron trap in NH<sub>3</sub>-nitrided and reoxidized nitrided oxide films is the bridging nitrogen center with its precursor being of the form  $(\equiv\text{Si})_2\text{NH}$ . They point out that N typically substitutes for O in  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  forming  $\equiv\text{Si}-\text{N}-\text{Si}\equiv$  bonds.<sup>56</sup> The way in which N might interact with a PLD to affect B diffusion is not known. However, some insight can be gained from studies of atomic transport in SiO<sub>2</sub> by N-bearing molecules. Table II lists the measured and anticipated activation energies for N diffusion in oxide according to the results of several studies.<sup>22,57,58</sup> In general, it is thought that N species diffuse interstitially, become trapped, and then exchange N with the O in the network.<sup>59</sup> We will assume that local transport of atomic N from the molecular species to the exchange site occurs via a PLD defect. The diffusion activation reaction can be written as



$$\Delta H_i = -1.13 \text{ eV} \quad [25]$$

Note that the activation energy for this type of diffusion is  $1.13 + 0.6 = 1.73 \text{ eV}$ , which is well within the range of observed activation energy values in Table II.

We assume that N competes with B for access to PLD diffusion sites.<sup>60</sup> This competition is shown schematically in Fig. 12 where a B atom and a N atom are trying to be activated through the same PLD. From Eq. 5 and 6, the B diffusion coefficient in oxide as a function of N concentration, [N], can be written as

$$D_B([N]) = \gamma \lambda^2 X_{\text{PLD}} X_{[\text{N}]} (\text{activation})^{-\nu} \quad [26]$$

Table II. Molecular nitrogen diffusion activation energies compared with the PLD model for atomic N.

| N diffusion species | $E_A$ (eV) | Source             |
|---------------------|------------|--------------------|
| NH <sub>3</sub>     | 1.6        | Hori <i>et al.</i> |
| NH <sub>3</sub>     | 2.0        | Elastic model      |
| N <sub>2</sub>      | 1.2        | Elastic model      |
| N <sub>2</sub>      | 1.2-1.4    | Vasquez            |
| N incorporation     | 1.6        | Vasquez            |

PLD N diffusion model:  $E_A = 0.6 + 1.13 \text{ eV} = 1.73 \text{ eV}$ .

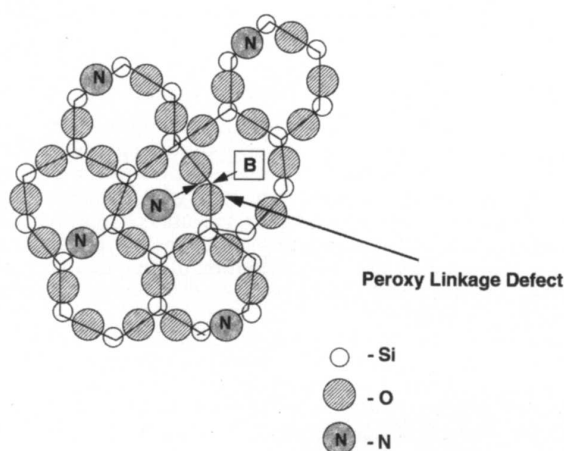


Fig. 12. Schematic drawing showing the competition between N and B for diffusion activation through a PLD site.

where  $X_{[N]}(\text{activation})$  is the probability of B activation via a PLD when N is present. We can equate this probability to the product of two probabilities

$$X_{[N]}(\text{activation}) = X_{[0]}(\text{activation}) \cdot X_{\text{PLD}}(N) \quad [27]$$

where  $X_{[0]}(\text{activation})$  is the probability of B activation when  $[N] = 0$ , and  $X_{\text{PLD}}(N)$  is the probability that a PLD is available for B activation for a given N concentration (fraction of available or uncontested B diffusion sites). Now,  $X_{\text{PLD}}(N)$  can be written as

$$X_{\text{PLD}}(N) = C_{\text{PLD}}(N)/C_{\text{PLD}}(0) \quad [28]$$

where  $C_{\text{PLD}}$  is the atomic density of PLDs. From Eq. 25 we can obtain the equilibrium ratio in Eq. 28 and express it as<sup>60</sup>

