Ab initio pseudopotential calculations of B diffusion and pairing in Si

Jing Zhu, Tomas Diaz dela Rubia, L. H. Yang, and Christian Mailhiot Lawrence Livermore National Laboratory, University of California, Livermore, California 94551

George H. Gilmer

Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974

(Received 6 February 1996)

The *ab initio* pseudopotential method was used to study the boron diffusion and pairing process in crystalline silicon. The results show that substitutional B attracts interstitial Si with a binding energy of 1.1 ± 0.1 eV. We show that B diffusion is significantly enhanced in the presence of the Si interstitial due to the substantial lowering of the migrational barrier through most likely a kick-out mechanism. The resulting mobile boron can also be trapped by another substitutional boron with a binding energy of 1.8 ± 0.1 eV, forming an immobile and electrically inactive two-boron pair along a $\langle 001 \rangle$ direction. It is also found that the pairing of these two boron atoms involves the trapping of a Si interstitial. Alternatively, two B pairs that do not trap the Si interstitial were found to be energetically unfavorable. All of these findings are consistent with experimental results. [S0163-1829(96)04631-0]

I. INTRODUCTION

Dopant diffusion in Si has been a subject of interest for many years.¹ However, despite much experimental²⁻⁴ and some theoretical work,⁵ not much is yet known about the atomic-scale migration mechanisms and paths of the dopants. These concerns are also of great technological consequence. As the minimum feature size of Si-based semiconductor devices decreases and gradually approaches the dopant diffusion length during processing conditions, lateral broadening of source-drain junctions caused by transient enhanced diffusion (TED) of implanted dopants during rapid thermal annealing becomes a critical process limiting the development of new technologies. In particular, B implantation followed by RTA at T>700 °C leads to broadening of the as-implanted B profile by several thousand Å in times as short as 15 min.⁶ Understanding and accurately modeling TED of dopants in silicon are therefore critical issues, from both a fundamental and a technological viewpoint.

Experimentally, dopant diffusion and TED can be studied by using dopant marker layers embedded in epitaxially grown Si superlattice structures. Excess Si interstitials can be injected from the surface by either surface oxidation or ion implantation. Excess vacancies can be generated using surface nitridation. The amount of dopant diffusion is monitored by measuring the dopant density profile using secondary-ion mass spectroscopy or spread resistance measurements and comparing to reference samples. In the case of B dopant in Si, several phenomena have been observed. First, B diffusion of the marker layer is significantly enhanced under oxidation or ion implantation. The amount of enhancement decreases as the marker layer is placed deeper in the bulk. On the other hand, when vacancies are injected through surface nitridation, B diffusion is initially suppressed. These results clearly show that B diffusion is dominated by the coupling of the B dopant to the Si self-interstitial. Moreover, on the basis of these experimental results, Cowern et al.²⁻⁴ have argued that B diffusion must proceed through a kick-out reaction mechanism. In this process, a Si self-interstitial (Si_i) kicks out a B_s atom into the interstitial position. This B_i is then capable of migrating long distances along the tetrahedral-hexagonal channels before falling back into a substitutional site. Second, when the local B concentration is high, an immobile and electrically inactive B region at the peak of the B density profile is commonly observed following oxidation or high dose implantation, even for B concentrations below the solid solubility limit in Si. The fraction of immobile B decreases as the depth of the marker layer increases. In the case of B ion implantation, at large enough dose, the implanted profile can also develop an immobile and electrically inactive B region, most likely due to B clustering and precipitation. However, these clusters have not been detectable in highresolution cross-section transmission electron microscopy (TEM), suggesting that the clusters only contain a few B atoms.

