

## Theoretical Studies of Self-Diffusion and Dopant Clustering in Semiconductors

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Density functional theory studies have been performed to investigate the mechanisms of self-diffusion in Ge and the clustering of B in Si. In the case of self-diffusion of Ge, we find within the harmonic transition state theory a diffusion prefactor for the vacancy mechanism which is in good agreement with experimental values. However, the activation energy is underestimated by nearly 1 eV when the PW91 functional is used. We propose a cluster correction procedure involving the hybrid B3LYP functional which leads to an activation energy of 3.1 eV in agreement with experiment. The contribution of interstitial and exchange mechanisms is negligible. The reaction pathway for the B cluster formation in Si has also been studied. The cluster  $B_3I_2$  has been identified as an intermediary in the formation of  $B_3I^-$ , a dominant cluster. The dimer method is found to be effective for finding transition states for complex systems. All of the steps identified to date have been shown to be diffusion limited.

### 1. Introduction

Diffusion in semiconductors is of great importance for semiconductor technology. As the dimensions of circuits shrink, an understanding of the atomistic-scale mechanism of diffusion processes will become crucial in order to accurately model and design future devices. A prerequisite to the understanding of dopant diffusion is the mechanism of self-diffusion in semiconductors since, for example, Ge, Sb, and As are believed to diffuse in Si by a mechanism involving vacancies in the Si lattice [1]. Accurate estimates for the formation energy and entropy of defects are therefore essential for determining dopant diffusion rates. It is also important to understand the clustering mechanisms since the formation rate of dopant clusters, e.g. B in Si, and the identity of the clusters actually formed will strongly influence the determination of the final profiles of active B in the substrate [2].

Theoretical calculations can give valuable insight into the diffusion mechanism since they allow the separation of the various contributions to the activation energy ( $E_a$ ) and

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the diffusion prefactor ( $D_0$ ). They can also help to identify the individual atomistic processes that lead to cluster formation. First-principles calculations, with no parameterization to measured properties, are most promising because the development of empirical or semi-empirical approaches is tedious, the experimental information is limited, and the accuracy of such approaches outside the fitted range is questionable.

## 2. Calculations

Our DFT calculations were carried out in two steps. First, a periodic cell with 64 atoms ( $\pm 1$  for the defects) was used to find the optimal atomic coordinates for the stable configurations and saddle points. For this, we used the VASP code [3]. The formation energy of interstitials I and vacancies V is well converged at this cell size, differing only by 3% or less when 1000 atoms are used [4]. The PW91 functional [5] combined with ultrasoft pseudopotentials [6] was used in these calculations. For the Ge calculations, we used a plane wave basis set with an energy cutoff of 174 eV and a  $4 \times 4 \times 4$   $k$ -point sampling mesh of the Monkhorst–Pack type [7]. This converges the defect energy to within 0.02 eV. The calculations presented here were performed on charge neutral systems since DFT/PW91 predicts Ge to be a metal. For the B/Si calculations, we used a cutoff of 231 eV and a  $k$ -point mesh of  $2 \times 2 \times 2$ .

Within the harmonic transition state theory (TST),  $E_a$  is obtained from the highest maximum along the minimum energy path (MEP) leading to the final state. We have used the climbing-image NEB method to find the MEP [8]. The prefactors for the Ge self-diffusion were calculated by constructing the force constant matrix at both initial state minima and saddle points [9]. Finite differences of 0.01 Å were used for the coordinates of atoms within a certain radius of the defect to evaluate the second derivatives. The resulting dynamical matrix was diagonalized to find the normal mode frequencies needed for the rate calculation.

For the B/Si calculations we employed the dimer method [10] which is an efficient method for finding multiple saddle points from a given local minimum. Between 10 and 25 dimers were run for each stable cluster to identify the pathways for cluster dissociation.

## 3. Ge Self-Diffusion

### 3.1 Previous experimental work

Various experiments, involving both  $^{71}\text{Ge}$  tracers [11] and  $^{70}\text{Ge}/^{74}\text{Ge}$  heterostructures [12], agree on  $E_a$  to be in the range of 2.95 to 3.14 eV and  $D_0$  in the range of 8 to 44  $\text{cm}^2/\text{s}$ .