$$X_{\text{PLD}}(N) = 1/[1 + K'_N \exp(1.13 \text{ eV}/kT)[N]] \quad [29]$$

Finally, we have

$$D_B([N]) = \gamma \lambda^2 X_{\text{PLD}} X_{[0]}(\text{activation}) \cdot X_{\text{PLD}}(N) \nu \\ = D_B/[1 + K'_N \exp(1.13 \text{ eV}/kT)[N]] \quad [30]$$

where  $D_B$  is the diffusion coefficient of B in pure  $\text{SiO}_2$ ,  $K'_N$  is the reaction constant, and  $[N]$  is the percentage of N present. Thus, according to the model, the effect of adding N to the oxide is to reduce B diffusivity due to N competition for PLDs. In effect, the presence of N raises the effective B diffusion activation energy by reducing the probability of diffusion activation via PLDs. From Eq. 30 it can be seen that at large temperatures or for small  $[N]$ , the denominator approaches a value of one and  $D_B([N]) \rightarrow D_B$ . However, at low temperatures or high  $[N]$ , the activation energy for B diffusion increases up to 1.13 eV above that observed for B diffusion in pure  $\text{SiO}_2$  ( $1.13 + 3.56 = 4.69 \text{ eV}$ ).

An increase in activation energy for B diffusion in nitrided oxides has been observed experimentally,<sup>18,20</sup> where a 4.42 eV energy was obtained for B diffusion through a 43 Å nitrided oxide containing 4% N. However, this energy is 0.27 eV less than expected from Eq. 30 when  $K'_N[N] \exp(1.13 \text{ eV}/kT) \gg 1$ . This difference can be accounted for by introducing the thin oxide correction from Eq. 23 for the 43 Å nitrided oxide. Thus, as N accumulates at the Si/SiO<sub>2</sub> interface the thin oxide contribution,  $D_{(\text{SiO})}$ , also decreases. Thus, the combined diffusivity now becomes

$$D_B([N]) = (D_B + D_{(\text{SiO})})/[1 + K'_N[N] \exp(1.13 \text{ eV}/kT)] \quad [31]$$

For thin oxides  $D_{(\text{SiO})}$  dominates, so the resulting activation energy for large  $[N]$  becomes 4.39 eV, remarkably close to Aoyama's result of 4.42 eV. Also, we can determine the

value of  $K'_N$  from Aoyama's data for B diffusion in nitrided oxides with  $[N] = 4\%$ , yielding  $K'_N = 5 \times 10^{-6}$ .<sup>60</sup>

Equation 31 is shown plotted in Fig. 13, and it can be compared with the data for the case of B diffusion in nitrided oxide with no F present. The agreement is good. It is interesting to see that Eq. 31 follows the B data in a curve that departs from Arrhenius behavior over the temperature range indicated. The term in the denominator of Eq. 31,  $K'_N[N] \exp(1.13 \text{ eV}/kT)$ , decreases with increasing temperature, and for  $[N] = 4\%$ , this term is less than one at  $T > 950^\circ\text{C}$ . The apparent activation, therefore, changes from approximately 4.39 eV at very low temperature to 3.26 eV at very high temperature, resulting in the changing slope of the B diffusivity curve. This result shows that the PLD diffusion model in  $\text{SiO}_2$  can be extended to nitrided oxides by using only one fitting parameter,  $K'_N$ , to predict the observed complex behavior in B diffusion.

**Fluorine effect in nitrided oxide.**—The effect of nitrided oxides on the diffusion of B when F is present can be calculated by recognizing that the effect of the F is to create additional PLD diffusion defects via Eq. 13. Thus the total fraction of PLDs in a nitrided oxide becomes<sup>60</sup>

$$X_{\text{PLD}}(\text{tot}) = X_{\text{PLD}}(N) + X_{\text{PLD}}(F) \quad [32]$$

