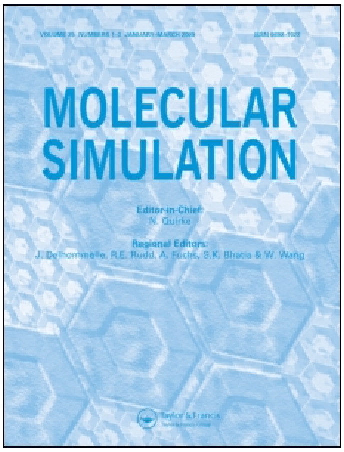

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A Tight-binding Molecular Dynamics Study of the Dissociation of Boron Clusters in c-Si

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Boron clusters with silicon self-interstitials have been implicated in the phenomenon of transient enhanced diffusion (TED) following ion implantation of boron and subsequent annealing steps. This paper explores possible dissolution mechanisms for boron–interstitial clusters during the simulation of a typical annealing process. Using tight-binding molecular dynamics (TBMD) and employing a Goodwin–Skinner–Pettifor sp-based TB model, we have been able to observe the complete dissolution of a B_4I_4 cluster into the surrounding crystalline silicon matrix. Many unsuccessful attempts to observe dissolution are also presented, highlighting the effect of cluster stability, temperature and the role of vacancies in cluster dissolution. Though we can make no unambiguous statements on the definitive dissolution mechanism of boron-defect clusters based on one successful dissolution event, we can hint at key events that appear to be important, such as the diffusion of self-interstitials (presciently predicted by Pelaz *et al.*), the "stranding" of boron atoms in their wake, and the importance of mobile boron–self-interstitial (B–I) pairs. The intrinsic diffusivity of boron in a c-Si lattice and its retardation of the diffusivity of Si self-interstitials is also discussed.

Keywords: Tight-binding method; Molecular dynamic simulation; TED; Boron clusters; Dissociation of clusters

INTRODUCTION

Our interest in the formation and dissolution of boron-defect clusters, e.g. B_mI_n (where B_m represents boron atoms and I_n represents their associated silicon self-interstitials) arises from a study of Transient Enhanced Diffusion (TED) of boron in silicon. TED is one of the most interesting problems in dopant diffusion that remains to be solved, both from a scientific and technological standpoint.

Since the first study by Hofker *et al.* [1], many people have investigated TED, both from an experimental and computational standpoint. For instance, an early paper investigated TED using both experiments and continuum-level simulation [2]. The authors identified several key problems in understanding this phenomenon, e.g. the number of interstitials arising from the implant, which contribute to the enhanced diffusion. Though the often-cited "+1" model [3], which assumes that each implanted ion generates one excess self-interstitial, is capable of estimating the extent of interstitials injected during TED, the model has never been verified by experiments. In addition, there is no detailed knowledge of the evolution of interstitial damage following ion implantation and during subsequent annealing steps. The third ambiguous feature of TED is the fact that the peak portion of implanted B profiles remains static and inactivated upon annealing, when an apparently critical dopant concentration is exceeded.

Benton *et al.* [4] studied the first two problems noted above using deep-level transient spectroscopy measurements to study the damage region produced by Si ion implantation. Their results suggest that the small interstitial clusters are either the precursors of extensive {311} defects or that they compete with {311} defects as a sink for self-interstitials. Haynes *et al.* [5] performed experiments to study the immobile and electrically inactive boron clusters during TED using plan-view transmission electron

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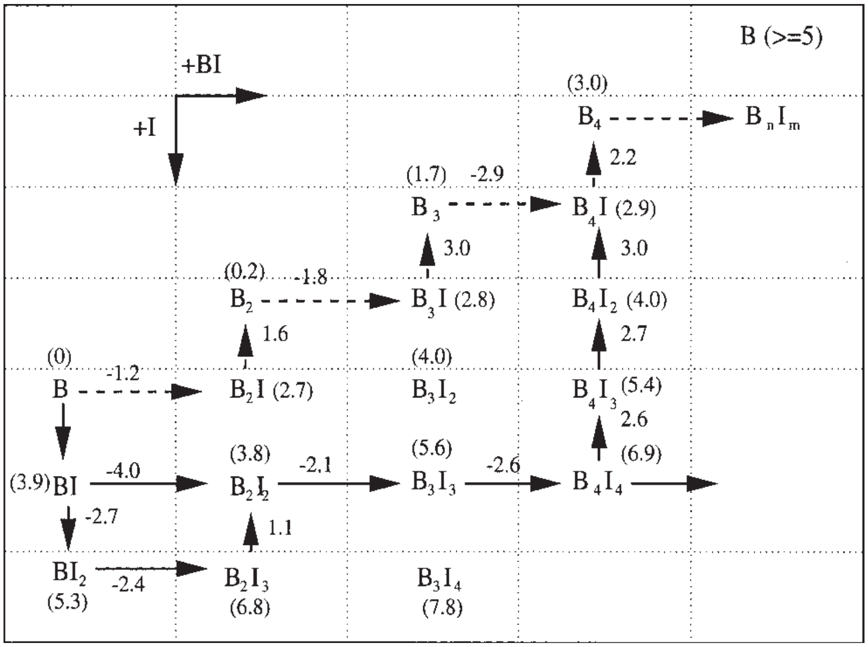


FIGURE 1 Schematic of different paths for the growth of B clusters showing formation energies and reaction energies from different boron clusters and reactions.

microscopy and suggested that B_sB_I clusters are formed during TED. Castell *et al.* [6] used secondary electron (SE) imaging in a scanning electron microscope (SEM) in combination with secondary ion mass spectrometry (SIMS) to investigate boron deactivation and TED of boron in a dopant superlattice. They believed that the deactivation of B marker layers was due to B–I and BI_2 defects. Independent of the location of the primary damage region, B deactivation can be explained through B_3I clustering mechanisms. The sizes of B defects and clusters were not measured from these experiments, but from a comparison of their data with the data existing in the literature. Given the difficulty of making experimental observations of the details of dopant-defect motion in solids, it is not surprising that the results, such as those described above, led to discrepancies in explaining what kinds of boron clusters are responsible for the experimental observations of boron deactivation and immobility during TED.

