First-principles study of the origin of retarded diffusion of boron in silicon in the presence of germanium

Liguo Wang and Paulette Clancy*
School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York 14853, USA

C. S. Murthy
IBM Corporation, East Fishkill, New York 12533, USA
(Received 18 December 2003; revised manuscript received 24 May 2004; published 20 October 2004)

Dopant diffusion plays an important role in the formation of ultrashallow junctions. To avoid unwanted transient enhanced diffusion of dopants, especially boron, other species (e.g., Ge, C, N, and F) are introduced into the Si substrate. Here, *ab initio* calculations have been carried out using a density functional theory code, DFT++, to investigate the origin of the experimentally observed retardation of boron diffusion in SiGe alloys. The formation energies of individual Si, B, and Ge point defects, and Si-B, Ge-B, and Si-Ge pair defects were calculated. Based on these calculations, the energetics of Si:Ge:B systems suggest that one mechanism to retard boron diffusion involves the effect of Ge atoms to decrease the number of available Si self-interstitials by increasing the migration energy and, concomitantly, to increase the migration energy of boron atoms. Our results also show that it is difficult for a Ge interstitial to approach a substitutional boron atom compared with a Si self-interstitial.

DOI: 10.1103/PhysRevB.70.165206 PACS number(s): 31.15.Ar, 66.30.Dn, 07.05.Tp

I. INTRODUCTION

The semiconductor industry has been following a long-term trend to increase transistor density by decreasing feature sizes on a chip for more than three decades. According to the International Technology Roadmap for Semiconductors (ITRS),[1] the minimum feature size (MPU physical gate length), which decreased from 10 μm in 1970 to 0.35 μm in 1995, and is proposed to decrease further to 0.018 μm in 2010 with related increases in device performance.With continued downscaling of Si device dimensions into the sub-100 nm range, ultrashallow junctions (i.e., $\sim$10 nm of drain extension junction depth) will be required within the nextdecade (i.e., 2010) to meet the goals of the ITRS.[1]

Of the common dopants in Si, boron is the only practical *p*-type dopant, but its use is hampered by the ability to form shallow junctions. The biggest problem associated with boron-doped ultrashallow junction formation is the anomalous diffusion of boron during annealing, arising from point defects introduced during ion implantation.[2,3] This effect is more pronounced in the "tail" region and is called transient enhanced diffusion (TED). In order to minimize boron TED, different methods have been proposed, such as fast-ramp rapid thermal annealing (RTA),[4,5] laser thermal processing (LTP),[6–9] and impurity doping (incorporating other species into the Si substrate).[10–16] Unlike fast-ramp RTA and LTP, where the time during which the system is at elevated temperatures ($>700\,^\circ$C) is decreased, impurity doping methods attempt to decrease the diffusivity of boron and thus suppress TED. Experiments showed that the boron diffusivity in strained as well as relaxed SiGe alloys decreased rapidly with Ge content up to 40% Ge (Refs. 10–16) but increased again at high Ge levels.[12,16] As pointed out by Paine *et al.*,[10] this must involve a changeover of dominant mechanism at some composition. At low Ge concentrations, boron diffusion is dominated by an interstitial-based mechanism.[10,17] At high Ge levels, it has been suggested that boron diffuses mainly *via* vacancies. Recently, Uppal *et al.* has called this suggestion into question based on his observation that there was little increase in boron diffusivity from 50% to 100% Ge.[16]

There are a number of potential explanations for the slower boron diffusion in SiGe alloys. The reduction was initially attributed to the effect of compressive strain on the self-interstitial concentration[11] since the self-interstitial formation energy increases linearly with increasing biaxial compressive strain and decreases with increasing tensile strain.[18] Recently Kuo *et al.* made detailed comparisons of boron diffusion in compressively strained SiGe with that in-relaxed SiGe with the same composition, and in tensile-strained Si with that in relaxed Si using inert-ambient furnace annealing of $Si_{1-x}Ge_x$ layers (where $x\approx 0.10$ and $x\approx 0.20$) grown epitaxially on various relaxed $Si_{1-y}Ge_y$ ($0\leqslant y\leqslant 0.20$) substrates at 800 °C.[12,19] They found no effect of strain on diffusivity. Making the assumption that boron diffusion is mediated by positively charged point defects, Moriya *et al.* pointed out that, as Ge content increased, the band gap narrowing may change the concentration of charged interstitials and give rise to the reduction in diffusivity.[20] However, more extensive diffusion studies using iso-concentration *p*-type and *n*-type backgrounds have shown that the contributions of charged and neutral point defects to intrinsic boron diffusion (the dopant concentration is less than the intrinsic carrier concentration) are of similar magnitude.[21,22] This rules out a strong reduction in intrinsic B diffusion due to band gap narrowing. Another explanation involves the pairing of boron and germanium atoms in the alloy,[11] consistent with the fact that the two atoms introduce compensating strain in the silicon lattice. Since germanium diffuses very slowly compared to boron in Si,[23] attraction

 ©2004 The American Physical Society

between germanium and boron atoms could conceivably slow boron diffusion in the SiGe alloy. So far, no consensus on the cause for this decrease in diffusivity has been reached.

This situation provides the motivation to use atomic-level computer simulations to study the effect on boron diffusion in Si due to the presence of Ge. Since dopants dissolve in the lattice to occupy substitutional lattice sites almost exclusively, only by interacting with native point defects (interstitials and vacancies) will dopant atoms be able to exchange lattice sites and diffuse over a long distance. Both experimental observations and theoretical studies indicate that diffusion of common dopants in Si is mediated either by native point defects, namely self-interstitials (Si_i) and vacancies (Si_v), or by a direct exchange mechanism which occurs in their absence. Various diffusion mechanisms have been considered: (1) a monovacancy mechanism; (2) a direct interstitial mechanism; (3) an interstitialcy mechanism, i.e., the diffusing defect is a complex formed by an impurity atom and a Si atom sharing the same lattice site; (4) a concerted exchange mechanism, in which two adjacent substitutional atoms switch position (theoretical calculations show that this is a possibility[24,25]). It has proven difficult to give a definitive assessment of the dominant diffusion mechanism, even for self-diffusion in Si.[26,27]

Our focus here will not reside in determining which mechanism is dominant; rather, we will try to understand the effect of Ge atoms on the formation and diffusion of different defects involving B, Ge, and Si atoms. The energetic and structural properties of B, Ge, and B-Ge defects in a Si matrix will be studied using *ab initio* calculations. By comparing the energies of all the point defects, a mechanism to explain retarded boron diffusion in SiGe will be proposed. A database of the energetic static properties of these systems will be built for future tight-binding and classical potential models and for use in continuum models to simulate boron diffusion in SiGe on experimentally realistic length and time scales.

