Structure and diffusion of interstitial boron pairs in silicon

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(Received 24 September 2003; published 8 January 2004)

Using the plane wave pseudopotential approach, the structure and mechanism of migration of an interstitial boron pair are proposed. The energy of the proposed configuration is lower by at least 0.2 eV in comparison to other interstitial boron pairs. The proposed model, which is equivalent to a B_2I_2 pair (using the notation where B_mI_n refers to m boron atoms and n silicon atoms occupying m regular sites), migrates in the $\langle 110 \rangle$ channel with energy barriers between intermediate sites not greater than 0.1 eV and a total energy barrier of 0.6 eV between stable sites. Conventional continuum and kinetic Monte Carlo models of formation of boron interstitial clusters (BIC's) do not consider the mobility of the proposed configuration in the growth process. Its stability against dissociation could have considerable implications for the modeling of transient enhanced diffusion of boron in silicon.

The relentless decrease of feature sizes of semiconductor devices introduces a serious problem in precise control of dopant distribution due to the phenomenon of transient enhanced diffusion (TED). Although this ultrafast diffusion occurs only for a short period after thermal annealing, swiftly diffusing species have sufficient amount of time to migrate for distances that are comparable to device feature size, creating a problem in monitoring the depth of dopant penetration into the material. It is believed that TED is induced by interactions between dopants and native defects (self-interstitials or vacancies), which are produced as a result of bombardment by energetic ions during the process of ion implantation.[1] In silicon, TED of boron, a widely used acceptor dopant, is caused predominantly by interstitials as generally agreed on the basis of experimental observations,[2] kinetic Monte Carlo simulations,[3] and *ab initio* modeling.[4–7]

On an atomic level it was proposed that boron diffuses via alternating "kick-out" and "kick-in" of boron atom by a self-interstitial.[4,5] In such a mechanism the boron atom at a substitutional site is displaced by a self-interstitial (kick-out) and forced to migrate until it falls into another substitutional site releasing a self-interstitial (kick-in). Using experiment, Cowern *et al.* estimated that kick-out is associated with an energy barrier less than 0.3 eV,[8] which is substantially lower than "kick-in" (1 eV), as obtained by *ab initio* calculations.[4] Furthermore, Monte Carlo simulations have shown that a kick-in reaction is usually followed by immediate kick-out and therefore boron atoms are not trapped at substitutional sites but migrate as boron-interstitial pairs.[9] In this study the migrational barrier of boron diffusion energy required to fit mean migrational path length was estimated to be 0.55 eV and kick-out and kick-in barriers were 0 and 0.8 eV, respectively.[9] Subsequent *ab initio* calculations[6,7] confirmed that boron diffuses forming a mobile boron-self-interstitial pair with energy barrier in the range 0.4–0.7 eV and kick-in dissociation barrier of 0.8 eV.

To realize shallow junctions ($<0.1 \mu$m) it is desirable to incorporate and electrically activate dopants with minimal surface damage and concentration of native defects. In lieu of ion implantation, boron can be incorporated by exposure of silicon to $B_2H_6 + H_2$ gas in oxygen-free atmosphere.[10]

Thus incorporated boron can be activated and forced to diffuse by rapid thermal annealing at a high temperature of $1000\,°$C.[10] Attempts have been made to reproduce an evolution of boron profiles under such experimental environments, with low concentration of self-interstitials using a kinetic Monte Carlo approach.[11] The main conclusion of that work was that neither boron-interstitial diffusion mechanism nor boron-interstitial plus boron clustering mechanisms can provide a good fit to experiment. Reasonable fit is only possible if mobile boron pairs are introduced into the model.[11] In response, Hwang *et al.* used *ab initio* calculations to demonstrate that the $\langle 100 \rangle$ pair of interstitial and substitutional borons (B_2I pair of Tarnow[12]) can be mobile with intermediate energy barriers below 1 eV and total energy barrier of 1.8 eV.[13] However, the magnitude of this barrier (in comparison to other barriers for boron diffusion) could well render the assumption of immobility of the B_2I pair to be fairly reasonable. This assumption, for example, was used in older models to explain reduced mobility threshold, incomplete activation, and threshold concentration of diffusion.[14]

More recently, however, the concept of BIC's has been significantly motivated by the work of Pelaz[15] and Caturla,[16] who presented a reaction pathway favoring the BI and further the BI_2 as the immobile species. The B_mI_n notation, which is widely used in continuum and KMC modelling,[14] does not provide any information about structural location of atoms except to identify the total number of atoms of each atomic type. However, to maintain compatibility, we follow this notation, although our atomic based calculations do allow us to differentiate clearly between structural compositions of atomic clusters.

