Simulations of dopant clustering in silicon: Dimer calculations using DFT forces

Graeme Henkelman[(a)], Blas Uberuaga[(a)], Scott Dunham[(c)] and Hannes Jónsson[(a,b)]

(a) Department of Chemistry, University of Washington, Seattle, Washington 98195, USA
(b) Faculty of Science, VR-II, University of Iceland, 107 Reykjavík, Iceland
(c) Department of Electrical Engineering, University of Washington, Seattle, Washington 98195, USA

ABSTRACT

We have carried out computer simulations to study the formation and break-up of boron clusters in crystalline silicon. Density functional theory was used to evaluate the interatomic interactions and dimer method used to find the mechanism and rate of the atomic rearrangement processes. The transition rates were calculated within harmonic transition state theory. The simulations have shown how the highly stable B_3I^- cluster in silicon can break up, both by a direct dissociation mechanism and by an interstitial mediated dissociation. The former has an activation energy of 4.3 eV, but the latter around 3.0 eV. The formation of the boron clusters is diffusion limited, i.e. attachment of boron interstitials involves lower barrier than diffusion. But, rearrangements of the boron clusters from one configuration to another turn out to have rather large activation barriers.

Keywords: dimer method, kinetic Monte Carlo, boron clustering, long time-scale

1 INTRODUCTION

The kinetic Monte Carlo (kMC) method applied to a system with well defined energy surface[1] is a very powerful algorithm for simulating long time-scale evolution in a system undergoing thermally activated hops. As long as the mechanism of the important transitions is known, the transition rate can be found from the energy surface and a consistent table of rates constructed. When dealing with solids, the harmonic approximation to transition state theory is typically accurate enough for the relevant range in temperature [2]. This reduces the problem to the task of finding all relevant saddle points on the rim of the potential ridge surrounding the energy minimum corresponding to a given state of the system. The problem is that the mechanism for the relevant transitions is typically not known beforehand. In a recently developed extension of the kMC method [3], the 'dimer method' [4] is used to find saddle points for a given state of the system. This extends the applicability of the kMC method to more complex systems.

Another limitation of typical kMC calculations based on an energy surface is the availability and accuracy of an empirical potential energy function that can be used to estimate the transition rates. By using directly the energy and atomic forces coming from density functional theory (DFT) calculations, this problem is reduced at the expense of CPU time. In the simulations presented here, we demonstrate that it is possible to carry out long time-scale kMC simulations with the dimer method based directly on DFT estimates of the energetics.

2 BORON CLUSTERING IN SILICON

In the electronics industry, silicon is doped with various elements in order to get the right electronic properties. Boron atoms, for example, have one less valence electron than Si and when they are placed in the silicon lattice, replacing silicon atoms, they form four bonds with neighboring silicon atoms and capture an electron from the crystal. This creates a positive hole that can then conduct current through the material.

As the devices have become smaller, the concentration of dopant atoms has been increased in order to get the same throughput of current. At present, the boron concentration is often sufficiently high that small B clusters will form in the silicon after implantation. This clustering deactivates the boron atoms, in that it reduces the number of electrons captured by the boron atoms and thereby the number of holes created in the crystal. Clustering also immobilizes the boron atoms. An understanding of the clustering mechanism and the rate of cluster formation is, therefore, critical for the prediction of boron dopant profiles.

In previous theoretical studies of boron clustering in silicon, the energetics of stable clusters were calculated[5], [6]. It was found that the B_3I^- cluster is particularly stable. There has, however, not been any prior study, as far as we know, of the kinetic pathways that lead to boron cluster formation. It is important to know the mechanism and rate limiting steps of boron cluster formation in order to accurately simulate the distribution and activity of boron dopants in devices. In this study we used the dimer method[4] and elastic band method[7], [8] to find transition mechanism while obtaining the atomic forces directly from density functional theory (DFT) calculations. The calculations give kinetic

pathways of boron cluster break-up as well as formation.

