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Self Diffusion in Silicon Using the Ackland Potential

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Abstract

The study of self-diffusion using the Ackland potential yields an activation energy which lies within the experimental range of 4-5 eV. This study yields a configurational entropy for the interstitial defect of the order of 4.2K. The formation energy of both interstitials and vacancies has been found to be 3.9 ±0.1eV. The migration energy of interstitials is 0.7±0.1 eV and it is 0.2 eV for the vacancies.

1. Introduction

Silicon self-diffusion is mediated by point defects such as self-interstitials and vacancies. These point defects also influence the diffusion properties of dopants in silicon thereby causing anomalous oxidation enhanced diffusion, transient enhanced diffusion etc. Understanding the nature of these point defects is therefore important to VLSI technology.

In this paper, an attempt has been made to estimate the diffusion pathways for silicon point defects using a classical atomic potential approach. Most existing potentials for silicon are not well suited for diffusion studies[1, 2, 3]. For example, vacancy migration studies using these potentials reveal that the split vacancy configuration is more favourable compared to the isolated vacancy, indicating that none of these potentials correctly represent the ground state of the vacancy [4]. A recent study of self-diffusion using the Stillinger-Weber potential has yielded very high formation energies for hexagonal, split and bond-centered interstitials[5]. In their study, the proposed mechanism for interstitial migration is via an "extended" interstitial which moves from one low-energy configuration to another, via the tetrahedral site. However, this pathway by itself does not contribute to the activation energy for self-diffusion because it does not involve motion through a substitutional site [6].

In this paper, the study of diffusion has been carried out using the Ackland potential [7]. The Ackland potential is unique because of its bond-based nature and the fact that it allows for assymetric structured bonding, which is not easily performed using conventional LDA (Local Density Approximation) methods.

2. Computational Procedure

Simulations were performed at 300 K using a 2x2x2 unit cell with a total of 64 atoms. Periodic boundary conditions were employed in a constant NVT (Number of particles, Volume and Temperature) ensemble and energy minimisation was performed using the Metropolis Monte Carlo algorithm with multiple moves. The total energy in the Ackland potential is of the form:

$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} Ae^{-\alpha r_{ij}} - \frac{1}{2}\sum_{i=1}^{N}\sum_{k=1}^{4} Br_{ik}e^{-\beta r_{ik}} + \sum_{i}\sum_{n=1}^{3}\sum_{m=n+1}^{4} C[\cos(\omega R_{k_m k_n}) + \frac{1}{3}]^2 \quad (1)$$

The last term in expression (1) is essential in order to stabilise reconstructed interstitial and vacancy formation energies. The parameter ω is adjusted so that the minimum of the function falls at the tetrahedral bond angle in the diamond structure for silicon.

During the calculation of the migration energies, the interstitial was constrained to move in a plane perpendicular to its direction of motion. At the saddle point, those bonds whose contribution to the total energy was very high were converted to "dangling" status. Such bonds do not contribute to the attractive as well as to the bond-bond repulsion terms in expression (1). In this plane, different bonding configurations were tried and the configuration which gave the least energy was selected to be the most probable one. Averages of the total energy after relaxation were taken, with an accuracy of ± 0.1 eV and plotted against the distance of the migrating atom from the center of mass of the simulation cell.

3. Results

A value of C=1.5 in expression (1) was found to give the most suitable values for the formation energies of defects. Both interstitials and vacancies were treated under identical conditions by using the same value of C. The formation energies of the T (Fig. 1a) and H (Fig. 1b) site interstitials were found to vary between 3.9 and 4.7 eV depending upon the bonding configuration. The formation energy of the split interstitial was found to be 4.6 eV. This configuration is three-fold coordinated, as shown in Fig. 1c and hence does not conform to the bonding rules for the ground state condition in the Ackland potential that every atom should be four-fold coordinated. In the <111> direction, a "buckled" configuration was found to be more favourable in comparison to the bond-centered configuration as shown in Fig. 2c . The formation energy of the vacancy was found to be 3.9 eV. The divacancy formation energy was found to be 8.5 eV for a typical configuration [4].

During the calculation of the migration energies, it was found that a migrating interstitial with one dangling bond has a higher energy (1.2-1.4 eV) as compared to an interstitial with two dangling bonds, except in the case of the split interstitial configuration, which has a comparable energy. The maximum possible saddle point energy along any pathway is hence the energy of this configuration with two dangling bonds at the interstitial. The migration energy was found to lie between 0.7-0.8 eV. The various pathways examined have been shown in Fig. (2), with the corresponding energy diagrams in Fig. 3. In addition the (T-B)' pathway (Fig. 2d) was also found to be favourable in contrast to [8]. The vacancy migration energy was found to have a low value of 0.2 eV. The split vacancy configuration was thus slightly higher in energy in comparison with the ground state vacancy.

The entropy of formation of a defect is the sum of the configurational entropy and the vibrational entropy. For the self-intersitial there are at least 68 different bonding configurations which yield the minimum energy of 3.9 eV. The configurational entropy for the self-interstitial component of self-diffusion is thus approximately 4.2K. This high value could explain the large entropy of 10K observed experimentally for silicon self-diffusion. This total entropy is a sum of the configurational, vibrational and migration entropies. No other calculation has ever yielded such a large value of the configurational entropy for the interstitial defect in silicon.