Due to a series of breakthrough developments in theoretical methods and rapid increases in computational power, ab *initio* methods based on the density functional theory (DFT) and the local density approximation (LDA) have been developed to the point that large systems with as many as a few hundred atoms can now be studied accurately. These calculations can then lead to a quantitative understanding of the energetics of single defects and impurities as well as their mutual interactions. Previously, Nichols, Van de Walle, and Pantelides⁵ carried out the most complete studies of the substitutional B and interstitial Si pair (B_s-Si_i) including the kick-out mechanism, using a 32-atom supercell. However, Löwdin perturbation theory⁸ was used to include plane waves from 10 to 20 Ry and in addition not all atoms were fully relaxed in the search for the low-energy configurations. No B pair result was included by Nichols, Van de Walle, and Pantelides. Tarnow, on the other hand, has studied several configurations of interstitial and substitutional B $(B_i - B_s)$ pairs⁹ in addition to B_s -Si_i pairs.^{10,11} However, small supercells together with small plane-wave cutoffs were used to determine the lowest-energy configuration and no accurate

54

4741



FIG. 1. Charge density contour plot on the $(\overline{110})$ plane through the [110]-split Si interstitial atoms. The positions of Si atoms are indicated by the filled circles.

values of the binding energies were provided.

In this paper we present results of an *ab initio* study to determine quantitatively the interaction of B_s with a Si_i and the energetics of B pairing in Si using 64-atom supercells. A fully converged set of plane waves was used to expand the electronic wave function with each atomic position fully relaxed according to the *ab initio* forces.

The rest of the paper is arranged as follows: In Sec. II, we discuss our calculational method; in Sec. III, we present our results of Si self-interstitials, B_s -Si_i pairs, as well as B-B pairs; the summary of this paper will be presented in Sec. IV.

II. METHODS

The present calculations use the density functional theory with the local density approximation to determine quantitatively the energetics of the interactions between point defects and B dopants in Si. A Ceperly-Alder¹² exchange-correlation potential parametrized by Perdew and Zunger¹³ was used. A nonlocal and norm-conserving pseudopotential constructed using the scheme of Troullier and Martins¹⁴ was used to describe the valance electron interactions with the atomic core. The nonlocal components of the pseudopotential were expressed in the separable form of Kleinman and Bylander.¹⁵ Typically, the calculations were performed in 32- and 64atom unit cells with a fixed volume corresponding to a Si-Si bond distance of 4.443 a.u. in pure Si, which is the experimental value of equilibrium distance (the theoretical equilibrium lattice constant is 1% less than the experimental value). A plane-wave basis set with a cutoff energy of 20 Ry was used to expand the electronic wave functions for both Si and B. We have tested up to 40 Ry for the plane-wave energy cutoff in 32-atom cells and found that the relative energies were all converged to within 0.1 eV.

Two to eight special **k** points in a 32-atom supercell and one to four special **k** points in a 64-atom supercell were used to sample the first Brillouin zone. The exact number of special **k** points used depends on the symmetry of the configurations and supercell sizes. Special care was taken to ensure that the **k** points used are equivalent to a $2 \times 2 \times 2$ special **k**-point mesh¹⁶ in the first Brillouin zone of a 64-atom supercell, which allows unambiguous analysis of effects of the supercell size. The **k**-point convergence has been checked by using up to a $4 \times 4 \times 4$ special **k**-point mesh in the 64-atom supercell and the relative (defect) energy differences were found to be converged within 0.1 eV in all cases tested. The conjugate gradient iterative scheme¹⁷ was used to obtain the self-consistent solutions of the one-electron Kohn-Sham equations.¹⁸ The Hellmann-Feynman theorem was used to evaluate the forces on all atoms that are allowed to move freely. The quasi-Newton method was used to find the relaxed atomic positions.

Unless specifically noted, we will report results for the 64-atom supercell. In addition, the result using a simple valence force model^{19–21} indicates supercell effects are less than 0.1 eV in the 64-atom cell system in all test cases we have studied. Therefore, we will not include the correction from the valence force model. All results presented here are for neutral systems. Charged defects are expected to play an important role, however, and their studies are currently under way.