Typically, a silicon crystal will contain a large number of boron clusters after implantation and annealing. Only a small fraction of the implanted boron atoms are then electronically active as dopants. This is typically fixed by rapid heating up to about 1000 $°C$. In order not to destroy the implantation pattern, the annealing time at this peak temperature is short, on the order of seconds. Assuming the prefactor for boron cluster breakup is a typical prefactor for atomic scale processes (a vibrational period), 10^{13} sec^{-1}, this means that the activation energy barrier for boron cluster break-up is ca. 3.3 eV.

2.1 The DFT calculation

The DFT calculations were carried out with the PW91 functional[9], ultrasoft pseudo-potentials [10] and a plane wave basis. The cell for the Si crystal consisted of 64 atoms subject to periodic boundary conditions. We used the VASP software[11]. The rate of transitions was estimated within harmonic transition state theory [2]. We carried out the long time-scale dynamics simulations by mapping out minimum energy paths for the dissociation processes. The algorithm we use is an extension of the kMC method where random numbers are used to choose between processes according to the relative rates. In our implementation of the method [3], the rates are estimated as the simulation proceeds, rather than by constructing a predefined table of events. Also, we do not map atoms onto lattice sites as is typically done in kMC simulations. The development of this new methodology is important for the study of problems such as boron clustering, since it is hard to guess *a priori* what processes will be important and how fast they will occur.

Given an initial state of the system, for example a $B_3I_2^-$ cluster, the dimer method is used to search for the mechanism of possible rearrangements of the atoms. In one case one finds that a BI pair gets dissociated from the cluster. In another case an interstitial, I, gets dissociated from the cluster. These different pathways can then be used to construct the minimum energy path for the capture of a I by a B_3I^- cluster to form $B_3I_2^-$ and subsequent ejection of BI to form B_2I. The process can then be repeated to get the pathway for dissociation of the B_2I cluster. The results of the calculation we have carried out so far are given below. A more complete report of this work will be given elsewhere.

2.2 Direct Break-up of B_3I^-

A minimum energy path for direct dissociation of the B_3I^- cluster to form BI^+ and B_2^{2-} clusters is shown in figure 1 (the charges are assigned on the basis of minimum energy . The activation energy for this process is 4.3 eV, high enough that the process would not be active at on the time scale of seconds at 1000$°C$ if a standard prefactor is assumed (10^{13} sec^{-1}).

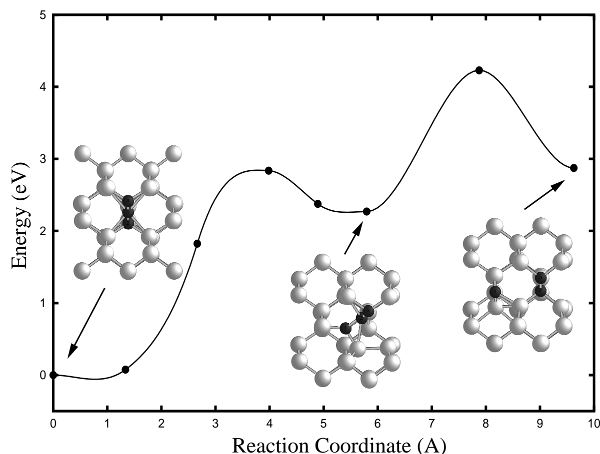

Figure 1: The minimum energy path for direct breakup of a B_3I^- cluster in silicon. The energy minimum far to the left corresponds to the nearly linear configuration of the three boron atoms. the minimum to the right corresponds to a boron dimer and a separate boron interstitial. The activation energy barrier for the break-up is high, 4.3 eV. The product B_2^{2-} is energetically unstable with respect to further break-up into individual B^- atoms at sites in the silicon lattice.

