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LETTER TO THE EDITOR

Correlation between migration mechanisms and small diffusion coefficient pre-factors for small dopant impurities in silicon

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Abstract. Dopant impurity migration paths and activation energies for self-interstitial-assisted migrations have been investigated based on first-principles and critical-path calculations. The calculated results reveal that B migration pathways have several choices. The present migration mechanisms suggest that B diffusion by the interstitialcy mechanism can show a small pre-exponential factor, while dopant impurities migrating by interstitial mechanisms can show large pre-exponential factors, corresponding to reported experimental results.

Although there have been extensive studies on III and V dopant impurity migrations in silicon by both experimental and theoretical methods, these studies have not yet come to a final conclusion on migration mechanisms [1]. The experimentally and theoretically obtained activation and migration energies are almost in agreement, providing an affirmative support for the theoretically proposed migration mechanisms [2]. Vacancy mechanisms can explain some of the dopant impurity migration behaviours in silicon, while interstitial mechanisms are in accordance with the relatively smaller dopant impurity migration behaviours. There still exists uncertainty concerning the widely spread differences among the pre-exponential factors in the diffusion coefficients experimentally obtained for the dopant impurities [3]. This factor ranges by two orders of magnitude according to the dopant species. The values of the pre-exponential factors are determined through the transition probability, the number of final configurations, the migration distance at one migration event, and the entropy term during each migration step [4]. In the case of the vacancy mechanism [5], the dopant impurity difference does not make much difference in the pre-exponential factors, because the migration event is dominated by the vacancy generation process, being a larger proportion of the activation energy. A successive impurity migration from a substitutional site is limited only by a path to a vacant nearest-neighbour site. In the case of the interstitial or interstitialcy mechanism, the migration event is also dominated by the generation process for a pair of an interstitial or interstitialcy dopant impurity and a self-interstitial, being generally a larger proportion of the activation energy [5]. The dopant impurity migration after this process, however, has various possibilities in the migration paths for one migration event. This suggests that the number of final configurations for the interstitial or interstitialcy mechanism may differ greatly depending on the dopant impurity migration paths and energies. This study reports on the differences in the consequent migration mechanisms for typical dopant impurities, B, Al, P, and As, using first-principles calculations. Based on the calculated results, the paper tries to elucidate the relation between

the migration mechanisms and the small pre-exponential factor for B, and to compare with experimental diffusion coefficients for dopant impurities reported so far.

The electronic-state calculations were performed using self-consistent pseudo-potential techniques within density-functional formalism in the local-density approximation. The norm-conserving pseudo-potential was employed, following the method of Bachelet, Hamann and Schluter [6]. The Perdew–Zunger and Ceperley–Alder correlations were implemented [7, 8]. Fictitious time derivatives of electronic wave functions were integrated to converge the electronic states on the basis of momentum-space formalism following the Car–Parrinello formalism [9, 10]. A super-cell geometry of 33-atom cells was used to achieve convergence with sufficient accuracy. An energy cut-off of 12 Ryd is employed for 1 k point to reduce the energy error to within 0.2 eV. The most probable migration path with the lowest migration energy involves the lowest saddle configurations. The migration path with the lowest saddle configuration has been found by moving an atom initiating migration along a valley on a potential energy surface towards the saddle configuration, while relaxing the other atoms into the lowest-energy configurations accordingly [11].

The present study is focused on smaller-impurity migrations assisted by self-interstitials. Stable configurations and migration pathways are not simple under the charge-neutral condition. To simplify the migration analysis in this study because of the higher symmetry conditions, and to compare the dopant migration behaviours with different valence charge states under the same Fermi-level condition, an electron is added to the B case and is subtracted from the P and As cases. The geometry of a dopant impurity and self-interstitial complex was first optimized before an impurity migration. A dopant impurity was placed at a substitutional site, and a self-interstitial was placed at the nearest stable interstice between lattice atoms. Then, the atoms in the system were relaxed to minimize the total energy in the system. The interatomic distances of the obtained stable hexagonal self-interstitial and dopant impurity complexes are 1.71 Å, 2.28 Å, 1.95 Å, and 2.36 Å for B, Al, P, and As, respectively. Si atoms adjacent to the substitutional B and P relaxed towards the dopant impurities because of their smaller covalent radius than Si. In the case of B, the substitutional B also relaxed toward the hexagonal self-interstitial, reducing the interatomic distance. Si atoms adjacent to substitutional As did not, however, show a remarkable relaxation because of the As covalent radius comparable with that of Si.

