First-principles calculations of interstitial boron in silicon

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We perform first-principles total-energy calculations to identify the stable and metastable configurations of interstitial B in Si. We calculate formation energies and ionization levels for several equilibrium ionic configurations in different possible charge states. In all charge states the ground state consists of a B atom close to a substitutional site and a Si self-interstitial nearby. The binding energy of the self-interstitial to the substitutional B is, however, rather weak, of the order of 0.2–0.3 eV. The ground state has negative-U properties in accordance with experiments. We find several charge-state-dependent metastable configurations of interstitial B energetically close to the ground state. We discuss on the basis of formation energies the role of excess Si interstitials in the activation of B diffusion and the charge-assisted transport mechanism in the activation of B diffusion.

I. INTRODUCTION

One of the main p-type dopants of Si is boron. B atoms dissolve to the substitutional positions in the Si lattice and act as acceptors. However, electron irradiation at cryogenic temperatures has been found to displace substitutional B atoms into an interstitial configuration.[1–3] In these studies this defect was also found to have negative-U properties, i.e., it is able to trap two electrons with the property that the second electron is more strongly bound than the first one. Tarnow[4] studied the charge state configurations of this defect with *ab initio* total-energy calculations. He found that the B atom in interstitial sites is metastable against the configuration of a substitutional B with a Si self-interstitial in the close vicinity. The symmetry of the substitutional B interstitial Si pair corresponded to the experimental observation.

The diffusion of B is considered to occur as interstitial diffusion.[5] Cowern *et al.*[6–8] proposed that the activation occurs through a kick-out mechanism. In this mechanism excess Si interstitials kick B atoms out of their substitutional positions to the interstitial region. B atoms migrate until a reverse kick-out process occurs. Increased diffusion of B is observed when implantation damage creates excess Si interstitials which interact with B atoms. The phenomenon is called transient-enhanced diffusion (TED). Zhu *et al.*[9] calculated the energy barriers and binding energies for the kick-out process for the neutral charge state. They also calculated binding energies for a complex containing two B atoms, which may be involved in the immobile[10] and electrically inactive[11] B regions observed in TED experiments at higher doses of B. Additional calculations by Zhu[12] were reported for the positive and negative charge states of the ground-state configuration of B_i and for some interstitial positions.

In this paper we report on our systematic first-principles calculations of the interstitial B in Si. We present improved results for the lowest-energy configuration reported by Tarnow,[4] who used a rather small supercell and basis set for the electron wave functions. These limitations may lead to nonconverged ionic configurations and electrical properties. In addition, we study several metastable structures with formation energies close to the ground state. We complement the work of Zhu *et al.*[9] and Zhu[12] by calculating systematically the formation and binding energies and the geometries for all the possible charge states of the structures. We discuss the effect of excess Si interstitials on the lowering of the activation energy of B diffusion. The kick-out reaction is considered on the basis of formation energies. Finally we investigate the metastable structures of interstitial B as the local-energy minima for B migration in the interstitial region. In particular, we find different minimum-energy positions for different charge states of B in the interstitial region, which is a necessary condition for charge-assisted migration by the Bourgoin mechanism.[13]

The paper is organized as follows. The computational methods are presented in Sec. II. In Sec. III the results for the stable and metastable states of interstitial B are discussed. The results are compared with experimental data and with previous theoretical studies of interstitial structures and B diffusion. The summary and the conclusions are given in Sec. IV.

II. METHODS

We use the plane-wave pseudopotential method[14] within the spin-polarized density-functional theory.[15,16] The local-spin-density approximation[16] is employed for the electron exchange and correlation. For Si we use a norm-conserving nonlocal pseudopotential[17] with the nonlinear core-valence exchange-correlation scheme.[18] For B we generated a Vanderbilt-type non-norm-conserving pseudopotential,[19] which allows us to use a lower kinetic-energy cutoff of the plane-wave expansion. With these pseudopotentials the total energies were found to be well converged with an 18-Ry kinetic-energy cutoff. The bonding properties of B were tested by calculating the bond length and the vibrational frequency of a boron dimer (B_2). We used core radii of 1.4 a.u. for both s and p channels and found the bond length of 1.58 Å, which is close to the experimental value[20] of 1.59 Å. The vibrational frequency of ~ 1035 cm^{-1} was also found to be close to the experimental value[20] of 1050 cm^{-1}. A softer pseudopotential with core radius of 1.6 a.u. for both s and p channels is used for calculating B in the Si crystal.