III. RESULTS

A. Si self-interstitial

The lowest-energy configuration for a neutral interstitial Si is the $\langle 110 \rangle$ dumbbell configuration. Its charge density along the (110) plane is shown in Fig. 1. In this configuration, two Si atoms displace along the [110] direction by about one bond distance, sharing one single lattice site. The two Si atoms were found to form a weak bond, as shown in Fig. 1, with a bond distance 3% longer than the normal Si bond length. All the atoms along the [110] direction going through the interstitital site relax outward. The relaxation is largest for the first-nearest-neighbor shell, about 6% of the bond distance away from their respective lattice sites. Interestingly, contrary to our original thought, all the atoms along the [110] direction going through the interstitial site also relax outwards with the nearest-neighbor atoms relaxing the most, about 6% of the bond distance, similar to the first nearest neighbors along the [110] direction. One reason is that the two dumbbell atoms displace from the lattice site not only along the [110] direction, but also along the [001] direction, compensating for some of the outward movement for atoms along the [110] chain while at the same time also pushing out the atoms along the [110] chain. Secondly, the bond distance between the interstitial and its first nearest

(b)



FIG. 2. Charge density contour plot on a $(\overline{110})$ plane of two substitutional boron and interstitial pair complexes. Si atomic positions are indicated by open circles while boron atomic positions are indicated by filled dots. Configuration (a) has the Si interstitial next to the boron atom while configuration (b) has the Si interstitial next to another Si atom, which is a nearest neighbor to the B atom.

neighbors along the $[\overline{1}10]$ chain expands more than 5%, indicating a weaker bond, which also pushes out the $[\overline{1}10]$ chain atoms. The stress field along the $[\overline{1}10]$ chain, however, dies off much more quickly than that along the closely packed [110] chain, even though the first shell atoms all relax by a similar amount.

The formation energy $E_f(Si_i)$ of such a Si interstitial can be defined as

$$E_f(\mathrm{Si}_i) = E(\mathrm{Si}_{65}) - \frac{65}{64}E(\mathrm{Si}_{64}), \tag{1}$$

where $E(Si_{65})$ is 65-atom supercell total energy including one Si interstitial and $E(Si_{64})$ is the 64 bulk atom total energy. The formation energy is 3.2 ± 0.1 eV, in excellent agreement with the 3.3-eV result from a recent *ab initio* calculation²² using the Car-Parrinello approach,²³ among other DFT-LDA calculations.^{24–29} The Si interstitial at the hexagonal site is only about 0.1 eV higher than the $\langle 110 \rangle$ self-interstitial configuration. As a matter of fact, the hexagonal interstitial has slightly lower energy than the $\langle 110 \rangle$ selfinterstitial in a 32-atom supercell calculation. This is because the $\langle 110 \rangle$ interstitial creates larger stress field in its neighboring Si lattice than the hexagonal interstitial, which may not be able to relax fully at a smaller 32-atom supercell. A larger 64-atom supercell will allow better relaxation of the stress, which further lowers the energy of the $\langle 110 \rangle$ interstitial compared to the hexagonal one.

B. Substitutional boron

Under equilibrium conditions and the limit of low B concentration, B atoms occupy substitutional sites in a Si diamond crystal lattice. In our calculations, we have found that the first-nearest-neighbor Si atoms relax towards the substitutional B atom by about 12%. It is interesting to note that in a Si vacancy, if we only consider symmetrical relaxations without Jahn-Teller distortions, the Si atoms in the firstneighbor shell relax inward by only about 11%. This can be understood because of the short Si-B bond distance and the fact that the first shell Si atoms tend to relax more to take full advantage of the bonding energy. In the case of a vacancy, however, there is no bonding energy to be gained by inward relaxation. (The Si-Si bond between the first shell atoms is not formed if only symmetrical relaxation is allowed. However, if Jahn-Teller distortion is allowed, the symmetry will indeed be lowered and there is bonding between first-shell atoms.) We have also compared the Si-B distance in a fictitious SiB compound with β -SiC structure. The bond distance is about 15% shorter than the Si-Si bond. Clearly, 12% bond distance reduction in the substitutional B case is a compromise between an ideal Si-B bond length (15%) and zero stress to the neighboring Si lattice (0%). The second-shell Si atoms have been relaxed by 3% of the bond distance.