In the scenario presented in Refs. 15 and 16, the growth mechanism is either by capture of a self-interstitial or a BI pair, since all other species are considered immobile. Moreover, according to the notation of Pelaz, the two possible pathways are (a) an interstitial rich path such as BI_2, B_2I_3, or B_2I_2 and (b) a low interstitial content path with high energy complexes such as B_2I, B_2, B_3I, or B_3. The *ab initio* calculations of the B_2I and B_2I_2 pairs presented in this work, however, reveal clusters involving both pathways (a) and (b). We furthermore present a scenario of diffusion of a stable

boron pair formed by two interstitial atoms. To reiterate, this stable complex (a) possesses an energy lower by at least 0.2 eV than other proposed models; (b) can migrate with a total energy barrier of only 0.6 eV with intermediate energy barriers below 0.1 eV. Moreover, the proposed structure is stable with respect to separation of boron atoms, as the binding energy exceeds the migrational barrier by a factor of 3. In addition the formation of this pair from a B_2I pair of boron atoms is energetically favorable by an energy of 1.2 eV.

Calculations are based on density functional theory in local density approximation (LDA) implemented in CASTEP code.[17,18] In this study Kerker-type pseudopotentials in Kleinmann-Bylander form are used.[19] The wave functions are expanded in plane waves with cut-off energy of 20 Ry. For integration of the Brillouin zone four special k points generated by Monkhorst-Pack method[20] are used, as the supercell consists of 64 atoms of crystalline silicon plus additional boron atoms. The cut-off energy, the size of the supercell, and the number of k points are identical to these used in Ref. 5, where the convergence of these parameters has been verified for defects that consist of 1–2 atoms (boron and/or silicon). For minimization of electronic energy, a density mixing scheme is used,[21] whereas for minimization of ionic energy, Hellmann-Feynmann theorem is utilized.[22] The relaxation of all presented configurations proceeds until the Hellmann-Feynmann force does not exceed 0.04 eV/Å.[23] For investigation of diffusion pathways the intermediate images between two stable sites have been obtained by constrained relaxation of the diffusing atom in the plane perpendicular to the line connecting the two stable sites. The diffusion of the proposed interstitial boron pair has been investigated in neutral state as this defect was found to be higher in energy in charged states for midgap position of the Fermi level.

To characterize stability of a model with respect to decay into smaller products, the binding energy was calculated as

$$E_{bind} = (E_1 + E_2) - (E_{(1+2)} + E_{perf}), \quad (1)$$

where $E_{(1+2)}$ is the total energy of a supercell that contains a combined cluster and E_1 and E_2 are total energies of supercells of separated products 1 and 2.

The pathway of formation of the mobile boron pair is illustrated in Fig. 1. In the initial stage the substitutional boron atom (B) captures silicon self-interstitial and becomes interstitial boron (BI). The binding energy associated with this process (1.1 eV) has been calculated using BI configuration of the lowest energy in which a boron atom is positioned at the substitutional site and the silicon atom at a nearby tetrahedral site. The calculated value is in reasonable agreement with the value reported by Zhu (1.1±0.1 eV).[5] Alternatively, the substitutional boron B may capture an interstitial boron and form a ⟨100⟩ boron pair reported by Tarnow. The binding energy in this case is 1.7 eV, which is also in good agreement with Zhu (1.8±0.1 eV). The ⟨100⟩ pair of Tarnow is depicted in Fig. 1. This structure presents ideal bonding for boron and silicon atoms: each boron atom is three-bonded, whereas each silicon atom is four-bonded. Moreover, as two boron atoms share one silicon site and are
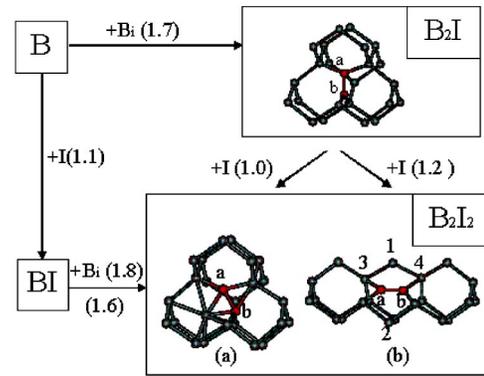

FIG. 1. (Color online) The diagram of boron cluster growth via the capture of either self-interstitial ($+I$) or a mobile boron interstitial ($+Bi$) with corresponding *ab initio* calculated binding energies given in eV. The model proposed by Tarnow is depicted as the inset for B_2I configuration (boron atoms are denoted as a and b), whereas the optimized structure of Liu *et al.* (Ref. 24) and the proposed model of B_2I_2 type are given as the inset with indices (a) and (b) correspondingly.

oriented in the ⟨100⟩ direction, the structural arrangements allow Si-B bonds and B-B bond to be shorter than Si-Si bonds.