We can account for the effect of N on  $X_{\text{PLD}}(F)$  by assuming that the  $[N]$  in  $\text{SiO}_2$  results in  $(100 - [N])\%$  fewer  $\text{Si-O-Si}$  reaction sites as they become replaced by  $\text{Si-N-Si}$ . Thus, the total B diffusion coefficient in Eq. 24 now becomes

$$D_T = D_B([N]) + AC(1 - [N]/100) \exp(-3.56 \text{ eV}/kT) \phi_{F_2}^{1/2} \quad [33]$$

where  $AC = 2.75 \times 10^{-10} \text{ cm}^2/\text{s}$  from Eq. 24 and 31. Equation 33 is plotted in Fig. 13 and is compared with B diffusivity data in nitrided oxide from Aoyama<sup>20</sup> for the F doses  $1 \times 10^{15}$  and  $1 \times 10^{16} \text{ cm}^{-2}$  with  $[N] = 4\%$ . Once again the agreement is good, and it is achieved by applying the basic diffusion model for B in  $\text{SiO}_2$  with one fitting parameter to account for the competition with N diffusion.

We can use Eq. 33 to calculate the retarding effect of N on B diffusion in  $\text{SiO}_2$ . The results are shown in Fig. 14 for both B and  $\text{BF}_2$  ( $5 \times 10^{15} \text{ cm}^{-2}$ ) implants into polysilicon over gate oxides that are 15 to 70 Å in thickness and annealed at  $900^\circ\text{C}$  in an inert ambient.<sup>60</sup> As  $[N]$  increases,  $D_T$  decreases for each oxide thickness shown, although the effect on the B implants is much more dramatic than for the  $\text{BF}_2$  implant. In Eq. 33 it can be seen that the multiplier  $(1 - [N]/100)$  of the  $\phi_{F_2}$  term has a small effect on the diffusivity of B when  $\phi_{F_2}$  is large. Also, for high F content films, the thin oxide correction term,  $D_{(\text{SiO})}$ , is much less important, even for 15 Å nitrided oxides. On the other

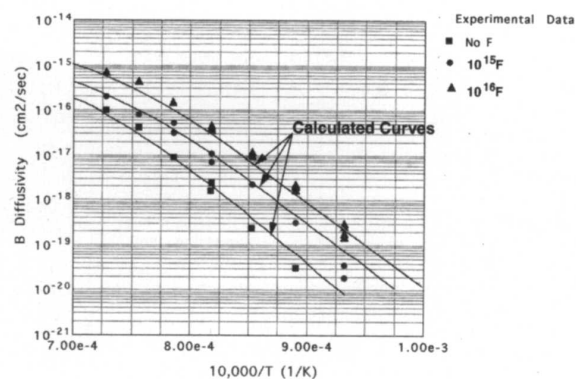


Fig. 13. Boron diffusivity in 4% nitrided oxide showing calculated curves and experimental data from Ref. 20 on the effect of F. Data and calculations are for B diffusion with no F (bottom curve),  $1 \times 10^{15} \text{ F}$  and  $1 \times 10^{16} \text{ F}$ . After Ref. 60.

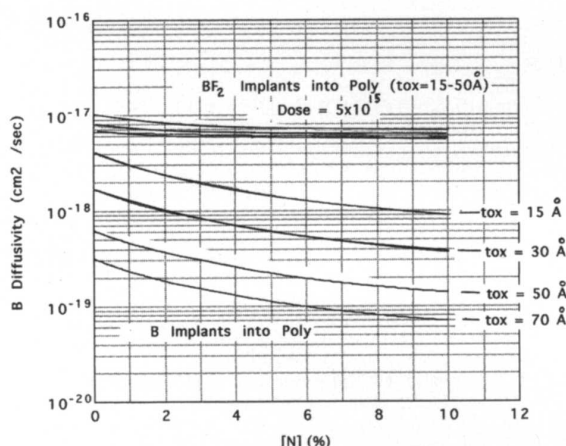


Fig. 14. Calculated B diffusivity in nitrided oxide as a function of N concentration for both B and BF<sub>2</sub> implants into poly-Si over the nitrided oxide. The B implants result in a strong oxide thickness dependence, thus limiting the effectiveness of nitridation for ultra-thin oxides. The effect of nitridation on B diffusion from BF<sub>2</sub> implants is predicted to be small as is the effect of oxide thickness. After Ref. 60.

