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Ab initio investigation of boron diffusion paths in germanium

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Experimental data indicate that boron diffuses very differently in Ge than in Si. To examine the kinetics of boron diffusion, density functional calculations were performed on a variety of boron diffusion mechanisms, including interstitial and vacancy-mediated paths, as well as a correlated exchange mechanism. It was found that although vacancy and correlated exchange mechanisms possess high diffusion barriers comparable with experiment, the barrier for interstitial-mediated diffusion lies around 3.8 eV and is similar to those found for boron diffusion in Si. This estimate is well below the experimental activation energy. The difference is attributed to the failure of the theory to include the effect of electronic excitations.

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I. INTRODUCTION

Despite continued advances in silicon-based transistor technology, there is a growing interest in technologies using other semiconducting materials. Germanium is one of these materials, appealing both due to its similarity to silicon, allowing relatively direct translation of current manufacturing techniques,[1] and for its superior low-field electron and hole mobilities.[2] In order to develop germanium-based devices, selective area doping must be achievable, and to this end, we study here the migration dynamics of boron in germanium.

Under equilibrium conditions, diffusion by all mechanisms is expected to lead to a diffusivity of the following form:

$$D = D_0 \exp\left(-\frac{Q}{k_B T}\right), \quad D_0 = \nu a^2 \exp\left(\frac{S_d}{k_B}\right), \quad Q = E_f + W, \tag{1}$$

where D is the diffusivity, Q its activation energy, ν and a are the attempt frequencies and elementary jump distances, E_f is the formation energy of the diffusing species, W is the barrier for its diffusion, and S_d is the entropic contribution to the formation and migration of the species, while k_B and T have their usual meanings. In the microscopic theory where S_d is neglected, which works reasonably well for B diffusion in Si, E_f is the formation energy for the boron interstitial relative to that of the isolated ionized substitutional B atom, and W is the migration energy of the interstitial through the lattice. νa^2 is estimated to be about 10^{-3}–10^{-2} cm^2/s and experimental values give $D_0 \sim 0.8$ cm^2/s and $E_d \sim 3.46$ eV.[3] Thus, the entropic factor S_d is rather modest. However, in Ge, boron diffusion is activated with $Q = 4.65$ eV and $D_0 \sim 10^5$ cm^2/s.[4] Clearly, the very large prefactor shows that the microscopic mechanism for boron diffusion in Si does not operate in Ge. The difference is very likely to arise from the excitation of electrons during the diffusion event, and this effect increases in the narrow gap material. Investigations of these effects[5] suggest that increases in Q and D_0 are linearly related according to the Meyer-Neldel rule, and for Ge, a 1 eV increase in Q is found, accompanied by an increase in D_0 of 10^5. This implies that the microscopic theory should calculate a low barrier for diffusion of boron around 3.6 eV, and together with a value of $D_0 \sim 0.1$ cm^2 s^{-1} will not fully describe the high T diffusion mechanics. We shall show that our calculations are in agreement with this.

Following implantation, thermal equilibrium of native defects does not occur, leading in some cases to transient enhanced diffusion (TED) of dopants. In Si, boron is found to undergo strong TED,[6,7] while in Ge, this TED is much weaker, and it has only recently been observed.[8] Indeed, the diffusivity of boron introduced by implantation or growth has been found to be the same in many experiments.[4,9]

A number of theoretical studies have been carried out for boron diffusion in silicon, but different groups find different diffusion paths although the overall barrier to diffusion is similar. Both theory and experiments favor an interstitial-mediated mechanism. One study[10] finds a diffusion path proceeding from the positive boron-interstitial (BI$^+$) complex whose formation energy is about 3.2 eV. This changes its charge state to neutral, then diffuses via the H site without true kick out, and with a barrier of 0.6 eV, leading to a total diffusion barrier of 3.8 eV. Another study[11] proposes different charge state dependent paths with Q values of 2.9 eV$+\mu_e$ in the neutral and 3.4 eV in the negative charge states, where μ_e is the Fermi energy or electron chemical potential, measured from the valence band top. A third investigation[12] finds a formation energy of 1.8 eV$+2\mu_e$ for BI$^+$ relative to the charged substitutional defect and a kick-out diffusion path with a total barrier of 1.2 eV giving a net diffusion barrier of $Q = 3.0$ eV$+2\mu_e$. Taking μ_e to be at midgap of ~ 0.6 eV yields a diffusion barrier of 4.2 eV.

