# Mechanism of Boron Diffusion in Silicon: An *Ab Initio* and Kinetic Monte Carlo Study

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An exhaustive first-principles study of the energetics of B-Si interstitial complexes of various configurations and charge states is used to elucidate the diffusion mechanism of B in Si. Total energy calculations and molecular dynamics simulations show that B diffuses by an interstitialcy mechanism. Substitutional B captures a Si interstitial with a binding energy of 0.90 eV. This complex is itself a fast diffuser, with no need to first "kick out" the B into an interstitial channel. The migration barrier is about 0.68 eV. Kinetic Monte Carlo simulations confirm that this mechanism leads to a decrease in the diffusion length with increasing temperature, as observed experimentally.

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Boron is an important dopant commonly used in silicon device fabrication. Understanding the mechanism by which it diffuses is necessary to model accurately manufacturing processes such as ion implantation and rapid thermal annealing. Despite this important technological driving force and the fact that it has been widely studied, substantial controversy remains regarding the fundamental atomic-level nature of diffusion of B and other dopants in Si.

The microscopic mechanism of dopant diffusion in Si has been a subject of extensive theoretical and experimental study for more than two decades [1]. In particular B and Si interstitials have been investigated in great detail by Watkins and co-workers, using electron paramagnetic resonance (EPR), deep level transient spectroscopy (DLTS), and optical spectroscopies [2]. Dopant diffusion studies under nonequilibrium point-defect concentrations in Si clearly suggest that B diffusivity is enhanced by self-interstitials and retarded by vacancies [3]. Most early workers assumed that this interstitial-mediated diffusion occurs through an interstitialcy mechanism, i.e., the diffusing defect is a complex formed by an impurity atom and a Si atom sharing the same site [3]. For heavier defect atoms like Au, a kick-out [4] mechanism was invoked in which the impurity is "kicked out" of a substitutional site by a self-interstitial and subsequently diffuses as an interstitial through the open channels in the silicon lattice until it "kicks in" displacing a substitutional Si atom into an interstitial site.

The emergence of efficient implementations of density-functional theory (DFT) has provided a tool for studying diffusion mechanisms on a microscopic level. The first DFT investigations of impurity diffusion in Si found that many dopants diffuse via a kick-out mechanism [5,6]. Nichols, Van de Walle, and Pantelides (NVP) proposed the diffusion path for B to be between the $H$ (hexagonal) and $T$ (tetrahedral) interstitial sites. Subsequently, Cowern *et al.* experimentally measured anomalous diffusion in the tails of a B concentration distribution for short times, corresponding to mean migration events per atom $\langle n \rangle \ll 1$ [7]. The one-dimensional spatial distribution of the dopant after diffusion has exponential tails, much longer than the Gaussian shape expected from Fick's second law. They proposed a diffusion mechanism involving fast-migrating intermediate species of the form

$$X_s + I \Leftrightarrow X_m . \quad (1)$$

Here $X_s$ is the immobile substitutional impurity, which through reaction with a self-interstitial ($I$) forms a fast-migrating species $X_m$, which diffuses at a rate $D_m$. This is consistent with the NVP mechanism where $X_m$ is an interstitial B. If $X_m$ is created at a frequency $g$, then for times $t < 1/g$ an initial $\delta$-function impurity distribution would in one dimension become [7]

$$s(|x|/\lambda, gt) = (1 - gt)\delta(x) + gt\exp(-|x|/\lambda) + \mathrm{O}((gt)^2),$$

where the first term represents atoms that have not yet diffused, and the second term represents atoms that have undergone a single migration event with mean projected path length $\lambda$, and $x$ is the position relative to the initial $\delta$ function. Cowern *et al.* were able to measure such diffusion tails, and by fitting to the B concentration profiles, to determine $\lambda$ and $g$. Si interstitial injection by oxidation was shown to increase the generation rate of the fast diffusing species without changing $\lambda$. This was taken as proof that a reaction of the form (1) was occurring.

More recently, the atomic detail of B diffusion in Si has been revisited by several authors, using more sophisticated DFT schemes [8,9]. Zhu and co-workers calculated the energy surface for the NVP mechanism [8]. They used 64 atom supercells and considered several possible charge states of the Si interstitial and the B-Si interstitial complex. The diffusion path predicted for the neutral species and its associated energy barriers is shown in Fig. 1(a).

