First-Principles Study of Boron Diffusion in Silicon

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(Received 14 June 1999)

In this Letter we investigate boron diffusion as a function of the Fermi-level position in crystalline silicon using *ab initio* calculations. Based on our results, a new mechanism for B diffusion mediated by Si self-interstitials is proposed. Rather than kick out of B into a mobile channel, we find a direct diffusion mechanism for the boron-interstitial pair for all Fermi-level positions. Our activation energy of 3.5–3.8 eV, migration barrier of 0.4–0.7 eV, and diffusion-length exponent of −0.6 to −0.2 eV are in excellent agreement with experiment.

PACS numbers: 66.30.Jt, 31.15.Ar, 71.15.–m, 71.55.Cn

Dopant diffusion in Si is an elementary process in electronic-device fabrication and has been studied extensively. Excellent reviews on this topic are given in Refs. [1] and [2], whereas more recent developments can be found in, e.g., Ref. [3]. Both experimental observations and theoretical calculations indicate that diffusion of common dopants in Si is mediated by self-interstitials (Si_i) or vacancies (Si_v). Experiments involving the injection of point defects into a B doped Si substrate have shown that B diffusion in Si is dominated to a degree of more than 98% by a Si_i mechanism [4], i.e., the mobile entity is expected to be a B atom paired with a Si_i. The B-Si_i pair is currently believed to diffuse via the so-called "kick-out" mechanism, which has been first suggested for diffusion of Al in Si by Watkins [5]. The equations for the kick-out mechanism have later been elaborated in more detail and applied successfully to the diffusion of Au in Si (see, e.g., Ref. [1], and references therein).

While experiments are able to find the total diffusion coefficient, they generally cannot determine the microscopic diffusion mechanism [6]. However, to accurately model dopant diffusion under conditions influenced by externally created defects, dopant pairing, or codiffusion of different dopants, it is important to know the atomic parameters governing point defect energetics.

First-principles calculations are able to provide information on the energetics for different diffusion pathways in Si. Currently, a kick-out mechanism is most widely accepted for B diffusion in Si, where first a B_s-$Si_i^{T_{2n}}$ pair is formed [Fig. 1(a), T_{Nn} denotes a tetrahedral interstitial in Nth neighbor position with respect to B_s] [7]. Subsequently, the B_s becomes interstitial (B_i) by being kicked out into a [110] channel connecting hexagonal [H, Fig. 1(b)] and T interstitial sites. This model further suggests that in the network of [110] channels, the B_i diffuses rapidly by performing a large number of jumps before being kicked back into a substitutional site releasing a Si_i (which may remain bound to the B_s).

Recent results within the local-density approximation (LDA) for the kick-out model for uncharged systems found a B_s-$Si_i^{T_{2n}}$ binding energy of 1.0 eV, a kick-out barrier of 1.0 eV, a migration barrier in the [110] channels of 0.3 eV, and a kick-in barrier of 0.6 eV [8]. Considering charged states, neutral pairs were found to be energetically unfavorable, with the positively charged B_s-$Si_i^{T_{1n}+}$ pair having the lowest energy for $E_F < 0.55$ eV (relative to the valence band edge), and the negatively charged B_i^{H-} favored otherwise. In p-type material, the kick-out, migration, and kick-in barriers were calculated to be 1.1, 0.2, and 0.4 eV, respectively [9].

Previous process modeling work that uses first-principles input has been primarily based on the neutral