C. Boron-Si pair

As discussed above, B diffusion in Si is drastically increased in the presence of excess self-interstitials, which leads to TED. Therefore, it is important to study the B_s -Si_i complexes. Configurations formed by a B_s and a Si_i can take one of at least three forms: B interstitial, which is formed by interstitial Si kicking out the substitutional B atom, B substitutional with Si interstitial close by, and B-Si interstitialcy (one B, one Si atom sharing one single site). The lowestenergy configurations we found are all of the second type. In Fig. 2, two lowest-energy configurations having similar total energy are shown together with their respective charge density contours on the (110) plane. Both have the B in the substitutional site and the Si interstitial close to a nearby tetrahedral (T) site. Configuration (a) has the Si interstitial next to the B atom while in configuration (b) the Si interstitial is next to another Si atom, which is a first nearest neighbor to the B. The two configurations have similar energy with the energy for configuration (a) only 0.13 eV lower than that of configuration (b). Both are lower in energy than a well separated neutral Si interstitial and neutral B substitutional. The binding energy of such a configuration relative to well separated neutral defects is defined by

$$E_b(\text{Si-B}) = E(\text{Si}_{65}) + E(\text{Si}_{63}\text{B}) - E(\text{Si}_{64}\text{B}) - E(\text{Si}_{64}),$$
(2)

where Si₆₃B is the substitutional B configuration in a 64atom supercell and Si₆₄B is the B-Si complex in a 65-atom supercell. The binding energy for configuration (a) and configuration (b) is 1.1 ± 0.1 and 1.0 ± 0.1 eV, respectively.

The binding energy between interstitial Si and substitutional B can come from several sources. One such source for the binding energy comes from the electronic structure contribution. The tetrahedral Si has a defect state close to the bottom of the conduction band, which in the neutral state is occupied by two electrons. The neutral substitutional B has room for one more electron to occupy the defect state near the top of the valence band. Therefore, the combined system can lower its total energy by transferring one electron from the state near the bottom of the conduction band of tetrahedral Si to the state near the top of the valence band of the substitutional B. This energy gain can more than offset the energy cost to convert a $\langle 110 \rangle$ interstitial to a tetrahedral (*T*) one. Another source is stress compensation. Interstitial



FIG. 3. Schematic energy diagram for the kick-out mechanism of B diffusion in Si. The substitutional B atom is being kicked out by an interstitial Si atom into the interstitial region. The resulting B interstitial can then migrate along the hexagonal-tetrahedralhexagonal path for quite a long distance before falling back to another substitutional site. The energy barrier for the initial kick-out is about 1.0 eV. The energy barrier for the final reverse kick-out in the absence of vacancies is 0.6 eV, which is much higher than the B interstitial migrational barrier 0.3 eV.

Si exerts a compressive stress on the Si lattice while substitutional B exerts a tensile stress. It is known from elasticity theory that two defects of opposite stress will attract each other, and that this interaction of elastic fields will lower the crystal energy. The third possible source can come from the electrostatic contribution due to this electron transfer from tetrahedral Si interstitial to B substitutional. However, since all of the defect states involved are very extended, this part of the contribution should be relatively small.

