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Ab initio investigation of phosphorus diffusion paths in germanium

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Ab initio calculations were performed to study phosphorus diffusion in germanium through vacancy and interstitial-mediated mechanisms as well as a correlated exchange mechanism without interaction with a mediating defect. It was found that the most favorable diffusion mechanism is sensitive to the position of the Fermi level within the band gap. For material with a midgap Fermi level, the neutral or singly positive phosphorus interstitial is the dominant diffusing species, while in n-type material, it is the doubly negative phosphorus-vacancy complex. For a Fermi level position of $E_v+0.5$ eV, a barrier for phosphorus diffusion via the doubly negative phosphorus-vacancy defect of ~ 2.5 eV was calculated, which is roughly ~ 1 eV below the equivalent process in Si.

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I. INTRODUCTION

Dopant diffusion is an important process in device fabrication in any material, and phosphorus is an important n-type dopant in both germanium and silicon devices. In this paper, we present extensive work on diffusion mechanisms of phosphorus in germanium. We have examined three primary atomistic methods of dopant diffusion: vacancy- and interstitial-mediated diffusion paths and correlated exchange (CE).

The germanium self-interstitial (I) and lattice vacancy (V) have been previously studied using the methods presented in this paper. The vacancy has been calculated to have diffusion barriers ranging from 0.3 eV in the doubly negative to 0.7 eV in the neutral charge states,[1] which compares to experimentally measured values of 0.2 eV for low temperature experiments[2] and 1.0 eV for high temperature.[3,4] Therefore, there is a good agreement for low temperature results, but high temperature experiments are not understood. An acceptor level for the vacancy has been observed to lie at $E_v+0.2$ eV (Ref. 5) or $E_v+0.14$ eV (Ref. 6) and single and double acceptor levels have been calculated using density functional theory (DFT) to lie at $E_v+0.20$ and 0.16 eV for the first and second acceptor levels, respectively.[7] The electrical levels of I have been experimentally measured as well, with the defect showing donor levels measured to lie between $E_c-0.2$ and 0.04 eV.[6,8–10] Calculations on cage-sited interstitials yield a donor levels at $E_c-0.08$ eV and $E_c-0.24$ eV.[11] I diffusion is estimated from experiment to have a barrier of ~ 0.6 eV,[5] and theory calculations give barriers of 0.5, 0.3, and 1.2 eV for the neutral, singly positive, and doubly positive charge states, respectively.[11] Taking these results together, it can be seen that the methods that have been used in this study give generally reasonable agreement with experimental data.

Interstitial-mediated diffusion involves either a kick-out mechanism and diffusion of interstitial phosphorus (P_i) or the diffusion as a unit of complexes formed of a phosphorus atom and a crystal self-interstitial (PI). These mechanisms have been previously studied by *ab initio* methods in silicon. One study on neutral defects found the most stable structure to be one where the phosphorus atom lay at an interstitial site between the bond center and the center of a hexagonal ring, which dubbed the X_2 configuration. This structure was found to have a formation energy of 2.7 eV and a migration barrier of 0.2 eV through motion around the hexagonal ring alongside reorientations between them, although these energies are calculated with respect to the neutral rather than positive substitutional phosphorus atom, and thus no Fermi level dependence is discussed.[12] A second study that included singly charged defects found larger energies of $3.5-\mu_e$ and 0.6 eV in the neutral charge state via a very similar path, with respect to singly positively charged substitutional phosphorus, where μ_e is the Fermi energy as measured from the valence band top. In the positive charge state, the $\langle 100\rangle$ split interstitial—dubbed the S interstitial—and hexagonal- (H-) site interstitial were found to be degenerate with formation energies of 3.1 eV and with a migration barrier of 0.3 eV through motion between the H-site and S interstitials. In the negative charge state, the structure and path were found to be as in the neutral case, but the energies rose to $4.1-2\mu_e$ eV for formation and 1.4 eV for migration, so this charge state was considered unimportant for the diffusion of the defects.[13] The latter study is in excellent agreement with experimental studies giving 3.68 and 3.43 eV diffusion barriers for the P_i^0 and P_i^+ defects, respectively.[14]

Vacancy-mediated diffusion has previously been proposed as a mechanism for germanium self-diffusion and diffusion of various fast-diffusing species in germanium.[3,15,16] The process involves the diffusion of bound phosphorus-vacancy (PV) complexes through motion of the vacancy.[17]

CE is a diffusion mechanism originally proposed by Pandey[18] for self- and dopant-diffusion in Si. This method involves diffusion without interaction with any other defects and proceeds through the rotation of the two atoms about their mutual bond center.