There has also been previous modeling work carried out on boron diffusion in Ge.[13] The formation energy of BI$^+$ is 2.77 eV$+2\mu_e$, relative to B$^-$ at a substitutional site, and the defect can migrate with a barrier of 0.9 eV via bond centers, although this must be followed by a subsequent reorientation with a barrier of 0.5 eV. The diffusion barrier is then 3.7 eV$+2\mu_e$, which if $\mu_e \sim 0.35$ eV gives a diffusion barrier of 4.4 eV. The authors quote a barrier of 4.5 eV although their reasoning is unclear. Somewhat, similar barriers are found for other charge states. However, as we noted above, this theory is unable to account for the exceptionally large prefactor, and according to the Meyer-Neldel rule, this implies that the calculated adiabatic barrier has to be significantly lower than the experimental result of 4.5 eV.

We discuss here the boron diffusion via interstitial, vacancy,[14–16] and concerted exchange mechanisms[17] using a density functional method. Such calculations have, in the past, been performed using one of the two methods to treat the boundary conditions. The supercell method uses periodic boundary conditions, forming an infinite superlattice as an approximation to the bulk. The cluster method models instead a nanoparticle, with the boundaries being surfaces to vacuum. Further refinement of the cluster method usually involves passivating the dangling bonds at the surface with hydrogen atoms, and holding the surface semiconductor and hydrogen atoms fixed while relaxing the bulk of the cluster. Both methods should tend to true bulk values in the limit of infinite size. Both cluster and supercell methods have problems associated with them, and this study used both methods for different calculations. The cluster method cannot be used to calculate formation energies, while supercell calculations suffer from a severe underestimation of the band gap due to the approximation to the exchange-correlation energy employed within the local density approximation of density functional theory. This underestimation is especially critical in germanium calculations, where the experimental band gap is small. It has been seen in previous studies that this underestimation can cause defect energy levels to reside within the bulk bands at **k** points often used to sample the Brillouin zone.[18,19] With the cluster methodology, this problem is mitigated by the increase in electron energies due to confinement within the cluster. Although an artificial solution, it allows for the study of charged defects in germanium. Due to these limitations, supercell calculations were used in this study to calculate formation energies of defects, while clusters were used to investigate their energy levels and migration energies. The clusters and supercells used were the largest feasible with the resources available to the authors, and similar conclusions have been reached in a previous paper by the present authors on the divacancy in germanium.[20]

Section II contains details of the modeling methods applied to the problem. Results are presented in Sec. III and are discussed in Sec. IV. The conclusions of the study are finally summarized in Sec. V.

II. METHOD

Calculations were performed using a local density functional code AIMPRO,[21] and the defect was embedded in hydrogen-terminated clusters and periodic supercells of germanium atoms. A Padé parametrization[22] of the exchange-correlation functional as proposed by Perdew and Wang[23] was used, and the core electrons were accounted for by the pseudopotentials of Hartwigsen *et al.*[24]

A real-space Gaussian contracted basis set consisting of (s,p,d) orbitals with (4, 4, 1) distinct exponents, respectively, and optimized for bulk Ge was used to expand the Kohn-Sham states. This basis set gives a relaxed lattice constant of 5.68 Å, 98.6% of the experimental value, and a bulk modulus of 73.6 GPa, 96.1% of experiment. The orbitals of the hydrogen surface atoms were expanded using contracted basis sets with four s and one p exponents and those of the boron atoms with an uncontracted basis consisting of four d orbitals.

The supercells used were cubic shaped and consisted of 216 atoms for the perfect crystal, with the Brillouin zone sampled using a Monkhorst-Pack sampling scheme of eight points (MP-2^3).[25]

The Ge clusters used were atom centered, near spherical in shape, and saturated with hydrogen atoms at the surface to passivate dangling bonds. The perfect clusters then comprised of 329 Ge and 172 H atoms. They were generated using the experimental lattice parameter (5.657 Å),[26] and the surface hydrogen-germanium bonds were relaxed prior to any calculations. The defect was then introduced and the cluster was relaxed, holding the terminating hydrogen and surface germanium atoms fixed.