Interstitial B, which plays an important role in the socalled "kick-out" B diffusion mechanism, has relatively higher energy than the lowest-energy B_s -Si_i complexes of Fig. 2. Interstitial B at the hexagonal (H) site has energy about 0.4 eV higher than the B_s -Si_i configuration of Fig. 2(b), and the tetrahedral (T) site energy is another 0.3 eV higher than the H site. For the neutral states, there is no additional energy barrier from one H site to another H site through a T site other than the energy difference between the T site and the H site, which is only 0.3 eV. The calculation of the energy barrier for the initial kick-out is much more complicated. It can be calculated by placing the B atom at a few points between substitutional position in configuration B and the final H position and then relaxing all the atoms except the B atom while maintaining the overall center-of-mass position unchanged. We have found that in a 32-atom supercell the migration barrier for the B atom to be kicked out and become an interstitial B from the configuration of the B_{s} -Si_i pair is about 1.0 eV. After that, the interstitial B can then migrate along the T-H path with 0.3-eV migration energy. These energy barriers are illustrated schematically in Fig. 3. Note that based on this picture, the barrier for the B in the T-H channel to return to the B-Si pair complex of Fig. 2(b) (the reverse kick-out reaction) is 0.6 eV, which is 0.3 eV higher than the migration energy barrier in the channel. The higher reverse kick-out reaction barrier compared to the interstitial migration barrier allows the B interstitial to migrate quite a long diffusion length before falling back to its substitutional position. The interstitial B diffusion length increases as the temperature decreases, contrary to the intuitive thinking. This is due to the fact that while at low temperature it takes longer for the interstitial B to overcome the migrational barrier of 0.3 eV to make a jump to another H site, it takes even longer for the B interstitial to overcome the reverse kick-out barrier of 0.6 eV. Therefore, the net effect is that, at low temperature, the B interstitial is able to make more jumps within the T-H interstitial channel before falling back to a substitutional position, resulting in a longer diffusion length. Futhermore, even when the B interstitial is being kicked back to its substitutional site, if the Si interstitial is still bound to the B atom, the B atom will still have a chance to be kicked into interstitial region and continue to migrate, adding to its diffusion length.

For certain dopant elements, a large percentage of dopant atoms never dissociate with the Si interstitial so that the diffusion length is long enough for the dopant atom to reach the surface or interface and segregate. For example, Griffin, Crowder, and Knight observed P segregation of up to 50% of the implant doses with low enough annealing temperatures at Si/SiO₂ interfaces.³¹ For B, this could also occur at sufficiently low temperatures. However, it is estimated from this calculation that the temperature would be too low to have any measurable diffusion.

The anomalous temperature dependence of interstitial B diffusion length is consistent with the experimental observation that the enhancement of B diffusion increases when the temperature decreases.³⁰ Cowern et al.²⁻⁴ were able to measure the diffusion length experimentally, which demonstrated such a temperature dependence unique to the diffusion mechanism through intermediate species. However, it is not possible to determine experimentally if the intermediate species is a B interstitial generated from a kick-out mechanism or a B-Si complex as shown in Fig. 2 since any intermediate species with a break-up barrier higher than its migrational barrier will demonstrate such a temperature dependence. On the other hand, from our calculation, we are able to determine that, at least within neutral defect systems, even though the initial kick-out barrier is similar to other migrational mechanisms in which the B atom stays substitutional, due to the fact that the interstitial B has a much longer diffusion length, the kick-out mechanism will still dominate.

Regardless of actual mechanisms for interstitial assisted B migration, compared to the approximately 4.9-eV migrational barrier for a concerted exchange mechanism without Si interstitials,⁵ the presence of excess interstitial flux greatly reduces the migrational barrier for B and increases B diffusivities that has been clearly demonstrated in B marker layer experiments.^{7,2-4} The enhancement of B diffusivity should increase with increasing Si interstitial density. Since Si interstitials come mainly from the surface or just below the surface in both the TED and surface oxidation experiments, the surface should have the highest self-interstitial density since the Si bulk may have various traps for self-interstitials such as vacancies or carbon impurities.³² This explains why B diffusivity is the largest near the surface and steadily decreases as the position of the B marker layer is deeper inside the bulk.⁷

D. Boron-boron pair

At higher B concentration, B dopant clusters will also become important, especially in the presence of a large excess of self-interstitials, which leads to a large number of mobile B atoms. Therefore, we have also carried out a study of a mobile B_i bound to a B_s . This is likely the first step for B clustering. We have identified the lowest-energy configuration to be two B atoms displaced along a (001) direction occupying one lattice site. The B-B pair forms a very strong bond of length about 68% of ideal Si-Si bond length. Since B has a smaller atomic size than Si, this configuration should create much less strain than if two Si atoms occupy the same two sites. We also note that in this configuration, each B has three nearest neighbors (two Si atoms and one B atom) while all Si atoms have four nearest neighbors. This is nearly the ideal coordination for both B and Si atoms in a covalent bonding environment. The pairing process can be described by the following reaction:

$$\mathbf{B}_{s} \cdot \mathbf{S}\mathbf{i}_{i} + \mathbf{B}_{s} \rightarrow \mathbf{B}_{i} + \mathbf{B}_{s} \rightarrow \mathbf{B}_{i} \cdot \mathbf{B}_{s}, \qquad (3)$$

i.e., a B_s -Si_i complex becomes mobile likely through a "kick-out" mechanism and then binds with a substitutional B, forming a B_i - B_s pair. Using the lowest energy for each configuration, we found that this reaction has a large energy gain of 1.8 ± 0.1 eV. Combined with 1.1-eV binding energy for the pairing of interstitial Si and substitutional B, the total energy gain for the reaction

$$\operatorname{Si}_{i} + \operatorname{B}_{s} + \operatorname{B}_{s} \rightarrow \operatorname{B}_{s} - \operatorname{Si}_{i} + \operatorname{B}_{s} \rightarrow \operatorname{B}_{i} - \operatorname{B}_{s}$$
 (4)

is 2.9 \pm 0.1 eV. This reaction is limited by the density of free Si interstititals as well as the B density and can only go significantly forward on the condition of both a large enough local B density and large amount of mobile Si interstitials. The resulting B_i-B_s pair is immobile due to its large binding energy as well as its strong bonding with its neighboring Si atoms. It is impossible to find a migration path that only breaks one or two bonds while still keeping two B atoms together. Moreover, we have found that this B_i-B_s pair is electrically inactive.

The interstitial-substitutional B pair was first studied using *ab initio* methods by Tarnow.⁹ However, supercell sizes and plane-wave cutoffs much smaller than those used in the present calculation were employed. In addition to the $\langle 100 \rangle$ split B pair, Tarnow has also proposed the $\langle 111 \rangle$ split configuration in which two B atoms split along a $\langle 111 \rangle$ direction sharing one single site. We have also studied the energetics of the $\langle 111 \rangle$ split B pair. The relaxed structure indicates a B-B bond length of 66% of the ideal Si-Si bond length. One of the B atoms splits away from the ideal lattice site but toward another Si atom in the $\langle 111 \rangle$ direction by 39% of the ideal Si bond length while the other one splits away along the opposite direction by 27% of the Si bond length. Moreover, our calculation shows that this configuration, while still electrically inactive, is about 0.2 eV higher in energy than the $\langle 001 \rangle$ split configuration.

The results presented above are consistent with recent TED experiments using δ -doped superlattices,⁷ which found immobile and electrically inactive B regions. These immobile B regions were found in the B marker layers closest to the surface where the Si interstitial flux is the highest, and

also in the B implanted region where large implant doses provided both the large interstitial flux and large B concentration required for the reaction to go forward. This immobile B region may also be the result of large clusters or even B precipitation, which would require higher-order processes than those described here. Nevertheless, the B clusters were not detectable in high-resolution cross-section TEM, suggesting that the clusters only contain a few B atoms.⁷ The $\langle 001 \rangle$ split configuration for B pairs is also consistent with the structure suggested by ion channeling experiments.^{33,34}

Our B clustering results also imply that a Si interstitial is trapped during the process of forming a B pair. We have also looked at the possibility that a Si interstitial is ejected back to the Si lattice while forming a B pair. In this case, both B atoms should be substitutional and the formation process can be expressed as

$$B-Si+B_s \rightarrow B_s - B_s + Si_i.$$
 (5)