There have been a number of experimental works previously published on phosphorus in germanium. Measurements performed on the depth of the *p-n* junction formed through phosphorus diffusion have yielded a barrier of ~2.5 eV.[19] Later work using spreading resistance probe techniques and secondary ion mass spectroscopy (SIMS) yielded a barrier of 2.07 eV,[20] while other SIMS studies report diffusion barriers of 2.3 or 2.85 eV with a doubly or singly negative diffusing species, respectively.[21,22] The first of these last also suggests possible evidence for transient enhanced diffusion effects. The PV defect, termed the E center, has also been experimentally studied previously. The defect is observed to possess two acceptor levels at $E_v+0.35$ and $E_c-0.23$ eV and anneals out between 100 and 150 °C.[23] Previous supercell-based theoretical work has calculated the binding energy of the related AsV defect as 0.6 eV in germanium.[24] This seems too low in comparison to the E center in silicon which anneals out at similar temperatures, around 150 °C for AsV and 125 °C for PV,[25] and is calculated to possess binding energies for AsV of 1.09,[26] 1.21,[27] or 1.34 eV (Ref. 24) according to a number of previous studies. The P$_i$ and PI defects have not been so well studied in germanium. It is expected that some similarities will be seen with the interstitial carbon–substitutional phosphorus pair in silicon, which exhibits a donor level at $E_v+0.48$ eV and an acceptor level at $E_c-0.38$ eV.[28]

Ab initio calculations are generally performed in one of the two methodologies. Supercell calculations use periodic boundary conditions to mimic bulk material, while cluster calculations use a nanoparticle, which is usually terminated with hydrogen atoms and with the surface layer of bulk held fixed. Both methods should tend to true bulk values as the size increases to infinity.

All calculations performed within the local density approximation of DFT suffer from an underestimation of the band gap. This is especially critical in calculations on germanium and similar low-band-gap materials, where it has been shown in supercell calculations to lead to a crossing of defect levels into the bulk bands at **k** points often used to sample the Brillouin zone.[1,29,30] In cluster calculations, this underestimation is mitigated by the confinement effects imposed by the cluster surface, which widens the band gap and allows for a more reliable study of charged defects. Formation energies, however, cannot be calculated through the cluster methodology due to the inequivalence of the atoms in the cluster. In this study, both supercell and cluster calculations were used to calculate the formation energies of charged defects, either through the use of charged supercells or neutral supercell calculations combined with energy levels calculated from charged clusters.

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,[31] and the defect was embedded in hydrogen-terminated clusters and periodic supercells of germanium atoms. A Padé parametrization[32] of the exchange-correlation functional as proposed by Perdew and Wang[33] was used, and the core electrons were accounted for by the pseudopotentials of Hartwigsen *et al.*[34]

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. The orbitals of the hydrogen surface atoms were expanded using contracted basis sets with four s and one p exponents and those of the phosphorous 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[35] sampling scheme of eight points (MP-2^3). 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),[36] and the surface hydrogen-germanium bonds were relaxed prior to any calculations. The defect was then introduced and the surrounding atoms were displaced to break symmetry before the atoms in the cluster were 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. Energy levels for the phosphorus-interstitial and phosphorus-vacancy complexes were calculated in two ways: the marker method[37] and the formation energy method. In the marker method, 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 as calculated in the cluster methodology is taken to be the difference in the position of their energy levels. In this study, the antimony-vacancy (SbV) donor level at $E_v+0.09$ and acceptor levels at $E_v+0.31$ and $E_c-0.30$ were used for the vacancy-related defect,[23,38] while the two separate sets of levels were used for the interstitial-related defects—the SbV levels and the single donor level of substitutional Se at $E_c-0.28$ eV (Ref. 39) and the single acceptor level of the vacancy-oxygen complex (VO) at $E_v+0.32$ eV.[40] These defects have well-characterized energy levels at similar positions to those studied here. In the case of the interstitial-related defect, different defects were used to try and ascertain which was the most suitable. In the formation energy method, the value of μ_e at which the formation energies are equal for defects with different charge states gives the position of the energy level in the band gap.

Formation energies for the various defects were calculated in the supercell using the formula

$$E_f(D)=E(D)+Q(E_v+\mu_e)-\sum_i n_i\mu_i, \qquad (1)$$

where $E_f(D)$ is the formation energy of defect D, $E(D)$ is the total energy of a supercell containing the defect, Q is the

TABLE I. Formation energies relative to P_{Ge}^{+} (E_f) and energy levels $[E(n-1/n)]$ in eV of the P*V* defect as calculated using neutral P*V* supercells and charged cluster calculations (cluster) or from the formation energies calculated for charged defects in the supercell (supercell).

