PHYSICAL REVIEW B, VOLUME 64, 075207

Atomic-scale characterization of boron diffusion in silicon

Paola Alippi,* L. Colombo, and P. Ruggerone
Istituto Nazionale per la Fisica della Materia and Department of Physics, University of Cagliari, Cittadella Universitaria, I-09042 Monserrato (CA), Italy

A. Sieck, G. Seifert, and Th. Frauenheim
Department of Physics, University of Paderborn, D-33098 Paderborn, Germany

(Received 22 December 2000; published 31 July 2001)

By means of density-functional based tight-binding molecular-dynamics (DF-TBMD) simulations, we investigated the diffusion dynamics of boron in crystalline silicon. First, the energetics of single B defects in silicon, given by the present model, has been compared to first-principle results, and a discussion is provided on the overall accuracy of the DF-TBMD parametrization. We then computed the migration energy in the range 900–1500 K, obtaining a value 0.66 eV. By direct analysis of computer-generated trajectories, we show that B diffusion is a self-interstitial assisted process, displaying no kick-out events. Rather, Si–B pairs clearly diffuse through an interstitialcy mechanism. We predict a diffusion pre-exponential factor $d_{\mathrm{B}}^{0}=1.1\times10^{-3}\ \mathrm{cm}^2/\mathrm{s}$.

DOI: 10.1103/PhysRevB.64.075207 PACS number(s): 71.55.−i, 66.30.Jt, 71.15.Ap, 71.15.Mb

I. INTRODUCTION

Controlling the behavior of diffusing dopant species is a fundamental issue in silicon device technology. In particular, any further development in ion-implantation techniques (especially related to the fabrication of shallow junctions) requires an improved atomic-scale understanding of the mechanisms governing dopant diffusion and dopant-silicon interactions. In the case of boron, experiments have shown[1] that it undergoes transient enhanced diffusion when a large concentration of intrinsic self-interstitial defects is created by the implant damage. On the other hand, boron diffusion profiles also show a portion of immobile and electrically inactive boron atoms,[2] suggesting the formation of immobile mixed clusters of boron atoms and Si interstitials. Although this issue represents a lively matter of discussion, an ultimate atomic-scale picture about boron diffusivity is still missing, as well as a quantitative estimation of diffusion coefficient.

Atomistic simulations are providing valuable information about the energetics and the possible reaction paths of mobile boron in the crystalline host. In fact, theoretical investigations[3–6] have substantiated the early experimental idea[1] that B diffusion is mediated and enhanced by the presence of self-interstitial atoms. The theoretical picture has been obtained considering different defect configurations containing a single boron atom in a silicon lattice and evaluating total-energy differences and energy barriers. Furthermore,[4–6] several possible charged states of the defect have been considered, as well as the formation of Si-B complexes.[7] As for the diffusion mechanism, two conflicting models have been proposed, both based on *ab initio* electronic structure calculations.[3–5] Zhu *et al.*[3] have proposed a kick-out mechanism in which B is able to diffuse alone through interstitial channels, once it has been kicked out from a substitutional site. More recently, this picture has been contrasted by the proposed interstitialcy mechanism.[4,5] In this case, B-Si pairs diffuse in the lattice, the configuration of the B atom being iteratively reversed from interstitial to substitutional and back. Diffusivity of B is thus predicted to be ruled by a sort of ‘‘concerted-exchange’’ mechanism. These two mechanisms look qualitatively different and imply different microstructural evolution of B-implanted silicon. However, they provide similar predictions for the B migration energy E_m, namely, $E_{\mathrm{m}}\simeq0.6$ eV.[4,5] Nevertheless, the estimation of the B diffusivity coefficient, at the temperatures of experimental interest, is hindered by the lack of knowledge of the diffusivity pre-exponential factor, not provided by total-energy calculations. The importance of this parameter might be crucial. As a matter of fact, there is not an ultimate experimental estimation for it. Furthermore, studies on surface diffusion have shown that large differences in the prefactors may come out from different diffusion mechanisms (like single hopping or concerted process).[8]