II. SIMULATION METHODS

In this study, a density functional theory code using the local density approximation (DFT-LDA), DFT++, developed by Ismail-Geigi and Arias,[28] was used to perform *ab initio* calculations of the energetics of boron in Si and SiGe alloys. DFT++ is a linear, basis-independent, matrix-based, and fully explicit formulation of generalized density function theories. The interaction between "cores" (nuclei plus core electrons) and valence electrons is described by generalized norm-conserving pseudopotentials.[29] For the exchange and correlation interaction, DFT++ uses the local density approximation (LDA) parametrized by Perdew *et al.*[30] This method has been very successful in calculating and predicting the structure of the hydrogen-boron complex in crystalline silicon.[31]

While for the sake of brevity it is not appropriate to go into great detail on the DFT++ method here, one point must be made. The calculated energy, and thus the energetic and structural properties of the system, depends critically on the sampling points and the plane-wave cutoff. Sampling points

TABLE I. Formation energies of interstitials in a Si matrix (eV).

	Tetrahedral I	Hexagonal I	(110) split I
Si_I	3.40	3.27	3.27
B_I	2.95	2.62	2.37
Ge_I	3.54	3.52	3.25
Si_IB_s	2.13	2.14	2.37
Ge_IB_s	2.48	2.47	2.55
B_IGe_s	unstable (3.21 unrelaxed)	2.79	2.55
Si_IGe_s	unstable (3.97 unrelaxed)	3.39	3.25

for Brillouin-zone integration were generated using the Monkhorst-Pack scheme[32] and convergence was checked with respect to the number of sampling points. As observed by Mercer *et al.*[33] and Li *et al.*,[34] Monkhorst-Pack parameters (3,3,3) are sufficient for the 64-atom cells. The plane-wave expansion cutoff is another crucial factor for determining the energetics of boron. To obtain an energy tolerance of 0.01 eV/atom or less, a cutoff of 16 hartree was used for the 64-atom cells. To determine the energetics of stable structures, atomic positions were relaxed until the largest forces were below 0.05 eV/Å.

III. RESULTS AND DISCUSSION

Experiments have shown that boron diffusion in Si is mediated mainly by Si self-interstitials.[17,26,27] A Si self-interstitial, migrating through the interstices of the lattice, approaches a substitutional boron atom (B_s). If the interaction causes the dopant atom to be displaced into an interstitial site, the boron atom will now migrate through the interstices as a boron interstitial (B_I) until it takes up a substitutional site again by dislodging a silicon atom from a substitutional site.

When Ge atoms are introduced into the system, there are four main kinds of locations that a Ge atom might occupy which could affect boron diffusion: (1) a substitutional location near a Si self-interstitial, thus affecting the latter's migration rate and its availability to interact with a nearby substitutional boron atom, B_s (described in Sec. III A below); (2) a substitutional location near a mobile boron interstitial which might affect its diffusion (Sec. III B); (3) a Ge atom taking the place of a Si self-interstitial (in the process becoming a Ge interstitial), thus affecting the number of Si self-interstitials available to interact with B_s atoms (Sec. III C); (4) a substitutional location near a B_s atom, which might alter the ease with which a nearby Si self-interstitial is able to displace a B_s atom (Sec. III D). This fourth location also serves to test the suggestion that stress compensation between Ge and B atoms could play a role. Summaries of the effect of the presence of a Ge atom in the four classes of situations listed above are given at the end of each section.

Several other structures, involving entities such as Si_I (Table I), B_I (Table I), Ge_s (Sec. III D), and B_s (Sec. III D), were also studied to understand more completely the energetic and structural changes introduced by the presence of

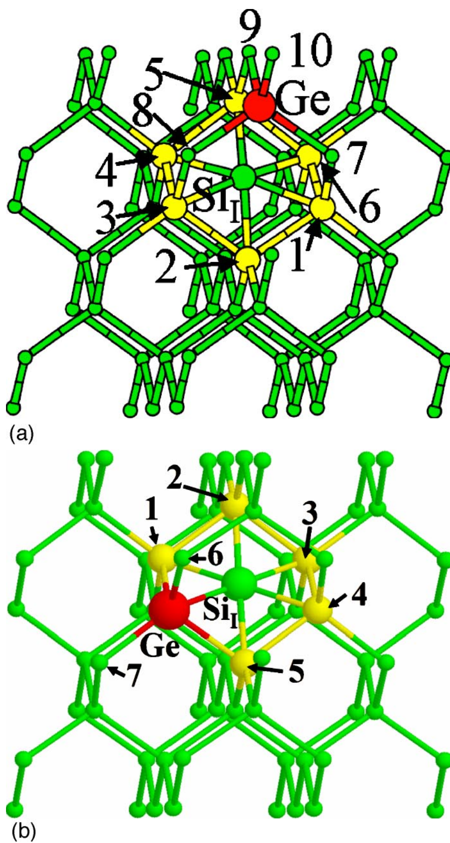

FIG. 1. (Color online) Si self-interstitials with a Ge atom involved in a Si matrix (lattice constant, 5.43 Å). (a) Relaxed tetrahedral interstitial. Red (largest grey) atom, Ge atom; large green (grey) atom, self-interstitial; yellow (large white) atoms, first NN of self-interstitial (atoms 1–6). (b) Hexagonal interstitial. Red (largest grey) atom, Ge atom; large green (grey) atom, self-interstitial; yellow (large white) atoms, first NN of self-interstitial (atoms 1–5).

Ge atoms. Due to limitations of space and in order to focus on the main goal of this paper, namely to study the effect of Ge on boron diffusion, only 12 out of the 24 structures we studied are discussed in detail in this paper. The rest of the structures are only cited in this paper to illustrate further the structural and energetic differences introduced by Ge atoms.

A. Effect of Ge on Si self-interstitial

The effect of Ge atoms on the formation energies of nearby Si self-interstitials was studied by placing a substitutional Ge atom as the first nearest neighbor (first NN) of a Si self-interstitial. All three main types of interstitials were considered: Tetrahedral, hexagonal, and 110-split interstitials.

