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Energetics of transient enhanced diffusion of boron in Ge and SiGe

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We study the energetics and migration of boron in Ge and ordered, Si-epitaxial $Si_{0.5}Ge_{0.5}$ via first-principles calculations, considering specifically the interstitial-mediated mechanism previously associated with B transient enhanced diffusion in Si. The temperature dependence of the migration length λ of a B-interstitial complex is calculated from migration barriers and dissociation energies. In Ge, the migration length hardly depends on temperature, while in SiGe it is similar to that in Si, due to the preference of B for Si-like equilibrium sites and diffusion paths. The calculated solubility of B in Ge is similar to that in Si, about 1×10^{19} cm^{-3}. In Si-epi strained SiGe the solubility is instead enhanced by two orders of magnitude, and in free-standing SiGe by one order of magnitude. The calculated activation energy for B diffusion in Ge ($\sim$4.5 eV) is considerably higher than in Si ($\sim$3.6 eV) and in our model SiGe, in accordance with recent experiments.

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I. INTRODUCTION

Substantial diffusion of dopants is known to occur during thermal processing of Si-based integrated microelectronic circuits.[1–4] As Ge and the SiGe alloy rapidly gain interest in Si-based electronics, an understanding of the energetics and diffusion of dopants therein becomes increasingly important. In this paper we analyze, by means of first-principles calculations, the behavior of B, the principal acceptor species of Si technology, in pure Ge and in the simplest realization of SiGe, the ordered 50% alloy, assumed to be grown epitaxially on Si.

It is generally accepted[2–4] that the transient enhanced diffusion (TED) of B in Si is related to the presence of a high nonequilibrium concentration of self-interstitials (henceforth denoted I). The atomic-level origin of TED is the much higher diffusivity of B–self-interstitial complexes compared to that of isolated substitutional B, as brought out by recent studies.[5,6] The ''easy'' diffusion event consists, in essence, in the formation of a B-I pair and its migration. The formation is a diffusion-limited process[3,7] whose rate has an upper bound $g=4\pi a D_{\mathrm{I}} C_{bulk} C_{\mathrm{I}}/C_{\mathrm{I}}^{*}$, with C_{I} being the actual concentration of self-interstitials, C_{I}^{*} being their equilibrium concentration, D_{I} being their diffusivity, C_{bulk} being the bulk density of lattice sites, and a being the capture radius of the interstitial by the impurity. Clearly, a high nonequilibrium concentration of self-interstitials favors the formation of the complexes of interest. The complex then diffuses by an interstitialcy mechanism, producing a net migration of the impurity. The event ends with pair dissociation and the ensuing escape of the self-interstitial.

The migration mechanism is efficient as long as the concentration of self-interstitials is high, and its transient character stems from the concurrent relaxation of the interstitial concentration towards its equilibrium value. Operating at conditions for which the transient time is shorter than the inverse of g, the possibility that a given impurity undergoes more than one migration event at a time can be neglected. In such conditions, the final B concentration exhibits an exponential tail[3,4] decaying over the mean length λ a pair may travel before dissociating, whereby λ is related to the diffusivity D_p and lifetime τ of the complex by

$$\lambda \propto \sqrt{D_p \cdot \tau}. \tag{1}$$

Since migration and dissociation[8] are Arrhenius-like processes with respective probabilities $\exp(-E_{\mathrm{migr}}/k_B T)$ and $\exp(-E_{\mathrm{diss}}/k_B T)$, λ has a thermal dependence $\exp(-E_\lambda/k_B T)$, with a diffusion length exponent E_λ related[5] to the pair migration and dissociation energies [see Eq. (1)] by