The present paper stands as a contribution to the above on-going discussion. In particular, it is aimed at providing a quantitative estimation of the diffusivity prefactor. At variance with previous investigations,[3–5] we did not guess the reaction path of diffusion from a total-energy landscape generated at zero temperature. Instead, we simulated the diffusivity of B at finite temperature, performing quantum-mechanical molecular-dynamics (MD) simulations in the range 900–1500 K. From several computer-generated trajectories, we extracted information on the involved atomistic mechanisms, as well as quantitative estimations of diffusion constants. Our approach, although conceptually simple and straightforward, is rather computer intensive, since atomic trajectories need to be followed for several tens of picoseconds in order to provide a reliable source of information. Because of such a heavy computational work load, we adopted a density-functional based tight-binding molecular-dynamics[9] (DF-TBMD) scheme, which allows to simulate, at finite temperature, the interplay between electronic structure and atom dynamics. This is an important issue when dealing with materials characterized by directional and covalent bonding.

At first, in Sec. II, we provide a validation of the method by comparing the Si:B energetics obtained in the DF-TBMD scheme to first-principle investigations. In Sec. III, we discuss the results obtained for B diffusivity, presenting our estimations of migration energy and the pre-exponential factor. Finally, conclusions are drawn in Sec. IV.

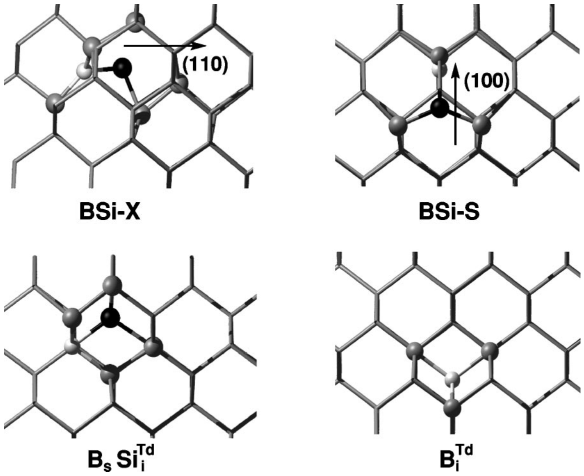

FIG. 1. Defect configurations relaxed at zero temperature: B atoms (white, smaller radius), Si self-interstitial (black, larger radius) and their first neighbor's (gray, larger radius) are shown over the underlying diamond lattice. The two dumbbell structures are in the upper panel, denoted as BSi-X (left) and BSi-S (right). In the lower panel, the $\mathrm{B}_s+\mathrm{Si}_i^{Td}$ (left) and the interstitial B in the tetrahedral position, B_i^{Td} (right) are shown.

II. ENERGETICS

The adopted DF-TBMD consists of a nonorthogonal TB scheme, where the two-center linear combination of atomic orbitals (LCAO) Kohn-Sham Hamiltonian and overlap matrix elements, are evaluated within the framework of an atomic orbitals formalism. For detailed descriptions of the method, we refer the reader to Refs. 9 and 10. The atomic eigenfunctions of a given atom type are obtained from a self-consistent calculation using density-functional theory in the local density approximation (DFT-LDA). In order to confine the range of valence electrons, the atomic calculations are actually solved for slightly contracted pseudoatoms. The potential added to the free-atom potential, has the form $\simeq (r/r_0)^2$, where r_0 is related to the covalent radius of the atom. In the present parametrization we used a confinement radius $r_0 = 1.74$ Å for Si atoms and 1.48 Å for B atoms.

The short-range repulsive potential (accounting for ion-ion interactions and correcting the double counting of electron-electron ones) is obtained from the difference between the band structure tight-binding energy and the corresponding total energy of a self-consistent DFT-LDA calculation for a given reference system, usually as simple as the diatomic molecule.[9] The difference decays rapidly with increasing interatomic distance and can be approximated by a polynomial expression in $(r-r_c)$, with a cutoff radius r_c, which is smaller than twice the nearest-neighbor distances. For the Si-B parametrization, we calculated the repulsive potential, taking as a reference system the $\mathrm{Si_4BH_{12}}$ configuration, i.e., a B atom surrounded by four Si atoms with hydrogens saturating the dangling bonds. The arrangement of the B-Si bonds in $\mathrm{Si_4BH_{12}}$ is in fact more similar to the environment seen by a B defect in a Si matrix than the simpler Si-B dimer reference system. We choose $r_c = 2.38$ Å (2.54 Å) for the Si-B (Si-Si) pair potential.