Interstitial boron pairs can be formed by aggregating two BI structures or by adding a self-interstitial to the ⟨100⟩ boron pair. Liu *et al.* proposed an interstitial boron pair B_2I_2 depicted in Fig. 1(a).[24] This pair can be naturally formed from the ⟨100⟩ boron pair of Tarnow by adding a self-interstitial. An alternative model of B_2I_2, proposed in this work is presented in Fig. 1(b). This configuration has an energy lower by 0.2 eV than the structure of Liu. The binding energy with respect to formation of this model from two BI is 1.8 eV, whereas the binding energy with respect to its formation from a ⟨100⟩ boron pair and a self-interstitial is 1.2 eV.

In the proposed model two boron atoms form a dumbbell, which lies in the plane of two parallel bonds of the silicon hexagonal ring ({112} plane of crystalline silicon). The boron dumbbell is oriented perpendicular to these two bonds and in the process of structural relaxation, boron atoms cause breaking of these silicon bonds by moving silicon atoms away from each other. Each of these silicon atoms, however, saturates its dangling electrons by forming bonds with boron atoms. In turn, each boron atom becomes three-bonded by forming two bonds with silicon atoms and one bond with the other boron atom. Although initially boron atoms were introduced symmetrically into the silicon ring, i.e., at equal distances from atoms 1 and 2 [Fig. 1(b)], in the process of relaxation the symmetry is broken and boron atoms move closer to atom 1.

The presence/absence of a bond between boron atoms and atoms 1 and 2 has been investigated using quantum theory of atoms in molecules (QTAM) of Bader,[25] using the methodology presented in Ref. 26. As expected, QTAM analysis reveals that boron atoms a and b are not bonded to distant atom 2 [Fig. 1(b)]. Moreover, no bond is formed between boron atoms a and b and atom 1, which is situated closer,
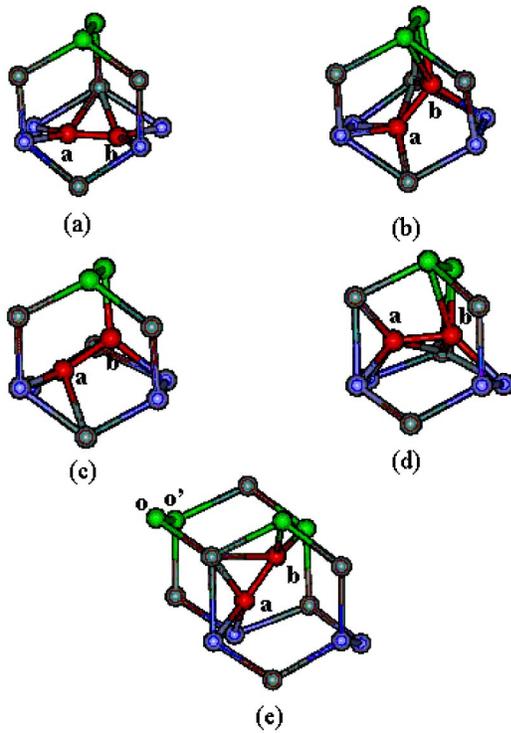
FIG. 2. (Color online) Migration of interstitial boron pair (the bonds are indicated based upon interatomic distance criteria only). (a) Initial stable structure; (b) metastable structure; atom b moves near hexagonal site of adjacent ring; (c) metastable midpoint configuration, atom a at the midpoint between structurally equivalent configurations at (b) and (d); (d) metastable structure; atom a lies in the plane of four atoms of adjacent hexagonal ring; (e) final stable structure equivalent to (a); atom b moves to the same plane of four silicon atoms as atom a in (d). Further migration can occur by either of atoms a or b being bonded to the silicon atoms o and o'.
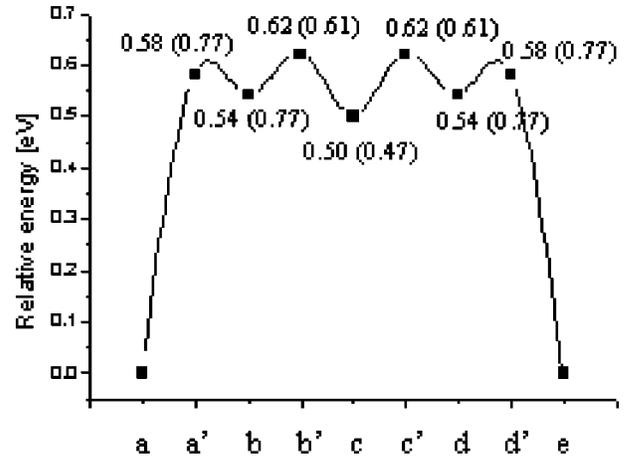