(a) *Tetrahedral Si_IGe_s*: An Si matrix containing a tetrahedral Si self-interstitial (Si_I) with one of its first NNs replaced by a Ge atom was relaxed using statics calculations until the largest force was below 0.05 eV/Å. Interestingly, and in contrast to the situation where no Ge is present, the tetrahedral Si_I is not stable in the presence of a Ge atom. The tetrahedral Si_I moves away from the substitutional Ge atom and forms a hexagonal interstitial without the Ge atom as its first NN [Fig. 1(a)]. By moving away from the Ge atom, the formation energy, defined as the energy difference between that of a supercell containing an interstitial and a supercell of the same atoms all on substitutional positions, drops considerably, by 0.67 eV (3.97 eV vs 3.30 eV). The final bond length between Si_I and Ge is 2.89 Å, much longer than the bond length between an isolated tetrahedral Si_I and its first NNs (2.35 Å), and the Ge atom moves slightly towards Si_I, which resulted in longer bond lengths between the Ge atom and its first NNs (2.40 Å away from atoms 7, 8, and 9, 2.42 Å away from atom 10) than in an isolated substitutional Ge atom (2.38 Å). Furthermore, in contrast to an isolated hexagonal Si_I, which stays between the planes formed by atoms 1-3-5 and by atoms 2-4-6, here, the Si_I stays above both planes, evidenced by the fact that the bond length between Si_I and atoms 1, 3, and 5 is shorter than that between the Si_I and atoms 2, 4, and 6 (2.38 Å vs 2.44 Å).On the other hand, the structural difference between the relaxed tetrahedral structure and an isolated hexagonal self-interstitial structure has little effect on the formation energies (3.30 eV vs 3.27 eV), in agreement with earlier studies of Si interstitials.[35–38]

(b) *Hexagonal Si_IGe_s*: A hexagonal Si_I with a Ge atom as one of its first NNs is shown in Fig. 1(b). After relaxation, the bond length between Si_I and its surrounding Si atoms changes very little (2.36 Å between Si_I and atoms 1, 2, 4, 5, and 2.37 Å between Si_I and atom 3). However, the effect of the nearby Si interstitial on a substitutional Ge atom (Ge_s) is quite different from an isolated Ge_s, where all the Si atoms relax outward with bond lengths of 2.38 Å (calculated in this work). Here, atoms 1 and 5 are constrained by the presence of the Si_I and could not move outward. To reach an energy minimum, the Ge atom moves up toward atom 6, which resulted in a shorter bond length between Ge and atom 6 (2.36 Å) and longer bond lengths between Ge and atoms 1 and 5 (2.54 Å). This is also evidenced by a larger bond angle (64.5° for angle 1-Si_I-Ge and 5-Si_I-Ge) than that observed in either the hexagonal Ge interstitial [Sec. III C (b)] or self-hexagonal interstitial cases (63°, calculated in this work). At the same time, the Ge atom moves toward atom 7 (2.39 Å, close to the bond length between Ge and Si_I, 2.41 Å). This structural difference, again, makes only a small difference in the formation energy (0.12 eV higher than that of the isolated hexagonal self-interstitial, 3.40 eV vs 3.27 eV).

(c) *Si-Ge split interstitial*: For a Si 110-split interstitial, two Si atoms share one lattice site. When one of these two self-interstitials is replaced with a Ge atom, two heterogeneous interstitial atoms share the same lattice site (Fig. 2). The Ge-Si split interstitial bond length is 2.47 Å, the same as that observed in the Ge tetrahedral interstitial case (Sec. III C (a)]. Due to the different sizes of the Ge and Si atoms, the bond is asymmetric with respect to the plane perpendicular to the bond direction. The Si_I is 2.49 Å away from atoms 1 and 2, while Ge_I is 2.51 Å away from atoms 1 and 2. For the same reason, the bond between Ge_I and atom 3 is longer than that between Si_I and atom 4 (2.37 Å vs 2.34 Å). This structural difference has virtually no effect on the formation energy (3.25 eV, only 0.02 eV lower than that of the split self-interstitials).

In an interstitial diffusion mechanism, the interstitials prefer to diffuse through (110) channels, following the path con-

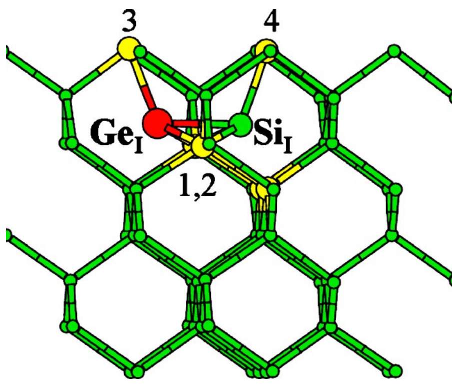

FIG. 2. (Color online) Ge-Si split interstitial in a Si matrix. Red (largest grey) atom, Ge atom; large green (grey) atom, self-interstitial; yellow (large white) atoms, first NN of interstitials.

necting the tetrahedral and hexagonal sites as shown in Fig. 3.[39–42] The formation energy difference between the tetrahedral and hexagonal interstitials is defined as the migration energy, E_m. For self-diffusion without any Ge atoms present, the migration energy is 0.13 eV (calculated in this work). However, in the presenceof a Ge atom, we were unable to find a stable structure involving a tetrahedral self-interstitial and a Ge atom. Even if a stable structure exists, its formation energy should be close to the value we calculated (3.97 eV) since the difference between the formation energies of the relaxed and unrelaxed tetrahedral self-interstitials (and boron interstitials) is less than 0.1 eV (calculated in this work). Therefore, the large energy difference between the tetrahedral and hexagonal self-interstitials when a Ge atom is present (0.6 eV) can be considered as representative of the migration energy of self-interstitials in the presence of Ge atoms. The higher migration energy should significantly decrease the diffusion of self-interstitials, thus decreasing the number of available interstitials to mediate boron diffusion; this result reveals one possible explanation for the retarded diffusion of self-interstitials in SiGe alloys. Furthermore, the energy difference between the split interstitial and the hexagonal interstitial is 0.14 eV (Table I) when a Ge atom is involved, compared to the almost zero energy difference (Table I) when no Ge atom is present. These results suggest that the Ge-Si_I pair is more difficult to dissolve into mobile interstitials compared to 110-split interstitials.

B. Effect of substitutional Ge on boron interstitials

After considering the effect of Ge atoms on the diffusion mediator, Si self-interstitials, the diffusion of boron interstitials in the presence of substitutional Ge atoms was studied. As above, three kinds of boron interstitials were studied: tetrahedral, hexagonal, and split interstitials.

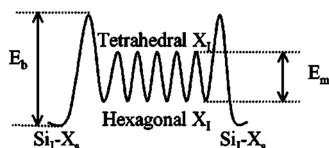

FIG. 3. Schematic of migration along the 110 channel. E_m is the migration energy and E_b is the energy barrier for an initial kick out. X is the test species which can be Si, Ge, or B.