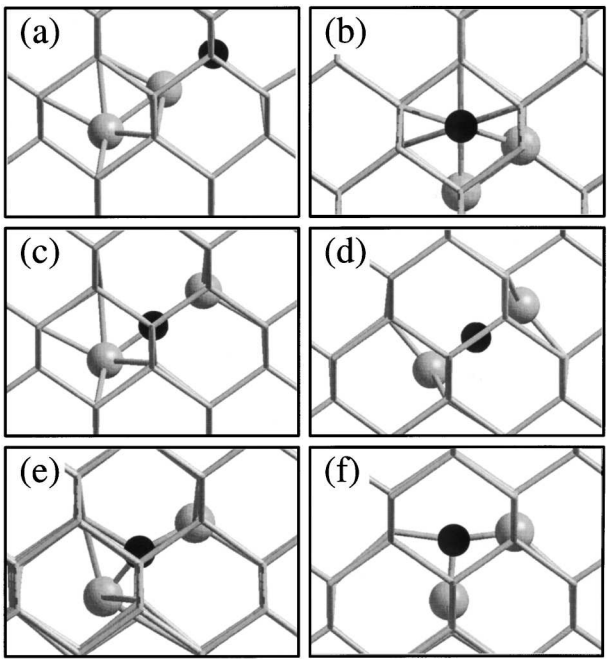

FIG. 1. Atomic configurations involved in interstitial-assisted B diffusion. Shown is a section of a [110] projection of Si. The large gray balls represent Si atoms involved in the process, the smaller black ball is the B atom; all other Si atoms are represented by a stick-only network. (a) B_s-$Si_i^{T_{2n}}$, (b) B_i^H, (c) B_s-$Si_i^{T_{1n}}$, (d) B_i^B, (e) B_i^X, and (f) B_i^S configuration.

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calculations of Ref. [8] (see, e.g., Refs. [10–12]). However, it has been shown that such models can describe B diffusion only within a narrow temperature and annealing time regime [13]. Therefore, we discuss in this Letter a scheme to perform a first-principles study of dopant formation and diffusion in semiconductors which includes more rigorous corrections for finite-size and other errors, as well as improved methods for finding saddle points. Using these techniques, we reinvestigate the Si_i-assisted diffusion of single B dopants in crystalline Si. Intermediate results of this work have been published before [14].

We perform our calculations both within the LDA [15] and a generalized gradient approximation (GGA) [16], since it is currently not understood which of these two flavors of density-functional theory give more accurate results for dopant defects in Si. The difference between the results gives us an estimate of the error introduced by the exchange-correlation functional. We use the efficient plane-wave ultrasoft pseudopotential code VASP [17]. We use optimized Si lattice constants of 5.46 Å (GGA) and 5.40 Å (LDA) as well as a kinetic-energy cutoff of 208 eV, 64-atom supercells, and a 4^3 Monkhorst-Pack **k**-point sampling, resulting in a combined convergence and finite-size error of $\sim$0.1 eV [14].

The formation energy (E_f) for a system with charge Q as a function of the Fermi level (E_F) can be calculated from the total energy of the charged system [$E_{tot}(Q)$], a neutral reference energy [$E_{ref} = E_{tot}(Si_{63}B) + E_{tot}(Si_{64})/64$ for interstitial B in a 64-atom supercell], and a valence band reference energy for the missing/excess electron(s) (E_v), giving $E_f(Q, E_F) = E_{tot}(Q) - E_{ref} + Q(E_v + E_F)$. We apply a monopole correction $e^2Q^2\alpha/(a_0\varepsilon)$ (α is the Madelung constant, a_0 the lattice constant of the cubic supercell, and ε the dielectric constant of Si) to charged systems which increases the total energy by 0.16 (0.64) eV for single (double) charged systems [18]. Furthermore, we add corrections for the too-small GGA (LDA) band gap of +0.54 (+0.59) eV, shifts due to the formation of bound states [19], and finite-size effects on conduction bands and associated shallow levels. The latter is demonstrated for a Si_i^{T+} interstitial, where the conduction band is occupied by one electron. In an infinite system, this electron would be at the conduction band minimum along the Γ-X direction of the Brillouin zone (BZ). In a 64-atom cell with $2 \times 2 \times 2$ **k**-point sampling, however, the conduction band value is taken at $\pi/(8a)(111)$ in the BZ, which has an energy 0.25 (0.30) eV higher than the conduction band minimum which we correct for. The application of this finite-size correction makes the difference in the total energy between $2 \times 2 \times 2$ and $4 \times 4 \times 4$ **k**-point sampling nearly disappear. Despite these corrections, one has to expect a considerable uncertainty in the results because of the uncertainty in the position of "deep" levels in density-functional calculations [20]. For the lowest-energy B-Si_i configurations for neutral and negative pairs, these levels are known from deep-level transient spectroscopy and could be corrected for (a shift to higher total energies between 0.1 and 0.4 eV) [21]. However, since such data do not exist for saddle points, we do not attempt such corrections to maintain a consistent treatment of all configurations.