$$2\,E_\lambda = E_{\mathrm{migr}} - E_{\mathrm{diss}}. \tag{2}$$

For B in Si, λ was experimentally measured[4] to obtain $E_\lambda \simeq -0.4\pm0.2$ eV. Theoretical estimates[4–6] match E_λ well enough (and vacancy-assisted B diffusion is known[9] to be sufficiently unlikely) to give credit to the above atomistic migration mechanism for B in Si. Here we provide estimates of the B migration length in Ge and SiGe within the same diffusion mechanism just outlined. Our estimates are derived from *ab initio* calculations of total energies, and thence formation, migration, dissociation, and activation energies of the defect configurations that, according to the mentioned atomistic model, are relevant for B diffusion. We validate a selection of the migration paths by a search using the nudged-elastic-band method.[10,11] While λ has not been measured yet for Ge or SiGe, our predicted formation energies, hence solubilities, and activation energies for diffusion can be compared with existing experiments, and turn out to be in reasonable agreement with data for Si and recent results for Ge.

II. METHOD

We simulate the relevant defects in zincblende-structure (occasionally tetragonally-distorted) periodic supercells containing 64 sites, and compute energies and forces within density-functional theory (DFT) in the local-density approximation (LDA), using the plane-wave pseudopotential method as implemented in Vienna Ab-initio Simulation Package (Ref. 11) and the ultrasoft pseudopotentials[12] provided therewith. The plane-wave basis is cut off at 208 eV, and Brillouin-zone integration is done on Monkhorst-Pack $4\times4\times4$ grids. The calculated lattice parameter of Ge, 5.62 Å, is used in all Ge calculations. $Si_{0.5}Ge_{0.5}$ is modeled as a tetragonally distorted zincblende epitaxial to Si, i.e. having the theoretical in-plane lattice constant of Si, 5.39 Å. The *c/a* ratio is found to be 1.035. The (ordered) alloy is stable, with a calculated formation enthalpy of -0.06 eV per f.u.

The formation energy of a defect configuration is as usual $E_f = E_{\rm tot} - \Sigma_s n_s \mu_s + Q\mu_e$ where $E_{\rm tot}$ is the total energy of the configuration, μ_s and $\mu_{\rm F}$ are the chemical potentials of, respectively, the atoms in the cell and the electrons added to or removed from it. In Ge calculations, $\mu_{\rm Ge}$ is the Ge bulk energy; in SiGe, we assume Si-rich conditions (the alloy is supposed to be grown epitaxially on Si), i.e., use $\mu_{\rm Si} = \mu_{\rm Si}^{\rm bulk}$ and impose $\mu_{\rm Si} + \mu_{\rm Ge} = \mu_{\rm SiGe}$ to get $\mu_{\rm Ge}$. Indeed, as the formation enthalpy of the alloy is very small, $\mu_{\rm Ge}$ is almost identical to its bulk value. For B, we calculate absolute formation energies, and solubilities vs temperature[13] adopting as solubility limit the metallic phase B_{50}. As discussed below, we find almost the same formation energy for B in Ge and Si, whereas in Si-epi SiGe the formation energy of B is lower by as much as 0.5 eV.

The formation energies of charged defects depend on $\mu_{\rm F}$, i.e., the Fermi energy in our $T=0$ calculation, which for a given set of impurities and defects determines self-consistently the doping conditions imposing charge neutrality. A thermal ionization level $\epsilon(q/q')$ is defined as the difference in total energy for the defect in charge states q and q' with full relaxation of atomic coordinates, i.e., equivalently, as the value of $\mu_{\rm F}$ at which charge state q' becomes favored over charge state q. Setting the position of these thermal ionization levels relative to band edges is a subtle, and in principle unsolved, issue. The levels are of course related to, but by no means identical with, the density-functional eigenvalues pertaining to defects states; when using electronic eigenvalues one should, in addition, confront the notorious LDA gap inaccuracy, and quasiparticle calculations would be needed. As we use thermal levels defined in terms of ground-state density-functional total energies, it seems natural to compare them with a gap estimate obtained[14] using the definition of gap[15] and the very same technical procedure used for defects, namely as a total-energy difference of undefected bulk cells with excess and deficit electrons.[14] (This procedure is similar in spirit, and in terms of quality of the results, to the "*k*-points gap" used recently[16] by Segev and Wei.) We found that the resulting values are usually in fair agreement with experiment; this is the case of Ge whose gap is estimated to be 0.67 eV. We therefore consider a comparison of the ionization-levels positions with the estimated gap to be justified, and we deem this procedure less arbitrary and more consistent than, e.g., using the experimental gap or the DFT eigenvalues in the comparison.