We use the supercell approximation with periodic boundary conditions. The calculated equilibrium lattice constant is 5.39 Å, which is slightly smaller than the experimental one of 5.43 Å. The discrepancy is typical for the local-density approximation (LDA) calculations. The calculated band gap of 0.47 eV is less than the experimental value of ~ 1.2 eV, an underestimation also typical for the LDA calculations. Our defect calculations are performed with 32 and 64 atom-site supercells. The $2\times2\times2$ Monkhorst-Pack[21] **k**-point sampling is used for both supercells. For all the necessary cases we have used the 64 atom-site supercell to ensure that a sufficient convergence of the atomic structure was obtained. In the defect calculations the ions are moved according to the Hellman-Feynman forces until the highest force component on any ion is less than 5 meV/Å. The ionic positions are first slightly randomized to ensure that no conserved symmetry would prevent the system from relaxing to the ground state.

The formation energies of dopants and dopant-defect complexes can be calculated as[22]

$$E_f^Q = E_D^Q + Q(E_v + \mu_e) - \sum_s n_s \mu_s, \tag{1}$$

where E_D^Q is the total energy of the supercell with the dopant or the complex in the charge state Q, E_v the top of the valence band, μ_e the electron chemical potential with respect to E_v, n_s the number of atoms of type s, and μ_s the chemical potential of an atom of type s. For Si μ_{Si} is the chemical potential of a Si atom in bulk Si, and for B we use μ_B which is the chemical potential of a B atom in the B_2 dimer. For our purposes the determination of μ_B was not critical, since the quantities of interest (the total-energy differences and the ionization levels of defects) do not depend on μ_B, provided that the defects compared contain the same number of B atoms. To compare the formation energies consistently, a proper alignment of E_v for the different defect supercells is needed. In Eq. (1) we therefore use the form[23,24]

$$E_v = E_v(\text{bulk}) + [V_{ave}(\text{defect}) - V_{ave}(\text{bulk})], \tag{2}$$

where $V_{ave}(\text{defect})$ is the average potential far from the defect center in the supercell, and $V_{ave}(\text{bulk})$ the corresponding value in the ideal bulk supercell. The correction takes into account properly the finite size of the supercell. The ionization level $\mu_e(Q/Q')$ is defined as the value of the electron chemical potential μ_e when two thermodynamically stable charge states Q and Q' have the same energy

$$E_D^Q + Q[E_v^Q + \mu_e(Q/Q')] = E_D^{Q'} + Q'[E_v^{Q'} + \mu_e(Q/Q')]. \tag{3}$$

We have studied the convergence of total energies, ionization levels and bond lengths of the defects with respect to supercell size. By increasing the supercell size from 32 to 64 atoms we find that the total energy differences are converged within 0.1 eV, the ionization levels within 0.03 eV, and the bond lengths within 3% of the bulk bond length for all the test cases. Furthermore, the point symmetries of the different defects and their relative positions in the formation energy diagram did not change.
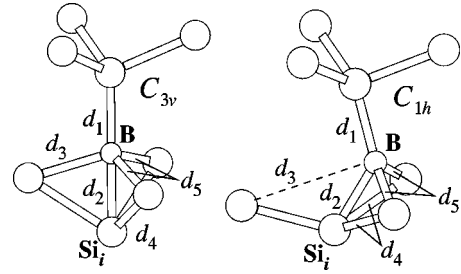

FIG. 1. Calculated atomic structure of the B_{Si}-Si_i defect in its two possible configurations. For the $1+$ charge state only the C_{3v} configuration is found, whereas for the 0 and $1-$ charge states both the C_{3v} and C_{1h} configurations are found. The bond lengths d_i are given in Table I.