Without a systematic method, diffusion saddle point configurations have to be simply guessed or estimated by dragging an atom from minimum to minimum across the saddle [7,8]. However, such methods cannot be expected to be reliable, especially if the diffusion involves the concerted motion of a number of atoms [22]. Therefore, we use the nudged elastic band method (NEBM) [22] implemented into VASP to determine minimum barrier energy diffusion paths between known initial and final geometries, typically local minima. The NEBM starts from a chain of geometries interpolating between the initial and final geometries. Then, the atomic configurations in the different geometries are iteratively optimized using only the ionic-force components perpendicular to the hypertangent. We determine the energy along the path by spline interpolation based on the total energy of the individual geometries and the tangential projection of the $3N$ force components on each geometry. This spline construction allows us to get the energy of the saddle point to within 0.01 eV using only four to eight geometries in most cases. The use of the NEBM might be the reason why we found a new Si_i-assisted B diffusion mechanism that had been previously overlooked using traditional search methods. Instead of a quantitative method such as the NEBM, MD simulations can be used to gain a qualitative understanding of diffusion processes, which has been done for B in Si in Ref. [23].

Si_i-assisted B diffusion starts from a bound pair of B and Si_i. The pair with the lowest formation energy that we find in the neutral case is B_s-$Si_i^{T_{1n}0}$ [Fig. 1(c)] with a formation energy of 2.8 (2.5) eV + E_F with respect to the lowest-energy B charge state, B^- [here and in the following, numbers without (with) brackets denote GGA (LDA) results]. This results in a binding energy of 0.9 (0.6) eV relative to neutral Si_i^{X0} and B_s^0 and 0.8 (0.5) eV with respect to the more stable dissociation products Si_i^{T+} and B_s^-. This binding energy is very similar to the sheer Coulombic attraction of a positive and a negative point charge ($\sim$0.6 eV) [2]. For the +1 charged system, B_s-$Si_i^{T_{1n}+}$ has the lowest formation energy in agreement with Ref. [9]. Our binding energy with respect to the dissociation products B_s^- and Si_i^{T++} is 1.0 (0.8) eV. For the −1 charged system, we find two dumbbell-like interstitials to have the lowest formation energies (we name them B_i^{X-} [Fig. 1(e)] and B_i^{S-} [Fig. 1(f)], since they are lattice sites shared between a B and a Si atom with approximately [110] and [100] orientations, respectively). B_i^{X-} has the lowest total energy, which is no surprise, since a negatively charged system with a B atom is very similar to a neutral Si_i system. We find a binding energy for B_i^{X-} of 0.5 (0.3) eV with respect to B_s^- and Si_i^{X0}. Our formation energies as functions

of the Fermi-level for the lowest-energy B-Si$_i$ pairs with respect to the B$_s$ ground state B$_s^-$ are shown in Fig. 2.