A more successful approach towards understanding this problem has come from computer simulation based techniques, as exemplified by the work of Pelaz *et al.* [7,8]. They have focused on explaining the immobility and deactivation of boron (i.e. the third problem outlined above) using an atomic-scale simulation approach using the Monte Carlo diffusion code DADOS [9]. The initial distributions of self-interstitials, vacancies and implanted ions needed by DADOS were calculated using the MARLOWE code [10] that is based on the binary collision approximation. Using these approaches, they have also suggested that BI_2 acts as an important precursor to B clusters. Further, they have suggested that boron precipitation and clustering occurs along two different possible paths (see Fig. 1): a generic low interstitial content path (dashed line) and a high interstitial content path (solid line). Thus, the preferred mechanistic pathway depends on the concentration of silicon self-interstitials.

Much of Pelaz *et al.*'s work was validated by a recent tight-binding statics calculations of the formation energies of both the high- and low-interstitial content routes [11]. According to the formation energy data, the low self-interstitial content path is characterized by low formation energy. The largest formation energy in this path is that of B_4I (2.9 eV), which is lower than the lowest formation energy of clusters involved in the high interstitial content path. If the concentration of self-interstitials is low (say, close to equilibrium conditions), this path is energetically favored. In contrast, the formation energies of the clusters involved in the high interstitial content path are high; however, the reaction energies are negative, which means that all reactions along this path are exothermic. When there are a large number of excess self-interstitials, the high interstitial content path will be the energetically favored one. Thus, the energetically favored boron precipitation path depends on the concentration of B_I, and hence the concentration of boron and self-interstitials available to facilitate boron clustering. In addition, this work showed that binding energies of B_mI_n clusters were lowest when $m = n$, i.e. when the clusters are neither B-rich nor interstitial-rich [11]. This conclusion is the same as that given by Pelaz *et al.* [8], though the approach was different.

TABLE I Comparison of the binding energies (in eV) for the release of I and BI in neutral reactions, as calculated by a tight-binding method [11] and LDA [13]

Reaction path	$BI_2 \rightarrow BI \rightarrow B$		$B_2I_2 \rightarrow B_2I \rightarrow B_2$	
Tight-binding method	2.70	0.20	3.00	1.60
LDA	1.45	0.79	1.12	3.50
Reaction path	$B_3I_2 \rightarrow B_3I \rightarrow B_3$		$B_3I_2 \rightarrow B_2I \rightarrow B$	
Tight-binding method	2.90	3.00	2.60	1.20
LDA	1.69	4.26	1.50	1.33
Reaction path	$B_4I_2 \rightarrow B_3I \rightarrow B_2$		$B_2I_2 \rightarrow BI$	
Tight-binding method	2.70	1.80	4.00	
LDA	1.29	3.31	1.66	
Reaction path	$B_4I \rightarrow B_3$		$B_4I_2 \rightarrow B_4I$	
Tight-binding method	2.90		3.00	
LDA	2.60		2.95	

Recently, there have been two *ab initio* studies of the formation energies of small B_mI_n clusters using LDA [12,13] and GGA [12] methods. Although they use similar approaches, Liu *et al.* suggest that the most stable structure is B_2I_3, whereas Lenosky *et al.* consider B_3I^{-1} to be particularly stable. Comparison of the binding energies for the release of Si self-interstitials and BI, estimated by the tight-binding method [11] and these two *ab initio* calculations are listed in Table I (for neutral reactions) and Table II (for charged reactions). As these tables show, the binding energies from the three studies show somewhat different values, reflecting the current difficulties in rationalizing these approaches.

Despite the qualitative agreement between investigations of the favored precipitation paths that enable boron clustering to occur, the situation for cluster dissolution is less unambiguous. Inspection of the tight-binding derived energies of boron dopant-defect clusters released during dissolution of clusters like B_4I_4, either by losing an interstitial or a B–I pair, are close enough such that they are within the accuracy of the tight-binding calculations themselves (around 0.3 eV). For example, a B_4I_4 cluster could fall apart either by releasing a mobile self-interstitial or by losing a mobile boron interstitial atom (B_I); both require 2.6 eV.

TABLE II Comparison of the binding energies for the release of I and BI in charged reactions, as estimated by two LDA calculations [12,13]

Reaction path	$BI_2 \rightarrow BI^+ \rightarrow B^-$		$B_2I_2 \rightarrow B_2I \rightarrow B_2^=$	
LDA [12]	1.90	0.40	1.20	2.10
LDA [13]	1.10	1.02	1.12	3.05
Reaction path	$B_3I_2 \rightarrow B_3I^- \rightarrow B_3^{3-}$		$B_3I_2 \rightarrow B_2I \rightarrow B^-$	
LDA [12]	0.40	4.50	1.00	0.80
LDA [13]	1.32	4.23	1.27	1.10
Reaction path	$B_4I_2 \rightarrow B_3I^- \rightarrow B_2^=$		$B_2I_2 \rightarrow BI^+$	
LDA [12]	1.70	2.70	1.60	
LDA [13]	0.69	3.00	1.20	
Reaction path	$B_4I^= \rightarrow B_3^{3-}$		$B_4I_2 \rightarrow B_4I^=$	
LDA [12]	3.20		3.00	
LDA [13]	2.75		2.40	

The intent of this paper is to use tight-binding molecular dynamics (TBMD) to investigate the dissolution of a boron-defect cluster, B_4I_4. The advantage of TBMD over the statics calculations is that the former is completely deterministic. The mechanism of dissolution will be governed solely by the interatomic forces and the thermodynamic constraints on the system (e.g. temperature). On the other hand, TBMD is remarkably slow computationally, which constrains the lower limit of temperature we can study and also the duration of the elapsed time we can simulate (certainly less than 1 ns). Note that an LDA study would be infeasible here. Thus, this paper constitutes a feasibility study for the capability of TBMD to observe boron-defect cluster dissolution in an accessible timeframe. Simulations of the characteristic diffusion of a boron atom in the absence of other defects are also given in this paper, in order to provide a baseline against which to view boron-defect diffusion within a larger cluster.

SIMULATION METHOD

The TBMD calculations used an NVT ensemble and a 216-atom supercell. The code involves a traditional diagonalization to solve the Hamiltonian matrix. Only one k point (Γ) was used, for the reason explained in a previous paper [11], namely that the Γ point is accurate enough to obtain the structure of defects and clusters, though it would not be accurate enough to calculate energetic properties to better than 0.3 eV. The time step was 1 fs. Each simulation was run for 250 ps (250,000 iterations of the PDEs). We chose B_4I_4 as our test cluster, being the largest cluster we can reasonably handle computationally. A larger cluster would require a larger cell than 216 atoms and, while simulations of 512 atoms are feasible, they are also excruciatingly slow for the series of eight simulations investigated here and inappropriate at this "proof of concept" stage.