For charged defects, a neutralizing background eliminates electrostatic divergencies, and a correction $Q^2\alpha/(2\epsilon L)$, in a.u., with α being the relevant Madelung constant, ϵ being the dielectric constant of Ge or SiGe (the former taken to be 16, the latter an interpolated value of 14), Q being the charge state, and L being the linear cell dimension, accounts for the spurious interactions between periodic images.[17] The next correction term (monopole-quadrupole interaction) is $\sim o(L^{-3})$, and found of order 0.01 eV for simple defects in Si.

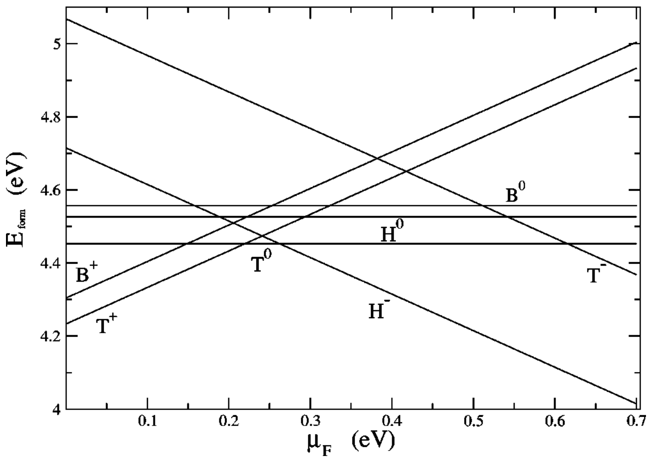

FIG. 1. Formation energy of *B* interstitials in Ge (*T*, tetrahedral; *B*, bond center; *H*, hexagonal).

III. RESULTS AND DISCUSSION

A. Boron in Ge: Energetics and diffusion

Substitutional, negatively charged $B_{\rm Ge}$ is the lowest-energy state of B in Ge. Its formation energy at $\mu_{\rm F}=0$ is 0.72 eV; the ionization level $\epsilon(0/-)$ is found resonant with the valence-band top (actually almost coincident with it), which is reasonable in view of the typical error bar of ±0.05 eV. Assuming zero formation entropy, the resulting chemical concentration limit of B in Ge at $T=1000$ K is 1.1×10^{19} cm^{-3}, accounting for acceptor charging.[13] For reference, our calculated formation energy of the neutral B acceptor in Si is 0.71 eV, the ionization level $\epsilon(0/-)$ is 0.03 eV (0.045 experimental), and the concentration at $T=1000$ K is 1.0×10^{19} cm^{-3}, in reasonable agreement with experiment given the neglect of formation entropy.

In Fig. 1 we show the formation energies for B interstitial configurations in Ge as a function of the Fermi level. These energies are over 3.5 eV higher than that of $B_{\rm Ge}$, completely ruling out "stand-alone" B migration. The singly positive tetrahedral site is the most stable in *p*-type conditions, while at $E_{\rm F}\sim0.25$ eV the lowest-energy configuration becomes neutral tetrahedral, with a marginal stability range, and then singly negative hexagonal site B (nearly a negative-*U* effect with change of site). This is analogous to the behavior reported for Si,[18] as we also verified directly. Also similarly to B:Si, the self-interstitial–boron complexes are found rather lower in formation energy, as shown in Fig. 2. The pair's lowest-energy configuration has C_{3v} symmetry, with the substitutional B coupled to the self-interstitial sitting on the trigonal axis towards the tetrahedral site. In the negative charge state, the self-interstitial distorts sideways, and the symmetry becomes C_{1h}. We also considered the B-I split-