Table 1. Possible pathways and their energies of migration and activation for B, P, Al, and As assisted by self-interstitials. SP, H, and T are split, hexagonal, and tetrahedral configurations, respectively.

Dopant	Pathway	E_m (eV)	E_a (eV)	Mechanism
B	SP→SP	1.0	4.4	interstitialcy
	H→SP→H	1.4	3.4	interstitialcy
	H→T→H	1.0	3.0	interstitial
Al	T→H→T	0.8	3.4	interstitial
P	H→T→H	1.1	3.4	interstitial
As	H→T→H	0.6	3.5	interstitial

The typical dopant impurity migration pathways, migration energies, activation energies, and migration mechanisms are summarized in table 1. B migration by interstitial-interchange

and interstitialcy-interchange mechanisms was examined first by moving an adjacent self-interstitial towards an impurity atom on the nearest substitutional site. As a self-interstitial moves towards the adjacent substitutional B, it does not directly push the substitutional B into an interstice but forms a metastable split configuration with the substitutional B, as shown in figure 1(a). The B atom replaced in a split configuration requires a further energy of 0.2 eV to relax into a more stable hexagonal configuration. Since a substitutional B and a self-interstitial transform easily into a stable split configuration (SP) during a migration process, it has been found that B has various migration pathways involving split configurations as intermediate structures. B in a split configuration can migrate from one split configuration to another split configuration by the interstitialcy mechanism, as shown in figure 1(b). In the cases of B relaxed into a stable hexagonal site (H), the dopant impurity migration occurs from the initial hexagonal site to a next hexagonal site through a split configuration by the interstitial mechanism and through a tetrahedral site (T) by the interstitial mechanism, as listed in table 1.

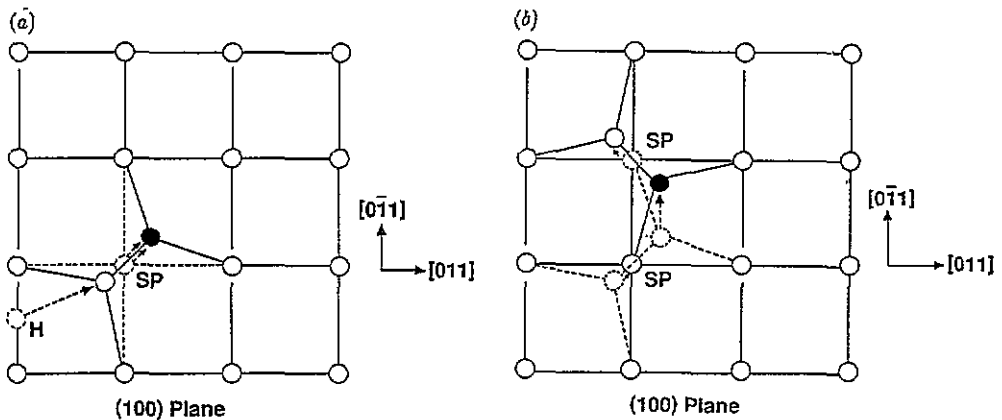


Figure 1. Schematic migration pathways for B by the interstitialcy mechanism (a) from a substitutional site to a split configuration and (b) from one split configuration to another split configuration. Dopant impurity and Si atoms are denoted by closed and open circles, respectively.