III. RESULTS AND DISCUSSION

A. Substitutional B

We have first studied B in the substitutional position in its neutral and negative charge states. For the negative charge state the nearest-neighbor silicon atoms relax inwards ~ 0.3 Å, which is $\sim 12\%$ of the bulk bond length, conserving the T_d point symmetry of the lattice. The fact that the B atom has a smaller ionic radius than Si explains the inward relaxation around substitutional B. In the neutral charge state, in addition to an inward relaxation of the same order, substitutional B induces a small symmetry-lowering relaxation. However, the distortion is weak and the wave function of the uppermost electronic state is accordingly delocalized in the supercell. Our results are in agreement with previous first-principles calculations of neutral substitutional B.[5,9]

The negative charge state is the lowest in formation energy for all the Fermi level positions in the band gap. Actually this means that the negatively charged impurity can bind a hole into a shallow effective-mass state. When reionized it acts as a shallow acceptor leaving a delocalized hole in the valence band. We consider the formation energy of B_{Si}^{1-} at $\mu_e = 0$ eV as a proper reference energy for comparing the formation energies of the other kinds of defects involving one B atom (B_i, B_{Si}-Si_i). The formation energies of these defects are found to be 2–3 eV higher than that for substitutional B_{Si}^{1-}. Therefore these defects do not cause compensation of acceptors in thermal equilibrium.

B. Substitutional B interstitial Si pair

Our simulations resulted in two types of structures for interstitial B. We discuss first the lowest-energy structure, denoted by B_{Si}-Si_i. It is characterized by the fact that the B atom stays close to its substitutional position, and a Si interstitial is trapped at a nearby tetrahedral site. The geometries obtained are depicted in Fig. 1 and the bond lengths of the defect are given in Table I. We use the same labeling of bonds as Tarnow[4] and give also his theoretical results for comparison. The other types of structures are discussed in Sec. III C.

In the $1+$ charge state the B_{Si}-Si_i defect has the C_{3v} point symmetry so that the B atom is at the substitutional site and the Si interstitial at a nearby tetrahedral site. For the 0 and $1-$ charge states we found two competing structures C_{3v} and C_{1h} whose total energies are within ~ 0.2 eV. In the

TABLE I. Calculated point symmetry groups and bond lengths of the B_{Si}-Si_i defect for the charge states $1+$, 0 and $1-$. The distances d_i are given in Å and refer to Fig. 1. In the perfect crystal the Si-Si bond length is 2.33 Å. The entries in parentheses correspond to the energetically higher configurations. Supercell of 64 atoms is used.

	Charge state	Symmetry	d_1	d_2	d_3	d_4	d_5
This work	$1+$	C_{3v}	2.08	2.03	2.19	2.51	2.19
	0	C_{3v}	2.05	2.03	2.19	2.49	2.19
	(0)	(C_{1h})	(2.00)	(1.98)	(3.06)	(2.51)	(2.10)
	$1-$	C_{1h}	1.98	1.94	3.40	2.52	2.04
	$(1-)$	$(\sim C_{3v})$	(2.03)	(2.03)	(2.16)	(2.44)	(2.20)
Tarnow[a]	$1+$	C_{3v}	2.08	2.07	2.51	2.51	
	0	C_{1h}	2.03	2.01	2.20	2.35	
	$1-$	C_{1h}	2.05	2.01	2.12	2.31	

[a]Reference 4.

C_{1h} configuration the B atom is displaced from the axial $\langle 111 \rangle$ position in the {110} plane. For the neutral charge state the C_{3v} configuration has a lower total energy by 0.21 eV, whereas in the negative charge state the C_{1h} configuration corresponds to the ground state by 0.13 eV. The ground-state ionic configuration of the neutral state and the corresponding total energy may be affected by an unphysical hybridization of the uppermost occupied electron state with the conduction-band states which are erroneously low in energy due to the underestimation of the band gap in the LDA. For the C_{1h} structure the uppermost occupied electron state is located at the middle of the band gap and its mostly p-type wave function is well localized around the B atom for both the 0 and $1-$ charge states.