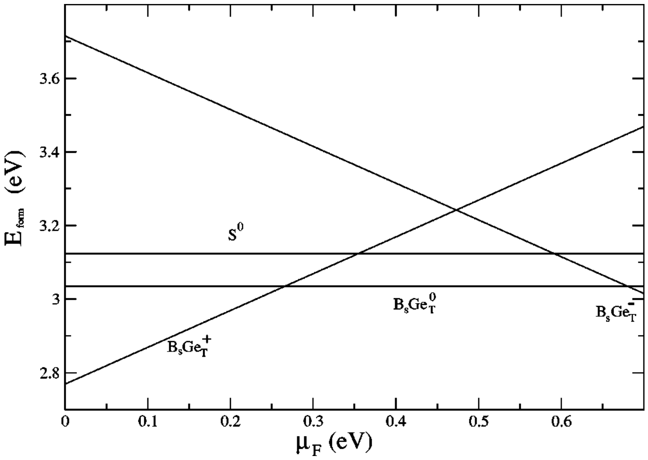

FIG. 2. Formation energy of B-I pairs in Ge. The pair has essentially the classical C_{3v} configuration (only the negative configuration distorts to C_{1h} symmetry). S is the [100] split interstitial.

TABLE I. Formation energy (eV) of B-related defects in SiGe at $\mu_F = 0$.

B_H^0	B_H^-	B_{T4Si}^+	B_{T4Si}^0
3.93	4.24	3.67	4.08
B_{T4Si}^-	B_{Si}-Si_I^+	B_{Si}-Si_I^0	B_{Si}-Si_I^-
4.57	3.06	3.41	4.08
B_{Ge}-Ge_I^+	B_{Ge}-Ge_I^0	B_{Ge}-Ge_I^-	B_{Ge}-Si_I^+
3.29	3.48	4.11	3.12
$B_{Ge}-Si_I^0$	$B_{Ge}-Si_I^-$	$B_ISi_I^+$ (S^+)	$B_ISi_I^0$ (S^0)
3.31	3.98	3.80	3.86

interstitial configuration (denoted by S) along a [100] direction, which is always neutral, and somewhat closer in energy to the B-I pair than in Si.

From the total energies of the various high-symmetry configurations, we can determine the dominant diffusion mechanism; the possible intermediate configurations are basically slight variations of the bond-center and hexagonal paths.[6] From Fig. 2 we see that over almost all of the gap only the positive and neutral pairs are stable, so we only consider the migration of these two pairs. For the positive pair, whose energy depends on E_F, we choose p-type conditions (i.e., $E_F = 0$), and assumed it to dissociate into negative B_{Ge} and the $Q = +2T_d$ self-interstitial. The latter has a formation energy[19] of 3.06 eV, and the positive pair has a formation energy of 2.77 eV, from which we obtain a binding energy for the positive pair of $E_{bind}(B-Ge_I^+) = 0.39$ eV. The barrier energy for the migrative step of the isolated T^{++} interstitial through a hex site was calculated to be[19] of 0.71 eV. The dissociation energy is then $E_{diss}(B-Ge_I^+) = 1.1$ eV. For the positive complex, the energy barrier for B-I migration is 1.3 eV through the hexagonal site and 0.9 eV through the bond-center. This preference for the bond-center-like path is analogous to that found in B:Si (Refs. 5,6) for the positive pair (although generally the hex is entropically favored as a pair sees four equivalent hex paths opposed to a single bond-center). To achieve *net* motion with successive bond-center steps it is necessary to either take a hex step, or to reorient the B-I pair. The energy barrier for the latter process may be grossly estimated as the energy of the B-I pair to the S_0 split interstitial. As this is about 0.5 eV (Fig. 2), the rate-limiting event is the bond-center diffusion. Assuming then the bond-center path, we read off Eq. (2) the exponent $E_\lambda = –0.1$ eV for the diffusion length. This value is well below the typical experimental error on E_λ for B:Si, so we conclude that a temperature dependence should be hardly observable for I-assisted B diffusion in Ge in p-type conditions.