The present DFT study is performed in both the local-density approximation (LDA) and the gradient corrected

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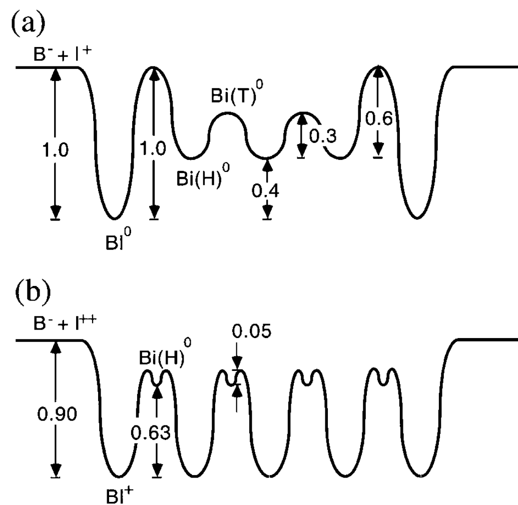


FIG. 1. Comparison of the diffusion path and energy barriers (a) for the kick-out mechanism as calculated by Zhu *et al.,* and (b) for the interstitialcy mechanism as calculated in this work. The vertical axis is energy in eV, the horizontal axis is reaction coordinate.

approximation (GGA, energies given in square brackets below), within a plane-wave pseudopotential scheme using the Vienna *Ab Initio* Simulation Package (VASP) [10]. We used Vanderbilt-type pseudopotentials [11] as supplied by Kresse and Hafner [10], and a uniform grid of $k$ points equivalent to a $4 \times 4 \times 4$ Monkhorst and Pack grid in the diamond cubic cell. We performed all of our final relaxed defect energy calculations in 128 atom unit cells, but performed molecular dynamics (MD) in 32 atom unit cells. The smaller supercells give errors of a few percent in the relative defect energies. The LDA energies of charged and uncharged B defects are shown in Fig. 2. All configurations are higher in energy than the B$I^+$ interstitialcy, which consists of B in a substitutional site and Si in a neighboring tetrahedral interstitial site.

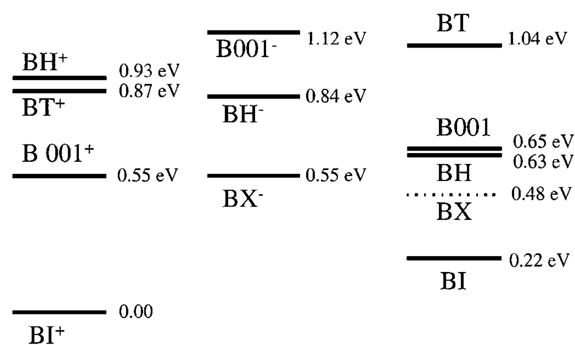


FIG. 2. Energy levels of B interstitials in various configurations and charge states, referenced to the energy of the B$I^+$ configuration ($B^-$ on a substitutional site with $Si^{++}$ in a neighboring tetrahedral interstitial site.) Charges are as indicated: $H$ = hexagonal interstitial site; $T$ = tetrahedral interstitial site; ⟨001⟩ = split interstitial in the ⟨001⟩ direction; and $X$ = split interstitial in the ⟨110⟩ direction.

This complex is formed by the electrostatic attraction between a negatively charged substitutional B and a double positively charged self-interstitial. The binding energy is 0.90 [1.03] eV. Note that unlike many previous works, the energetics presented in this paper are true LDA [GGA] values, and contain no adjustable parameters (e.g., the band gap) that are fitted to experiment.

In order to investigate the energy barriers between these various configurations, we performed constant-volume *ab initio* MD using a 3 fs time step and the Verlet algorithm. The total energy was well converged at each time step. We performed MD from various starting configurations using a temperature thermostat set at 1200 or 1500 K. Each simulation proceeded for several picoseconds. The B$H$ interstitial rapidly diffused into a B$I$ defect at both temperatures, within about half a picosecond. The B$I$ defect was stable for the length of the simulations. We also examined several other defects. The B$T$ interstitial with +1 charge went to B$I^+$ in a similarly rapid time, as did the ⟨001⟩ B split interstitial with +1 charge. We also simulated the B$X^-$ defect at 1500 K. It failed to diffuse at all, indicating that this is the most stable geometry for a negatively charged B interstitial.