We performed MD runs at two temperatures, 1000 and 1200°C respectively. Typical experimental annealing temperatures following ion implantation normally lie in a range between several hundred degrees and about 1000°C. Clearly, the higher the temperature, the easier it is to perform MD simulations. Hence, the choice of 1200°C for some of the simulations was made to facilitate dissolution without, presumably, changing the dominant mechanisms.

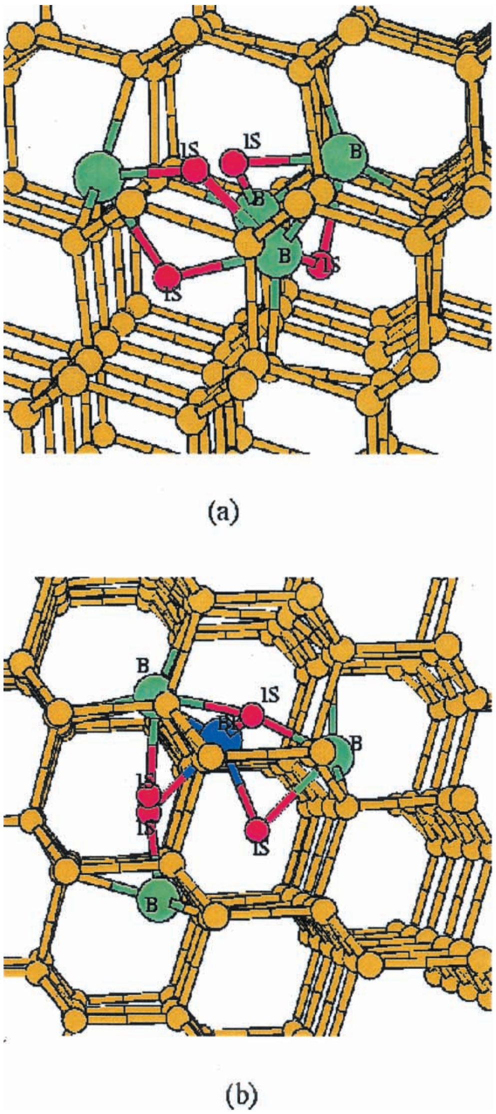


FIGURE 2 Structure of B_4I_4 clusters. Boron atoms are shown artificially large for clarity. Si lattice atoms are shown in brown, substitutional boron atoms are large and green, large blue atoms are interstitial boron, and small red atoms are Si self-interstitials. (a) $E_f = 7.6$ eV; (b) $E_f = 6.9$ eV. (Colour version available online.)

The initial structure for the B_4I_4 cluster was, in half of the cases, a relatively stable cluster identified by the previous statics calculations [11] with a formation energy of 7.6 eV (Fig. 2a). In the other half of the cases, the most stable cluster identified by the statics calculations, one with a formation energy of 6.9 eV (see Fig. 2b) was used as the starting point. Comparison of these cases would allow us to see if the precise nature of the starting point affected the dissolution mechanics. In order to mimic real annealing conditions in semiconductor processing, one vacancy was placed in the vicinity of the cluster in some of the cases, providing insight into the way in which a vacancy influences the dissociation process of boron-defect cluster.

The method used here for simulations of the diffusion of a single boron atom in c-Si is the same as that described above for the dissociation of boron-defect clusters. A system size of $216 + 1$ atoms with periodic boundary conditions was used to produce the trajectories of a boron atom (initially an interstitial) through a Si lattice at 1200°C over a period of 250.0 ps.

In the results and figures associated with this paper, we distinguish atoms in terms of their location in the lattice. A lattice atom is defined as one within 1 Å of a perfect lattice position. An interstitial atom (whether Si or B) is defined as any atom, which is not within 1 Å of a lattice site. A vacancy is defined as a lattice site without an atom within 1 Å of the site. When the distance between a boron atom and a self-interstitial is less than 2.32 Å, they are considered as a B–I pair, including both B_I–I (Fig. 4a) and B_S–I pairs (Fig. 4b). If the boron atom can move freely through the open channel of the matrix without interacting with any self-interstitial, it is regarded as a mobile atom (Fig. 4c).

The diffusivity of a boron atom of self-interstitial is an ensemble-averaged value that is achieved by partitioning the whole run into a number of time intervals Δt, and then averaging the diffusion results over all these time origins. The diffusivity is calculated for each time interval using the well-known Einstein formula

$$D = \frac{[\vec{x}(t) - \vec{x}(0)]^2}{6t} \tag{1}$$

which is exact in the limit $t \longrightarrow \infty$, and where $\vec{x}(t)$ is the location of the defect at time t. Typically, Δt is 300 fs and more than 100 origins are considered to get the average diffusivity.

DIFFUSION OF AN ISOLATED BORON ATOM

Over a time period of 250.0 ps, the diffusivity of a boron atom was found to be 2.4×10^{-5} cm^2/s, which is approximately the same order of magnitude as that for a Si self-interstitial [14]. Since the boron atom may diffuse by various mechanisms, each of which can be associated with a characteristic diffusivity, the value reported above may actually be a composite quantity. These mechanisms include migration via a direct interstitial mechanism, a vacancy, a $\langle 110 \rangle$ split interstitial, and via coordinated push of B_s–I pairs. Previous statics calculations based on transition state theory [15] showed that the diffusivity of a boron atom via a direct interstitial migration (i.e. through the open channels of the matrix) is much higher than those of the other mechanisms, being about 10^{-3} cm^2/s at 1200°C. This value is about four or five orders of magnitude larger than those of the other three mechanisms listed above. In the TBMD simulation performed here, the boron atom was found to migrate via the direct interstitial mechanism only. These observations confirm the tendency predicted by statics calculations [15]. The characteristic diffusivity of a *mobile* boron atom calculated from TBMD simulation is about $10^{-4}\,\mathrm{cm}^2/\mathrm{s}$ at 1200°C, which is about one order of magnitude smaller than that predicted by transition state theory. This discrepancy is probably due to the assumption of constant migration energy in the statics calculation, which is inappropriate at the high temperature considered in the simulation.

We used a visualization tool, XMOL [16], to trace the dynamic motion of the boron atom. From this XMOL analysis, we found that, although the size of a boron atom is smaller than that of a silicon atom, it is relatively easy for it to push a Si atom out of its lattice site. The boron atom migrated to a lattice site very early in the simulation (0.45 ps) and stayed there, in a substitutional position for most of the time. The fraction of time spent by a boron atom in a substitutional site versus an interstitial position is shown in Fig. 3. By the conclusion of the simulation, the ratio of time spent as an interstitial boron, including the atom as a single mobile boron and as a B_I–I pair, was only about 0.2. This is the reason why the average diffusivity of a boron atom in c-Si ($2.4 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{s}$) is much lower than the characteristic diffusivity of a boron atom via a direct interstitial migration ($10^{-4}\,\mathrm{cm}^2/\mathrm{s}$).