We now come to the neutral pair, and view it as composed by the B_s^- and the T^+ self-interstitial. Using the formation energy[19] for the latter, 3.16 eV, the binding energy of the neutral pair is 0.22 eV. (The pair energy depends no more on E_F.) The dissociation migrative steps of the self-interstitial is through the hexagonal site, and the energy barrier for this step is 0.62 eV, yielding a total dissociation energy of 0.84 eV. The lowest barrier for the pair migration step through the hexagonal site is 0.87 eV (practically identical to that, 0.9 eV, on the bond-center path). Then we get $E_\lambda = 0.02$ eV, i.e., essentially zero, confirming the prediction of marginal to absent temperature dependence of I-assisted B diffusion in Ge.

From the same data just discussed, we easily calculate the activation energies for B diffusion in Ge in the form of a B-I complex; these turn out to be 4.30 eV for the positively charged complex (relevant in p-type conditions) and 4.53 eV for the neutral complex (probably relevant in intrinsic and postimplant conditions). The latter data agree well with a recent experimental result[20] of 4.6±0.3 eV. Our theoretical value for B in Si is 3.60 eV, which also compares satisfactorily with 3.75 eV experimental.[4] Thus, B diffusion is appreciably less efficient in Ge than in Si, due in equal parts to larger formation and migration energies.

B. Boron in SiGe: Energetics and diffusion

In SiGe, the possible configurations of the relevant complexes proliferate considerably compared to Ge or Si because many configurations actually occur in different variants (e.g., two distinct T_d sites with Ge or Si neighbors), and two distinct self-interstitial species are involved. The same goes for self-interstitial variants (e.g., Si-Ge, Ge-Ge, Si-Si dumbbells on Si- or Ge-substituting sites, etc.), which are described in detail elsewhere.[19]

In SiGe, negatively charged Ge-substituting B has the lowest formation energy, 0.19 eV at $\mu_F = 0$, i.e., over 0.5 eV lower than in either Ge or Si. The chemical concentration limit is thus much higher, 1.8×10^{21} cm^{-3} at $T = 1000$ K. This results in part from epitaxial strain: indeed, in unstrained, free-standing SiGe, the formation energy is 0.35 eV, with a concentration limit of 2.0×10^{20} cm^{-3} at $T = 1000$ K. This is, in any case, a good order of magnitude higher than in either Si or Ge.

Negative Si-substituting B is 0.28 eV higher than Ge-substituting B, a difference presumably attributable to the preferred binding of B to Si than to Ge. The (much higher) formation energies of the other B-related defect configurations considered here ($\mu_F = 0$ is assumed for charged defects) are reported in Table I. In Fig. 3 we also show the

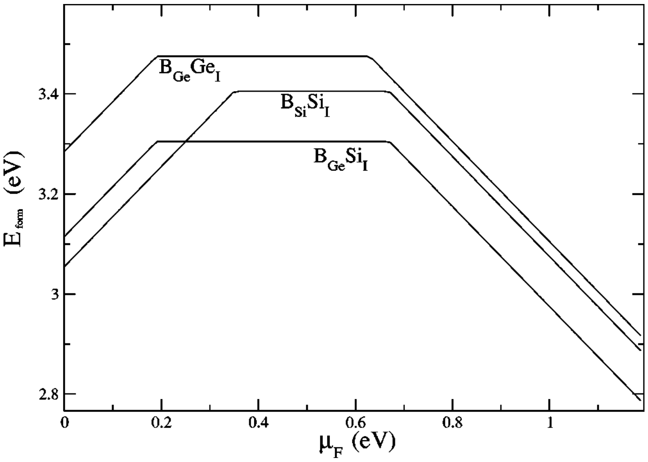

FIG. 3. Formation energy of B-I pairs in SiGe.