Energetically the positive and negative charge states are stable for the low and high positions of the Fermi level in the band gap, respectively. In contrast, the neutral charge state is both in the C_{3v} and C_{1h} configurations higher in energy than the positive or negative charge state and can therefore be considered metastable. Thus the defect forms a negative-effective-U system. Using for the neutral state the total energy corresponding to the C_{3v} configuration, we obtain the ionization levels of $\mu_e(1+/0)$ and $\mu_e(0/1-)$ at 0.66 and 0.55 eV above the valence-band maximum, respectively. The net effective correlation energy U is then ~ -0.1 eV. With the total energy of the C_{1h} configuration the ionization levels are at 0.87 and 0.34 eV ensuing a rather strong U of ~ -0.5 eV. Experimentally the existence of the negative-U behavior for interstitial B has been conclusively demonstrated by Harris et al.[25] They found the $\mu_e(1+/0)$ donor level close to the conduction band edge at $E_c - (0.13 \pm 0.01)$ eV and the $\mu_e(0/1-)$ acceptor level at $E_c - (0.37 \pm 0.08)$ eV. For the correlation energy U they found the value of $-(0.24 \pm 0.09)$ eV. The direct comparison of the positions of theoretical and experimental ionization levels is difficult due to the underestimation of the band gap in the LDA. Especially, the electron states close to the conduction band, e.g., for the neutral charge state in the C_{3v} configuration, may be somewhat inaccurately described. However, we think that the agreement between experiment and theory is reasonable, especially when the total energy corresponding to the C_{3v} configuration of the neutral state is used. The rather large lattice rearrangement which we find between the

neutral and negative charge states reflects nicely the negative-effective-U behavior. Another experimental result is that the neutral charge state should in fact have the low-symmetry of C_{1h}.[1] The missing of a strong symmetry lowering in our ground state may again be due to the hybridization of the deep level and the conduction-band states. The fact that the neutral defect has a metastable state with the correct symmetry gives a hint that the correct ground state could also have this symmetry.

The first-principles calculations by Zhu[12] resulted in the same positive charge state configuration for the B_{Si}-Si_i defect as the present ones. However, his stable negative charge state configuration is the interstitial B at the hexagonal site instead of the B_{Si}-Si_i configuration. In our calculation B at the hexagonal site is ~ 0.2 eV higher in energy than the B_{Si}-Si_i defect. One possible reason for this discrepancy is the fact that Zhu used the experimental lattice constant. We have used the theoretical lattice constant throughout the calculations in order to avoid residual stresses. The differences between the configurations obtained by Tarnow[4] and us are clearly visible in Table I. For example, in his results for the $1-$ charge state the B atom relaxes from the $\langle 111 \rangle$ axis towards the opposite direction on a {110} plane than in our results. The differences are probably due to the fact that he has used a smaller supercell. This means that in his results the defect-defect interaction is larger.

The electronic properties of the B_{Si}-Si_i defect can be compared to those of the substitutional B and the *isolated* Si interstitial separately. In the $1+$ charge state of B_{Si}-Si_i the B atom is close to the substitutional site and creates a shallow acceptor level. The acceptor level is filled, giving an effective charge of $1-$ for the B atom. Then the nearby Si interstitial would be nominally in the $2+$ charge state. This is the situation in p-type material. In n-type material the pair is in the $1-$ charge state and the effective charge of the Si interstitial is neutral. These charge states of the Si interstitial are in agreement with first-principles calculations[26] for isolated Si interstitials. According to those calculations for interstitial Si the $1+$ charge state is not stable for any Fermi level position. The T^{2+} defect (Si at the tetrahedral-interstitial site) is the ground state in p-type material, and the T^0 defect is a metastable configuration in n-type material. The comparison between B_{Si}-Si_i and Si_i can be also made with re-

TABLE II. Formation energies of substitutional B and Si self-interstitial in their well-separated and paired configurations. The energy zero is the formation energy of B_{Si}^{1-} at $\mu_e = 0$ eV. Supercell of 64 atoms is used.

