We propose a novel mechanism for the diffusion of a diboron pair in Si, based on first principles density functional theory. We find a reaction pathway along which the boron pair diffuses from one lowest energy configuration of [B-B]$_i$-(001) to an equivalent structure at an adjacent equivalent site through three local minimum states denoted as [B-B]$_i$-(111), B$_i$-B$_i$, and B$_i$-B$_i$-Si$_i$. The activation energy for the diffusion is estimated to be 1.81 eV in the generalized gradient approximation. A kinetic model suggests that the diboron diffusion plays an important role in determining diffusion profiles during ultrashallow pn junction processing (which requires high boron-dopant concentration as well as high annealing temperature).

As the gate length of semiconductor devices decreases to the diffusion length of dopants by transient enhanced diffusion (TED), it becomes crucial to achieve a precise control of diffusion profiles during implantation as well as postimplantation thermal treatment. Ion implantation followed by thermal annealing is currently the most widely used method for semiconductor doping. This has led to extensive recent investigations into diffusion mechanisms of dopants [1,2]. However, many questions remain unresolved, particularly on the fundamentals of boron diffusion and clustering at high doping levels ($>10^{18}$ cm$^{-3}$) inherent to ultrashallow pn junction fabrication in Si.

Boron is a major $p$-type dopant in silicon-based devices. It has been thought that the boron substitution-Si interstitial pair, (B$_i$-Si)$_i$, is mainly responsible for B TED [2,3] via the so-called “kick-out” mechanism [4,5] or the direct interstitial hopping mechanism [6,7]. However (vide infra), the TED mechanism does not explain the concentration-dependent diffusion observed at high B concentrations ($>10^{18}$ cm$^{-3}$) during high temperature annealing ($=1200^\circ$C) where B clustering is insignificant [8]. Here B diffusion is enhanced with B concentration, leading to shoulder in diffusion profiles [9]. Thus, there must be some other mechanism that significantly facilitates TED at high concentration.

For high concentrations, a mobile B$_i$-Si$_i$ species may be captured by a second B complex to form a stable multiboron cluster. Such clustering impedes B TED substantially. For instance, upon annealing 600 $^\circ$C, B TED is noticeable only at <10$^{18}$ cm$^{-3}$, where cluster formation is insignificant. In this case, the displacement of diffusion profiles becomes larger as the B concentration decreases, exhibiting a tailing behavior [10]. Given the tendency of increased retardation by clustering at higher concentrations, we consider it is unlikely that B$_i$-Si$_i$ diffusion is responsible for the anomalous shouldering, suggesting that there must exist some other diffusing component.

Based on a kinetic model, Vandenbossche and Baccus [11] showed that including a mobile and inactive substitutional-interstitial boron cluster (B$_i$-B$_i$) gave the best agreement with the experimental results of Inada et al. [12]. However, based on ab initio density functional theory (DFT) studies Zhu et al. [5] claimed that “B$_i$-B$_i$ is (relatively) immobile; it is impossible to find a migration path that only breaks one or two bonds while still keeping two B atoms together.” Consequently, diboron diffusion has been neglected in more recent theoretical studies [13].

Using ab initio DFT we have reexamined the diffusion of the diboron (B$_i$-B$_i$) pair in Si. We find a new mechanism for diffusion of a boron pair that leads to a total energy barrier of 1.81 eV. Using a kinetic model we show below that when the B concentration and annealing temperature are both very high the contribution of B$_i$-B$_i$ diffusion can be comparable to or exceed that of B$_i$-Si$_i$ diffusion. Indeed this mechanism leads to rates that explain the observed shoulder in TED. Our new mechanism involves diffusion of the dimer from one lowest energy [B-B]$_i$-(001) configuration to another equivalent configuration through three local minimum states: [B-B]$_i$-(111), B$_i$-B$_i$, and B$_i$-B$_i$-Si$_i$. We find that the energy barriers for jumping from one local minimum structure to another are each less than 1.0 eV, suggesting that the boron pair can easily change configuration at high temperatures.