The reliability of the actual parametrization for Si:B interactions in the crystalline environment has been tested, performing DF-TBMD calculations on cubic, periodically repeated cells, containing 216 Si atoms and one B impurity, and using the Γ-point approximation for Brillouin-zone integration. We relaxed the configurations by means of finite-temperature simulated annealing. The atomic structures relaxed at zero temperature are shown in Fig. 1, while the total-energy values are reported in the first column of Table I. Also, only neutral defects were considered in the present paper.

The energy landscape, provided by DF-TBMD for Si:B, indicates that the lowest-energy structure (hereafter referred to as BSi-X) consists of a Si self-interstitial and a B atom sharing the same lattice site, with the Si-B dimer lying in the $\langle 110\rangle$ direction. The first column of Table I reports total-energy differences between all considered defects structures and the BSi-X one. The DF-TBMD BSi-X structure is actually slightly tilted with respect to the ideal dumbbell configuration by an angle θ from the $\langle 110\rangle$ direction. The BSi-S structure, with the Si-B dimer oriented along the $\langle 100\rangle$ direction, has been found to be 0.2 eV higher in energy from the BSi-X. The $\mathrm{B}_s+\mathrm{Si}_i^{Td}$ geometry, where B sits on a substitutional site stabilizing a Si self-interstitial in a nearby tetrahedral position, is further up in energy (+0.31 eV), together with the configuration B_i^{Td}, i.e., the interstitial B in the tetrahedral position. The interstitial hexagonal B_i^{Hx} is the highest-energy structure in our picture (+0.68 eV).

With respect to *ab initio* results, we obtain the lowest-energy defect structures in the same energy range, but there are differences in the details of the calculated energetics. Previous first-principle calculations[4–6] found that the ground state is the positively charged $(\mathrm{B}_s+\mathrm{Si}_i^{Td})^+$ complex. We have not taken into account charged defects, hence a direct comparison is not possible. However, first-principle results[4,5] indicated also that the same configuration, $\mathrm{B}_s+\mathrm{Si}_i^{Td}$, is the lowest-energy one among neutral defects.

We independently performed total-energy calculations in the framework of the density-functional theory in the local

TABLE I. Energetics of the Si:B defect configurations from DF-TBMD (first-column) and VASP (second-column) calculations. Total-energy values are referred to the respective ground-state configurations, indicated by arrows (see the text). The values in parentheses in the second column are DFT-LDA values extracted from Ref. 4.

	DFTB	VASP	(DFT-LDA)
BSi-X	→0.0	0.6	(0.26)
BSi-S	0.20		(0.43)
B_i^{Td}	0.27		(0.82)
$\mathrm{B}_s+\mathrm{Si}_i^{Td}$	0.31	→0.0	(0.0)
B_i^{Hx}	0.68		(0.41)

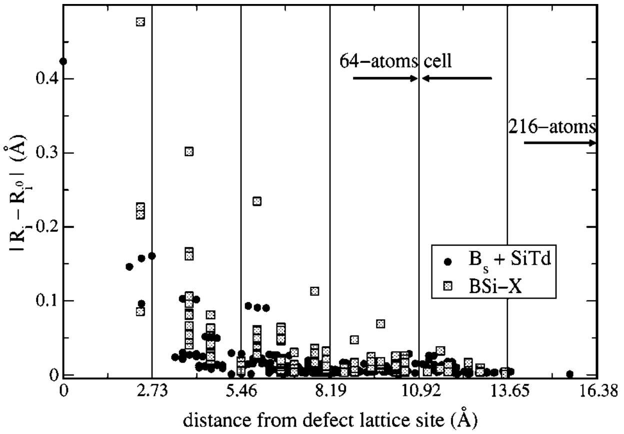

FIG. 2. Strain field $|\mathbf{R}_i - \mathbf{R}_i^0|$ as a function of the distance from the defect site. All quantities are in Å.