In both clusters and supercells, the defect was introduced and the position of the surrounding atoms was disturbed to break the symmetry and facilitate rebonding where necessary. Formation energies were calculated using

$$E_f(D) = E(D) - n_{\mathrm{Ge}}\mu_{\mathrm{Ge}} - q(E_v + \mu_e) - \mu_{\mathrm{B}}, \qquad (2)$$

where $E_f(D)$ is the formation energy of defect D charged with q electrons, $E(D)$ is the total energy of a supercell containing the defect, and $n_{\mathrm{Ge}}\mu_{\mathrm{Ge}}$ is the number of germanium atoms in the supercell multiplied by their chemical potential. Here, μ_e is the Fermi energy relative to the top of the valence band E_v. μ_{Ge} is the chemical potential of Ge, calculated from supercells containing a perfect crystal structure, while μ_{B} is the chemical potential of boron. The activation energy for the diffusion of boron is the difference in formation energy between boron in its equilibrium state and a saddle point and is independent of μ_{B}.

Migration energies and paths were calculated using the improved tangent nudged elastic band (NEB) method.[27] In this method, initial and final configurations are linearly interpolated to give a chain of intermediate structures or images. For the correlated exchange (CE) runs, an intermediate structure is also introduced to avoid the migrating atoms attempting to pass through one another due to symmetry constraints. In all cases, the initial and final structures are held fixed, and the images are then relaxed, with consecutive images interacting via virtual "elastic bands." Relaxation is continued until the forces on the atoms in each image, including the elastic band forces, vanish.

Energy levels for the boron-interstitial complexes were calculated using the marker method.[28] Here, a marker defect with experimentally well defined energy levels is used to aid in the calculation of the energy levels of the defect being studied. The difference in ionization energies for the two defects is taken to be the difference in the position of their energy levels. In this study, the donor level of substitutional

Se at $E_c-0.28$ eV (Ref. 29) and the acceptor level of the vacancy-oxygen complex at $E_v+0.32$ eV (Ref. 30) are used as markers.

In addition to the calculations described below of activation energies for boron diffusion, alternative calculations were performed for the interstitial-mediated diffusion path. In the alternative calculations, the formation energy of the neutral interstitial was calculated from the supercell and for the positive and doubly positive charge states from energy levels calculated in the cluster methodology.[31] Binding energies between the boron and self-interstitial atoms as well as the migration barriers presented below were then calculated in clusters. This method, while minimizing reliance on supercell calculations, added several extra stages to the calculations. We have presented the simpler calculations below, as we believe that the extra stages likely add more uncertainty to the calculations than the use of the supercell code to calculate formation energies of charged defects, although we concede that this assessment is not entirely certain. Using the alternate method gives activation energies lower by ~0.2–0.5 eV.

Similar methods have been used in the past to study various defects in germanium including vacancy-oxygen complexes,[32] vacancy-donor complexes,[19] oxygen interstitial structures,[33] single vacancies,[18,34] and divacancies,[35] as well as boron-interstitial structures in silicon.[36,37]

III. RESULTS

A. Interstitial-mediated diffusion

Calculations were performed within the supercell and cluster methods to establish the most stable configuration for the BI complex in germanium. Several BI structures were studied: substitutional boron with *T*-site and *H*-site Ge self-interstitials, *T*- and *H*-site boron interstitials, and ⟨110⟩ and ⟨100⟩ split interstitials (BI_{110} and BI_{100}). Supercell results for the neutral defects gave BI_{100} as being more stable than BI_{110} but by only 0.02 eV. Subsequent cluster method calculations gave the latter structures as the most energetically favorable in the neutral and singly negative charge states, while the singly positive charge state exhibited a structure with a substitutional boron atom and an adjacent tetrahedral Ge interstitial (BI_T). The energy difference between competing structures was seen to be no more than 0.3 eV. The cluster results for the defect's structure are in agreement with previous work[13] and are also very similar to those found for BI complexes in silicon.[37] The formation energy of BI^+ in the supercell relative to B_s^- was found to be $2.5\text{ eV}+2\mu_e$, while the formation energies of BI^0 and BI^- defects relative to B_s^- are $3.2\text{ eV}+\mu_e$ and 3.8 eV.

Energy levels were calculated in clusters as described above. The donor level is found to lie at $E_c-0.10$ eV and the acceptor level at $E_v+0.29$ eV. This implies that the structural changes indicated above give rise to a negative-*U* system in which the neutral charge state is not stable for any Fermi energy position, similar to BI in Si.[38] Using the experimental band gap of 0.66 eV, consistent with the use of the empirical marker method for energy level calculations, the (−/+) transition is found to lie at $E_c-0.23$ eV.