energy of B–self-interstitial pairs vs the Fermi level. Here we assume a supersaturation of Si self-interstitials, as is generally the case in implanted or surface-oxidized complementary metal-oxide semiconductor samples: this allows us to neglect most configurations involving $\mathrm{Ge_I}$, whose formation probability is marginal compared to that of Si-containing pairs. An exception is $\mathrm{B_{Ge}}$-$\mathrm{Ge_I}$, because it may be formed during the migration event of a pair.

We are now in a position to evaluate an interstitialcy diffusion mechanism analogous to that considered for Ge and Si. Migration mechanisms in the alloy are complicated by the fact that the pair may change its composition as it diffuses, for example, from a Ge site to a Si site, as summarized in Fig. 4. Fortunately, in the ordered alloy, the independent intermediate configurations for each pair are just two and nondegenerate. From the data in Table I, we find that the hex path is energetically favored over the bond-center, with a migration barrier of 0.62 eV ($\mathrm{B_{Ge}}$-Si), 0.45 eV ($\mathrm{B_{Ge}}$-Ge), and 0.52 eV ($\mathrm{B_{Si}}$-Si).

While not considering thermal disorder explicitly, we can estimate the effects of the disorder generated by the pair migration. A Si interstitials binding to $\mathrm{B_{Ge}}$ produces an antisite $\mathrm{Si_{Ge}}$ upon B migration via the reactions in the lower panel of Fig. 4; final configurations are only slightly higher in energy (~ 0.1 eV), so that the reactions are not energetically impeded. Comparing the *isolated* defects involved, we find that the energy drops by 1.5 eV as the B-I complex becomes asymptotically separated from the $\mathrm{Si_{Ge}}$ antisite. Also, the cost of a pair of noninteracting complementary antisites, i.e., the cost of a Si-Ge site exchange, is estimated[19] in ~ 10 meV ($\mathrm{Si_{Ge}}$ and $\mathrm{Ge_{Si}}$ have $E_{\mathrm{form}} = -1.65$ eV and 1.67 eV, respectively), and that an antisite neighboring a pair changes the migration energy of the latter by ~ 10 meV. Thus, disorder along the pair migration path should modify negligibly the migration energetics, and the following considerations still hold in the presence of disorder.

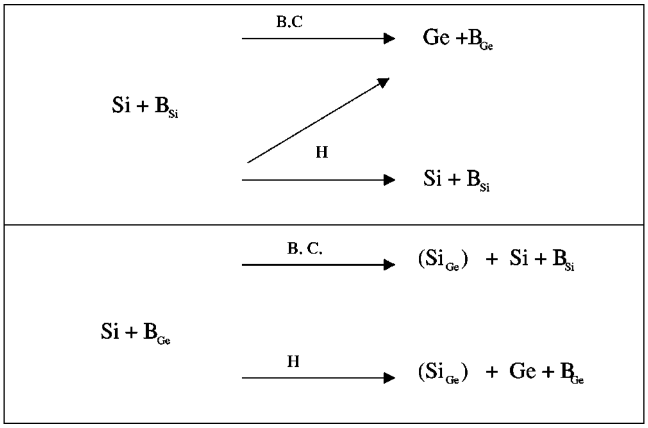

FIG. 4. Schematic of the various possible B-I diffusion reactions in SiGe. Antisite defects may form as a result of the diffusion process (see text for discussion).