We have found that the lowest-energy configuration for a B_s - B_s pair is two B atoms occupying neighboring lattice site relaxing towards each other to form a strong B-B bond. The bonding character between the two B atoms is evident in Fig. 4(a) where the charge density contour on the [110] plane containing both B atoms is shown together with the atomic positions. Interestingly, another configuration, which is shown in Fig. 4(b), with these two B atoms relaxing away from each other, therefore unbonded, is also a total-energy local minimum. The unbonded configuration has near perfect coordinations for both B and Si atoms, and creates a smaller stress than the bonded configuration. However, in a 32-atom cell calculation the bonded structure is still lower in energy by 0.5 eV. This is because the bonding energy between two B atoms is large enough to offset the energy costs of the imperfect coordination number and the large stress field. It is interesting to note that in a smaller eight-atom supercell calculation, the bonded configuration has higher energy than the unbonded one. It is not surprising, though, since the eightatom cell does not allow sufficient stress relief, thus biasing the results towards low stress configuration. Our calculations also show that, primarily due to the large formation energy to create a free Si interstitial, the reaction in Eq. (5) has an energy cost of 1.7 eV, compared to an energy gain of 1.8 eV if the Si interstitial is trapped as in Eq. (3). Furthermore, the bonded configuration of the B substitutional pair is electrically active, which is contrary to the experimental finding. Therefore, the present calculation does not favor the importance of reejecting all Si interstitials during the B clustering process, at least when only two B atoms are involved.

IV. SUMMARY

In summary, we have used *ab initio* methods with a 64atom supercell, well converged **k**-point sampling, and full relaxation of atomic positions, to study the neutral Si interstitial and its pairing with a B substitutional atom, as well as the pairing of two B atoms in Si. For Si_i, we find the lowestenergy configuration to be the $\langle 110 \rangle$ dumbbell with a 3.2 ± 0.1 -eV formation energy, in excellent agreement with previous calculations.²² The hexagonal interstitial is only 0.1 eV higher in energy within LDA. For B_s, we found the firstnearest-neighbor shell Si atoms relax inwards by 12% of the



FIG. 4. Charge density contour plot on the (110) plane of two substitutional boron pair configurations. Si atomic positions are indicated by open circles while boron atomic positions are indicated by filled dots. Configuration (a) is the bonded configuration between the two substitutional boron atoms while configuration (b) is the nonbonded configuration between the two boron atoms.

Si-Si bond length with a relaxation energy of about 1.2 eV. The electronic structure of the substitutional B is consistent with the behavior of an electron acceptor. We have also identified two almost degenerate (0.1-eV energy difference) lowenergy configurations of the B_s-Si_i pair with binding energies of 1.1 ± 0.1 eV relative to the energy of the well seperated neutral B_s and Si_i . Furthermore, we have found that the migration barrier for B diffusion in Si is greatly reduced in the presence of Si, with diffusion occurring predominantly through the kick-out mechanism. This is the source of transient enhanced diffusion in which the B diffusivity is much enhanced in the presence of excess Si interstitials. We have also found that a mobile B_i can be trapped by a B_s atom to form a B_i - B_s pair. The lowest-energy configuration of such a B_i - B_s pair is the (001) split configuration where all B and Si atoms have the perfect coordinations. The total energy gain going from two separated B_s and one Si_i to the formation of a B_i - B_s pair is 2.9 ± 0.1 eV. The resulting B_i - B_s pair is immobile and electrically inactive. These results are all consistent with the experimental findings that, under high Si interstitial flux, there exists an immobile and electrically inactive B region at the peak of B density profile. Additionally, we have studied an alternative process in which a B_s - B_s pair is formed with Si_i returned to the bulk. Our calculations show that this reaction is unlikely since it is energetically unfavorable and the resulting B-B pair is electrically active, contrary to the experimental findings. Finally, we would like to emphasize that all results mentioned above are from calculations of neutral systems.