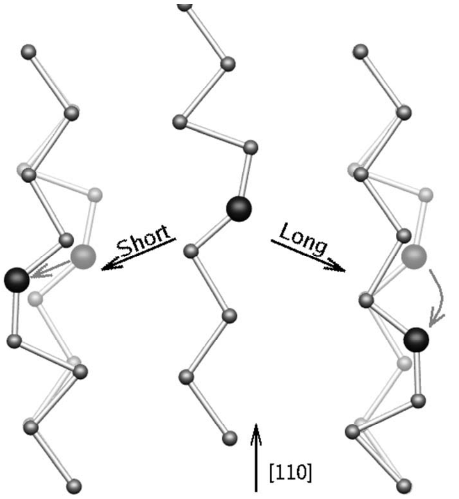

FIG. 1. Diagram showing the mechanisms involved in the diffusion of singly negative BI_{110}. The smaller, light gray balls represent germanium atoms and the larger, black balls the boron. In the center is the initial configuration, showing the distorted ⟨110⟩ chain containing the split interstitial. The faded chains on each side are the central image repeated as a guide to the reader. To the left is shown the short diffusion step, where the boron atom moves from one germanium to the next along the chain. To the right is shown the long diffusion step, where the boron atom skips a germanium atom and forms a split interstitial with the next atom along.

The negative-*U* nature of BI suggests that diffusion only occurs in the positive or negative states as these are the stable ones. For the BI_{110} structure, the boron atom is considered to diffuse along the ⟨110⟩ chains in the crystal and to rotate between different chains. The diffusion along the chain occurs by steps of one or two atoms, termed "short" and "long" steps, respectively, where the boron atom forms a new split-interstitial structure with the atom it moves to. This path is depicted in Fig. 1. The BI_T structure diffuses through movement of the boron atom to an adjacent crystal site. The interstitial atom drops into the substitutional site just vacated, and the germanium atom at the site the boron atom is moving to is displaced to a *T* site. This path is depicted in Fig. 2. Kick-out mechanisms were also calculated, wherein the boron atom jumps into and diffuses along the ⟨110⟩ channels in the crystal.

For BI_{110}^-, the diffusion of the defect as a complex is calculated to have barriers of 0.78 eV for the long, 1.50 eV for the short, and 0.31 eV for the rotation steps. The diffusion would therefore proceed as that for the neutral self-interstitial, through long and rotation steps only, with a saddle point along the ⟨110⟩ chain lying at bond-center sites distorted toward an adjacent tetragonal site ($B_{BC\text{-}T}$). The kick-out diffusion path is a little more complicated. The defect first reorients with a barrier of 0.31 eV to a dumbbell lying in a ⟨110⟩ direction perpendicular to the chains (B^*_{110}), lying 0.1 eV above the more stable B_{110} defect. Diffusion can then proceed to an adjacent B^*_{110} position via a metastable B_H defect. The total barrier for the kick-out diffusion was found to be 0.68 eV, similar to the barrier for diffusion without kick out.

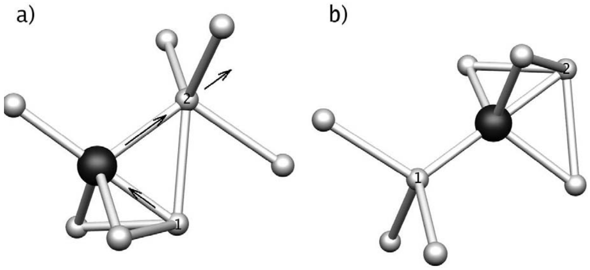

FIG. 2. Diagram showing the proposed mechanism for diffusion of BI_T. The light gray balls represent germanium atoms, while the large black ball represents the boron atom. The arrows indicate the direction of atomic movements, and the numbered germanium atoms are used to clarify the atomic movement. Interstitial germanium atoms are at T sites, with three of the surrounding atoms shown.