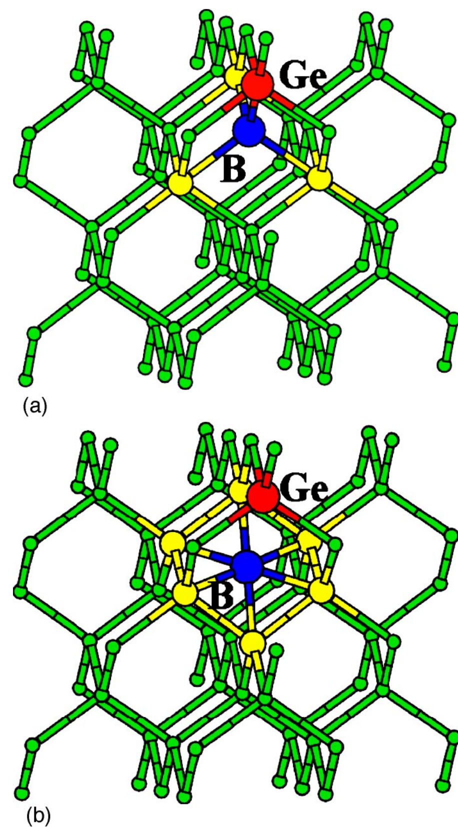

FIG. 4. (Color online) Tetrahedral boron interstitial with a Ge atom involved in a Si matrix. (a) Unrelaxed tetrahedral interstitial, (b) relaxed hex-away structure. Blue (large dark) atom, B atom; red (large grey) atom, Ge atom; yellow (large white) atoms, first NN of the interstitial.

(a) *Tetrahedral* B_IGe_s: As observed for a tetrahedral self-interstitial with a Ge_s as its first NN [Sec. III A (a)], the tetrahedral boron interstitial is also not stable in the vicinity of a Ge_s atom [Fig. 4(a)]. The boron atom moves away from Ge and forms a hexagonal interstitial without the Ge_s as its first NN, as shown in Fig. 4(b). The B-Si bond length is the same as the value of 2.20 Å observed in the case of an isolated hexagonal boron interstitial (data not shown). In addition, the arrangement of the boron interstitial and its surrounding Si atoms is the same as that of an isolated hexagonal boron interstitial. The distance between the B and Ge atoms is 3.51 Å, much larger than that observed for a hexagonal self-interstitial with a Ge atom as its first NN [2.89 Å, Sec. III A (b)]. Thus, there is little interaction between the boron interstitial and the Ge atom. The formation energy should then be expected to be close to that of an isolated hexagonal boron interstitial; this, indeed, is the case (2.67 eV vs 2.62 eV). This behavior is the same as that observed in the case of a tetrahedral self-interstitial with a Ge atom as its first NN, whose formation energy is just 0.03 eV higher than that of the isolated tetrahedral Si_I.

(b) *Hexagonal* B_IGe_s: When one first NN of a hexagonal boron interstitial was replaced by a Ge atom, the boron

TABLE II. Bond lengths between a hexagonal boron interstitial and a Ge atom in a Si matrix (Å).

B-Ge	B-1,5	B-2,4	B-3	Ge-1,5	Ge-6	Ge-7	1-2, 4-5	3-2,4
2.464	2.238	2.141	2.100	2.368	2.375	2.405	2.337	2.365

atom moved away from the Ge atom. The bond length between the boron atom and the surrounding atoms decreased from the Ge atom to atom 3 (2.46 Å between B and Ge, 2.24 Å between B and atoms 1 and 5, 2.14 Å between B and atoms 2 and 4, 2.10 Å between B and atom 3), as shown in Table II. The bond lengths between the boron atom and atoms 2, 4, and 3 are shorter than the B-Si bond length (2.19 Å) in the isolated hexagonal boron interstitial case (data not shown). The same phenomenon was observed in the B_s-Ge_s case (described below): The boron atom moved away from the Ge atom to form stronger bonds with Si atoms than with the Ge atom. At the same time, this movement gives more room for the Ge atom to relax, which resulted in the bond length between the Ge atom and atom 7 being a little longer than that in the case of an isolated substitutional Ge atom (2.40 Å vs 2.38 Å) and the bond lengths between the Ge atom and atoms 1 and 5 being almost identical to that in the isolated substitutional Ge atom case (2.37 Å vs 2.38 Å). The bond length between the Ge atom and atom 6 is the same as that in the isolated substitutional Ge atom case since the bond is perpendicular to the hexagonal interstitial plane. The formation energy of the hexagonal boron interstitial with a Ge atom as its first NN is 2.79 eV, 0.17 eV higher than that of the isolated hexagonal boron interstitial without any Ge atom involved (2.62 eV, Table I). This is similar to the hexagonal self-interstitial with a Ge atom as its first NN [described above in Sec. III A (b)], where the formation energy is 0.12 eV higher than that of the isolated hexagonal self-interstitial without any Ge atom involved (calculated in this work). These results again confirm that the B-Si interaction is stronger than the B-Ge interaction.

(c) *B-Ge split interstitial*: The B-Ge split interstitial is shown in Fig. 5(b). As in the B-Si split interstitial case (data not shown), the B atom is much closer to the lattice site than the Ge atom. The B-Ge bond length is longer than the B-Si bond length observed in the B-Si split interstitial case (2.02 Å vs 1.97 Å). The bond lengths between the Ge atom and its surrounding Si atoms are longer than those observed in a Ge-Si split interstitial case [2.38 Å vs 2.34 Å; 2.57 Å vs 2.51 Å, Sec. III A (c)]. The bond lengths between the B atom and atoms 3 and 4 are the same as observed in the B-Si split interstitial case, the bond length between the B atom and atom 2 is also very close to that observed in the B-Si split interstitial case (1.98 Å vs 1.99 Å). Due to the weaker B -Ge and Ge-Si bonds, the formation energy of the B-Ge split interstitial is 0.18 eV higher than that of the B-Si split interstitial. This is similar to the observation for the hexagonal boron interstitial with a Ge atom as its first NN case [described in Sec. III B (b) above], where the formation energy is 0.17 eV higher than that when no Ge is present.

The addition of a Ge atom causes the formation energy of boron interstitials to increase in a similar manner to that observed for a Si self-interstitial with a Ge atom as its first NN. The migration energy of boron increases from 0.33 eV (calculated in this work) in a Si matrix to 0.42 eV when one Ge atom becomes a first NN of the boron interstitial. Thus the diffusion of mobile boron atoms is somewhat suppressed.

C. Effect of Ge interstitials in Si

In SiGe alloys, a fraction of any interstitials present in the lattice will be Ge atoms which may also play a role in boron diffusion. Here we will investigate the effect of Ge *interstitials* in Si in order to understand the different role of Ge and Si interstitials in the boron diffusion process.

Ge interstitials (Figs. 6 and 2) resemble Si self-interstitials (data not shown) in terms of structural properties. However, there are some changes in the bond length and the formation energy due to the larger size of Ge atoms, as described below.