Consistent with early speculations [11], the observed diffusion behavior of Cu in Ge has shown that self-diffusion in Ge is vacancy mediated [13]. This means that diffusion is a two step process consisting of the generation and migration of a vacancy. Assuming that both processes are thermally activated,  $E_a$  for self-diffusion is given by the sum of formation and migration energy.

### 3.2 Vacancy mechanism

When an atom is removed from a lattice site to create a vacancy, the neighboring four atoms relax towards the vacant lattice site by 0.36 Å. This relaxation is quite local since

the second neighbors only move by 0.02 Å. However, the force constants are affected over many neighbor shells. From convergence tests we find that the prefactor calculated using a small cutoff radius is less than half the value using a large radius.

The V formation energy is predicted by PW91 to be 2.2 eV. The migration path is simple: One of the four neighbors moves into the vacant site. The migration barrier is low, 0.2 eV, giving an overall  $E_a$  of 2.4 eV.

The vibrational formation entropy for V is quite high,  $9.18k_B$ . This value is obtained by extrapolating the entropies found for various cutoff radii to infinity using an exponential form. The calculated harmonic prefactor for the V diffusion is  $\nu = 2.4 \times 10^{12} \text{ s}^{-1}$ . The prefactor is then  $D_0 = (fzva^2/2d) \exp(S_{\text{form}}/k_B) = 5 \text{ cm}^2 \text{ s}^{-1}$ . Here,  $f = 1/2$  is the correlation factor [14],  $z = 4$  the coordination number,  $a = 2.5 \text{ Å}$  the nearest neighbor separation, and  $d = 3$  the dimensionality of the system. These calculated values are only slightly smaller than the experimental values [11, 12].

### 3.3 B3LYP correction

The PW91 calculations predict an  $E_a$  that is about 0.7 eV lower than experimental values. This large discrepancy is consistent with results obtained for other vacancy diffusers in Si [15]. A comparison with experiments is more conclusive for Ge since the experimental results are more consistent than for Si.

We present a procedure where B3LYP [16] calculations on clusters are used to correct the PW91 results. The B3LYP functional includes Hartree-Fock exchange and has been shown to give better results than the PW91 functional for small molecules, in particular for quantities crucial to the current work such as the activation energy for the Si–Si bond breaking in disilane [17]. The atomic configuration of the periodic system obtained from the PW91 calculations is used. From this, a cluster of a given radius is cut out and capped with H-atoms to eliminate dangling bonds. Both B3LYP and PW91 calculations are performed on the same cluster using the Gaussian98 code [18]. This procedure is repeated for clusters of different sizes and an extrapolation to infinite size is carried out. The difference between the B3LYP and PW91 calculations gives the correction which is added to the periodic PW91 results. The consistency between cluster and periodic system calculations has been demonstrated for Si adatom binding and surface diffusion where it was found that the two approaches give similar results apart from structural relaxation effects [19].

While the formation energy of a defect with respect to an atom in the perfect crystal,  $E_f$ , can be calculated from the periodic cell PW91 calculation the cluster calculations can only give the formation energy with respect to an isolated atom,  $E'_f$ . In the infinite cluster limit the difference between the two values is the cohesive energy of the crystal,  $E_f = E'_f - E_{\text{coh}}$ . We use the PW91 calculation of  $E_f$  but add a correction given by the difference between the B3LYP and PW91 cluster calculations of  $E'_f - E_{\text{coh}}$ . The best estimate then becomes  $E_f + \Delta E'_f - \Delta E_{\text{coh}}$ . In a cluster, the surface atoms are not equivalent to the interior atoms and so, in principle, one would have to use an infinite cluster for these calculations. For a cluster representing the perfect crystal structure the size dependence can be modeled as  $E = Ah + Bg$  where  $h$  is the number of H–Ge bonds and  $g$  is the number of Ge–Ge bonds. In order to extract  $\Delta E_{\text{coh}}$ , we have carried out calculations for three different clusters, containing 5, 17, and 35 Ge atoms, respectively, and fitted the difference between B3LYP and PW91 results to  $\Delta E = h \Delta A + g \Delta B$ .