In the neutral charge state, the diffusion as a complex is calculated to have barriers of 0.76 eV for the long, 0.63 eV for the short, and 0.16 eV for the rotation steps. The diffusion would therefore proceed via the short and rotation steps with a barrier of 0.63 eV and a saddle point structure of a bond-center boron interstitial (B_{BC}). This kick out diffusion path proceeds with, first, a reorientation to a B^*_{110} structure via a structure with a substitutional boron atom adjacent to a $\langle 111\rangle$ self-interstitial structure ($\mathrm{B}_s\mathrm{I}_{111}$). From the B^*_{110} structure, the boron is kicked out into the interstitial channels, where it diffuses between H-site configuration (B_H) saddle points and interstitial minima at a site between the H and the T sites ($\mathrm{B}_{H\text{-}T}$). No barrier is observed to kick in from the $\mathrm{B}_{H\text{-}T}$ to B^*_{110}, and the total barrier is calculated to be 0.43 eV.

In the positive charge state, the diffusion proceeds, as shown in Fig. 2, with a barrier of 0.60 eV. The saddle point for this path is a split interstitial in the $\langle 111\rangle$ direction, after which the defect relaxes into a B^*_{110} structure, 0.28 eV above the stable BI_T structure. The diffusion continues with the defect passing through a B_{BC} structure before arriving at the final BI_T position. For the kick out mechanism, the barrier to kick out is calculated to be 0.89 eV, with the boron atom moving to a tetrahedral interstitial position (B_T) of 0.45 eV above the BI_T structure. It then faces a 0.70 eV barrier for further diffusion through the B_H site or a 0.44 eV barrier to return to a BI_T position. This gives a total barrier for kick-out migration of 1.15 eV above the BI_T structure.

All these results, both the paths and the calculated barriers, lie close to equivalent calculations previously performed for boron in silicon.[11,12] When compared with the earlier theoretical work in germanium, the barriers calculated here are lower in all cases, but the paths taken are the same.[13]

Total energy barriers for the migration of boron through an interstitial-mediated mechanism can be calculated by summing the formation and migration barriers for the defects. If we take μ_e to be at midgap at the temperature where diffusion is observed, we get 4.5, 3.9, and 3.8 eV for the singly negative, neutral, and singly positive charge states and similar to what is found theoretically for boron diffusion in Si. As stated above, this is an upper limit to the diffusivity since the experiment indicates that large entropic effects are present.

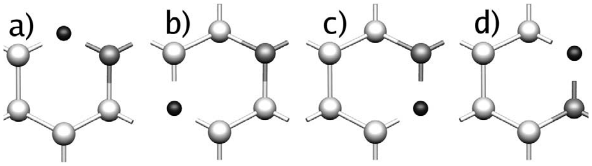

FIG. 3. Migration path for the boron-vacancy complex. In the figure, the smaller, lighter gray atoms are Ge, the larger, darker one is B, and the isolated black atom indicates the vacant site. [(a) and (b)] The vacancy diffuses around the six-membered ring. [(c) and (d)] Having arrived back at the B atom, the vacancy exchanges places with it, resulting in a net motion of the defect of one crystal site.

B. Vacancy-mediated diffusion

Vacancy-mediated diffusion is the method associated with most fast-diffusing impurities and self-diffusion in germanium. Boron-vacancy defects are calculated using the supercell methodology to have formation energies of 3.0 eV$+\mu_e$ and 3.4 eV in the neutral and singly negative charge states, respectively.

In the vacancy-mediated path, illustrated in Fig. 3, a vacancy is formed and diffuses to the impurity atom to form a defect complex. This complex then diffuses through motion of the vacancy as it travels around the six-membered rings in the Ge crystal and then exchanges position with the impurity atom.

NEB runs were performed within the cluster methodology in the singly negative and neutral charge states. These give an exchange barrier for the boron atom to cross the vacancy of 2.6 eV in the negative charge state and 2.8 eV in the neutral state. When combined with the formation energy of the boron-vacancy complex, this gives a total diffusion barrier for boron by the vacancy-mediated path of 6.0 eV for the negative and 5.8 eV$+\mu_e$ in the neutral charge states. The barrier for the negative charge state is shown in Fig. 4. These