hand,  $D_T$  for the B implant case shows a strong dependence on [N] and  $t_{ox}$ . For example, in a 70 Å nitrided oxide with 4% N,  $D_T$  for  $\phi_{F_2} = 0$  is 2.5% of the diffusivity in a similar nitrided oxide with  $\phi_{F_2} = 5 \times 10^{15} \text{ cm}^{-2}$ . However, when  $t_{ox}$  decreases to 15 Å,  $D_B([N])$  at  $\phi_{F_2} = 0$  increases to become 21% of  $D_T$  at  $\phi_{F_2} = 5 \times 10^{15}$ . Thus, N does not act as a barrier to B diffusion through oxides. On the contrary, low percentage concentrations of N in oxide films will have a diminishing effect on B diffusion as the oxide thickness is scaled down and while high dose BF<sub>2</sub> implants are in use for doping p<sup>+</sup> gates and for creating p<sup>+</sup> source/drain regions.

### Discussion

Returning again to Fig. 1, it is useful to check our models by seeing if they can reduce the wide range of B diffusion coefficient data to the intrinsic B diffusivity curve shown in Fig. 5. Equations 24 or 33 were solved for  $D_B$  for the experimental conditions behind each datum. This sometimes involved subtracting larger numbers from each other resulting in negative values for  $D_B$  when the experimental data were smaller than the calculated values. These results were not included in Fig. 15. The usable data show a much tighter distribution than the raw data in Fig. 1, and a best exponential fit to these data yields a curve that agrees fairly well with  $D_B$  from Fig. 5.

There have been numerous reports of the conditions under which B penetration occurs as determined by direct measurements using SIMS<sup>61</sup> or flatband measurements on MOS capacitors or transistors.<sup>12,49,50,62-65</sup> Many of these results are summarized in Fig. 16 where diffusion lengths, as calculated from Eq. 24 or 33 under the reported experimental conditions, are plotted vs. the reported gate oxide thicknesses. The filled-in data points refer to those results where B penetration was observed, whereas the unfilled data points represent no B penetration. In general the models do a good job of predicting B penetration or non-penetration, but there are a few exceptions. The results of Zhang<sup>61</sup> were obtained by ion implanting  $1 \times 10^{16} \text{ B/cm}^2$  at 15 keV into 3000 Å of polysilicon over 30, 60, and 100 Å pure oxides. Only the anomalous results are highlighted in Fig. 16 at 30 and 60 Å and are indicated by the symbol, ■. Zhang's results show substantial B penetration for 10 s anneals at 1050 and 1100°C, whereas the models predict that the diffusion depth of B in the gate oxide should be <20 Å. Although no follow-up study was performed, it is reasonable to suspect that the oxide-polysilicon gate stack

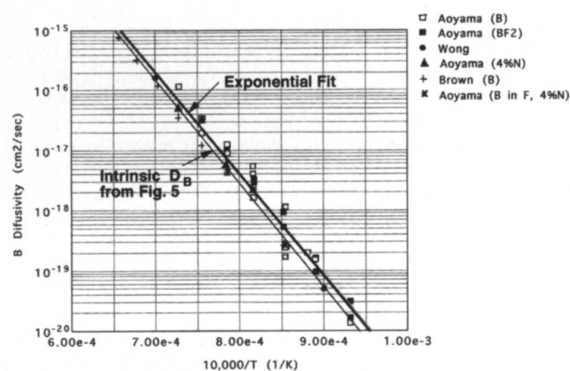


Fig. 15. Recalculated data from Fig. 1 where the intrinsic B diffusivity coefficient is extracted from the raw Fig. 1 data based on Eq. 24 or 33. A best exponential fit to these extracted data is compared with the intrinsic B diffusion coefficient from Fig. 5. This result implies that the models apply to a large range of experimental conditions.

sees substantially higher temperatures than would be measured on a bare calibration wafer.<sup>66</sup> As a result, it is critical that the actual local temperature of the devices on the wafer be known before applying Eq. 24 or 33.