(a) *Tetrahedral Ge_I*: The presence of a tetrahedral Ge interstitial introduces compressive strain into the Si matrix. The surrounding Si atoms relax away from an interstitial Ge

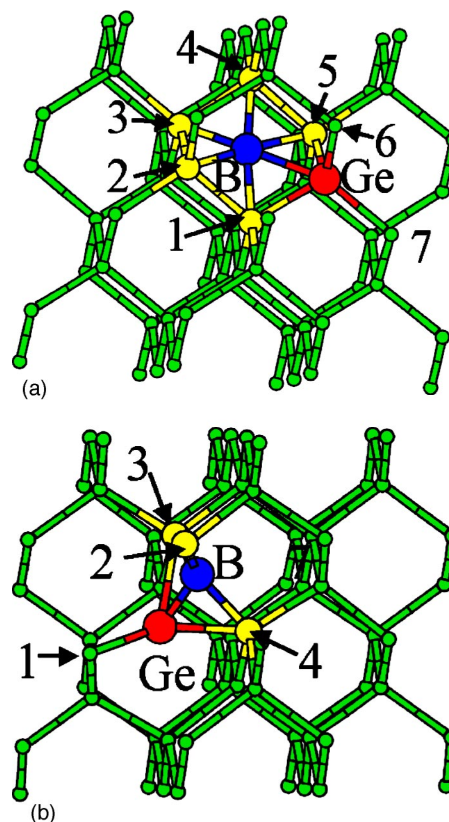

FIG. 5. (Color online) Boron interstitials close to a Ge atom involved in a Si matrix. (a) Hexagonal interstitial, (b) split interstitial. Blue (large dark) atom, B atom; red (large grey) atom, Ge atom; yellow (large white) atoms, first NN of the boron interstitial.

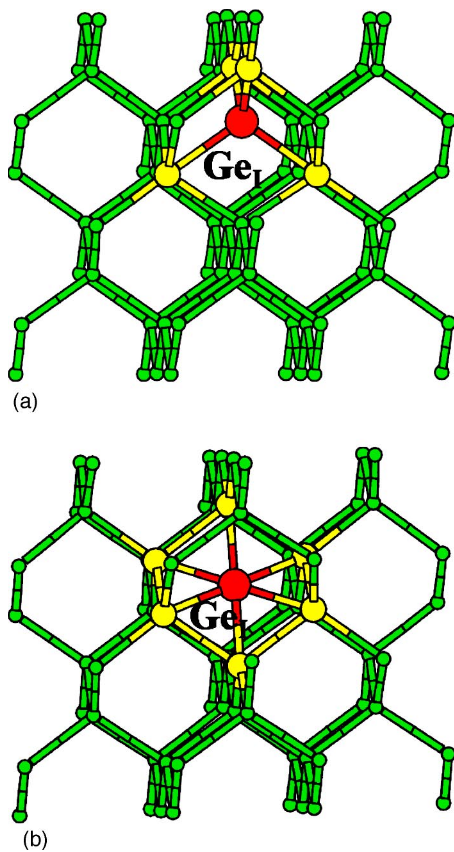

FIG. 6. (Color online) Tetrahedral and hexagonal Ge interstitials in a Si matrix. (a) Tetrahedral interstitial, (b) hexagonal interstitial. Red (large grey) atom, Ge atom; yellow (large white) atoms, first NN of the Ge interstitial.

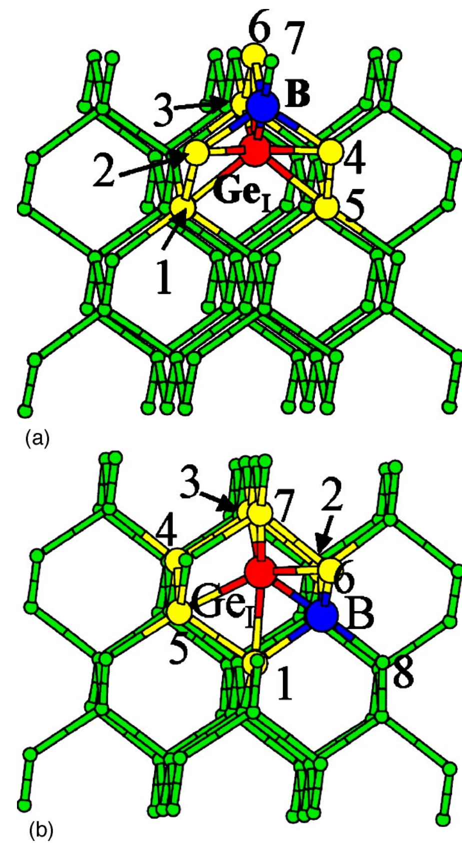

FIG. 7. (Color online) Ge interstitials with a boron atom involved in a Si matrix. (a) Tetrahedral interstitial, (b) hexagonal interstitial. Blue (large dark) atom, B atom; red (large grey) atom, Ge atom; yellow (large white) atoms, first NN of Ge atom.

atom, as observed in the relaxation of Si atoms surrounding a substitutional Ge atom (data not shown). The Ge-Si bond length is 2.47 Å and the Si-Ge_I-Si bond angle is the same as observed in the tetrahedral self-interstitial case (109.5°, calculated in this work). The formation energy of the Ge tetrahedral interstitial is 3.54 eV, 0.14 eV higher than the formation energy of the tetrahedral self-interstitial (calculated in this work), presumably resulting from the size difference between Ge and Si atoms.

(b) *Hexagonal* Ge_I: The hexagonal Ge interstitial also pushes away surrounding Si atoms, resulting in a Ge-Si bond of 2.40 Å, considerably longer than that between a self-interstitial and surrounding Si atoms (2.25 Å, calculated in this work). As a result, the bond length between the Si atoms surrounding the Ge atom is longer than that for a hexagonal self-interstitial case (2.51 Å vs 2.35 Å). The surrounding atoms not only move outward along the Ge-Si bond direction, but also move away from each other.

The Si-Ge_I-Si angle is 63.3°, larger than that of the Si -Si_I-Si in the hexagonal self-interstitial case (62.9°, calculated in this work). The angle between the surrounding Si atoms is 108.5°, smaller than 109.6° in the hexagonal self-interstitial case (note that these six atoms are not in the same plane). The change of the angles between the surrounding Si atoms has the same sign as observed in the hexagonal boron interstitial case (data not shown) where the surrounding Si atoms move towads the boron atom and away from each other at the same time. Here, however, the magnitude of the changes is smaller and thus the energy change is not as large. The formation energy of a Ge hexagonal interstitial is 3.52 eV, 0.25 eV higher than that of the hexagonal self-interstitial (calculated in this work), while (for comparison) the formation energy of the hexagonal boron interstitial is 0.65 eV lower than that of the hexagonal self-interstitial.

(c) *Tetrahedral* Ge_IB_s: In the case of an isolated Ge tetrahedral interstitial in a Si lattice, the bond lengths between the Ge atom and its four equivalent first NNs is 2.47 Å, and 2.75 Å for the six second NNs. When one of the first NNs of the tetrahedral Ge_I is replaced by a substitutional boron atom, the Ge atom is pulled towards the boron atom, the B-Ge bond length is 2.06 Å [smaller than that in the B_s -Ge_s case (2.16 Å, calculated in this work), and larger than that in the case of a B-Ge split interstitial (2.02 Å, calculated in this work)]. The bond lengths between the Ge atom and its three first NNs increase from 2.47 Å to 2.52 Å. Furthermore, three more bonds are formed between the Ge atom and atoms 2, 4, and 6 [Fig. 7(a)], with bond lengths of 2.53 Å. This relaxation pattern is the same as that observed in the case where a tetrahedral self-interstitial has a B_s atom as its first NN (data not shown). But the bond lengths are significantly longer here due to the larger size of Ge atoms (2.07 Å vs 1.99 Å, 2.52 Å vs 2.48 Å, 2.53 Å vs 2.49 Å).