Defect	Formation energy (eV)
B_{Si}^{1-}	$-\mu_e$
$Si_i^{2+}(T)$	$2.06 + 2\mu_e$
$Si_i^0(X)$	3.30
$(B_{Si}\text{-}Si_i)^{1+}$	$1.82 + \mu_e$
$(B_{Si}\text{-}Si_i)^0$ (C_{3v})	2.48
$(B_{Si}\text{-}Si_i)^{1-}$ (C_{1h})	$3.03 - \mu_e$

spect to the defect ionization levels. The level $\mu_e(2+/0)$ for the Si interstitial at the T site was found to be at about 0.85 eV (Ref. 26) (a negative-effective-U behavior as for the B_{Si}-Si_i pair), whereas the level $\mu_e(1+/1-)$ of B_{Si}-Si_i is in our calculations at 0.60 eV. Thus the levels are rather close to each other. The level shift is due to the fact that the nearby B atom distorts the potential around Si_i.

We have calculated the binding energy of the B_{Si}-Si_i defect with respect to well separated substitutional B and Si interstitial. Substitutional B was calculated in the negative charge state. The formation energies for these defects are listed in Table II. According to Lee *et al.*[26] the $Si_i^{2+}(T)$ and $Si_i^0(X)$ defects are lowest-energy configurations for the isolated Si interstitials. T denotes the tetrahedral interstitial and X the $\langle 110 \rangle$-split configuration. Table III contains the binding energy of the B_{Si}-Si_i defect. The bonding of the Si interstitial to the substitutional B is weak, of the order of 0.2–0.3 eV for the stable charge states. This is along the fact that the mobility of Si interstitials is high.[27] For the positive charge state the binding energy comes from the Coulombic interaction and the atomic relaxations. In the negative charge state the Coulombic interaction must be ruled out, but the two electrons in the localized state and the lower symmetry of the defect lead to a binding energy of the same order through atomic relaxations and rebonding.

The binding of the B and Si atoms is important in modeling the TED mechanism, in which different kinds of migration and clustering processes can take place. It is important to note that calculations that include only the neutral charge state result in higher and seemingly erroneous binding energies of the order of 1 eV.[9] Binding of structures containing two B atoms have been studied recently by first-principles calculations.[9,12]

To conclude, our calculations corroborate the result of Tarnow[4] that the substitutional B interstitial Si pair is the

TABLE III. Binding energy of the substitutional B interstitial Si pair (B_{Si}-Si_i). The binding energy is calculated with respect to the well separated B_{Si} and Si_i defects. Supercell of 64 atoms is used.

	Defect	E_b (eV)
This work	$(B_{Si}\text{-}Si_i)^{1+}$	0.24
	$(B_{Si}\text{-}Si_i)^{1-}$ (C_{1h})	0.27
Zhu[a]	$(B_{Si}\text{-}Si_i)^{1+}$	0.22

[a]Reference 12.

TABLE IV. Formation energies for the different charge states and configurations of interstitial B with respect to the ground state. For the neutral and negative charges of the ground state the C_{3v} and C_{1h} configurations are used, respectively. Energies are given in eV and correspond to Fermi level at the top of the valence band ($\mu_e = 0$ eV). T, H, S, and B denote the tetrahedral, hexagonal, B-Si interstitialcy, and bond-centered sites, respectively. Supercell of 32 atoms is used.

Charge state	B_{Si}-Si_i	T	H	S	B
1+	0	0.98	1.14	0.94	1.34
0	0	-	0.58	0.61	1.21
1−	0	-	0.24	-	1.20

configuration responsible for the negative-U properties related to interstitial B. We have made the identification on the basis of the structural, electrical and energetical properties. The other possible structures can be ruled out by their high formation energies and point symmetries in disagreement with experiment.