The assumption that nitrided oxides result in a uniform distribution of nitrogen throughout the oxide has been made in our analysis. It turns out that this is really the best case scenario for reducing B penetration. Recently Ganesh *et al.*<sup>67</sup> have compared B penetration in uniformly nitrided oxides prepared in a high pressure N<sub>2</sub>O ambient to atmospheric N<sub>2</sub>O oxides that showed N pileup at the Si/SiO<sub>2</sub> interface. Reduced B penetration resulting from BF<sub>2</sub> implants into polysilicon gates was measured for the uniform N-doped oxides relative to those oxides exhibiting N pileup.

Recently, N ion implantation in silicon followed by thermal oxidation has been described as a method for reducing B penetration through 25 Å thick gate dielectrics.<sup>68</sup> During oxidation apparently all of the N diffuses into the growing oxide and piles up at the Si/SiO<sub>2</sub> interface. It is

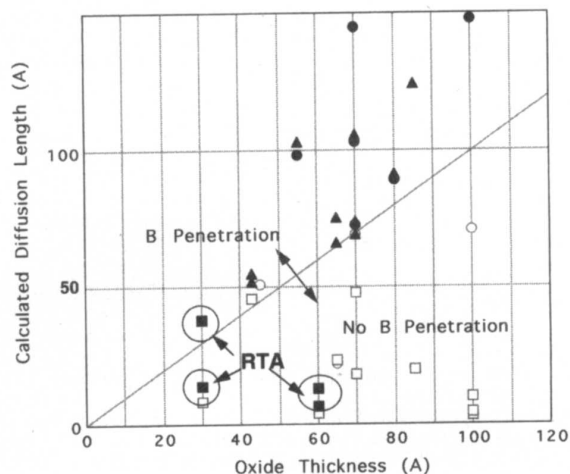


Fig. 16. Calculated B diffusion length vs. oxide thickness comparing theory and experimental results on B penetration. Data represent B penetration through nitrided oxides (●) and SiO<sub>2</sub> (▲), and no penetration through nitrided oxide (○) and SiO<sub>2</sub> (□). The special case where RTA is applied resulting in anomalous penetration is indicated with the symbol (■).

not known, however, whether or not this N pileup affects the transport of B across the interface. Measurements of Morimoto *et al.*<sup>31</sup> show that more B piles up on the oxide side of the interface for a nitrided oxide relative to pure thermal SiO<sub>2</sub>. At the polysilicon/oxide interface, similar transport effects may also be observed.

It is known that if the gate is codoped with phosphorus, then B penetration through the gate oxidized is suppressed. There may be two reasons for this: (i) B transport to the polysilicon/oxide interface may be reduced as a result of reducing B diffusion in the presence of P. There is the well-known Fermi-level effect<sup>69</sup> in diffusion, and P atoms may clog the grain boundaries causing additional reduced B diffusion; (ii) P also diffuses in SiO<sub>2</sub> via the PLD (see Table I) which means that it is also competing with B for diffusion-activation sites in the same way as N in our model.

### Conclusions

We have proposed physical models that explain reported experimental results on B diffusion in SiO<sub>2</sub>, particularly in the presence of F, H<sub>2</sub>, and N and as a function of oxide thickness. The most likely diffusion defect, the peroxy radical, appears to mediate the diffusion of B as well as As, P, and Ga, based upon consistent defect formation energies. However, under H<sub>2</sub> annealing conditions it appears that the precursor to the NBOHC becomes important in enhancing B diffusion with a [H<sub>2</sub>]<sup>1/2</sup> dependence.

When F is present in the oxide from etching residues or from a BF<sub>3</sub> implant, the role of F is to break Si–O bonds so that reactions with O are possible and additional PLDs formed. This in turn enhances the diffusion of B with a [F<sub>2</sub>]<sup>1/2</sup> dependence. In addition we have proposed that excess PLDs can be formed at the Si–SiO<sub>2</sub> interface due to the reactions of excess SiO. These interface PLDs exist in concentrations that exceed the bulk PLD concentration because the formation energy is one-half the bulk value, resulting in thin regions of high B diffusivity. As the oxide thickness is scaled down,  $t_{ox}$  becomes an increasingly large fraction of the thickness of this interface region, which is described by a characteristic distance,  $\lambda_c = 16$  Å. The resulting increase in B diffusivity in the thinned oxides becomes measurable for  $t_{ox} < 80$  Å.