Our *ab initio* MD simulations suggest that various B interstitials are separated by a negligible barrier from the B$I$ and B$I^+$ configurations. This fact makes the NVP mechanism untenable. Instead, we propose that the B$I^+$ complex, which is the lowest energy B interstitialcy, is itself the fast-diffusing intermediate species $X_m$ in Eq. (1). The path for this migration is through a low-energy interstitial configuration. The ⟨001⟩ split interstitial with a +1 charge cannot be this state, since going through this geometry does not lead to net motion of the B. Instead, we expect that B diffuses through the $H$ site with zero charge. A detailed MD investigation of the transition from the B$H$ interstitial to B$I$ complex over the temperature range 200–1200 K implies that this barrier is about 0.05 eV. Thus the total migration barrier is 0.68 [0.73] eV. This is close to 0.6 eV, as measured by Watkins *et al.* [2]. The mechanism is shown in Fig. 1(b). Based on a Si self-interstitial formation energy of 3.23 [3.71] eV, it gives a B equilibrium diffusion energy of 3.01 [3.41] eV.

Hence we propose a different microscopic mechanism for the diffusion of B in Si. This model leads to a diffusion-limited interstitialcy mechanism for the forward reaction in Eq. (1) involving no kick-out, but simply the capture of a self-interstitial by a substitutional B. This reaction rate can be shown to be [12]

$$g = 4\pi a D_I C_{\mathrm{Si}}(C_I/C_I^*), \qquad (2)$$

where $D_I$ is the interstitial component of self-diffusion, $a$ is the capture radius of a self-interstitial by a B impurity, $C_{\mathrm{Si}}$ is the number density of Si lattice atoms, and $C_I$ and $C_I^*$ are the concentrations of Si self-interstitials in the experiment and in equilibrium, respectively. Cowern *et al.* fitted their experimental data using Eq. (2) and obtained

such close agreement that they concluded that the kick-out barrier must be $<0.3$ eV [7]. This is consistent with the present model, in which there is no kick-out and hence no barrier.

For the reverse reaction in Eq. (1), our model suggests a dissociation barrier $E_{\mathrm{diss}}$ which is the binding energy of $B^-$ and $I^{++}$, plus the energy required to remove the Si interstitial one jump distance away from the B (0.9 eV [8]), so that they do not immediately recombine. The projected migration length takes an Arrhenius form:

$$\lambda = \lambda_0 \exp(-E_\lambda/k_B \mathrm{T}) \propto \sqrt{D_m \tau}\,, \qquad (3)$$

where $D_m$ is the diffusivity and $\tau$ is the lifetime of the mobile species. $D_m$ is governed by the migration energy of the mobile species $E_m$, while $\tau$ is a function of $E_{\mathrm{diss}}$. Thus

$$(D_m \tau) \propto \exp[(-E_m + E_{\mathrm{diss}})/k_B T],$$

which inserted in (3) gives $2E_\lambda = E_m - E_{\mathrm{diss}}$. Cowern *et al.* measured $E_\lambda = -0.4 \pm 0.2$ eV. Note that direct measurement of $\lambda$ is a very challenging experimental problem, but $E_\lambda$ can be determined from the relation $E_m - E_{\mathrm{diss}} = Q_B - Q_{\mathrm{SD}}$, where $Q_{\mathrm{B}}$ is the activation energy for B diffusion and $Q_{\mathrm{SD}}$ is the activation energy for the interstitial component of self-diffusion. Recent experiments give $Q_{\mathrm{SD}} = 4.95$ eV [13] and $Q_{\mathrm{B}} = 3.75$ eV [14]. Thus these values predict $E_\lambda$ to be about $-0.60$ eV, compared to $-0.59$ [$-0.62$] eV from our model.

To confirm that the proposed diffusion mechanism is consistent with the experimental data, we have used the energetics from the first principles calculations in a kinetic Monte Carlo simulation. The binding energy of the $\mathrm{B}I^+$ was 0.90 eV and its migration energy was 0.68 eV, as found in the *ab initio* LDA calculations. In the middle of the **x** axis of a simulation box 400 nm on a side, we introduced a B $\delta$-function of magnitude $2.8 \times 10^{18}$ cm$^{-3}$ (the same peak concentration as in the experiment [7]). Since the concentration of Si interstitials was found experimentally not to affect $\lambda$, we simply added a background concentration of $1 \times 10^{14}$ cm$^{-3}$ Si interstitials. Periodic boundary conditions were used along all three axes. (No B reached the boundary along the $x$ axis during the simulation time.) Simulations were run until approximately 10% of the B atoms had moved out of the original spike, at which time the B profile was fit by Eq. (1) above to extract $\lambda$. Simulations were performed at temperatures from 600 to 900 °C to obtain the temperature dependence of $\lambda$.