density approximation for the two neutral-charge configurations, $\mathrm{B}_s+\mathrm{Si}_i^{Td}$ and BSi-X. DFT-LDA calculations were done within a plane-wave pseudopotential scheme, using the Vienna *Ab initio* Simulation Package [VASP (Ref. 11)]. We used ultrasoft pseudopotentials, a cutoff energy $E_c = 257.1$ eV, $4\times4\times4$ grid for the k-points sampling, and a $2\times2\times2$ supercell (64 atoms).

We obtained an energy difference $E_{\mathrm{tot}}(\mathrm{BSi}\text{-}X)\text{-}E_{\mathrm{tot}}(\mathrm{B}_s+\mathrm{Si}_i^{Td})\simeq 0.6$ eV, slightly larger than the value reported by Sadigh *et al.*[4] In agreement with the previously published results, the $\mathrm{B}_s+\mathrm{Si}_i^{Td}$ structure has the lowest energy. It is worth noticing that, according to the present VASP calculations, the BSi-X complex is actually an unstable structure that converts into the $\mathrm{B}_s+\mathrm{Si}_i^{Td}$ during the atomic relaxation procedure we followed. However, for the sake of comparison, we reported in Table I the total energy of the metastable BSi-X complex.

Since the DF-TBMD calculations were performed using the larger $3\times3\times3$ unit cell (216 atoms), we wanted to investigate the convergency of the VASP results with respect to the size of the unit cell. In order to clarify whether the 64-atom cell is large enough to contain the lattice relaxation created by the defect structure, we calculated the atomic strain field of the two DF-TBMD configurations. In Fig. 2 the quantity $|\mathbf{R}_i - \mathbf{R}_i^0|$ is shown as a function of the distance from the defect site, where $\mathbf{R}_i^0$ and $\mathbf{R}_i$ are the atomic positions before and after the relaxation. Although the relaxation, induced by the BSi-X complex, has a wider spatial extension compared to that of $\mathrm{B}_s+\mathrm{Si}_i^{Td}$, it decays to zero well within the 64-atom cell boundaries. Thus, we can conclude that the convergence with respect to the cell size is fully achieved with a 64-atom cell.

In the second column of Table I, we report the first-principle total energy values available from Ref. 4. Total energies of the Si:B defect structures are all contained in the same energy window found for the DF-TBMD results. Reference 4 finds that the interstitial B_i^{Hx} rapidly diffuses into the ground-state configuration. In the same way, the small barrier ($\simeq 0.05$ eV) around the B_i^{Hx} configuration, calculated by Windl *et al.*,[5] confirms that B_i^{Hx} lies in a very shallow minimum. Our DF-TBMD results are in agreement with this finding; the B_i^{Hx} is not stable upon the annealing cycles, at any finite temperature. All other DF-TBMD structures are instead stable.

We remark, however, that the features of the energy landscape are somewhat different in the two pictures. DF-TBMD parametrization does not reproduce, in all details, the *ab initio* results with regard to the ground-state configuration and the relative energies with respect to it. Deviations could be, however, within the uncertainties of DFT-LDA calculations, as the discrepancy between the present calculated value of $E_{tot}(\mathrm{BSi}\text{-}X)\text{-}E_{tot}(\mathrm{B}_s+\mathrm{Si}_i^{Td})$ (0.6 eV) and the result of Ref. 4 (0.26 eV) suggests. However, DFT-LDA and DF-TBMD energy differences are of the same order of magnitude, which should lead to a reliable value for the migration energy. Despite the present DF-TBMD model being parametrized, we believe that the correct gauge for B interstitial energy is well reproduced.