The XMOL analysis was instrumental in allowing us to determine the complex relationship between boron atoms and self-interstitials. When the boron atom diffuses to the vicinity of a lattice site and pushes a silicon atom into an interstitial position, they always form a B–I pair (Fig. 4a) and continue to compete for this lattice site. After the boron atom enters this substitutional position, the B–I pair may continue to exist (Fig. 4b), leaving the self-interstitial in its vicinity, trying to return to its original position. It usually takes a long time for the silicon atom to retake the lattice site, since the boron atom prefers staying in a substitutional position (Fig. 4c). If the B–I pair separates, the self-interstitial diffuses away and enters a lattice site by ejecting a neighboring silicon atom. Our observations suggest that the new self-interstitial thus formed appears to be trapped by the boron atom and cannot migrate further away. It keeps moving around neighboring silicon atoms trying to push them out of the lattice, but most of the time it fails (Fig. 4d). The distance between the boron atom and the self-interstitial during this period is approximately equal to that for a second nearest neighbor; this allows the boron atom to remain in the lattice site for a long period of time. In the simulation reported here, for example, the boron atom was observed to stay continuously in a substitutional site for more than 100.0 ps after a B–I pair separated. The simulation showed that self-interstitials formed as a result of boron diffusion remain within the "capture radius" of the boron atom for a considerable length of time and their diffusivity is thus decreased. We estimated the diffusivity of self-interstitials formed transiently during this simulation to be approximately $10^{-6}\,\mathrm{cm}^2/\mathrm{s}$, which is about one order of magnitude lower than that in the absence of the boron atom, showing the impact of a boron atom in impeding the diffusion of a self-interstitial.

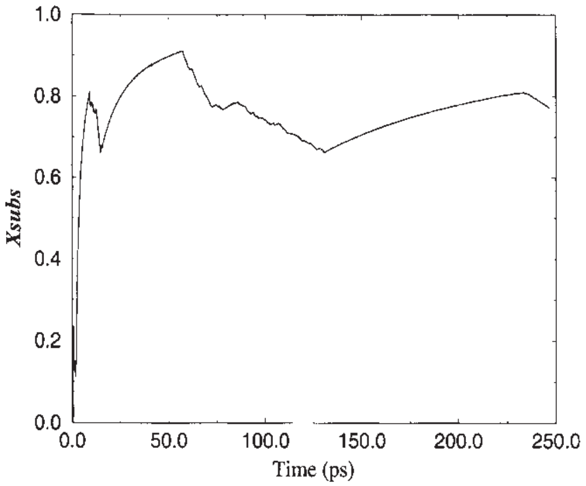


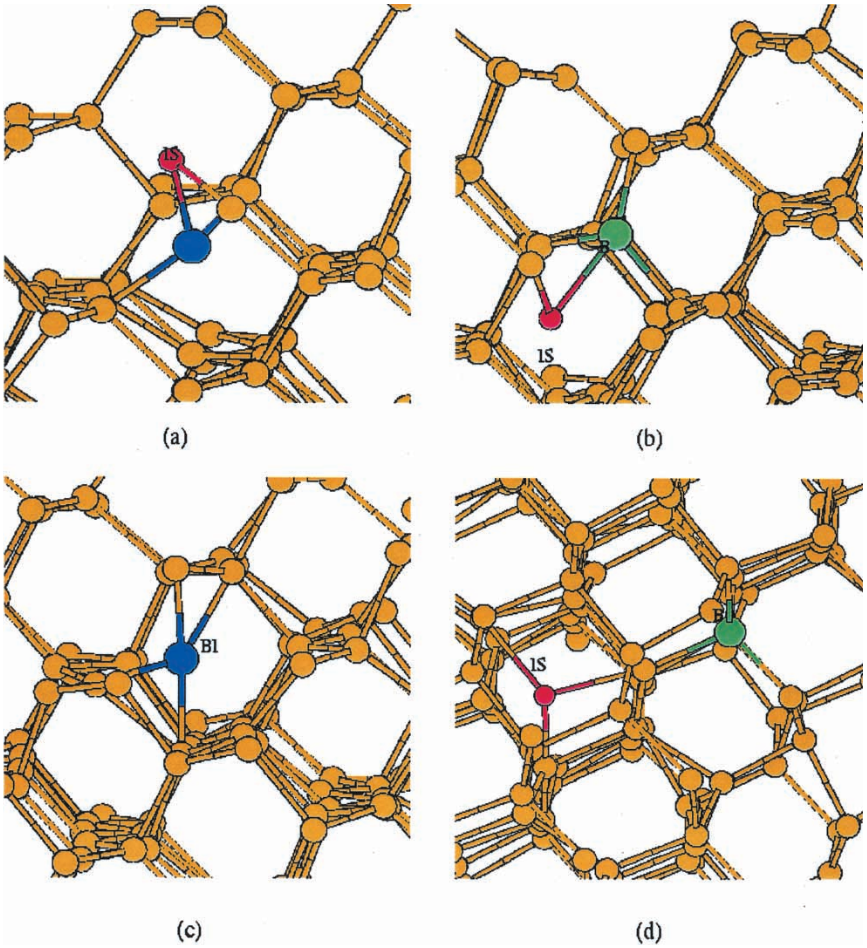
FIGURE 3 Running average of the fraction of time spent by a boron atom in a substitutional site compared to that in an interstitial position, X_{subs}, as a function of time.

DISSOCIATION MECHANISM

We performed eight TBMD simulations, summarized in Table III, to see the effect of cluster stability, temperature, and the role of a vacancy in cluster dissolution.

