Theoretical Investigations of Diffusion and Clustering in Semiconductors

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ABSTRACT

Density functional theory studies of two systems have been conducted: mechanisms of self-diffusion in Ge and clustering of B in Si. In the case of self-diffusion of Ge, we find for the vacancy mechanism within harmonic transition state theory a diffusion prefactor which agrees well with experiment but 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 brings the activation energy to 3.1 eV, agreeing with experiment. The interstitial and exchange mechanisms contribute negligibly.

The reaction pathway of B cluster formation in Si has also been studied, with the cluster B_3I_2 being 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.

Keywords: self-diffusion, clustering, density functional theory, dimer method, B3LYP functional

1 INTRODUCTION

Diffusion in semiconductors is of great importance to 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 understanding dopant diffusion is an understanding of self-diffusion in semiconductors, since, for example, Ge, Sb and As are believed to diffuse in Si by a mechanism involving a vacancy in the Si lattice [1]. Accurate estimates of the formation energy and entropy of defects are therefore essential for determining dopant diffusion rates. It is also important to understand clustering mechanisms, as the rate of formation of dopant clusters, such as B in Si, and the identity of the actual clusters formed will have a large role in determining the final profiles of active B in the substrate [2].

Theoretical calculations can give valuable insight into the diffusion mechanism, since they can separate the various contributions to the activation energy (E_a) and the diffusion prefactor (D_0). They can also help identify individual atomistic processes that lead to cluster formation. First-principles calculations, with no parametrization to measured properties, hold the greatest promise 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 (± 1 for the defects) was used to find optimal atomic coordinates for stable configurations and saddle points. For this, we use the VASP code [3]. The formation energy of I and V is well converged at this cell size, differing only by 3% or less when 1000 atoms are used [4]. The PW91 functional [5] was used in these calculations combined with ultrasoft pseudopotentials [6]. 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 done 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 harmonic 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 for finding the MEP [8]. The prefactors for 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 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.

The B/Si calculations 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 pathways via which that cluster dissociated.

Computational Nanoscience 2001, (www.cr.org), ISBN 0-9708275-3-9.

3 GE SELF-DIFFUSION

3.1 Previous Experimental Work

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

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 creation and migration of a vacancy. Assuming both processes are thermally activated, E_a for self-diffusion is 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 inwards towards the vacant lattice site by 0.36 Å. This relaxation is quite local, the second neighbors only moving 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 cut-off radius is less than half the value found 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 entropy of formation for V is quite high, $9.18k_B$. This value is obtained by extrapolating to infinity the entropy found for various cutoff radii using an exponential form. The total formation entropy is then $S_{form} = 9.18k_B$. The calculated harmonic prefactor for the diffusion of V is $\nu = 2.4 \times 10^{12}s^{-1}$. The prefactor is then $D_0 = (fz\nu a^2/2d)\exp(S_{form}/k_B) = 5$ cm^{2}s^{-1}. Here, $f = 1/2$ is the correlation factor [14], $z = 4$ the coordination number, $a = 2.5$ Å the nearest neighbor separation, and $d = 3$ the dimensionality of the system. This result is just below the range of experimental values [11], [12].

3.3 B3LYP Correction

The PW91 calculations predict an E_a that is about 0.7 eV lower than experiment. These results are consistent with the large discrepancy noted for other vacancy diffusers in Si [15]. Comparison with experiment 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 activation energy for Si-Si bond breaking in disilane [17]. The atomic configuration of the periodic system obtained from the PW91 calculations is used, from which 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 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 a correction which is added to the periodic PW91 results. The consistency between clusters 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 calculations, 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 is the cohesive energy of the crystal, $E_f = E'_f - E_{coh}$. We use the PW91 calculation of E_f but add to that a correction given by the difference between the B3LYP and PW91 cluster calculations of $E'_f - E_{coh}$. The best estimate then becomes $E_f + \Delta E'_f - \Delta E_{coh}$. In a cluster, the surface atoms are not equivalent to the interior atoms and, 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 (or 'surface') atoms and g is the number of Ge ('bulk') atoms. In order to extract ΔE_{coh}, we have carried out calculations for three different clusters, containing 5, 17, and 35 Ge atoms, and fitted the difference between B3LYP and PW91 results to $\Delta E = h\Delta A + g\Delta B$. The slope gives $\Delta B = \Delta E_{coh} = -0.6$ eV. The V formation energy, $\Delta E'_f$, was calculated using three clusters. The results were fitted with an exponential form and an infinite size extrapolation obtained. This 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 saddle point and 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_a is therefore 0.7 eV larger than the PW91 result, in excellent agreement with the experimental estimate.