III. DIFFUSION

The computer generated atomic trajectories were collected during very long simulations, playing special attention to assure the highest numerical accuracy and stability. In particular, the Si:B system was at first equilibrated at the desired temperatures by means of constant-temperature, constant-volume simulations. Then, we followed the mobile B dynamics generated in the microcanonical ensemble, using a time step as small as 0.5 fs.[12] The quantitative estimation of diffusion constants was provided by the calculation of the square displacement $|\Delta r_{\mathrm{B}}(t)|^2$ of B and by the random-walk equation for diffusivity, namely, $d_{\mathrm{B}}=\lim_{t\to\infty}|\Delta r_{\mathrm{B}}(t)|^2/6t$. From the behavior of d_{B} as a function of the temperature T, we extrapolate the value for the migration energy $E_m = (0.66\pm0.08)$ eV. This value is in excellent agreement with the 0.6 eV experimental value[1] and also compares well with previous *ab initio* predictions ranging from 0.4 to 0.6 eV.[4,5]

Let us first discuss the relevant characteristics of the diffusion process deduced from the analysis of the atomic trajectories. Starting with a configuration where B sits in a substitutional site, we did not observe any B diffusion until a silicon self-interstitial (SiI) approaches the substitutional B. When this occurs, a Si-B complex is formed. Its actual geometry changes in time, exploring the different configurations BSi-X, $\mathrm{B}_s+\mathrm{Si}_i^{Td}$, and BSi-S. Eventually B is converted into an interstitial position. It is worth remarking that we never observed the so-called *kick-out* mechanism discussed in Ref. 3. From the interstitial position, in fact, the boron atom falls soon into the closest lattice site, kicking out a SiI, which either diffuses away (if the ‘‘kick’’ was strong enough) or stays bound to the boron atom, iterating a new diffusion event. We remark that whenever the SiI diffuses away from the substitutional B, we did not observe any further B diffusion. This implies that diffusion, via a direct exchange mechanism (i.e., B switching between two substitutional sites) results to be unlike. Our simulations thus provide support to the picture that B diffusion is a self-interstitial assisted process.

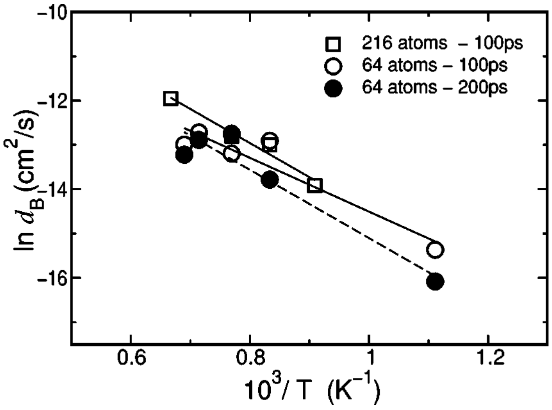

FIG. 3. Arrhenius plot for B diffusion in silicon. The extrapolated values for the migration energy and the diffusivity prefactor are discussed in the text.

In Fig. 3, d_B is reported as a function of the inverse of the temperature 10^3/T, on a semilogarithmic plot. Each set of points refer to a different choice of the simulation parameters. The lower computational load of our tight-binding method, with respect to *ab initio* MD, allowed us, in fact, to test the convergence of the DF-TBMD results, varying the total number of atoms in the unit cell (from 64 to 216) and the total length of the simulation time (from 100 to 200 ps). We can observe that the combined use of a larger unit cell (216 atoms) and a shorter simulation time (100 ps) compares well with the results obtained with the smaller supercell and longer molecular-dynamics runs.

The diffusivity shows a nice Arrhenius-like behavior; $\ln d_B$ is linear with $1/T$ in the whole range of temperatures investigated. This obviously indicates that the same mechanism is responsible for B diffusivity, at both high and low temperatures. The order of magnitude of B diffusivity varies between $d_B = 1.3\times10^{-6}$ cm^2/s at $T = 900$ K, $d_B = 0.2\times10^{-5}$ cm^2/s at $T = 1200$ K, and $d_B = 0.6\times10^{-5}$ cm^2/s at $T = 1500$ K. We extrapolated the value of the migration energy E_m and give a prediction for the diffusivity prefactor $d_B^0 = (1.1\pm0.4)\times10^{-3}$ cm^2/s. This value is of the same order of magnitude as the prefactor obtained for typical single hopping processes assuming a rate $\Gamma = 10^{13}$ s^{-1} (a Debye phonon frequency). This is an important qualitative feature of the B migration path. In fact, our results prove that the present interstitialcy mechanism does not exhibit an anomalous large prefactor as was otherwise suggested in other diffusion processes.[8]