C. Metastable states of interstitial B

Completely different types of equilibrium structures are found when the B atom is not relaxed to the substitutional site but resides in a true interstitial position or forms an interstitialcy with a Si atom. We find four different kinds of metastable geometries for B_i: hexagonal (H), tetrahedral (T), split-configuration (B-Si interstitialcy) (S), and bond-centered (B) positions. The formation energies of these configurations with respect to the ground state are given in Table IV and shown graphically in Fig. 2. Doubly negative or positive charge states were not found stable. For all Fermi level positions the interstitial configurations are higher in formation energy than the B_{Si}-Si_i defect.
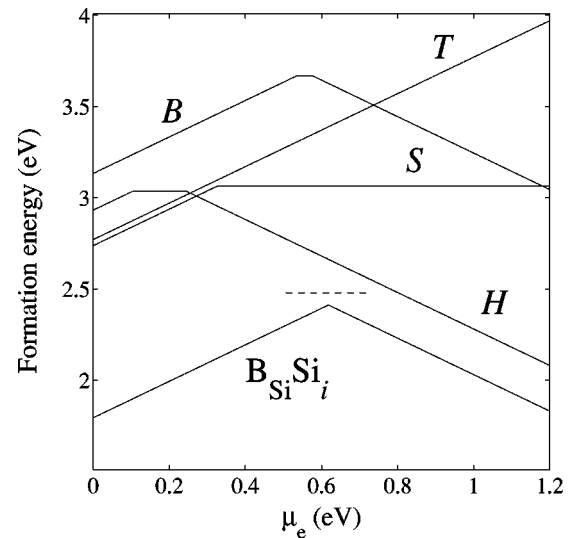

FIG. 2. Formation energies for interstitial B configurations as a function of the position of the Fermi level (μ_e) as calculated with 32-atom supercells. The dashed line represents the metastable neutral charge state of the B_{Si}-$Si_i(C_{3v})$ defect. The energy zero for the formation energy is the formation energy of B_{Si}^{1-} at $\mu_e = 0$ eV. The experimental band gap value is used as the upper limit of the Fermi level.

For the $1+$ charge state we find three metastable states, S, T, and H, with energies within 0.2 eV about 1 eV above that of ground state. In the S configuration the B and Si atoms share the same lattice site and are oriented along the $\langle 100 \rangle$ direction. The B-Si bond length is 1.87 Å and the symmetry of the defect C_{2v}. The electronic level $\mu_e(1+/0)$ is found in the gap at $E_v + 0.33$ eV. For the T site the T_d symmetry is preserved with a 2% inward relaxation of the nearest-neighbor Si atoms. The T site is stable only for the $1+$ charge state, which suggests that this structure is stabilized by removing electrons from dangling bonds. A similar explanation has been given for the stability of the $Si_i(T^{2+})$ defect.[26] The hexagonal H site is higher in energy by ~ 0.2 eV compared to the S configuration. The ionization level $\mu_e(1+/0)$ of H is at about $E_v + 0.10$ eV. About a 5% inward relaxation of the nearest-neighbor ions is observed for H in all its charge states. The formation energy difference between the T^+ and H^+ configurations agrees well with the value given by Zhu,[12] but the energy difference of these defects with respect to the ground state differs by ~ 0.4 eV as compared with his value.

For the 0 charge state we find the S and H sites, which are very close in energy (within 0.05 eV), as metastable ones. The geometry of the S site is unaltered in comparison with the $1+$ charge state. For H a ionization level $\mu_e(0/1-)$ is found at about $E_v + 0.25$ eV. For the H^0 configuration the formation energy with respect to the ground state is about 0.6 eV, which is close to the value of 0.4 eV given by Zhu et al.[9]

For the $1-$ charge state the H site is the only important one, and it is only about 0.2 eV above the ground state. The bond-centered site B was found to be the highest metastable state in energy for all the charge states. This is due to the compressive stress induced on the nearest-neighbor Si atoms. The two nearest atoms of B are displaced outwards ~ 0.7 Å and the symmetry of the configuration is D_{3d}.

An interesting feature concerning the structures is the crossing of the formation energy curves: in p-type material the S^{1+} or the T^{1+} positions are the lowest in energy, whereas in n-type material the H^{1-} position is the most likely metastable defect. The implications are addressed in Sec. III E.