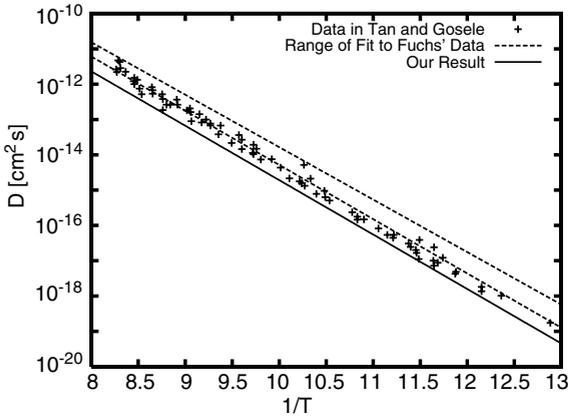


Fig. 1. Comparison between our calculated results (solid line) and experimental data (the two dashed lines give a range of values taken from [12], + gives values taken from [20])

Combined with the energy difference between B3LYP and PW91 for the isolated Ge atom, we find  $\Delta E_{\text{coh}} = \Delta E_{\text{atom}} - 2\Delta B = -0.6$  eV. The V formation energy,  $\Delta E_{\text{f}}^{\text{V}}$ , was calculated using three clusters. The results were fitted using an exponential form and thus an infinite size extrapolation obtained. The total B3LYP correction to the formation energy turns out to be 0.6 eV for the vacancy.

For V migration the difference between the energy of the saddle point and the initial state cluster configurations is calculated with each functional and the difference applied as a correction to the periodic PW91 results. The correction is small, 0.1 eV. The B3LYP corrected  $E_{\text{a}}$  is therefore 0.7 eV larger than the PW91 result in excellent agreement with the experimental data.

Our results are compared with experimental data in Fig. 1. The diffusion constant predicted by theory agrees well with the available experimental data.

### 3.4 Concerted exchange and interstitial mechanisms

For completeness, we report our results for the exchange and I diffusion mechanisms. The concerted exchange involves a swap of two adjacent atoms [21]. The PW91 calculation of  $E_{\text{a}}$  gives 3.6 eV which is 1.2 eV larger than the value for the V mechanism at the same level of theory. The B3LYP correction increases  $E_{\text{a}}$  by 0.5 eV to 4.1 eV which is significantly larger than the experimental value for self-diffusion. The harmonic prefactor for an exchange event is  $\nu = 4.5 \times 10^{14} \text{ s}^{-1}$  which gives an overall diffusion prefactor of  $D_0 = 1.1 \text{ cm}^2 \text{ s}^{-1}$  which is much smaller than the experimental value. The exchange mechanism is therefore predicted to be unimportant for the Ge self-diffusion.

We have found two stable configurations for I: Two Ge atoms can share a lattice site (X) or the interstitial can sit in a tetrahedral site (T) bonded to four neighbors. The PW91 calculations predict X, which has a formation energy relative to the perfect crystal of 3.2 eV, to be more stable than T by 0.3 eV. An estimate of the B3LYP correction increases the formation energy by about 1 eV.

A migration path for I from an X site to a neighboring T site is found to have an activation energy of 0.6 eV. The path to go from a T site to the nearest T site has an energy barrier of 0.2 eV which is slightly lower than the barrier for a hop to X. The lowest energy pathway for I migration is therefore  $X \rightarrow T \rightarrow T \rightarrow \dots \rightarrow X$ .

The PW91 calculations give a harmonic prefactor for the  $X \rightarrow T$  hop of  $\nu = 3 \times 10^{12} \text{ s}^{-1}$ . The I formation entropy is  $S_{\text{form}} = 3.70k_B$ . Thus,  $D_0 = 0.01 \text{ cm}^2 \text{ s}^{-1}$  with  $f = 1$  [14] assumed and  $E_a \approx 4.8 \text{ eV}$ . The I mediated diffusion mechanism is therefore predicted to be unimportant.

## 4. Clustering in Si

### 4.1 Stable clusters

Two previous theoretical studies of B clustering in Si have focused on the energetics of stable clusters [2, 22]. Both found  $B_3I^-$  to be one of the dominant clusters under implant annealing conditions. Liu and coworkers also found that  $B_3I_2$  and  $B_3I_2^-$  have similar energy depending on the Fermi level [23].

Both of these studies assume that cluster formation is diffusion limited, i.e. the barrier for the formation of a cluster from smaller components is just the migration barrier of the mobile species. Equivalently, this means that the barrier for cluster dissociation is given by the sum of the cluster binding energy with respect to the smaller components and the migration barrier of the mobile fragment that diffuses away. The goal of this work is to test this assumption by looking at the atomic mechanisms responsible for cluster formation. We will focus on two clusters,  $B_3I^-$  and  $B_3I_2$ .