All atomic structures (Fig. 1) were optimized using the local density approximation (LDA) [14] to DFT, as implemented in the CPMD V3.3 package [15]. Then at the optimum structure (either a minimum or a saddle point), we evaluated the energy using the generalized gradient approximation (GGA) [16]. The LDA and GGA values are virtually identical as shown in Fig. 2 so that we present only the GGA numbers in the text. These calculations used a nonlocal, norm-conserving pseudopotential [17] and a plane-wave cutoff energy of 20 Ry. The defect systems considered in this study were modeled using a 192-atom supercell with a fixed volume that yields a Si-Si bond distance of 2.35 Å in pure Si. All atomic positions were allowed to relax fully until all residual forces were smaller than 5 × 10$^{-4}$ Hartree/Bohr. Because of the large supercell, we use just one $k$ point at $\Gamma$ for the Brillouin-zone (BZ) integrations.
Figure 1 shows the structures along the pathway for diffusion of a boron-boron pair in Si. This involves four stable states: (i) \( {\text{B-B}} \), (ii) \( {\text{B-B}} \), (iii) \( {\text{B}} \), and (iv) \( {\text{B}} \) (with optimized atomic structures presented in Fig. 3).

Here \(( {\text{B-B}} )\) is the lowest energy configuration. As shown in more detail in Fig. 3(a), it has a normal 1.597 Å B-B single bond with each B forming a normal 2.00 Å bond to two Si atoms. In addition, each B has the ideal \( sp^2 \) planar bonding configurations while each neighboring Si is essentially tetrahedral.

In the first transition state (TS1), the lower B atom (denoted \( B_a \)) moves to the left along a \( 110 \) direction pushing the upper B atom (denoted \( B_b \)) in the opposite direction. This leads to the \(( {\text{B-B}})\) structure in Fig. 3(b) in which \( B_a \) forms normal 2.05 Å bonds to three Si, while \( B_b \) forms a compressed 1.94 Å bond to one Si and a compressed 1.56 Å donor-acceptor bond to \( B_b \). Again the two B atoms are bonded to share a single lattice site but are now displaced along a (111) direction.

The second transition state (TS2) involves displacement of the B dimer along the (111) direction away from the Si bonded to \( B_a \). This leads to the \( B_s-B_i \) state in which \( B_a \) has normal to long bonds (2.08, 2.23, 2.23, and 2.29 Å) with all four Si atoms, making it a \( B_s \), while \( B_b \) has a normal bond 1.65 Å to the \( B_s \) and long bonds (~2.24 Å) to three of the Si, making it a \( B_i \). One can visualize the bonding here in terms of \( B_b \) as \( B^- \) and \( B_a \) as \( B^+ \). Here, the bond between \( B_b \) and the upper layer Si atom, broken during the first step, is restored.

Next, \( B_b \) kicks into a lower layer Si site and the kicked-out Si atom (denote \( Si_c \)) moves into an interstitial position along a (111) direction, leading to the \( B_s-B_i-Si_i \) state. The third transition state (TS3) shows that the adjacent Si, originally bonded to \( Si_c \), simultaneously forms bonds with \( B_b \). The result is that both boron atoms become substitutional (think of them as \( B^- \)) while \( Si_c \) is displaced to an interstitial site (think of it as \( Si^{2+} \)). The \( B_s-B_i-Si_i \) state leaves the B-B bond broken (2.231 Å compared to 1.60). However, two B atoms remain strongly connected (at 1.956 and 2.203 Å) through the Si interstitial, \( Si_c \), but with the Si atom bonded more strongly to the kicked-in B atom. In addition to the two B, \( Si_i \) has bonds to four other

![FIG. 1. The pathway for boron dimer diffusion in Si.](image1)

![FIG. 2. Energetics (DFT/GGA in eV) along the reaction pathway for boron dimer diffusion in Si. LDA results are in parentheses.](image2)

![FIG. 3. Structures for minima along the reaction pathway for boron dimer diffusion in Si. (a) \([B-B]_{s-}(001)\), (b) \([B-B]_{s-}(111)\), (c) \(B_s-B_i\), (d) \(B_s-B_i-Si_i\).](image3)
Next, the Si interstitial (Si\textsubscript{i}) jumps down to become an interstitial in the (111) direction from B\textsubscript{h}, leading to a new equivalent B\textsubscript{s}-B\textsubscript{s}-Si\textsubscript{i} state. This involves the fourth transition state (TS4).

Next, we continue through TS5 (equivalent to TS3) but with Si\textsubscript{i} displacing B\textsubscript{s} to the interstitial position. Then TS6 (equivalent to TS2) with B\textsubscript{h} bonding to three Si atoms and B\textsubscript{s} bonding to one Si. Finally TS7 (equivalent to TS1) takes us to another lowest energy configuration, [B-B]\textsubscript{1}-(001), but displaced in the (−111) direction from the original. Simultaneously Si\textsubscript{c} has moved in the ⟨−111⟩ direction.