- ¹For a review, please see P. M. Fahey, P. B. Griffin, and J. D. Plummer, Rev. Mod. Phys. **61**, 289 (1989).
- ²N. E. B. Cowern, K. T. F. Janssen, G. F. A. van de Walle, and D. J. Gravesteijn, Phys. Rev. Lett. **65**, 2434 (1990).
- ³N. E. B. Cowern, G. F. A. van de Walle, D. J. Gravesteijn, and C. J. Vriezema, Phys. Rev. Lett. 67, 212 (1991).
- ⁴N. E. B. Cowern, G. F. A. van de Walle, P. C. Zalm, and D. J. Oostra, Phys. Rev. Lett. **69**, 116 (1992).
- ⁵C. S. Nichols, C. G. Van de Walle, and S. T. Pantelides, Phys. Rev. Lett. **62**, 1049 (1989); Phys. Rev. B **40**, 5484 (1989)
- ⁶A. E. Mitchel, Nucl. Instrum. Methods B 37/38, 379 (1989).
- ⁷ P. A. Stolk, H. J. Gossmann, D. J. Eaglesham, D. C. Jacobson, and J. M. Poate, Appl. Phys. Lett. **66**, 568 (1995); P. A. Stolk, H. J. Gossmann, D. J. Eaglesham, and J. M. Poate, Nucl. Instrum. Methods **96**, 187 (1995)
- ⁸P.-O. Löwdin, J. Chem. Phys. **19**, 1396 (1951).
- ⁹E. Tarnow, J. Phys. Condens. Matter 4, 5405 (1992).
- ¹⁰E. Tarnow, Europhys. Lett. **16**, 449 (1991).
- ¹¹E. Tarnow, Europhys. Lett. **17**, 157 (1992).
- ¹²D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).
- ¹³J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- ¹⁴N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991).
- ¹⁵L. Kleinman and D. M. Bylander, Phys. Rev. Lett. 48, 1425 (1982).
- ¹⁶H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
- ¹⁷ M. Teter, M. Payne, and D. G. Allan, Phys. Rev. B 40, 12 255 (1989).
- ¹⁸P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W.

Charged state effects are also essential to the full understanding of dopant diffusion in Si and such studies are currently under way.

ACKNOWLEDGMENTS

The authors acknowledge useful discussions with Dr. P. A. Stolk, Dr. D. J. Eaglesham, Dr. J. L. Benton, and Dr. J. M. Poate. This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

- Kohn and L. J. Sham, *ibid.* 140, A1133 (1965).
- ¹⁹P. N. Keating, Phys. Rev. 145, 637 (1966).
- ²⁰R. Martin, Phys. Rev. B 1, 4005 (1970).
- ²¹G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B 21, 5662 (1980).
- ²²P. E. Blöchl, E. Smargiassi, R. Car, D. B. Laks, W. Andreoni, and S. T. Pantelides, Phys. Rev. Lett. **70**, 2435 (1993); R. Car, P. Blöch, and E. Smargiassi, Mater. Sci. Forum **83-87**, 433 (1992).
- ²³R. Car and M. Parrinello, Phys. Rev. Lett. 55, 2471 (1985).
- ²⁴G. A. Baraff and M. Schlüter, Phys. Rev. B 30, 3460 (1984).
- ²⁵Y. Bar-Yam and J. D. Joannopoulos, Phys. Rev. B **30**, 2216 (1984); Phys. Rev. Lett. **52**, 1129 (1984).
- ²⁶R. Car, P. J. Kelly, A. Oshiyama, and S. T. Pantelides, Phys. Rev. Lett. **52**, 1814 (1984).
- ²⁷P. J. Kelly and R. Car, Phys. Rev. B **45**, 6543 (1992).
- ²⁸D. J. Chadi, Phys. Rev. B 46, 9400 (1992).
- ²⁹J. Zhu, L. H. Yang, C. Mailhiot, T. Diaz de la Rubia, and G. H. Gilmer, Nucl. Instrum. Methods B **102**, 29 (1995).
- ³⁰P. A. Packan and J. D. Plummer, Appl. Phys. Lett. 56, 1787 (1990).
- ³¹P. B. Griffin, S. W. Crowder, and J. M. Knight, Appl. Phys. Lett. 67, 482 (1995).
- ³²P. A. Stolk, D. J. Eaglesham, H. J. Gossmann, and J. M. Poate, Appl. Phys. Lett. **66**, 1370 (1995).
- ³³M. L. Swanson, Vacuum **39**, 87 (1989).
- ³⁴P. J. M. Smulders, D. O. Boerma, B. Bech Nielsen, and M. L. Swanson, Nucl. Instrum. Methods B 29, 417 (1987).