### 4.2 Formation and breakup of $B_3I^-$

According to the previous works of Liu et al. [2] and Lenosky et al. [22], the dominant B cluster is  $B_3I^-$ . We have run 10 dimers from this cluster. Of the interesting results, two led to simple exchange processes of one B atom with another. One of the dimer runs led to the beginning dissociation of the cluster. When a second dimer is started from the basin found from the first run, a full dissociation of  $B_3I^-$  to  $B_2^{--} + BI^+$  is found (charge state assumptions are based on the works of Liu et al. and Lenosky et al.).

The activation energy for the reaction  $B_2^{--} + BI^+ \rightarrow B_3I^-$  is about 1.5 eV. This is a rather high barrier to overcome. We now consider an alternative pathway which involves formation of  $B_3I_2$  as an intermediate step.

### 4.3 Formation and breakup of $B_3I_2$

The study of  $B_3I_2^-$  is not finished yet, so here we will focus only on  $B_3I_2$ .

Of the dimers run from this structure four locked on to zero-curvature modes, two were reorientations of the original cluster (identical in structure but rotated with respect to the original geometry), one resulted in a distorted structure, and one led to the beginning of the dissociation of the cluster.

The original cluster which involves three B atoms in a trigonal structure bonded to a Si atom can rotate so that the B atoms are bonded to a different Si atom in the same tetrahedron. This does not lead to a net diffusion of the cluster but rather a reorientation. This process has a barrier of 0.8 eV.

The other interesting process we found leads to the dissociation of the cluster. This reaction involves an intermediate state in which the three B atoms form a linear chain in the Si crystal which is degenerate in energy with the original cluster. The minimum

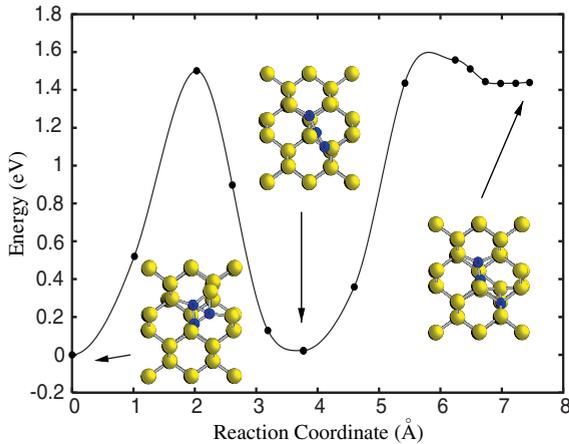


Fig. 2 (online colour). Minimum energy path for the breakup of  $B_3I_2$  into  $B_2I$  and  $BI$ . The reverse barrier for the formation of  $B_3I_2$  is only 0.2 eV

energy path for this reaction is shown in Fig. 2. The barrier for a transition from one structure to the other is 1.48 eV. Overcoming a second barrier of 1.58 eV leads to the products  $B_2I$  and  $BI$  with an energy of 1.42 eV above the original cluster. This is already in good agreement with the infinite separation energy of these individual products of 1.5 eV found by Liu et al. The reverse barrier of joining  $B_2I$  and  $BI$  to form  $B_3I_2$  is only 0.16 eV which is smaller than the diffusion barrier of  $BI$  in bulk Si [23]. Thus, the formation of the  $B_3I_2$  cluster from  $B_2I$  and  $BI$  is diffusion limited.

#### 4.4 Cluster formation pathway

One possible path for the  $B_3I^-$  cluster formation is then  $B_2I + BI \rightarrow B_3I_2 \rightarrow B_3I^- + I^+$ , where  $B_3I_2$  might be neutral or negative and thus  $I^+$  might be neutral or positive (more work has to be done to determine the charges of all of the species). We have found that the first step of this reaction has a forward activation energy of 0.2 eV. We have identified an atomic scale process for the second step for both neutral and negatively charged  $B_3I_2$  though we have not determined an energy for that step yet.

## 5. Conclusions

These two examples of density functional studies of the mechanisms important to understand atomic scale diffusion illustrate both the possibilities of this approach as well as the descriptive power of atomic scale studies. We have been able to describe the detailed atomic mechanism responsible for Ge self-diffusion and have found a possible pathway for B clustering in Si. The methods employed in these studies are just beginning to be applied to first principles calculations and as they gain wider use the types of problems that can be addressed will correspondingly grow.

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