**Energetics.**—Figure 2 presents the potential diagram for the boron-pair diffusion. There are four energy barriers along the diffusion pathway. The first barrier (TS1) from [B-B]\textsubscript{1}-(001) to [B-B]\textsubscript{1}-(111) is estimated to be 0.52 eV in LDA (GGA). The [B-B]\textsubscript{1}-(111) configuration is less stable than the [B-B]\textsubscript{1}-(001) configuration by 0.27 eV, but the barrier of 0.25 eV for returning back to the [B-B]\textsubscript{1}-(001) state implies that the [B-B]\textsubscript{1}-(111) configuration could be stable even at high temperatures.

The second barrier (TS2) from [B-B]\textsubscript{1}-(111) to B\textsubscript{s}-B\textsubscript{s} is 0.27 eV, while the formation energy difference between the two configurations is 0.20 eV. Thus with a return barrier of only 0.07 eV, this state is probably not stable.

Next, TS3, the kick-in of the B interstitial into the lower layer Si site requires a rather large energy barrier of 1.00 eV. Here the B\textsubscript{s}-B\textsubscript{s}-Si\textsubscript{i} configuration is stabilized with a sizable barrier of 0.78 eV for the reverse jump, suggesting that this state might also be stable.

Since the energy barriers for jumping across these local minimum structures are ≲ 1.0 eV, we expect that the B-B pair easily switches its configuration from [B-B]\textsubscript{1}-(111) to B\textsubscript{s}-B\textsubscript{s}-Si\textsubscript{i} at high temperatures.

TS4 leads an energy barrier of 1.12 eV. Thus, assuming steady state kinetics, the overall activation energy required for boron pair diffusion is estimated to be 1.81 eV (the largest barrier). This energy barrier is far smaller than the value 3.5 eV generally quoted for B\textsubscript{h} diffusion [18]. We see below that the diboron pair is an important diffusing component responsible for boron TED.

**Role in dopant profiling.**—We first estimate the diffusivity of B\textsubscript{s}-B\textsubscript{s}:

\[
D_m = D_0 \exp(-E_m/k_BT),
\]

where \(D_0\) is the prefactor and \(E_m\) is the diffusion energy barrier. The Debye frequency of Si (\(\nu_D = 10^{13} \text{ sec}^{-1}\)) and a jump distance of \(\delta = 2.5 \text{ Å}\) suggest \(D_0 = \nu_D \delta^2/6 = 1 \times 10^{-13} \text{ cm}^2/\text{sec}\). This leads to a diffusivity of \(3.8 \times 10^{-11} \text{ cm}^2/\text{sec}\) for \(E_m = 1.81 \text{ eV}\) at 1000 °C. This value is about 4 orders of magnitude larger than the value of \(D_m(B) = 0.757 \times \exp(-3.46/k_BT) \text{ cm}^2/\text{sec} = 5.2 \times 10^{-15} \text{ cm}^2/\text{sec}\) for B\textsubscript{h} diffusion [18]. Although the predicted B\textsubscript{s}-B\textsubscript{s} diffusivity is still far smaller than the B\textsubscript{s}-Si\textsubscript{i} diffusivity of \(1.6 \times 10^{-6} \text{ cm}^2/\text{sec}\) [for \(E_m(B\textsubscript{s}-Si\textsubscript{i}) = 0.68 \text{ eV}\) [6]], the larger binding energy for B\textsubscript{s}-Si\textsubscript{i} [19] leads to a diffusion length for B\textsubscript{s}-B\textsubscript{s} comparable to that of B\textsubscript{s}-Si\textsubscript{i} at high temperatures [20].