In contrast to the previously proposed B diffusion mechanism [8], we find that B$_i^S$ (and not B$_i^T$) plays the central role in diffusion (even though it is not stable in the neutral charge state). In the neutral case, we start from B$_s$-Si$_i^{T_{1n}0}$ [Fig. 1(c)], which has the lowest formation energy. We find the B$_s$ atom to migrate via the B$_i^{S0}$ [Fig. 1(f)] to an B$_i^{H0}$ [Fig. 1(b)] interstitial by a buckling of the Si-B-Si$_i$ triple dumbbell with a migration barrier of 0.2 (0.4) eV. The saddle point configuration is found to have a C_2 symmetry. We find the diffusion path between two neighboring H sites also to contain the S interstitial, from where another B$_s$-Si$_i^{T_{1n}}$ configuration can be accessed without barrier, or another H site can be reached over a barrier of 0.1 (0.1) eV [Figs. 3(a) and 3(b)]. This suggests an immediately following B$_i^{H0} \rightarrow$ B$_s$-Si$_i^{T_{1n}0}$ step to be the most probable event after the B$_s$-Si$_i^{T_{1n}0} \rightarrow$ B$_i^{H0}$ portion of the diffusion step.

For systems with positive charge, we find a one-step process B$_s$-Si$_i^{T_{1n}+} \rightarrow$ B$_s$-Si$_i^{T_{1n}+}$ with no intermediate metastable interstitial position, a bond-centered interstitial B$_i^{B+}$ [symmetry D_{3d}, Fig. 1(e)] as saddle point, and a migration barrier of 0.8 (1.2) eV [Figs. 3(c) and 3(d)]. However, there is a second, competing process, especially for the LDA calculations, which has B$_i^{H+}$ (symmetry D_{3d}) as the saddle point, with a migration barrier of 1.0 (1.3) eV [Figs. 3(e) and 3(f)]. Even if the barrier for this process is slightly higher than for the previous one, it can be assumed to be equally important, at least in the LDA case, since it has an "entropic advantage": For the one-step process, there is one possible diffusion path, which will move the B atom one bond length, d. For the latter process, however, the B atom can be pushed over six symmetry-equivalent B$_i^{H+}$ saddles to 20 different lattice sites, where one is the initial site itself, and four are d, nine 1.6d, and six 1.9d away. This moves the B atom in an average hop 1.5d away from its original site. For negatively charged systems, we find a B$_i^{X-} \rightarrow$ B$_i^{S-} \rightarrow$ B$_i^{X-}$ path with an intermediate metastable B$_i^{S-}$ configuration, a saddle point geometry with C_s symmetry, and a migration barrier of 0.6 (0.5) eV [Figs. 3(g) and 3(h)].

In Figs. 2(a) and 2(b), we show the overall activation energy for B diffusion which ranges from 2.8 to 3.8 (2.9 to 3.5) eV, depending on the Fermi-level position. B diffusion parameters measured experimentally are generally reported based on a Fermi-level-dependent diffusivity of the form $D_B = D_B^0 + D_B^+(p/n_i) + D_B^{++}(p/n_i)^2$, where D_B^0, D_B^+, and D_B^{++} are the diffusivities in intrinsic material due to diffusion via neutral (relative to the B ground state B$_s^-$, therefore negatively charged pairs), positive and double positive defects. Taking values from midgap, we predict activation energies of 3.75 (3.47) eV for D_B^0, and of 3.61 (3.45) eV for D_B^+, in excellent agreement with the experimental findings of 3.25–3.87 eV [2,24]. The calculations also find that although the dominant pair is positively charged in p-type material, B diffusion is dominated by neutral pairs, consistent with the approximately linear dependence of B diffusivity on carrier concentration (p/n_i) seen experimentally [25,26]. Our migration barriers for pairs as a function of the Fermi-level position are shown in Fig. 2(c). Between a Fermi level of 0.3 and 0.6 eV, the migration energy is found to be between 0.7 and 0.4 eV for