Based on the PLD network defect model for the diffusion of B in SiO<sub>2</sub>, we have proposed an extension of that model to account for the effect of nitridation. We assume that the effect of adding N to the oxide is to reduce B diffusivity due to N competition for PLDs. In effect, the presence of N raises the effective B diffusion activation energy by reducing the probability of diffusion activation via PLDs. We have shown that as the gate oxide is scaled below 50 Å in thickness, additional chemical processes act to increase B diffusivity in nitrided oxides, thus reducing the impact of nitridation as a diffusion barrier. For [N] < 10% the model predicts that nitridation has a negligible effect on B diffusion if p<sup>+</sup> poly gate doping is performed with high dose BF<sub>3</sub> implants.

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## Chemical Compatibility of (La<sub>0.6</sub>Ca<sub>0.4</sub>)<sub>x</sub>Fe<sub>0.8</sub>M<sub>0.2</sub>O<sub>3</sub> with Yttria-Stabilized Zirconia

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### ABSTRACT

LaFeO<sub>3</sub>-based perovskites are of interest as cathode material for the development of advanced solid oxide fuel cells operating at temperatures significantly lower than 900°C. The compatibility of the selected materials is necessary to guarantee long-term operation of a solid oxide fuel cell. Systematic investigations on the reactivity between the solid electrolyte yttria-stabilized zirconia (ZrO<sub>2</sub> + 8 mole percent Y<sub>2</sub>O<sub>3</sub>) and the perovskites (La<sub>0.6</sub>Ca<sub>0.4</sub>)<sub>x</sub>Fe<sub>0.8</sub>M<sub>0.2</sub>O<sub>3</sub> ( $x = 1, 0.9$ ; M = Cr, Mn, Co, Ni) were carried out. The results obtained are discussed.

### Introduction

The following three temperature regions are designated by Steele<sup>1</sup> for the operation of solid oxide fuel cells (SOFCs) by considering the materials properties: above 900°C (0°C = 273.15 K) using zirconia-based electrolytes with a thickness of about 150 μm, 700 to 900°C by employing thin layers of zirconia-based electrolytes supported by a thick electrode, and 500 to 700°C by selecting ceria-based electrolytes. Temperatures lower than 700°C are possible in principle with zirconia-based electrolytes depending on the extent of the practical reduction of the layer thickness. The cathode material in these SOFCs has to meet the following requirements: high electrical conductivity, thermal and chemical compatibility, compatibility with the electrolyte, and high catalytic activity for oxy-

gen reduction. The perovskite oxides La<sub>1-x</sub>A<sub>x</sub>MO<sub>3</sub> (A = Sr, Ca; M = Cr, Mn, Fe, Co) have been extensively studied for applications above 900°C since they show good electrical conductivity.<sup>2-5</sup> Yokokawa *et al.*<sup>6,7</sup> elucidated the chemical interactions of many of these perovskites with zirconia-based electrolyte. The compositions La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> are most widely used due to their good chemical and thermal compatibility with yttria-stabilized zirconia (YSZ) and their high catalytic activity for oxygen reduction.<sup>4,5,8</sup> Syskakis *et al.*<sup>9</sup> studied the reactions between YSZ and La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> as well as La<sub>0.79</sub>Sr<sub>0.16</sub>Mn<sub>0.9</sub>Co<sub>0.1</sub>O<sub>3</sub>.

Commercialization of SOFCs requires lowering the operating temperatures below 900°C. Possible materials for the development of cathodes for use at these temperatures are Sr-substituted lanthanum ferrites La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3</sub>.<sup>10,11</sup> Good electrical properties are reported at temperatures between 600 and 800°C for La<sub>1-x</sub>Sr<sub>x</sub>Fe<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub>,  $x = 0.2$  to  $0.4$ .<sup>11</sup> The stability and compatibility of the selected materials under operating conditions is a neces-

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