Dissociation of Clusters in the Absence of a vacancy

For the case where the temperature was 1000°C, and no vacancy was present in the simulation in the initial configuration, the cluster with a formation energy $E_f = 7.6\,\mathrm{eV}$ failed to dissociate within the elapsed time of the simulation (240 ps). At the end of this run, the B_4I_4 cluster remained intact and did not show any imminent tendency to dissolve. Although mobile entities such as B_I and B–I pairs were formed transiently during the simulation, they always recombined with the remainder of the cluster. Throughout the simulation, even though the precise atomic positions constituting the configuration of the cluster changed constantly with time, the relative positions of the four boron atoms did not change significantly; they stayed in substitutional sites for most of the time. This tendency agreed with the result of the boron diffusion simulation described in



(a) (b) (c) (d)

FIGURE 4 Typical sequence in the diffusion of an isolated boron atom at 1200°C. B = substitutional boron atom; BI = interstitial boron atom; IS = Si self-interstitial. Same color key as Fig. 1. (a) Formation of a B_I–I pair; (b) Formation of a B_s–I pair; (c) Creation of a mobile boron atom; (d) After the B–I pair separates, the self-interstitial appears to be trapped by the boron atom and cannot migrate further away for some time. (Colour version available online.)

the "Diffusion of an isolated boron atom" section. The configuration of the cluster changed mainly due to the displacement of the self-interstitials. But they were not able to escape the cluster; they remained within its interatomic force field.

In order to hasten the dissolution process, an MD run from the same initial structure as above was performed at a higher temperature, 1200°C. However, while the cluster dynamics were more rapid, the net result was the same as that at the lower temperature, i.e. the cluster remained intact. The key events observed during this run were essentially the same as those at the lower temperature.

TABLE III Summary of all TBMD runs

Temperature (°C)	*Running time* (ps)	*Initial structure*	*Dissolved?*
1000	240	B_4I_4 $E_f = 7.6\,\mathrm{eV}$	No
	240	B_4I_4 $E_f = 7.6\,\mathrm{eV} + \mathrm{V}$	No
	180	B_4I_4 $E_f = 6.9\,\mathrm{eV}$	No
	150	B_4I_4 $E_f = 6.9\,\mathrm{eV} + \mathrm{V}$	No
1200	240	B_4I_4 with $E_f = 7.6\,\mathrm{eV}$	No
	240	B_4I_4 $E_f = 7.6\,\mathrm{eV} + \mathrm{V}$	Yes
	180	B_4I_4 $E_f = 6.9\,\mathrm{eV}$	No
	180	B_4I_4 $E_f = 6.9\,\mathrm{eV} + \mathrm{V}$	No

TBMD simulations of the time evolution of a B_4I_4 cluster with a lower formation energy, $E_f = 6.9\,\mathrm{eV}$, at both 1000 and 1200°C respectively, did not produce any significant dissolution within the observation period. No new phenomena were observed relative to the preceding runs, and—if anything—this cluster was even more resistant to dissolution than the runs with the formation energy of 7.6 eV (as would be expected, given its lower formation energy).

The net result of all these investigations showed that, in situations corresponding to experiments in which the concentration of self-interstitials remains high, clusters of the size of B_4I_4 are stable over a timescale of at least 250 ps. Unfortunately, the simulation runtime is ten orders of magnitude too short compared to experimental conditions, where annealing is performed on the order of minutes. In addition, the simulation conditions do not approximate real annealing conditions in which interstitials can be lost by annihilation with vacancies, by being trapped by impurities and surface segregation. In the simulation, the concentration of interstitials remains constant (and high). Providing an avenue for the loss of self-interstitials during the simulation in order to mimic experimental annealing conditions had to be considered if any progress was to be made in studying cluster dissolution.

Dissociation of Clusters in the Presence of a vacancy

The simplest way to emulate real annealing conditions was to place a vacancy in the vicinity of the cluster. Our hope was that the vacancy would destabilize the cluster and hasten the dissolution process. Accordingly, we re-studied the TBMD time evolution of a B_4I_4 cluster in the presence of a single vacancy at both 1200 and 1000°C respectively.

We placed the vacancy in a tetrahedral lattice site near the $E_f = 7.6\,\text{eV}$ cluster in its initial configuration; the shortest distance between the vacancy and any of the four self-interstitials, was 4.5 Å (see Fig. 5a). This positioning of the vacancy was intentionally within the so-called "capture radius" of the cluster to ensure annihilation of the vacancy with some atom in the cluster [17]. The effect of including the vacancy proved to be important; it allowed us to observe the only cluster dissolution among all the simulations we tested. The key events are shown in the time sequence shown in Figs. 5–9.

For the case where the temperature was 1200°C, we found that the vacancy diffused towards the cluster very quickly. By 1.5 ps, the vacancy had

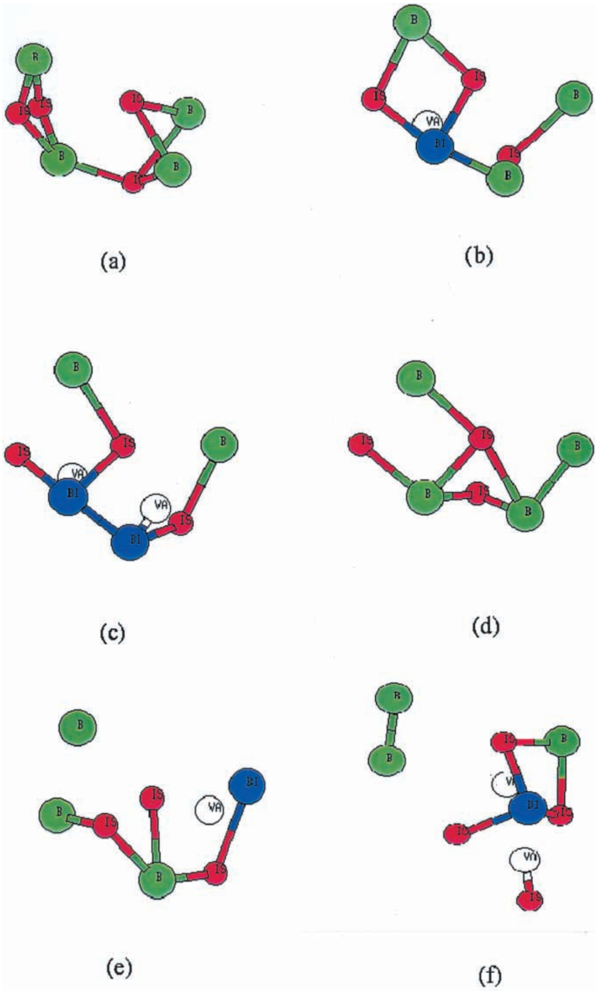


FIGURE 5 Key events in the TBMD simulation at 1200°C for a system containing B_4I_4 plus a vacancy in the time span: 0–70.0 ps. Same color key as Fig. 1; vacancies are shown as white circles. The surrounding matrix Si atoms are not shown for clarity. These diagrams are two-dimensional projections of the three-dimensional simulation cell. B = a substitutional boron atom; BI = a interstitial boron atom; VA = a vacancy; IS = a Si self-interstitial. (a) initial structure with $E_f = 7.6\,\text{eV}$, as obtained by statics calculations; (b) after 1.5 ps, the implanted vacancy had already annihilated one self-interstitial; (c)–(e) the three remaining self-interstitials moved around the four boron atoms, trying to displace them from their lattice sites; (f) boron interstitials may push nearby lattice Si atoms out of position during the competition, creating vacancies. (Colour version available online.)