In the case of Al, P, and As with a large covalent radius, dopant impurity migrations were also examined by moving an adjacent self-interstitial towards an impurity atom on the nearest substitutional site. A self-interstitial pushes the substitutional impurity atom into an interstice, without forming a split configuration as an intermediate structure. The dopant impurities such as Al, P, and As are pushed away and relaxed into interstices, because no metastable intermediate configuration is achieved in these cases. The replaced Al has been found to relax into a neighbouring tetrahedral site, as shown in figure 2(a), while the replaced P and As have been found to relax into neighbouring hexagonal sites, as shown in figure 2(b). Al relaxed in a tetrahedral site migrates from the initial tetrahedral site to a next tetrahedral site through a hexagonal site by the interstitial mechanism as listed in table 1. P or As relaxed in a hexagonal site migrates from the initial hexagonal site to a next hexagonal site through a tetrahedral site by the interstitial mechanism as listed in table 1. Therefore, the migration pathways of dopant impurities with a large covalent radius are almost limited to interstitial migrations. The possibility of migration through a split configuration is scarce compared with B migration.

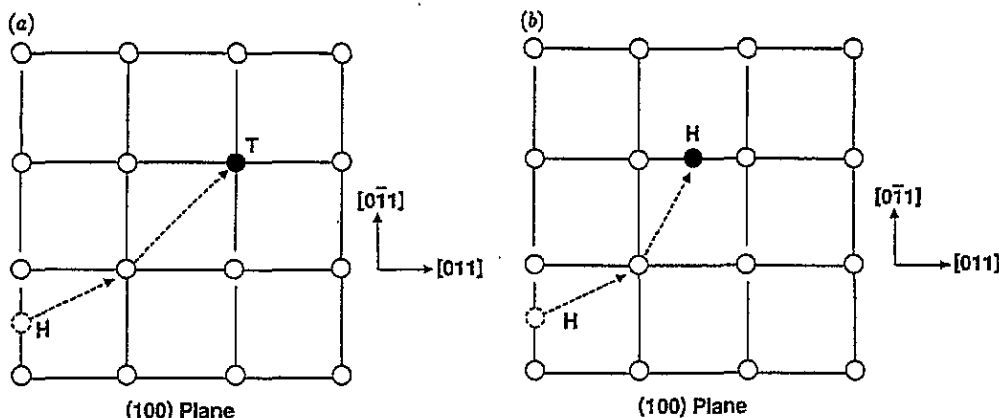


Figure 2. Schematic dopant impurity migrations by the interstitial mechanism from a substitutional site to (a) a tetrahedral configuration for Al and (b) a hexagonal configuration for P and As. Dopant impurity and Si atoms are denoted by closed and open circles, respectively.

The remarkable difference in migration mechanisms between B and the other dopant impurities is mostly due to the difference between the covalent radii of the dopant impurities. For the cases of dopant impurities with a small covalent radius such as B, the dopant impurity pushed away by a self-interstitial is stable in a split configuration with a self-interstitial because of the small atomic distance, even if the self-interstitial goes slightly beyond the substitutional site.

What should be recalled here is the pre-exponential factor difference in the diffusion coefficients between interstitialcy and interstitial migration mechanisms. The diffusion coefficient D is expressed by using the geometric factor Z_i , the jumping distance s_i , the vibration frequency ν_i , the entropy term S_i , and the activation energy E_i^a associated with the i th migration mechanism, where the sum runs over all contributing mechanisms [12],

$$D = \sum_i Z_i s_i^2 \nu_i e^{S_i/k} e^{-E_i^a/kT}. \quad (1)$$

In the case of interstitialcy mechanisms as seen in the B case, an interstitial impurity needs to change the moving direction by more than 90° at each migration event, and a self-interstitial is also required to move at each migration event. This process has little chance of continuing the migration for several lattice distances during one event, and consumes relatively large energies to remake the bonds between atoms, as seen in table 1. On the basis of these considerations, the interstitialcy migration is likely to occur step by step at each migration event. The entropy term S_i is a function of the migration barriers [13]. The entropy term must be, therefore, small in this case. The consequence of migration by the interstitialcy mechanism will be a small pre-exponential term. The step-by-step migration mechanism also applies to migration by the vacancy mechanism. The pre-exponential factor for the vacancy mechanism is also small.