FIG. 3. Diagram of relative energy along the migration path. The relative energies (the energy of the most stable site is set to zero) are measured along the vertical direction. Letters a, b, c imply the configurations with the same indices as in Fig. 2, whereas a', b', etc. are used to designate the barrier sites. LDA energies are given for each intermediate site and GGA values are attached in parentheses.

although the corresponding distance between the atoms exceeds the bond length $a-3$ and $b-4$ by only 11%. It should be mentioned, however, that electric charge is accumulated in the interatomic region of atoms 1, a, b since the Laplacian of charge density is positive in the area of the triangle formed by these atoms.

The possibility of gap states introduced by this model has been investigated by calculating the energy bands of the structure. We found two defect-localized occupied states, whose bands lie above the highest occupied band of the perfect structure at Γ point and one unoccupied defect-localized state, whose band lies below the unoccupied bands at the X point of the Brillouin zone of a perfect structure. These results are, however, tentative due to the well known inability of DFT-LDA to calculate positions of energy levels in agreement with experiment, and therefore more appropriate techniques should be used for investigation of this aspect of the electronic structure of the defect.

The migration of the boron pair has been investigated. The most energetically favorable mechanism, which we found, is a series of consecutive moves of boron atoms that result in reorientation of a boron pair into an identical structure, in which the dumbbell lies in the plane of four atoms of the adjacent hexagonal ring (Fig. 2). To clarify the mechanism of migration, we wish to point out that the low energy boron pair is very similar to an elementary two-atomic unit of self-interstitial $\langle 110 \rangle$ chains[27] which form the cores of extended {311} defects.[28] Diffusion of the pair in the $\langle 110 \rangle$ channel of crystalline silicon can be viewed as its reorientation in such a way, which at each step two boron atoms occupy alternating sites similar to those of the $\langle 110 \rangle$ chain. A more detailed discussion of structural transformation in the process of migration is presented below.

In the initial stage atom b of the structure in Fig. 2(a) moves towards the hexagonal site of an adjacent ring [Fig. 2(b)]. The relaxed configuration does not fall back to its initial structure in Fig. 2(a). Its energy is higher by 0.54 eV than that in Fig. 2(a). The barrier for atom b to fall back into the structure in Fig. 1(a) is 0.04 eV. Thus, the total barrier between the stages 2(a) and 2(b) is 0.58 eV. In the second stage, atom a moves into the plane of silicon atoms of the adjacent hexagonal ring [Figs. 2(c) and 2(d)]. In passing, atom a undergoes a barrier of 0.08 eV and reaches a stable intermediate site in Fig. 2(c). The energy of the configuration in Fig. 2(c) is lower by only 0.04 eV than that of the structure in Fig. 2(b). At the next stage the configuration in Fig. 2(d) is formed. Its structure is equivalent to configuration in Fig. 2(b). In the final stage, configuration in Fig. 2(d) is transformed to the lowest energy structure [Fig. 2(e)], identical to configuration in Fig. 1(a), via moving atom b with the barrier of 0.04 eV. Further migration can continue as the boron dumbbell propagates in the $\langle 110 \rangle$ channel [Fig. 2(e)]. At the next step of the pair reorientation, either of atoms a or b should form bonds with the silicon atoms o and o' [Fig. 2(e)] for further migration of the entire structure.

The total energy diagram of migration in which the energy of the most stable structures in Figs. 3(a) and 3(e) is set

to zero is summarized in Fig. 3. Comparison shows that total GGA barrier (0.77 eV) is slightly higher than LDA results (0.6 eV). The obtained GGA value is lower than that found for $\langle 100 \rangle$ interstitial-substitutional boron pair, whose total barrier of reorientation is 1.8 eV.[13] Moreover, as it was mentioned already, the binding energy of the proposed boron cluster with respect to separation of two boron atoms is 1.8 eV and release of the self-interstitial is 1.2 eV. Therefore, the proposed model is indeed capable of migration over long distances prior to separation of boron atoms or transforma-

tion into another boron pair as the binding energies exceed total diffusion barrier by the factors of 3 and 2, respectively.

Finally, as the proposed complex already consists of two interstitials, it may be assumed that larger stable structures, which include at least three atoms (boron and/or silicon), are unlikely to be mobile. Therefore our finding together with previous calculations of boron and diboron diffusion reveals that the previous scenarios of boron cluster growth used widely in kinetic Monte Carlo and continuum models need to be revisited.

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