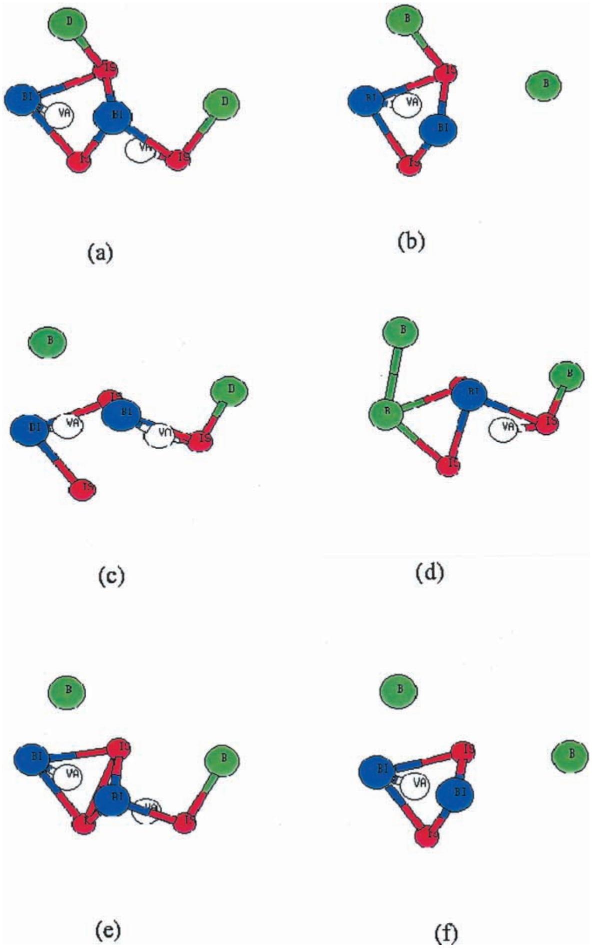


FIGURE 6 (a)–(f) Same simulation (and color code) as in Fig. 5 for the time period: 70.0–75.0 ps. (a) generation of two vacancies by the movement of two substitutional boron atoms from their lattice sites can be seen more frequently; (b)–(e) an interstitial (B or Si) moves into one of the vacant sites and is then kicked out by the movement of the other interstitials; (f) one self-interstitial occupied this position and the other interstitials turned their attention into competing for the remaining vacancy. (Colour version available online.)

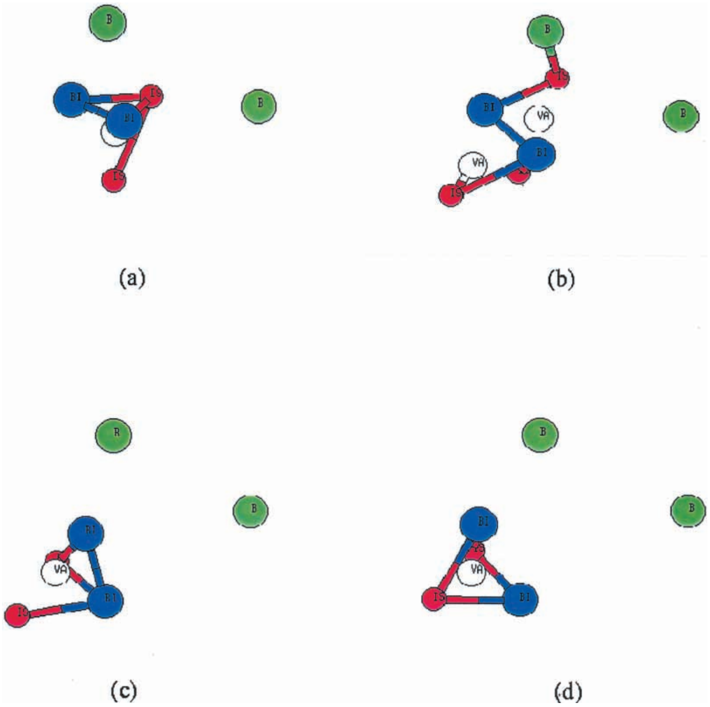


FIGURE 7 Same simulation as in Figs. 5 and 6 for the time period: 75.0–78.0 ps. (a) the remaining cluster formed a $(B_I)_2I_2$ ringed cluster around a vacancy forming ($(B_I)_2I_2V$); (b) a boron interstitial attempted to push out a neighboring lattice Si atom, which generated a new vacancy; (c) and (d) the concerted motion of this self-interstitial into the vacancy and the push of a peripheral Si atom from its lattice site by a interstitial boron atom had the net effect of moving the B_2I_2 ring away from its original location and farther away from the stranded boron atoms left in substitutional sites. (Colour version available online.)

annihilated one interstitial in the cluster. This time scale is the same as Zawadzki [17] obtained for pure Si. In her TBMD calculation, when the initial distance between a tetrahedral interstitial, I, and a vacancy, V, is 4.5 Å, the mean annihilation time is 2 ps. During the first 70 ps of simulation, the three remaining self-interstitials moved around the four boron atoms, trying to displace them from their lattice sites (see Fig. 5b–e). One or two vacancies can always be found inside the cluster. The creation of these vacancies was usually due to the movement of the boron atoms being pushed out of lattice sites by Si self-interstitials. If a boron interstitial did not move far away from its initial position, it always returned to its original site readily. Otherwise, Si self-interstitials would move quickly toward this vacancy and compete with the interstitial boron atom for this lattice position. Boron interstitials may also push a nearby lattice Si atom out of its position during the competition. Therefore, sometimes, yet another vacancy generated outside the cluster can be seen (Fig. 5f). Despite these local competitions, the relative positions of the four boron atoms did not change significantly for 70 ps.