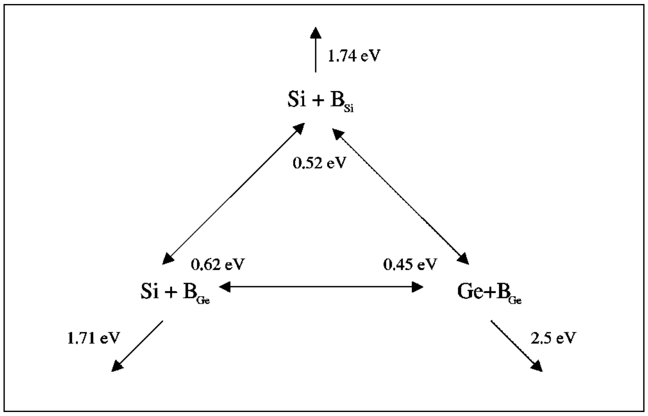

FIG. 5. Schematic of the B-I diffusion mechanism in SiGe. Internal numbers are migration barriers, outer ones are dissociation energies. The migration barriers are very similar, while the dissociation of the Ge pair energetically unfavorable.

We restrict ourselves to neutral pairs, which we view as the assembly of negative substitutional B and a positive self-interstitial. As discussed in detail elsewhere, the lowest-energy positive self-interstitials are T_d-site Si with four Si nearest neighbors, and the analogous Ge self-interstitial, both with formation energy[19] of 2.30 eV. From the migration barrier through a hex site (1.25 eV and 1.8 eV for, respectively, the Si and Ge self-interstitials[19]) and the pair binding energies of 0.37 eV ($\mathrm{B_{Si}}$-Si), 0.46 eV ($\mathrm{B_{Ge}}$-Si), and 0.49 eV ($\mathrm{B_{Ge}}$-Ge), we get the dissociation energies, and Table I provides the migration barriers. For convenience we summarize the result in Fig. 5: the key features are the similarity of the pair migration barriers and the higher dissociation barrier for the $\mathrm{B_{Ge}}$-Ge pair, ~ 2.5 eV vs ~ 1.7 eV for the other pairs. We can then neglect the relatively unlikely $\mathrm{B_{Ge}}$-Ge dissociation, and estimate the diffusion length exponent from an average dissociation and migration energy for the other two complexes, obtaining $E_\lambda \simeq -0.58$ eV, a value rather close to that obtained for B:Si.

The activation energy for B diffusion (in the neutral pair form) is found to be 3.83 eV, closer to Si (3.75 eV experimental, 3.60 eV theoretical) than to Ge (4.6 eV experimental, 4.5 eV theoretical). This results mostly from the migration energy in SiGe being similar to that in Si and smaller than in Ge. Qualitatively, this relates directly to (a) the preponderance of Si-pairs dissociation, with Ge pairs playing essentially the role of intermediate states, and to (b) the fact the diffusion through the hex site is Si-like, in that B actually transits through the asymmetric ring binding preferentially to Si atoms. (Specifically, in the saddle configuration, B sits in the plane of the three Si atoms in the hex ring, and decidedly off-center from the (111) axis through the crystallographic *H* site, so as to have two out of three Si ring members at 2.17 Å and one at 2.74 Å, while two out of three Ge members are at 2.27 Å and one at 2.84 Å.)

IV. SUMMARY

In summary, we have studied from first principles the energetics and migration energies of B in Ge and SiGe, and its consequences for solubility and diffusion activation. The solubility of B in Ge is similar to that in Si, about 1×10^{19} cm^{-3}; in (Si-epi strained) SiGe the solubility is instead enhanced by two orders of magnitude, and in free-standing SiGe by one order of magnitude. The calculated activation energy for B diffusion in Ge ($\sim$4.5 eV) is considerably higher than in Si ($\sim$3.6 eV) and in our model SiGe ($\sim$3.8 eV), in accordance with recent experiments. The migration length λ of a B-I complex in Ge is found to hardly depend on temperature, while in SiGe that dependence is similar to that of Si. The similarity of the λ energy dependence and of the activation energies is due to the preference of B for Si-like equilibrium sites and diffusion paths, and the preferred complex formation with Si interstitials.

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