D. Boron diffusion, thermal equilibrium

The impurity diffusion can be divided to two main mechanisms: the defect-mediated mechanism and the concerted exchange mechanism. According to Nichols et al.[5] B diffuses predominantly as an interstitial impurity. B diffusion occurs through a kick-out reaction and a subsequent channel diffusion.[6–8] Experimental values for the activation energy of diffusion under equilibrium conditions have been reported in the range 3.2–3.9 eV for intrinsic Si.[28] Under equilibrium conditions the activation energy (Q^*) can be expressed as a sum of the formation (E_f) and migration (E_m) energy for the diffusing species

$$Q^* = E_f + E_m. \tag{4}$$

In the previous studies the migration energy has been estimated negligible[5] or found to be rather small 0.2–0.3 eV.[9,12] A substantial contribution to the activation energy comes therefore from the formation energy.

Following the work of Nichols et al.,[5] the formation energy for the interstitial B can be defined with respect to substitutional B in the absence of any other defects

$$E_f(B_i) = E_f(Si_i) + [E(B_i) - E(B_{Si} - Si_i)]$$
$$= 2.06 + 2\mu_e + 0.74 \sim 2.8 \text{ eV} + 2\mu_e, \tag{5}$$

where $E_f(Si_i)$ is the formation energy of a Si self-interstitial (Table II), $E(B_i)$ the total energy of B at an interstitial position, and $E(B_{Si} - Si_i)$ the total energy of the system of well separated substitutional B and Si self-interstitial (Tables III and IV). The bracketed term in Eq. (5) corresponds to the energy which is obtained by exchanging the positions of an interstitial Si_i and a substitutional B_{Si}. Above we have assumed the T^{2+} configuration for the self-interstitial which is according to Lee et al.[26] the lowest-energy configuration for Si_i as $\mu_e < 0.7$ eV. The corresponding lowest-energy configuration for B_i is the T^{1+} site. B_{Si} was calculated in the negative charge state. Finally, we use the value of 0.2 eV for E_m. We thus obtain

$$Q^* \sim 3.0 \text{ eV} + 2\mu_e \tag{6}$$

for Fermi level positions below the midgap. At midgap $Q^* \sim 4.2$ eV, which agrees well with the earlier calculated values[5,12] but is slightly higher than in experiments.[28]

The formation energy diagram (Fig. 2) suggests that the energy of exchanging a Si interstitial and a substitutional B is lower if electrons are trapped during the exchange process. For Fermi level positions near midgap this means that the substitutional B atom is exchanged to the S or H interstitial positions, which are lower in formation energy than the T position. However, in thermal equilibrium the frequency of electron and hole capture is not high, and therefore this kind of mechanism is improbable.

E. Boron diffusion, excess of self-interstitials

The thermal activation energy of B diffusion is significantly lower in conditions where excess self-interstitials are present, for example after electron irradiation[1] or in processes where transient release of vacancies and interstitials is important.[27] After electron irradiation the thermal activation energy for the isolated interstitial B in p-type boron-doped Si is 0.6 eV.[1] Furthermore, the diffusion is strongly enhanced under optical or electrical injection.[27] To calculate the activation energies for diffusion under injection of excess point defects Nichols et al.[5] developed a theory of nonequilibrium diffusion. The component of the B diffusivity attributable to the interstitial-mediated mechanism has the activation energy

$$Q' = E_{inj} - \Delta E + E_m, \tag{7}$$

where E_{inj} corresponds to the activation process of the interstitial injection itself, $-\Delta E$ is the energy difference $[E(B_i) - E(B_{Si} - Si_i)]$ as in Eq. (5), and E_m the migration energy of the diffusing species. Since we want to calculate the activation energy corresponding to the measured value after electron irradiation, we assume that the lattice already contains excess Si interstitials so that E_{inj} can be neglected. E_m is assumed to be 0.2 eV as in Sec. III D. $-\Delta E$ corresponds to the energy cost of the kick-out reaction

$$B_{Si}^{1-} + Si_i^{2+}(T) \rightarrow (B_{Si}\text{-}Si_i)^{1+} \rightarrow Si_{Si} + B_i^{1+}(T), \qquad (8)$$
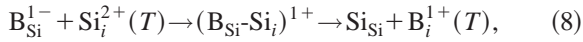
where the lowest-energy configurations are used. The reaction energy is obtained by using the binding energies and the relative formation energies of Tables III and IV, respectively. For the activation energy of B diffusion via this reaction we find $Q' = 0.98 - 0.24 + 0.2 \sim 0.9$ eV, a slightly higher value as compared with experiments.[1] The result is valid for Fermi level below the midgap.