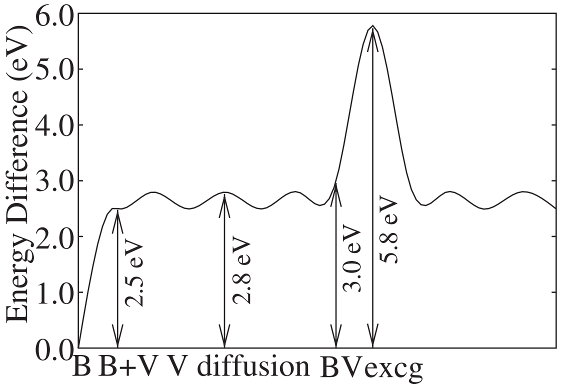

FIG. 4. Migration barrier for vacancy-mediated boron diffusion in the singly negative charge state. The energy scale is given relative to the isolated substitutional boron atom. The process shown involves the formation of a vacancy distant to the boron atom, diffusion of the vacancy to the boron atom to form a complex (BV), then the exchange of the boron and vacancy in the complex (excg) before the vacancy diffuses away from the boron again.

energies imply that vacancy related mechanisms are unlikely to compete with the interstitial-mediated diffusion mechanism.

C. Correlated exchange

CE is a mechanism for impurity or self-diffusion, which does not require interaction with other defects. Two adjacent substitutional atoms rotate about their bond center, with little change in interatomic distance. The migration path was found to be very similar to that proposed by Pandey for self-diffusion in silicon.[17] The diffusion barrier for this method was calculated for the negatively charged system, as the B dopants are expected to be in this charge state for the temperatures at which diffusion takes place, and it was found to be 4.1 eV.

IV. SUMMARY AND DISCUSSION

Vacancy-mediated diffusion is observed in these calculations to possess a high energy barrier of ~6 eV, significantly higher than that for the other methods, and in contrast to results suggesting it as the method for self-diffusion and some fast-diffusing species in germanium.[14–16] This suggests that vacancy-mediated diffusion is not the diffusion path boron takes in germanium.

Boron-interstitial structures were found to be in agreement with previous theoretical work in germanium[13] and also very similar to those found in silicon.[12,37] Boron-interstitial complexes were seen to diffuse either as a unit or through kick-out mechanisms. In the positive charge state, the diffusion as a unit exhibited a lower energy barrier of 0.6 eV, while in the neutral and singly negative, the kick-out mechanism was slightly more favorable at 0.4 and 0.7 eV, respectively. Total energy barriers, including the formation energies of the boron interstitial with respect to substitutional B^- for diffusion in the $+$, 0, and $-$ charge states, were then given as $3.1+2\mu_e$, $3.6+\mu_e$, and 4.5 eV, respectively. Taking μ_e to be at midgap, around 0.35 eV, gives barriers of 3.8, 3.9, and 4.5 eV, respectively.

Correlated exchange has been investigated and is observed to have a diffusion barrier of 4.1 eV in the singly negatively charged case, and thus it is less likely to be the dominant diffusion process than the interstitial-mediated mechanism.

Prior theoretical work on boron diffusion in silicon has concentrated on the interstitial-mediated diffusion method using a kick-out mechanism to create interstitial boron impurities which then diffuse within the $\langle 110\rangle$ channels with low diffusion barriers. A total activation energy for this process of 3.2–3.6 eV dependent on charge state is reported.[10–12] This is very close to the energy barriers reported here.

The experimental value of D_0 for boron diffusion in Ge reveals that the mechanism for boron diffusion in Ge is distinct from that of Si. In the latter, D_0 is around the value that can be expected for a microscopic mechanism via thermally generated boron interstitials. The same process in Ge yields similar barriers around 3.8 eV and about 0.9 eV below the experimental values for the activation energy for boron diffusion. However, this result applies to $T=0$ and the inclusion of electronic thermal excitations has been previously estimated to increase the observed energy barrier by ~1 eV and the preexponential factor by $\sim 10^5\ \mathrm{cm}^2/\mathrm{s}^5$, which brings the diffusivity into closer agreement with experimental values.

V. CONCLUSION

Boron diffusion was studied through atomistic *ab intio* modeling methods. Diffusion was found to proceed most readily via an interstitial-mediated mechanism, with a barrier of ~3.8 eV in the positive charge state. In order to explain the discrepancy between this value and experimental results of ~4.6 eV as well as the experimentally measured prefactors of $\sim 10^5\ \mathrm{cm}^2/\mathrm{s}$, electronic thermal excitations not considered in the $T=0$ atomistic model must be invoked.[5] These excitations would be expected to increase the diffusion barrier to ~4.8 eV, much closer to the experimental value.

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