At low B concentrations, the concentration of the boron dimer, B\textsubscript{s}-B\textsubscript{s} is quite small, leading to negligible diffusion. However, the B\textsubscript{s}-B\textsubscript{s} population rises rapidly with the total B density. Using a kinetic model, we have simulated the variation of B\textsubscript{s}-Si\textsubscript{i} and B\textsubscript{s}-B\textsubscript{s} concentrations with respect to the total boron concentration. The result is displayed in Fig. 4. In this calculation, we take into account only the formation/dissolution of B\textsubscript{s}-Si\textsubscript{i} and B\textsubscript{s}-B\textsubscript{s} pairs; that is, \(B_s + Si \leftrightarrow B_s-Si_i\) and \(B_s + B_s-Si_i \leftrightarrow B_s + B_s \leftrightarrow B_s-B_s\). This neglects many details in the interactions between B and Si atoms, but such simplified kinetics should give a reasonable description in the overall physical picture, especially for variations in the concentration. As the total boron concentration is increased, the concentration of B\textsubscript{s}-B\textsubscript{s} pairs increases *almost quadratically*. In contrast, B\textsubscript{s}-Si\textsubscript{i} increases *sublinearly* at high concentration region due to suppression by B\textsubscript{s}-B\textsubscript{s} clustering. That is, the mobile B\textsubscript{s}-Si\textsubscript{i} species is more quickly captured by the increased B\textsubscript{s} to produce B\textsubscript{s}-B\textsubscript{s}. At 10\(^2\) cm\(^{-3}\), the equilibrium concentrations of B\textsubscript{s}-B\textsubscript{s} are predicted to be 2.2 \times 10\(^{19}\) while B\textsubscript{s}-Si\textsubscript{i} is 1.7 \times 10\(^{15}\) cm\(^{-3}\); the B\textsubscript{s}-B\textsubscript{s} concentration is 4 orders of magnitude larger than the B\textsubscript{s}-Si\textsubscript{i} concentration.

Based on the equilibrium concentrations \(C_{eq}\) and the diffusivities \(D_m\), we can compare the contributions of B\textsubscript{s}-B\textsubscript{s} and B\textsubscript{s}-Si\textsubscript{i} to B TED:

\[
2D_m(B_s-B_s)C_{eq}(B_s-B_s)/D_m(B_s-Si_i)C_{eq}(B_s-Si_i),
\]

where the factor of 2 arises since two boron atoms are
carried upon $B_x$-$B_i$ diffusion. For $10^{20}$ cm$^{-3}$, the relative contribution of $B_x$-$B_i$ is estimated to be 0.4–0.6 at 1000 °C, but it drops rapidly as the B concentration and/or the temperature decreases. This indicates that the $B_x$-$B_i$ component should be as important as the $B_x$-$Si_i$ pair in determining diffusion profiles when both B concentration and annealing temperature are very high.

In addition to Vandenbossche and Baccus’s work [11], the role of $B_x$-$B_i$ diffusion can also be inferred from the observation of anomalous shouldering in diffusion profiles [9]. Clearly, such behavior cannot be explained by $B_x$-$Si_i$ diffusion alone. If $B_x$-$Si_i$ diffusion were dominant, the diffusion profile would evolve into a “tailed shape” due to increased trapping of $B_x$-$Si_i$ at higher concentration. Alternatively, it would have a “Gaussian shape” for single component diffusion (in the absence of trapping). On the other hand, since the $B_x$-$B_i$ concentration increases almost quadratically with B concentration, B TED appears to be facilitated at higher concentration when $B_x$-$B_i$ diffusion becomes important [9]. Given that such shouldering is observed only during high temperature annealing at the region of high B concentrations, we conclude that $B_x$-$B_i$ diffusion plays a key role in defining the diffusion profiles.

In conclusion, from first principles DFT calculations we have identified a favorable diffusion pathway for the diboron pair in Si. The diffusion energy barrier is estimated to be 1.81 eV in GGA. A kinetic model suggests that a $B_x$-$B_i$ pair becomes an important diffusing component when both boron-dopant concentration and annealing temperature are very high.

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[12] T. Inada et al., Appl. Phys. Lett. 58, 1748 (1991), they performed thermal annealing at 800 °C for 30 min and at 1000 °C for 10 sec after the predeposition step for B concentration of $4 \times 10^{20}$ cm$^{-3}$ at the surface.
[19] The binding energy of $B_x$-$B_i$ tends to be greater than that of $B_x$-$Si_i$ by about 0.7 eV [5].
[20] The projected diffusion length is given by $\lambda = \sqrt{6D_{\text{diss}}/D_{\text{diss}}}$, where $D_{\text{diss}}$ is the dissociation rate. Since a species must diffuse one jump away from the cluster to be dissociated, for $B_x$-$B_i$, the dissociation rate can be simplified as $D_{\text{diss}} = \nu_p \exp\left[-\left(E_m(B_x-Si_i) + E_p(B_x-B_i)\right)/k_B T\right]$. Taking $D_m(B_x-B_i) = 0.001 \times \exp(1.84/k_B T)$, $E_m(B_x-Si_i) = 0.68$ eV [6], and $E_p(B_x-B_i) = 1.6$ eV [estimated 0.7 eV larger than $E_p(B_x-Si_i) = 0.9$ eV [6]], we obtain $\lambda = 1.9$ nm at 1000 °C. This value is comparable with the value $= 2$ nm estimated for $B_x$-$Si_i$ diffusion [3,6].