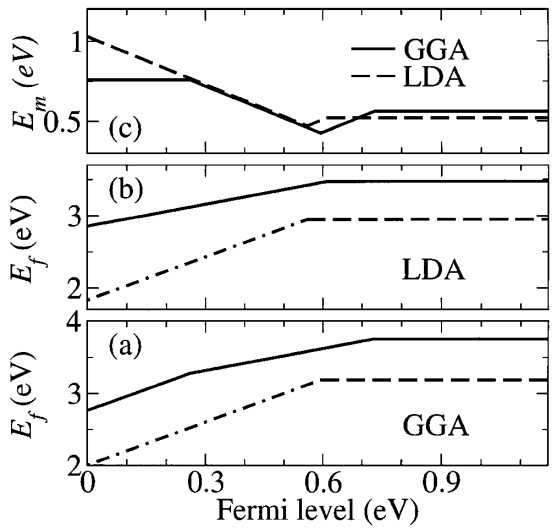

FIG. 2. (a) GGA and (b) LDA formation energies as a function of the Fermi level for the B-Si$_i$ complexes with the lowest formation energy with respect to B$_s^-$. The different lines show the following: dashed-dotted, B$_s$-Si$_i^{T_{1n}+}$; dashed, B$_i^{X-}$; solid, diffusion saddle (or activation energy). (c) shows the migration energy for B-Si$_i$ complexes: solid, GGA; dashed, LDA.

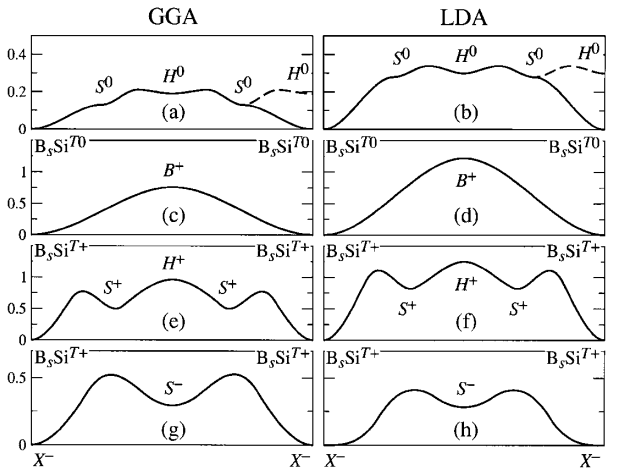

FIG. 3. Nudged-elastic band total energy (eV) for different charge states, relative to the energy of the initial system of B-Si$_i$ complexes as a function of the hyperdistance of the system from the initial configuration (arbitrary units). Charge states: (a), (b) neutral; (b), (c) and (d), (e) positive; and (f), (g) negative. Left column GGA, right column LDA results. The letters in the figures denote interstitial configurations.

both LDA and GGA calculations, in excellent agreement with experimental values around 0.6 eV [27].

We find that the dissociation of B_s and Si_i is self-interstitial limited (i.e., we do not find a barrier for B_s-Si_i dissociation above the diffusion barrier for Si_i). Therefore, the energy dependence E_λ of the migration length [28] is governed by half the difference between the activation energies of the B_s-Si_i pair diffusion and dissociation (which is the activation energy for Si_i diffusion). A low boundary for the activation energy for Si_i diffusion is given by the results of uncorrected first-principles calculations, i.e., $E_a = E_f + E_m = 3.79 + 0.31 = 4.10$ eV at midgap (GGA [29]). The experimental numbers show some scattering with an upper limit of about 5 eV for the Si_i activation energy (e.g., 4.95 eV from Ref. [30]). Taking the midgap first-principles result and high-value experiment as low and high boundaries for Si_i diffusion, respectively, we calculate a range for E_λ of -0.3 to -0.7 eV, in excellent agreement with an experimental value of -0.4 ± 0.2 eV [28].

Summarizing our work, our *ab initio* calculations suggest a new mechanism for B diffusion mediated by Si self-interstitials. We find no kickout, but rather a direct diffusion mechanism for boron-interstitial pairs for all Fermi-level positions. Our activation energy of 3.2–3.6 eV, interstitial migration energy of 0.3–0.7 eV, and diffusion-length exponent of -0.7 to -0.3 eV are in excellent agreement with the experimental values of 3.25–3.87 eV [2,24], 0.6 eV [27], and -0.4 ± 0.2 eV [28], respectively.

We thank Art Voter for very helpful discussions.

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