Because of the extra bonds formed, the formation energy is 2.48 eV, which is 1.06 eV lower than that of an isolated Ge tetrahedral interstitial (as calculated here). Due to the larger size of the Ge atoms, the formation energy decrease is smaller than that observed in the tetrahedral self-interstitial with a Ge atom as its first NN case (1.27 eV).

(d) *Hexagonal* Ge_IB_s: The Ge hexagonal interstitial with a substitutional boron atom as its first NN is shown in Fig. 7(b). The Ge atom is pulled towards the boron atom, the Ge-B bond length is 2.06 Å, and the bond between the Ge atom and atom 4 increases from 2.39 Å in the isolated Ge hexagonal interstitial case to 2.87 Å. The bond lengths between Ge, and rest of the surrounding atoms (atoms 1, 2, 3, and 5) are 2.50 Å. Two more bonds are formed between the Ge atom and atoms 6 and 7 with bond lengths of 2.60 Å and 2.58 Å, respectively. As for the atoms around the boron atom, the bond lengths between the boron atom and atoms 1, 2 (2.26 Å), and 6 (2.18 Å) are longer than those between the boron atom and atom 8 (2.07 Å). This is probably due to the fact that atoms 1, 2, and 6 have formed bonds with the Ge atom, which therefore has less freedom to move towards the boron atom. In contrast, atom 8, which receives little influence from the Ge atom, can move freely to the boron atom.

The relaxation pattern is the same as that observed in the case of a hexagonal self-interstitial with a boron atom as its first NN with longer bond lengths around the Ge interstitial (data not shown). Furthermore, the boron atom moves away from the interstitial (towards atom 8) compared with that in the self-interstitial with a boron atom as its first NN case (data not shown). Thus the bond length between the boron atom and atom 8 is shorter, and the bond lengths between the boron atom and atoms 1, 2, and 6 are longer here. The formation energy of the Ge hexagonal interstitial with a substitutional boron atom as its first NN is 2.47 eV, which is the same as that of the Ge tetrahedral interstitial with a boron atom as its first NN [as described in Sec. III C (c) above].

In SiGe alloys, if a Ge interstitial is unable to kick out a B_s atom to make it a mobile interstitial, B_I, boron diffusion will be decreased. As shown in Table I and described above, the formation energies of Ge_IB_s are about 0.3 eV higher than those of Si_IB_s. Thus it is somewhat more energetically difficult for a Ge interstitial to approach a B_s atom, thus decreasing the number of mobile boron interstitials. However, this does not imply that it is difficultfor a Ge interstitial close to a B_s atom to kick it out. In the kick-out event, the system starts with a B_s-Si_I (or B_s-Ge_I) complex, passes through a transient state, and reaches the final B_I-Si_s (or B_I-Ge_s) state. The energy difference between the initial configuration and the transient state is defined as the kick-out energy barrier, which indicates how easily the kick-out will occur. Due to the expense of calculations needed to search for the transient state, the energy difference between the initial and final states was calculated instead of the kick-out energy barrier. This energy difference controls how many kick-out events will occur. In SiGe, the energy difference between a Ge-B split interstitial and a hexagonal B_I with a Ge_s is around 0.3 eV, which is smaller than that between a Si-B split interstitial and a hexagonal B_I in Si (0.5 eV, see Table I). This indicates that it is easier for a Ge interstitial close to a B_s atom to kick out the B_s than would occur in Si. But this does not lead to enhanced boron diffusion. Due to the higher migration energy of boron in SiGe, the boron interstitial will be constrained to the vicinity around the Ge atom. This will be shown clearly in subsequent molecular dynamics simulations of the behavior of a classical (Stillinger-Weber) potential in a similar situation.[43]

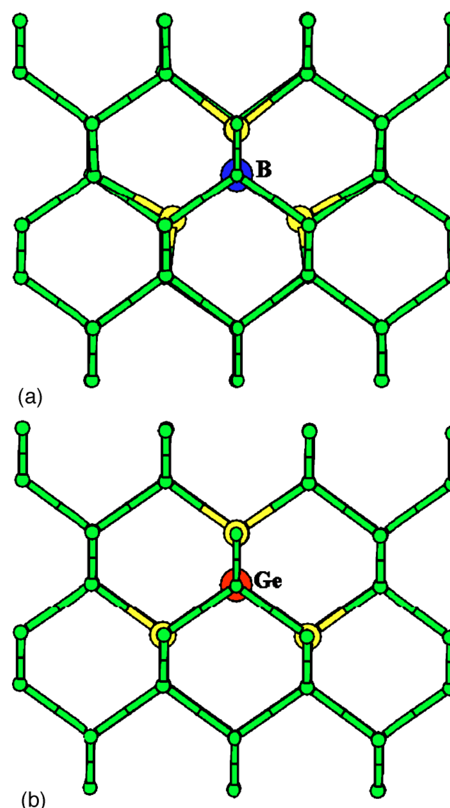

FIG. 8. (Color online) Relaxation of substitutional boron and Ge atoms in a Si matrix. (a) B_s in Si. Blue (large dark) atom, B atom; yellow (large white) atoms, first NN Si atoms. (b) Ge_s in Si. Red (large grey) atom, Ge atom; yellow (large white) atoms, first NN Si atoms.

D. The interaction between B_s and Ge_s and the role of compensatory stress relief

Dopant atoms dissolve in the lattice to almost exclusively occupy substitutional lattice sites, making necessary a study of the interaction between nearby substitutional B and Ge atoms. This may also be used to test the suggestion that stress compensation between Ge and B atoms could play a role in the retarded boron diffusion in SiGe alloys. The following positions were investigated: (1) in which the Ge atom is far away from the B atom (i.e., no B-Ge interaction is involved); (2) the Ge atom is a first NN of B_s; (3) the Ge atom is a second NN of B_s; (4) the Ge atom is a third NN of B_s; (5) the Ge atom is a fourth NN of B_s.

Compared to a substitutional boron [B_s, Fig. 8(a)], a substitutional Ge atom [Ge_s, Fig. 8(b)] introduces compressive strain into a Si matrix. To minimize the system's total energy, the surrounding Si atoms relax outwards. As shown in Fig. 8(b) and Table III, the first shell Si atoms (first NN) relax

TABLE III. Relaxation of Si atoms around Ge_s and B_s in a Si matrix (Å).