2.3 Interstitial Aided Break-up of B_3I^-

After implantation of dopants, the silicon crystal is typically rich in defects, in particular Si interstitial atoms. These interstitials can play an important role in the break-up of dopant clusters. Figure 2 shows an alternative route for the dissociation of tri-boron clusters (read from right to left). If interstitials are present and do not need to be generated thermally, this process requires a significantly lower activation energy than the direct dissociation shown in figure 1. The attachment of the Si interstitial to the tri-boron cluster is down-hill in energy, by about 1 eV. The interstitial rich cluster had previously been found to be particularly stable [5]. The barrier for the attachment of the Si interstitial is small, less than 0.2 eV, slightly lower than the migration barrier of Si interstitials [12]. Our simulations have revealed several different configurations of this cluster with similar energy. For Fermi-level that is close to mid-gap, the neutral and negatively charged clusters, $B_3I_2^-$ and B_3I_2 are also nearly degenerate [13]. We have, in figure 2, constructed a path where a $B_3I_2^-$ cluster looses its excess charge before dissociating further (at reaction coordinate of 13 Å). The barrier for breaking up the B_3I_2 cluster is 1.5 eV to form B_2I and a BI pair. The B_2I cluster is still stable with respect to individual B atoms in the lattice by 2.0 eV [5]. The transition state

for this final step is only very slightly higher than the final state energy and the overall activation energy barrier for the break-up of the $B_3I_2^-$ cluster is calculated to be 3.0 eV. This is significantly lower activation energy than the direct dissociation shown in figure 1. We therefore conclude that an interstitial rich environment opens up lower energy pathways for dissociation of the B_3I^- cluster. The calculated activation energy for interstitial aided breakup is in excellent agreement with recent experimental measurements based on Hall effect [14].

Reading the energy landscape shown in figure 2 in the opposite way, from left to right, one sees that the addition of a BI pair to a B_2I cluster involves a small activation energy barrier, 0.15 eV. Since the diffusion of a BI pair has an activation energy barrier of 0.4 - 0.7 eV [15], the growth of the two-boron cluster to a three-boron cluster is diffusion limited.

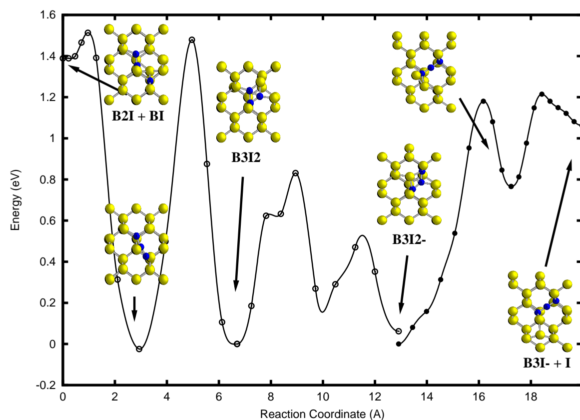

Figure 2: The minimum energy path for interstitial mediated break-up of a B_3I^- cluster in silicon. The energy minimum far to the right corresponds to the nearly linear configuration of the three boron atoms and a separated Si-interstitial (in a hex channel). The intermediate minima correspond to the interstitial rich tri-boron cluster in various configurations, both charged (at reaction coordinate of 13 Å) and neutral (for smaller reaction coordinate). The minimum to the far left corresponds to a B_2I cluster and a separate boron interstitial, BI. The activation energy barrier for this part of the break-up process is 1.5 eV. The product, B_2I, is energetically stable with respect to further break-up into individual B^- atoms at sites in the silicon lattice by 2 eV and the overall activation energy barrier is 3.0 eV.

3 Conclusions

We have presented here an example of a simulation of a sequence of activated events in a complex solid system where DFT calculations of the energy and atomic forces were used directly to find mechanism and rate of each step in the time evolution of the system. These kinds of calculations are at present time CPU intensive but doable. Each dimer search for a saddle point takes on the order of a couple of days on a personal computer. A cluster of personal computers can handle the calculation well because the algorithm, which includes several independent dimer searches, can easily map onto a heterogeneous cluster of computers.

The break-up of tri-boron clusters in silicon is found to be facilitated by the addition of an interstitial to form the B_3I_2 cluster which subsequently undergoes fragmentation. The estimated barrier, approximately 3.5 eV, is quite consistent with the fact that fast heat ramps to 1000 $^\circ C$ for a few seconds can be used to re-activate boron dopant after implantation. The direct break-up of the B_3I^- cluster requires a significantly larger activation energy, 4.3 eV.

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