Our results are compared with experiment 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 mechanism. The concerted ex-

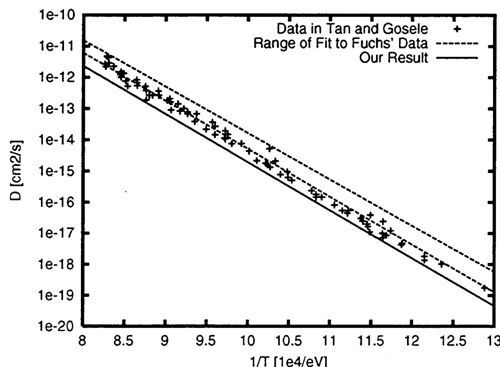

Figure 1: Comparison between our calculated results (dashed line) and experimental data (the two dotted lines give a range from [12], + give values from [20]).

change involves a swap of two adjacent atoms [21]. The PW91 calculation of E_a gives 3.6 eV, which is 1.2 eV larger than the V mechanism at the same level of theory. The B3LYP correction increases E_a by 0.5 eV to 4.1 eV, significantly larger than the experimental value. The harmonic prefactor for an exchange event is $\nu = 4.5 \times 10^{14}$ s^{-1} which gives an overall diffusion prefactor of $D_0 = 1.1 \mathrm{cm}^2\mathrm{s}^{-1}$, much smaller than the experimental estimate. The exchange mechanism is therefore predicted to be unimportant for 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 to be more stable by 0.3 eV, which has a formation energy relative to the perfect crystal of 3.2 eV. An estimate of the B3LYP correction increases the formation energy by about 1 eV.

A migration path of 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 T to the nearest T has a barrier of 0.2 eV, slightly lower than a hop to X. The lowest energy pathway for I migration is therefore X→T→T→...→X.

The PW91 calculations give a harmonic prefactor for the X→T hop as $\nu = 3 \times 10^{12}$ s^{-1}. The I formation entropy is $S_{form} = 3.70 k_B$. Thus, $D_0 = 0.01$ cm^{2}s^{-1} with $f = 1$ [14] in this case and $E_a\tilde{4}.8$ eV. The I mediated diffusion mechanism is therefore predicted to be unimportant.

4 B 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 $B_3I_2^-$ were degenerate in energy depending on the Fermi level.

Both of these studies assume that cluster formation is diffusion limited, or that the barrier for formation of a cluster from smaller components is just the migration barrier of the mobile species. Equivalently, this assumption says that the barrier for cluster dissociation is 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 focus on two clusters, B_3I^- and B_3I_2.

4.2 Formation of B_3I^-

Based upon the previous work of Liu [2] and Lenosky [22], the dominant B cluster is B_3I^-. We ran 10 dimers from this cluster. Of the interesting results, two lead to simple exchange processes of one B atom with another. One of the dimer runs leads to the beginnings of the 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 (the charge states are assumed based upon the work of Liu and Lenosky).

The activation energy for the reaction B_2^{--} + BI^+ → B_3I^- is about 1.5 eV. This is a high barrier to overcome and is thus unlikely to be overcome at typical temperatures. Because of the difficulty of forming B_3I^- from smaller clusters, we look at a larger cluster, B_3I_2, as an intermediate step.

4.3 Formation and Breakup of B_3I_2

Liu has found that B_3I_2 and $B_3I_2^-$ are degenerate in energy, depending on the Fermi energy. The study of $B_3I_2^-$ is ongoing, so here we discuss only 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 results in a distorted structure, and one leads 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 are bonded to a different Si atom in the same tetrahedron. This does not lead to net diffusion of the cluster, but rather just a reorientation. This process has a barrier of 0.8 eV.

The other interesting process 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 energy path for this reaction is shown in Fig. 2. The barrier to go 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

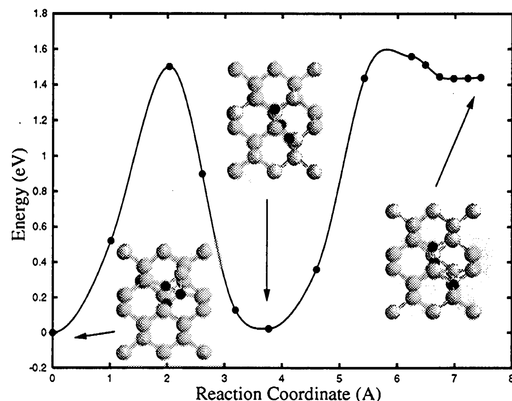

Figure 2: Minimum energy path for the breakup of B_3I_2 into B_2I and BI. The reverse barrier, for the formation of B_3I_2, is only 0.2 eV.

an energy of 1.42 eV above the original cluster. This already agrees well with the infinite separation energy of these individual products of 1.5 eV found by Liu. 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 B Cluster Formation Pathway

One possible path to B_3I^- cluster formation is then $B_2I + BI \rightarrow B_3I_2 \rightarrow B_3I^- + \imath$, where B_3I_2 might be neutral or negative and thus $\imath$ might be neutral or positive (more work needs 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 a atomic scale process for the second step, for both neutral and negatively charged B_3I_2, though we do not have an energy for that step yet.

5 CONCLUSIONS

These two examples of density functional studies of mechanisms important for understand large 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.

We acknowledge Art Voter and Rich Martin for helpful discussions. BPU acknowledges financial support from Motorola. This work was funded by the National Science Foundation grant number CHE-9710995 and by the Semiconductor Research Corporation contract #2000-MJ-761.

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