	First NN	Second NN	Third NN	Fourth NN
Perfect crystal	2.351	3.840	4.502	5.430
Ge_s	2.378	3.846	4.502	5.430
Ratio of relaxation	1.011	1.002	1.000	1.000
B_s	2.078	3.769	4.494	5.430
Ratio of relaxation	0.884	0.982	0.998	1.000

away from the substitutional Ge atom by about 1% of the regular Si-Si bond length. This relaxation is much smaller than that of a B_s in a Si matrix, as shown in Fig. 8(b) and Table III. There is little relaxation beyond the third shell of Ge_s.

The cohesive energy of B_s, Ge_s and the B_sGe_s complex was calculated using the following equation:

$$E(\text{cohesive}) = -[E(X_m\text{Si}_{n-m}) - E(\text{Si}_n) \times (n-m)/n], \quad (1)$$

where $E(X_m\text{Si}_{n-m})$is the total energy of $(n-m)$ Si atoms with m test species X, and $E(\text{Si}_n)$ is the energy of n Si atoms. The cohesive energies of a Ge_s atom and a B_s atom are 6.24 eV and 5.23 eV, respectively.

The interaction between a Ge_s and a B_s is shown in Fig. 9. The Ge atom moved towards the B atom and the bond length is decreased to 2.16 Å. However, the cohesive energy is close to the sum of the cohesive energy of an isolated Ge_s and an isolated B_s, shown in Table IV. Thus there is no energetic benefit in bringing the two atoms together. The reason may lie in the following analysis: Although the total number of defective bonds decreases from 8 to 7 as a Ge_s and a B_s become first nearest neighbors, the bond length (and hence the bond strength) is changed. Three B-Si bonds (2.06 Å) are shortened by 0.01 Å compared with an isolated B_s, and three Ge-Si bonds (2.41 Å) are enlarged by 0.03 Å compared to an isolated Ge_s. Furthermore, the B-Ge bond length is 2.16 Å, much larger than the B-Si bond length. In

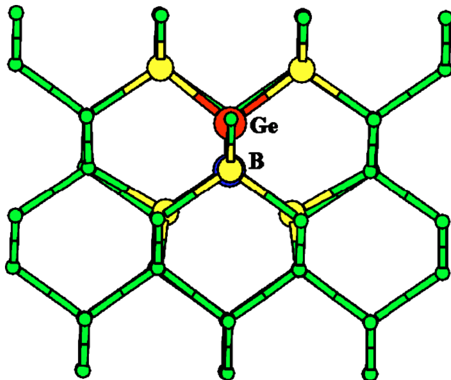

FIG. 9. (Color online) Interaction between B_s and Ge_s in a Si matrix (Ge_s at the first NN position). Blue (large dark) atom, B atom; red (large grey) atom, Ge atom; yellow (large white) atoms, first NN of a Ge_s or a B_s.

TABLE IV. Interaction between Ge_s and B_s in a Si matrix (eV).

Position of Ge_s	First NN	Second NN	Third NN	Fourth NN
Cohesive energy (eV)	11.40	11.45	11.45	11.45

this complicated interaction, the benefit of bringing two opposing defect centers is counterbalanced by the extra energy required to create defective bonds of B-Si, Ge-Si, and B -Ge. Three other initial positions of the Ge and B atoms were also investigatedwith the cohesive energies shown in Table IV. The cohesive energy increases very little (0.05 eV), i.e., the system energy becomes energetically a little more stable as the separation between Ge and B increases to second NN. Thus, the interaction between a Ge_s and a B_s atom has little effect on the energy of a B_s, and is unlikely to contribute much to the retardation of boron diffusion in SiGe alloys.

From Table I, it is evident that the energetics of interstitials involving a boron atom and a Ge (or Si) atom have significantly lower formation energies than that of the isolated corresponding interstitials. This is in good agreement with elasticity theory that two defects of opposite strain will attract each other, and that this interaction of elastic fields will lower the crystal energy. However, there is little interaction between the substitutional Ge and boron atoms. The reason may lie in the local environment around the defects. If the atoms can move relatively freely, the interaction between the two defects of opposite strain will be strong and the total energy of the system can be lowered. If the atoms are restricted to lattice sites, the energy gained by the bringing together the two defects of opposite strain will be small and will be counterbalanced by the distortion of other bonds. For the same reason, the formation energy of a vacancy with a Ge as its first NN is lowered where the formation energy of a vacancy with a Ge as its second NN is increased. These calculations then suggest that strain compensation is not important.

IV. CONCLUSIONS

A study of the energetics of interstitial defects in Si involving boron and Ge atoms has revealed information that may help explain retarded boron diffusion in SiGe alloys. These results are summarized in Table I. We conclude the following.

(1) The presence of Ge increases the migration energy of B_I.

The migration energy is defined as the energy difference between the tetrahedral and hexagonal interstitial sites which connects the diffusion path of interstitials. When a Ge atom becomes a first NN of a boron interstitial, the migration energy increases from 0.33 eV (in a Si matrix) to 0.42 eV. Although the absolute value of the difference (0.09 eV) is not large, we contend that this difference is significant (it is around 1/4 of the migration energy of self-interstitials in a Si matrix).

Furthermore, the tetrahedral boron interstitial is not stable in the presence of Ge_S, and moves away to form a hexagonal boron interstitial without the Ge atom as its first NN. The energy of this relaxed structure is 0.08 eV lower than the hexagonal boron interstitial with a Ge atom as its first NN. Our calculations predict that boron interstitials prefer to stay close to the Si rather than the Ge atom (creating lower formation energies in Si).

(2) The presence of Ge increases the migration energy of a self-interstitial, and decreases the number of self-interstitials available to mediate boron diffusion

The migration energy of a Si self-interstitial increases significantly, from 0.13 eV (in Si) to 0.58 eV (in SiGe). Just as was observed for boron interstitials in the presence of Ge_s, the Si tetrahedral interstitial moves away from substitutional Ge atoms to a hexagonal interstitial without the Ge atom as its first NN. It is difficult for a self-interstitial to pass a substitutional Ge atom, thus decreasing the total number of effective self-interstitials which can assist substitutional boron atoms to diffuse.

(3) Ge_I has difficulty in approaching and kicking out B_s into an interstitial position (B_I).

As shown in Table I, the formation energies of Ge_IB_s are about 0.3 eV higher than those of Si_IB_s. Thus it is somewhat more energetically difficult for a Ge interstitial to approach a B_s atom, thus decreasing the number of mobile boron interstitials.

Of the three observations given above to explain the experimentally observed retarded boron diffusion, the second one (increasing the migration energy of Si_I) is energetically the most important. The migration energy of Si_I increased from 0.13 eV in Si to 0.58 eV in SiGe, which is much more significant than the migration energy increase for a B_I atom (0.42 eV in SiGe vs 0.33 eV in Si) and is likely to contribute the most to the retardation of boron diffusion. The first observation (increasing the migration energy of B_I) is also important as will later be confirmed by molecular dynamics simulations with a classical Stillinger-Weber potential.