Capturing of electrons or holes under optical or electrical injection may affect the activation process of B first through the formation energy. As an example we assume that the Fermi level is below the midgap, there are excess self-interstitials and also mobile electronic charge in the lattice. If two electrons are trapped, the kick-out process may take the form

$$2e^- + B_{Si}^{1-} + Si_i^{2+}(T) \rightarrow (B_{Si}\text{-}Si_i)^{1-} \rightarrow Si_{Si} + B_i^{1-}(H), \qquad (9)$$
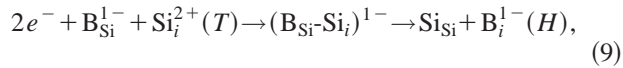
where the lowest-energy configurations corresponding to the charge states are used. For this reaction we obtain $Q' = 0.24 - 0.27 + 0.2 \sim 0.2$ eV. The $-\Delta E$ part of the activation energy is practically suppressed and the diffusion is enhanced as found in experiment.[27] The weakness of the reaction (9) is the assumption that the atomic configurations should change on a timescale of electron trapping and detrapping, which may be unrealistic.

The second mechanism enhancing the diffusion under optical or electrical injection is the lowering of the migration energy through carrier captures. The different charge-assisted mechanisms have been proposed by Bourgoin and Corbett.[13] Charge-assisted transport can be expected if the defect or the diffusing species have different possible charge states which have different migration barriers or minimum energy positions. For B in the true interstitial position or in the interstitialcy position we indeed find different minimum energy positions: for the $1+$ charge state the tetrahedral and the interstitialcy positions compete for the lowest-energy configuration, whereas for the $1-$ charge state the hexagonal position is the lowest-energy one. For a wide range of Fermi level positions the neutral charge state is energetically less favorable than the negative one as can be seen in Fig. 2. Cyclic trapping of two electrons and two holes could therefore lead to lowering of E_m and thereby to increased diffusion. This is in agreement with the results by Troxell and Watkins[3] obtained at cryogenic temperatures under minority-carrier injection in p-type electron-irradiated Si. According to them charge-assisted migration of B occurs through trapping of two electrons and holes. Charge-assisted migration has been proposed by Lee et al.[26] also for Si self-interstitials. However, extensive studies of the migrational barriers should be performed to complete the picture.

IV. CONCLUSIONS

We have performed first-principles calculations for interstitial B in Si for all the possible charge states and bonding configurations. The formation of electrically compensating defects containing one B atom in an otherwise pure crystal is energetically unfavorable. However, in the presence of Si self-interstitials the formation of interstitial B related defects is expected. The lowest-energy structure, the substitutional B interstitial Si pair, corresponds to the negative-U defect found in experiment. In the thermal equilibrium conditions the activation energy for B diffusion was found to be about 3.0–4.2 eV for Fermi level positions below the midgap. The excess Si interstitials lower considerably the activation energy of B diffusion to a value of the order of 1 eV. Our calculations for the charged metastable interstitial states of B are in agreement with the Bourgoin transport mechanism for the charge-assisted B diffusion.

Recently, two articles closely related to our work appeared [B. Sadigh et al., Phys. Rev. Lett. **83**, 4341 (1999); W. Windl et al., Phys. Rev. Lett. **83**, 4345 (1999)]. We have checked our results against the identified interstitial configurations and the formation and binding energies reported in these Letters. For the stable and metastable configurations of B_i the present results agree closely with those reported in the two Letters. Only in two cases (T^0 and S^{1-}) we do not find a metastable minimum whereas Sadigh et al. do. The formation and binding energies agree within 0.2 eV (0.4 eV) with the values of Windl et al. (Sadigh et al.). The relative stability of the configurations in Table IV is also the same as that reported by Sadigh et al. It should be noted that for comparing our results with those of Windl et al., we added a term correcting for the defect charge-neutralizing background interaction in the same manner as they did.

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