IV. CONCLUSIONS

In this paper, we developed a new DF-TBMD representation for Si-B interactions and we have applied it to the study of B migration in Si. Our investigation shows, by means of very long-time MD simulations, that B migrates through an interstitial mechanism for which a Si self-interstitial atom is also involved. The computed migration energy is in agreement with available experimental data and other theoretical calculations. We further provide a prediction for the diffusion prefactor.

Furthermore, we have shown that, although considering the electronic structure within an approximate DFT treatment, the present simulation method allows for the study of the diffusion processes in a crystalline environment by means of a reliable description of the bond dynamics occurring during dopant defect migration. There is, however, room for improving the overall accuracy of the method and work in this direction is in progress. In particular, effort is focused on a better modeling of the delicate energy balance between Si-Si and Si-B bonds in such heteroatom defects and, possibly, on the role of charged states.

ACKNOWLEDGMENTS

This work was performed in the framework of the P. A. "SIMS" project funded by INFM-Sez. E. We also acknowledge computational support by the INFM under the Parallel Computing Initiative.

---

*Author to whom correspondance should be addressed. Email address: paola.alippi@dsf.unica.it

[1] G.D. Watkins, Phys. Rev. B **12**, 5824 (1975); D.J. Eaglesham, P.A. Stolk, H.-J. Gossmann, and J.M. Poate, Appl. Phys. Lett. **65**, 2305 (1994).

[2] M. Jaraiz, G.H. Gilmer, T.D. de la Rubia, and J.M. Poate, Appl. Phys. Lett. **68**, 409 (1996); L. Pelaz, M. Jaraiz, G.H. Gilmer, H.-J. Gossmann, C.S. Rafferty, D.J. Eaglesham, and J.M. Poate, *ibid.* **70**, 2285 (1997).

[3] J. Zhu, T. Diaz de la Rubia, L.H. Yang, C. Mailhoit, and G.H. Gilmer, Phys. Rev. B **54**, 4741 (1996); J. Zhu, Comput. Mater. Sci. **12**, 309 (1998).

[4] B. Sadigh, T.J. Lenosky, S.K. Theiss, M.-J. Caturla, T. Diaz de la Rubia, and Majeed A. Foad, Phys. Rev. Lett. **83**, 4341 (1999).

[5] W. Windl, M.M. Bunea, R. Stumpf, S.T. Dunham, and M.P. Masquelier, Phys. Rev. Lett. **83**, 4345 (1999).

[6] M. Hakala, M.J. Puska, and R.M. Nieminen, Phys. Rev. B **61**, 8155 (2000).

[7] W. Luo, P.B. Rasband, and P. Clancy, J. Appl. Phys. **84**, 2476 (1998); T. Lenosky, B. Sadigh, S.K. Theiss, M.-J. Caturla, and T.D. de la Rubia, Appl. Phys. Lett. **77**, 1834 (2000); X.-Y. Liu, W. Winde, and M. Masquelier, *ibid.* **77**, 2018 (2000).

[8] *Surface Diffusion*, edited by M. C. Tringides (Plenum, New York, 1997).

[9] D. Porezag, Th. Frauenheim, Th. Koehler, G. Seifert, and R. Kaschner, Phys. Rev. B **51**, 12 947 (1995).

[10] M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, Th. Frauenheim, S. Suhai, and G. Seifert, Phys. Rev. B **58**, 7260 (1998).

[11] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); **49**, 14 251 (1994); G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); Phys. Rev. B **54**, 11 169 (1996).

[12] The atom dynamics has been solved with the velocity Verlet method. In the constant-temperature simulations, a velocity-rescaling algorithm has been employed as a temperature thermostat.