After that time, the dynamic behavior of the boron cluster changed more dramatically. Generation of two vacancies by the generally uncoordinated movement of two formerly substitutional boron atoms from their lattice sites into interstitial positions can be seen more frequently. This kind of dynamic motion produced two boron interstitial atoms and the three remaining self-interstitials competing for two vacancies. This also left two boron atoms in substitutional sites nearby. Between 70 and 75 ps (see Fig. 6), it was common to see a self-interstitial move into one of the vacancies and then be kicked out by the movement of nearby interstitials (B or Si). Finally, one self-interstitial occupied one of the vacancies and the other interstitials turned their attention into competing for the remaining vacancy. Thus, we now have a dynamic $(B_I)_2I_3$ cluster and two nearby B_s atoms.

The annihilation of one of the two vacancies by a self-interstitial left two boron interstitials and two self-interstitials competing for the single remaining vacancy, producing a B_2I_2 ringed cluster around the vacancy (B_2I_2V, see Fig. 7a). B_2I_2 rings are known to be a prevalent structure in tight-binding studies of B-doped Si [18]. The annihilation also stranded the other two boron atoms occupying the substitutional sites, a small distance from the B_2I_2V ring. At some point in this competition, a boron interstitial attempted to push a neighboring Si atom out of its lattice site which generated a new vacancy, temporarily creating a $B_2I_2V_2$ transition state (Fig. 7b). After 80 ps, one of the self-interstitials in the B_2I_2V ring moved into the original vacancy in Fig. 7a, thus annihilating it.

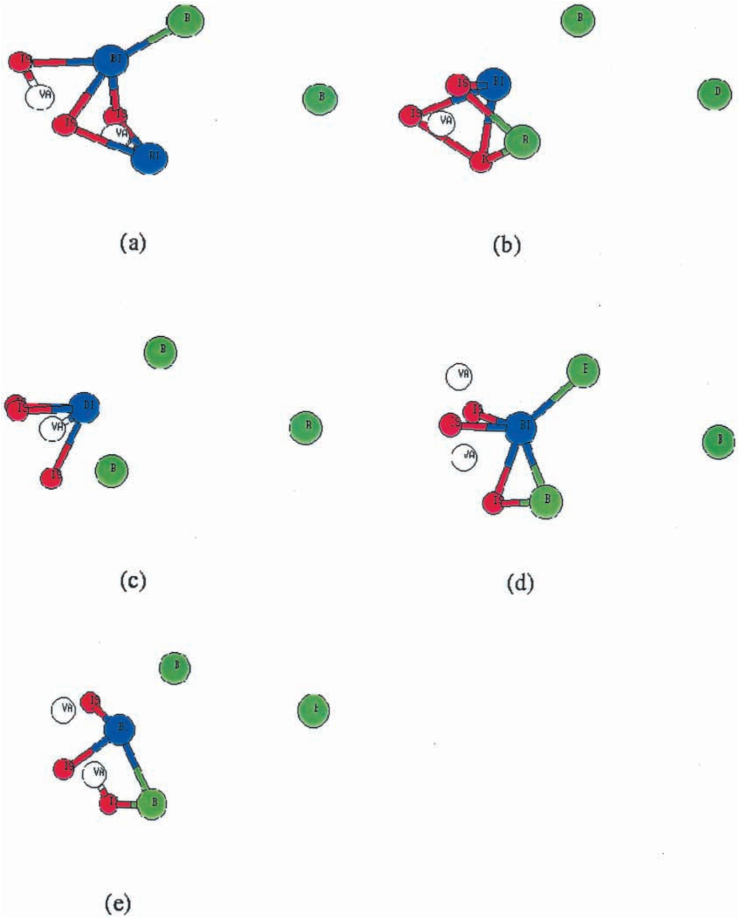


FIGURE 8 Same simulation as in Figs. 5–7 for the time period: 80.0–90.0 ps. (a)–(c) In a similar manner to that in Fig. 7, one boron atom in the $(B_I)_2I_2V$ ring created a second vacancy by pushing a neighboring Si atom from its lattice site. This allowed the other boron atom to occupy the vacancy in the former $(B_I)_2I_2V$ ring and created a B_II_3V defect; (d) and (e) the single remaining boron atom pushed a neighboring Si atom from its lattice site creating a second vacancy and a new self-interstitial. (Colour version available online.)

The concerted motion of this self-interstitial into the vacancy and the push of a peripheral Si atom from its lattice site by an interstitial boron atom has the net effect of moving the B_2I_2 ring away from its original location and farther away from the stranded boron atoms in substitutional sites (Fig. 7c and d).

In a similar manner to the competition described in the preceding paragraph, one boron atom in the B_2I_2V ring created a second vacancy by pushing a neighboring Si atom from its lattice site. This allowed one of the two interstitial boron atoms to occupy the vacancy in the former B_2I_2V ring and created a BI_3V defect (see Fig. 8a–c).

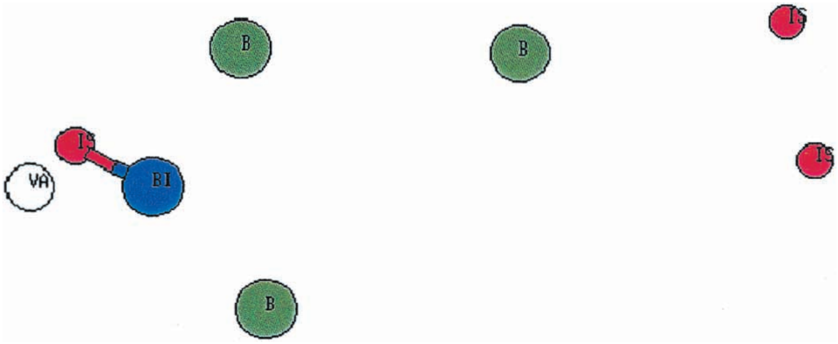


FIGURE 9 Final part of the simulation shown in Figs. 5–8 for the time period: 95.0–100.0 ps. After 95 ps, two of the self-interstitials in the B_II_3V ring diffused away from the boundary of the unit cell and left a B–I pair as the final fragment of the cluster. (Colour version available online.)