Since the diamond structure has wide interstice rows along the $\langle 110 \rangle$ direction, a migration through interstices along these directions by an interstitial mechanism possibly occurs as several lattice distances for one migration event. This is mostly due to the fact that an interstitial impurity moving along the $\langle 110 \rangle$ direction need not change its moving direction greatly (less than 71° at stable and saddle configurations) and does not need a large

migration energy because of loose bonds with adjacent atoms, as seen in table 1. If a dopant interstitial impurity is given a large energy sufficient for migration, it can migrate through interstices for several lattice distances. This inevitably increases the pre-exponential factors for interstitial migration mechanisms.

Table 2. Experimentally obtained diffusion coefficient parameters for dopant impurities [3]. $D = D_0 \exp(-E_a/kT)$ is a carrier-concentration-independent term.

Dopant	D_0 (cm ² s ⁻¹)	E_a (eV)
H	0.009	0.48
B	0.037	3.46
Al	1.385	3.41
P	3.85	3.66
As	0.066	3.44

In comparison with the theoretical results calculated in this study, the diffusion pre-exponential factors and activation energies obtained experimentally by Fair [3] are listed in table 2. The experimental results are diffusivities at intrinsic conditions for the carrier concentration. The activation energies of the dopant diffusion coefficients listed in table 2 agree fairly well with the theoretical results shown in table 1. This does not mean that the dopant impurity diffusions occur solely by the interstitial-assisted mechanism as shown in table 1, since the experimental data shown here include contributions from both vacancies and self-interstitials. The pre-exponential factors of the dopant impurity diffusions differ greatly by more than two orders of magnitude from B to P according to the dopant species. The difference between these factors is largely the result of the migration mechanism difference during one migration step. As the covalent radius of the dopant impurities is decreased, dopant impurity diffusion is dominated by an interstitial or interstitialcy mechanism rather than a vacancy mechanism, which has already been indicated by experimental results [1].

Although the pre-exponential factor has a tendency to increase from a larger dopant impurity to a smaller dopant impurity, this factor decreases dramatically for B. The pre-exponential factor for B is also far smaller than that for the other group III element Al with a larger covalent radius. Although B may diffuse through a vacancy mechanism, it is not, however, a dominant mechanism for all the migration behaviours. B diffusion has been observed to be enhanced in an O₂ ambience where the self-interstitial concentration is high, and has been observed to be retarded in an N₂ ambience where the vacancy concentration is high [1]. This indicates that B prefers self-interstitials rather than vacancies for migration. When migration pathways for B found in this study are compared with those for Al, P, and As, B has various choices for migration pathways because of the interstitialcy mechanisms. If we can assume that interstitialcy migration often occurs for B, this explains well the fact that the pre-exponential factor for B is far smaller than those for Al and P. When the pre-exponential factor for As is compared with those for B, Al, and P, As has the smallest pre-exponential factor next to B. This experimental result contradicting the assumption indicates that Al and P diffusions occur primarily by an interstitial mechanism at intrinsic conditions, while As diffusion occurs primarily by a vacancy mechanism at intrinsic conditions as evidenced by experimental and theoretical results [1, 2]. Since a vacancy migration occurs step by step at a single event, the vacancy mechanism for As migration has caused the second-smallest entropy term.

H diffusion in Si is much faster than the dopant impurities. H, however, has an even smaller pre-exponential factor than that for B (table 2). H has several stable interstitial configurations and diffuses through various pathways in interstices through these stable configurations [14, 15]. These migration pathways and mechanisms will be largely the reason for the small pre-exponential factor of H diffusion. From the point of view of small-impurity diffusion behaviours in semiconductors, B shows a diffusion mechanism closer to that of the even smaller H diffusion, rather than those for Al or P. The paper has been devoted to elucidating the relation between dopant impurity migration mechanisms and their diffusion coefficient values for small dopant impurities such as B. The migration mechanisms for dopant impurities have been revealed to have strong relations with the values of the diffusion coefficients. By extending this method to dopant impurities in Si and calculating the diffusion coefficient given by (1), the widely ranging values of the diffusion coefficients will be more rigorously explained.

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