4. Conclusion

The Ackland potential yields an activation energy for self-diffusion that lies within the experimental range of 4-5 eV. The formation energy for interstitials and vacancies is equal to 3.9 eV. Both the types of defects could therefore contribute to self-diffusion. However, the migration energy of the silicon interstitial is 0.7 eV whereas that for the vacancy is 0.2 eV.

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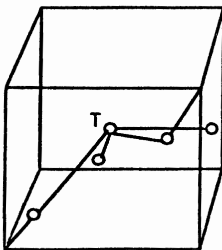

Fig. 1a: Tetrahedral site bonding configuration giving formation energy=3.9eV For a unit cell (0,0,0) to (1,1,1), T (0.5,0.5,0.5) is linked to (0.75,0.25,0.25), (1.0,0.5,0.5), (0.75,0.75,0.75) and (0.5,1.0,0.5).

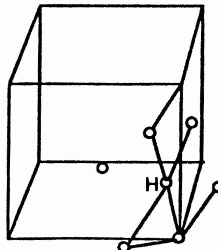

Fig. 1b: Hexagonal site bonding configuration giving formation energy = 3.9 eV. For a unit cell (0,0,0) to (1,1,1) H (0.875,0.875 ,0.375) is bonded to (1.25, 0.75,0.25),(1,1,1), (0.75,0.75,0.75) and (0.5,1.0,0.5).

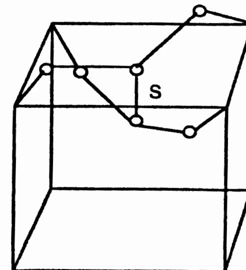

Fig. 1c: Split interstitial bonding configuration giving formation energy=4.6 eV. For a unit cell (0,0,0) to (1,1,1), S is bonded to (0.75,0.75,0.75), (0.25,0.25,0.75) and (0.5,0.5,1.0).

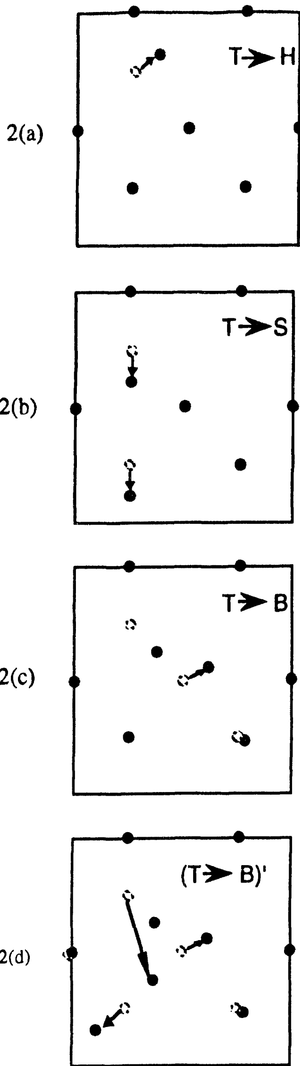

Fig. 2. Migration of silicon interstitial along (a) Tetra-Hex, (b) Tetra-Split (c) Tetra-Bond centered sites. (d)Tetra-B' site displayed in the (110) plane.

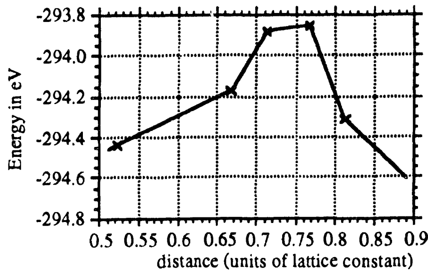

Fig. 3(a) Total energy curve of migrating interstitial along the TH path.

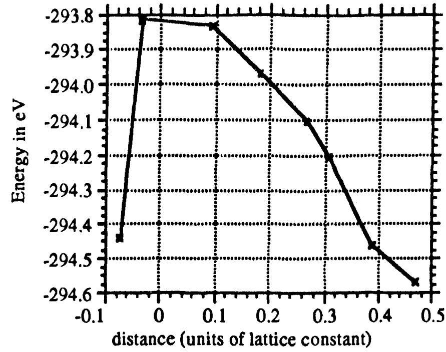

Fig. 3(b) Total energy curve of migrating interstitial along the TS path.

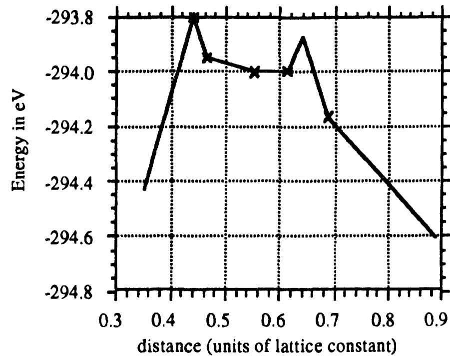

Fig. 3(c) Total energy curve of migrating interstitial along the TB path.

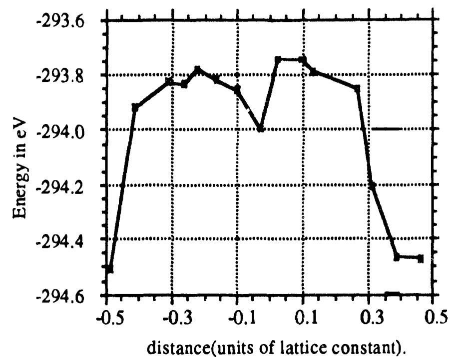

Fig. 3(d). Total energy curve of the migrating interstitial along the (T-B)' path.