ACKNOWLEDGMENTS

The authors would like to thank Professor Tomas Arias for providing us with the DFT++ *ab initio* code and the Cornell Center for Material Research (CCMR) for computing facility. L. W. would also like to thank the IBM Corporation for financial support through an IBM Co-operative Graduate Fellowship. Dr. Cheruvu S. Murthy is warmly thanked for numerous discussions and helpful suggestions.

*Author to whom correspondence should be addressed.

[1] *The International Technology Roadmap for Semiconductors* (International Sematech, Austin, Tx, 2001).
[2] W. K. Hofker, H. W. Werner, D. P. Oostheok, and N. J. Koeman, Appl. Phys. **4**, 125 (1974).
[3] T. E. Seidel, D. J. Linscher, C. S. Pai, R. V. Knoell, D. M. Mather, and D. C. Johnson, Nucl. Instrum. Methods Phys. Res. B **7/8**, 251 (1985).
[4] A. Agarwal, A. T. Fiory, and H. L. Gossmann, Semicond. Int. **22**, 71 (1999).
[5] A. T. Fiory, J. Electron. Mater. **31**, 981 (2002).
[6] A. G. Cullis, H. C. Weber, and N. G. Chew, Appl. Phys. Lett. **36**, 547 (1980).
[7] R. F. Wood, J. R. Kirkpatrick, and G. E. Giles, Phys. Rev. B **23**, 5555 (1981).
[8] J. Narayan, O. W. Holland, W. H. Christie, and J. J. Wortman, J. Appl. Phys. **55**, 1125 (1983).
[9] J. Narayan, O. W. Holland, W. H. Christie, and J. J. Wortman, J. Appl. Phys. **57**, 2709 (1984).
[10] A. D.N. Paine, M. Morookz, A. F.W. Willoughby, J. M. Bonar, P. Phyillips, M. G. Dowsett, and G. Cooke, Mater. Sci. Forum **196–201**, 345 (1995).
[11] P. Kuo, J. L. Hoyt, J. F. Gibbons, J. E. Turner, R. D. Jacowitz, and T. L. Kamins, Appl. Phys. Lett. **62**, 612 (1993).
[12] P. Kuo, J. L. Hoyt, J. F. Gibbons, J. E. Turner, R. D. Jacowitz, and D. Lefforge, Mater. Res. Soc. Symp. Proc. **379**, 373 (1995).
[13] W. T. Fang, P. B. Griffin, and J. D. Plummer, Mater. Res. Soc. Symp. Proc. **379**, 379 (1995).
[14] R. F. Lever, J. M. Bonar, and A. F.W. Willoughby, J. Appl. Phys. **83**, 1988 (1998).
[15] N. R. Zangenberg, J. Fage-Pedersen, J. Lundsgaard Hansen, and A. Nylandsted Larsen, Defect Diffus. Forum **194–199**, 703 (2001).
[16] S. Uppal, A. F.W. Willoughby, J. M. Bonar, A. G. R. Evans, N. E. B. Cowern, R. Morris, and M. G. Dowsett, Physica B **308–310**, 525 (2001).
[17] P. Kuo, J. L. Hoyt, and J. F. Gibbons, Appl. Phys. Lett. **67**, 706 (1995).
[18] A. Antonelli and J. Bernholc, Mater. Res. Soc. Symp. Proc. **163**, 523 (1990).
[19] P. Kuo, J. L. Hoyt, J. F. Gibbons, J. E. Turner, and D. Lefforge, Appl. Phys. Lett. **66**, 580 (1995).
[20] N. Moriya, L. C. Feldman, H. S. Luftman, C. A. King, J. Bevk, and B. Freer, Phys. Rev. Lett. **71**, 883 (1993).
[21] A. F. W. Willoughby, A. G. R. Evans, P. Champ, K. J. Yallup, D. J. Godfrey, and M. G. Dowsett, J. Appl. Phys. **59**, 2392 (1986).
[22] N. E. B. Cowern and D. J. Godfrey, Compel **6**, 59 (1987).
[23] J. C. Bean, A. T. Fiory, R. Hull, and R. T. Lynch, in *First International Symposium on* Si *Molecular Beam Epitaxy*, edited by J. C. Bean (Pennington, New Jersey, 1985).
[24] K. C. Pandey, Phys. Rev. Lett. **57**, 2287 (1986).
[25] A. Antonelli, S. Ismail-Beigi, E. Kaxiras, and K. C. Pandey, Phys. Rev. B **53**, 1310 (1996).
[26] P. M. Fahey, P. B. Griffin, and J. D. Plummer, Rev. Mod. Phys. **61**, 289 (1989).
[27] S. M. Hu, Mater. Sci. Eng., R. **13**, 105 (1994).
[28] S. Ismail-Beigi and T. Arias, Comput. Phys. Commun. **128**, 1 (2000).
[29] D. R. Hamann, Phys. Rev. B **40**, 2980 (1989).
[30] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, and D. J. Singh, Phys. Rev. B **46**, 6671 (1992).
[31] P. J. H. Denteneer, C. G. Van de Walle, and S. T. Pantelides, Phys.

Rev. B **39**, 10 809 (1989).
[32] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[33] J. L. Mercer, J. S. Nelson, A. F. Wright, and E. B. Stechel, Modell. Simul. Mater. Sci. Eng. **6**, 1 (1998).
[34] H. Li, P. Kohli, S. Ganguly, T. A. Kirichenko, and P. Zeitzoff, Appl. Phys. Lett. **77**, 2683 (2000).
[35] J. Zhu, T. D. dela Rubia, L. H. Yang, C. Mailhiot, and G. H. Gilmer, Phys. Rev. B **54**, 4741 (1996).
[36] P. E. Blochl, E. Smargiassi, R. Car, D. B. Laks, W. Andreoni, and S. T. Pantelides, Phys. Rev. Lett. **70**, 2435 (1993).
[37] M. Tang, L. Colombo, and T. Diaz de la Rubia, Mater. Res. Soc. Symp. Proc. **396**, 33 (1996).
[38] B. W. Roberts, W. Luo, K. A. Johnson, and P. Clancy, Chem. Eng. J. **74**, 67 (1999).
[39] Y. Bar-Yam and J. D. Joannopoulos, Phys. Rev. Lett. **52**, 1129 (1984).
[40] G. A. Baraff and M. Schlüter, Phys. Rev. B **30**, 3460 (1984).
[41] R. Car, P. J. Kelly, A. Oshiyama, and S. T. Pantelides, Phys. Rev. Lett. **52**, 1814 (1984).
[42] P. J. Kelly and R. Car, Phys. Rev. B **45**, 6543 (1992).
[43] L. Wang and P. Clancy, J. Appl. Phys. **96**, 1939 (2004).