Figure 3 is a plot of $\lambda$ vs inverse temperature. Simulation results are the filled circles. Clearly this mechanism reproduces the experimentally observed decrease in $\lambda$ with increasing temperature; the fit gives $E_\lambda = -0.5$ eV. The dashed line is the best fit and the shaded region is the approximate range that Cowern *et al.* found for their experimental data. In the simulation, the prefactor for $\mathrm{B}I^+$ migration $D_0(\mathrm{B}I^+) = 1.2 \times 10^{-3}$ cm$^2$/s, based on the Debye frequency of Si. That for $\mathrm{B}I^+$ dissociation was taken 2 orders of magnitude higher so that the absolute magnitude of $\lambda$ is on the same order as is found experimentally. This is not an unreasonably high value for the prefactor: the dissociation of $\mathrm{B}I^+$ involves a diffusive hop of a Si interstitial, and we find $D_0(I) \cong 2$ cm$^2$/s based on experiments of Coffa and Libertino [15].

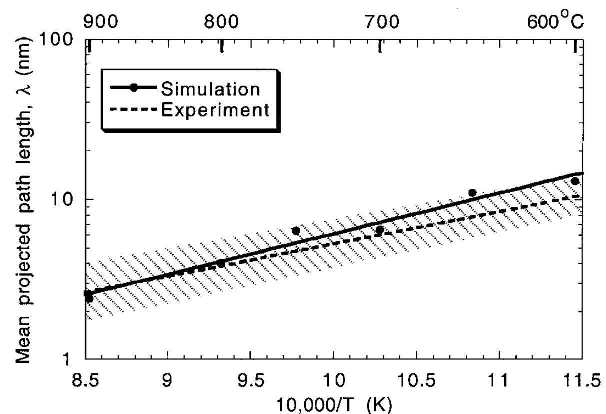


FIG. 3. Kinetic Monte Carlo simulations of the mean projected path length of B from a spike of concentration $2.8 \times 10^{18}$ cm$^{-3}$ using energies calculated from first principles (points). This gives $E_\lambda = -0.5$ eV. The dashed line is the best fit and the shaded region is approximately the range of Cowern's experimental data [7].

Additional support for the interstitialcy mechanism is provided by its calculated activation volume $V^*$, which characterizes the change with pressure of the Gibbs free energy of the diffusion event. It can be shown that $V^* = V(\mathrm{B}H) - V(B_s^-) - V(\mathrm{hole})$ for the interstitialcy mechanism, while $V^* = V(\mathrm{B}T) - V(B_s^-) - V(\mathrm{hole})$ for the NVP mechanism. $V(X)$ is the volume change from perfect Si that is required to minimize the total energy of a supercell containing the defect $X$. In units of the volume per atom of crystalline Si, $\Omega$, we find $V(\mathrm{B}H) = -1.03\,[-1.02]\,\Omega$, $V(\mathrm{B}T) = -0.94\,[-0.91]\,\Omega$, $V(\mathrm{B}_s^-) = -0.12\,[-0.087]\,\Omega$, $V(\mathrm{hole}) = -0.79\,[-0.78]\,\Omega$. The uncertainty in these numbers is about 0.005 $\Omega$. These results combine to give $V^* = -0.11\,[-0.15]\,\Omega$, while the NVP mechanism gives $V^* = +0.006\,[-0.023]\,\Omega$. A recent experimental study of the pressure dependence of B diffusion found $V^* = -0.17 \pm 0.01\,\Omega$ [16], very similar to our value.

In conclusion, we have identified the fundamental atomic diffusion pathway of B dopant in Si, based on first-principles DFT energetics obtained within both LDA and GGA. While it is not generally feasible to use *ab initio* MD to provide activation barriers directly, it does constitute a practical tool for probing small energy barriers close to saddle points once they are identified. We find that B diffuses by an interstitialcy mechanism, where a B-Si interstitial complex is the diffusing species, rather than via a kick-out mechanism. The new mechanism is consistent with experimental measurements of diffusion length and activation volume.

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