TABLE IV Key dissolution steps for B_4I_4

Key dissolution step	*Time frame* (ps)
$B_4I_4 + V \rightarrow B_4I_3 + Si_s$ (1)	1.5
$B_4I_3 \rightarrow B_s + B_s + (B_I)_2I_3 + 2V$ (2)	70
$(B_I)_2I_3 + 2V \rightarrow (B_I)_2I_2V + Si_s$ (3)	75
$(B_I)_2I_2V + V + I \rightarrow B_II_3V + B_s$ (4)	85–90
$B_II_3V + V + I \rightarrow B_IIV + Si_s + (2I)$ (5)	≥95

The above process was repeated when the single remaining boron atom pushed a neighboring Si atom from its lattice site creating a second vacancy and a new self-interstitial (see Fig. 8d and e). This allowed one of three self-interstitials to occupy the vacancy in the former BI_3V ring, creating a new BI_3V defect. After 95 ps, two of the self-interstitials in the BI_3V ring diffused away from the boundary of the unit cell and left a B–I pair as the final fragment of the cluster (see Fig. 9). Thus, the cluster fell apart in ~100 ps. The key dissolution steps are summarized in Table IV. An XMOL movie of the cluster dynamics is available on our web page (http://www.cheme.cornell.edu/graduate/research/ck77/research.html) to help readers visualize the complex process of dissolution.

For a lower temperature of 1000°C, the annihilation time of one self-interstitial in the cluster by the implanted initial vacancy was the same as that at 1200°C, but the kinetics are more sluggish. At the end of the simulation (240 ps), the relative positions of the four boron atoms had not changed significantly, and the cluster remained intact. The dynamic behavior of this cluster was similar to that observed in the first 70 ps at 1200°C. No migration of boron atoms or release of self-interstitials was observed during the simulation. We also performed the same simulations for the more stable $E_f = 6.9$ eV cluster at 1200 and 1000°C respectively. Both these cases failed to dissociate within the observation period and the clusters still existed in relatively stable states. The annihilation time of a self-interstitial in the initial configuration by the implanted vacancy is about 2.5 ps in both these cases, slightly longer than that of the $E_f = 7.6$ eV cluster reflecting its greater stability.

Pelaz *et al.* proposed a mechanism for the dissociation process [19]: the dissolution of boron-defect clusters may occur in a quasi-equilibrium condition by the capture of Si interstitials and then the release of an B interstitial. From their point of view, boron cluster dissolution is just the reverse process of precipitation. The results from the TBMD simulations described here show some elements of this model, particularly the motion of interstitials, but suggest that the process is much more complex. In Liu *et al.*'s LDA calculations, they consider B_2I_3 to be a particularly stable cluster. But in our simulation, the transformation of B_2I_3 into a B_2I_2 ringed cluster is easily observed. The difference may be due to the existence of the vacancy inside the cluster in our case or, of course, may reflect differences in the modeling approaches. Simulation of diffusion of a single boron atom confirmed that boron strongly prefers to stay in a substitutional site, but also showed that the self-interstitial seems to be trapped by the proximity of a boron atom and vice versa. Thus, it is not easy for boron-defect clusters to emit boron interstitials during the dissolution process. For the case described here in which the cluster dissolved, we learnt that the boron cluster fell apart due to the migration of interstitials (whether B or Si) shadowing the movement of a faster moving vacancy, leaving boron atoms stranded in substitutional sites farther away from the remaining cluster. The vacancy migrates in what may be termed an exchange mechanism. Boron interstitials remaining in the cluster will push a nearby Si atom from its lattice site creating a second vacancy. This allows one of the interstitials in the cluster to move into the site of the original vacancy and then the others move toward the new one, thus producing a new defect.

CONCLUSIONS

We have simulated the diffusion of an isolated boron atom at 1200°C. The average diffusivity of a boron atom in c-Si is approximately the same order of magnitude as that for a Si self-interstitial, $\sim 2.4 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{s}$, while the diffusivity when the boron atom is actually mobile in the lattice (as compared to being immobile on a lattice site) is about one order of magnitude higher ($\sim 10^{-4}\,\mathrm{cm}^2/\mathrm{s}$). The simulation showed that the boron atom clearly preferred staying in a lattice site (~80% of the elapsed time). It is relatively easy for boron atoms to displace a lattice Si atom and form a B–I pair. This self-interstitial may retake the lattice site, but it usually takes a long time to do so since the boron atom has a higher affinity for the substitutional position. The presence of the boron atom retards the diffusion of a self-interstitial by roughly an order of magnitude at 1200°C. This unexpected result has implications when considering the value of the diffusion constant of self-interstitials obtained experimentally, since boron is invariably used as a marker of self-interstitial location.

For the simulations of boron-defect cluster dissolution, we have been able to observe the complete dissolution of a B_4I_4 cluster into the surrounding crystalline silicon matrix at 1200°C within 100 ps. This result suggests that boron clusters may fall apart due to the migration of interstitials (whether B or Si), as in Pelaz *et al.*'s work, but also highlighted the role played by spontaneously generated vacancies. Other attempts to observe cluster dissolution failed within the same observation period, reflecting the effect of cluster stability, temperature and the role of vacancies in cluster dissolution.

It is unwise to assume that the dissolution mechanism observed for one single boron cluster is the only, or even the dominant, mechanism for the dissociation of boron-defect clusters in general. There are any numbers of reasons why these results may be, in essence, anecdotal. One drawback of this approach is the limited observation time of MD, here ~250 ps. Although one vacancy was placed in the vicinity of the cluster to approach the real annealing conditions, we have still simplified the situation by neglecting the presence of impurity traps and surface effects. Their influence on the dissociation mechanism is still unknown. Another factor in the tendency for dissolution may be the choice of potential model. For example, if the Kwon model [20] was used instead of GSP tight-binding model [21], we might get different results due to the enhanced stability of the split interstitial relative to the tetrahedral one in the GSP model.

Near the end of the stimulation, two self-interstitials moved across the boundary of the unit cell. However, due to the use of periodic boundary conditions and the small system size considered here, they re-entered the cell, close enough to interact with the remaining B–I pair and later recombined to form a new cluster. The present system size allows no room for interstitials to diffuse away to get clear of the influence of the cluster. A large cell would help ameliorate this situation, but the time necessary for a $O(N^3)$ 512-atom simulation for 250 ps would take approximately six months of exclusive CPU time on a single processor. In future, this problem can be solved by use of an $O(N)$ tight-binding method, such as that due to Goedecker [22], and/or hyperdynamics [23]. A fully quantum mechanical simulation, say by a LDA method, is unfortunately impractical over the time scales and system sizes studied in this tight-binding work.

The results described here are clear enough to say that, under annealing conditions, large boron clusters such as B_4I_4 are not stable and they will readily fall apart into smaller ones (cluster dissolution in under a nanosecond would be considered extremely fast by experimental yardsticks). This simulation also showed that the dissolution mechanism cannot be captured by simple pathways such as that shown in Fig. 1. Since we have only one successful test run so far, the statistics are certainly not good enough to determine the dissociation mechanism; but, as a proof of concept, it shows that such a study is feasible.

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