E_f			$E(n-1/n)$		
Charge	Supercell (eV)	Cluster (eV)	Level	Supercell (eV)	Cluster (eV)
+	2.16	2.10	(0/+)	$E_v+0.07$	$E_v+0.13$
0	$2.23-\mu_e$	$2.23-\mu_e$	(−/0)	$E_v+0.08$	$E_v+0.43$
−	$2.31-2\mu_e$	$2.66-2\mu_e$	(=/−)	$E_v+0.23$	$E_v+0.38$
=	$2.54-3\mu_e$	$3.04-3\mu_e$			

defect's charge state, E_v is the calculated level of the germanium valence band, μ_e is the Fermi energy as measured from the valence band, and $n_i\mu_i$ is the number of each species of atom in the supercell multiplied by their chemical potential. μ_{Ge} is calculated from supercells containing a perfect crystal structure. The diffusion barrier is defined as the difference in formation energy between the saddle point and the singly positive substitutional phosphorus P_{Ge}^{+}, whose formation energy is

$$E_f(P_{Ge}^{+}) = E(P_{Ge}^{+}) + E_v + \mu_e - \mu_P - n_{Ge}\mu_{Ge}, \qquad (2)$$

which makes the diffusion barrier independent of the chemical potential of phosphorus μ_P. The formation energies of defects in the cluster are found from the energies of neutral defects calculated in supercells and the energy levels of the same defects as found in clusters. For some defects, a binding energy was calculated between the phosphorus and the associated intrinsic defect. This was calculated either by comparing the supercell-calculated formation energies of the combined defect with those of the isolated P_{Ge}^{+} and appropriately charged intrinsic defect or by separating the component defects within a suitably charged cluster.

Migration energies and paths were calculated using the improved tangent nudged elastic band method.[41] In this method, initial and final configurations are linearly interpolated to give a chain of intermediate structures or images. For the 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. Similar methods have been used in the past to study various defects in germanium including vacancy-oxygen complexes,[42] vacancy-donor complexes,[29] oxygen interstitial structures,[43] single vacancies,[1,7] divacancies,[30,44] and boron diffusion.[45]

III. RESULTS

A. Vacancy-mediated diffusion

Formation energies relative to P_{Ge}^{+} and energy levels of the P*V* complex were calculated via the two methods described in Sec. II and are reported in Table I. The binding energy between the P_{Ge}^{+} and $V^{=}$ in the PV^{-} defect is calculated to be 0.6 eV by the supercell method. Using the singly negatively charged cluster, the total energy rises by 0.33, 0.64, and 0.82 eV with respect to the bound defect as the component defects are moved to the second-, third-, and fourth-neighbor positions, respectively. Thus, the binding energy is calculated in the cluster to be at least 0.82 eV. It can be seen that the energies calculated by relying on the formation energies found in charged supercells and those calculated by relying on the energy levels found in the cluster using the marker method are not in agreement. Taking the experimental germanium band gap of 0.66 eV, it can be seen that the marker method results for energy levels are in good agreement with experimental values of $E_v+0.35$ and $E_c-0.23$ eV (Ref. 23) for the first and second acceptor levels of the P*V* defect, while the formation energy method results are not in agreement. In addition, it should be noted that while the first acceptor level is calculated to lie above the second in the marker method, the energy difference between the two is too small to say with any confidence whether the defect should exhibit negative-*U* behavior.

The diffusion path considered for the bound P*V* defect is the same as has been examined for the boron-vacancy defect in a previous paper by the present authors.[45] In this path, the defect diffuses through motion of the vacancy around the six-membered rings that comprise the crystal. The barriers for both the motion of the vacancy out to a third-neighbor distance to the P atom and for the exchange of the P atom across the vacancy were calculated. The diffusion was considered in three charge states, which ranges from the neutral to the double negative; as these are the charge states, the defect is expected to exhibit in *n*-type material. In all these states, the barrier for the exchange of phosphorus across the vacancy dominated the barrier for motion out to third neighbor and back. The barriers for diffusion of the P*V* E center are then 1.6, 1.3, and 1.0 eV in the neutral, singly negative, and doubly negative charge states, respectively.

Combining these results with the formation energies of the P*V* defects, as given in Table I, yields total diffusion barriers reported in Table II. These vary with the position of the Fermi level and for a midgap value for μ_e, where the diffusion barrier is found to lie between 2.7 and 3.5 eV, with the barrier decreasing in more heavily doped material.

TABLE II. Total diffusion energies in eV for the PV and PI defects as calculated through the supercell-based formation energy (supercell) and cluster-based marker (cluster) methods. Se/VO and SbV represent the markers used in different cluster calculations.

PV			PI			
Charge	Supercell (eV)	Cluster (eV)	Charge	Supercell (eV)	Cluster	
					Se/VO (eV)	SbV (eV)
0	$3.8-\mu_e$	$3.8-\mu_e$	+	3.3	3.5	3.3
–	$3.6-2\mu_e$	$4.0-2\mu_e$	0	$3.6-\mu_e$	$3.6-\mu_e$	$3.6-\mu_e$
=	$3.6-3\mu_e$	$4.0-3\mu_e$	–	$4.4-2\mu_e$	$4.5-2\mu_e$	$4.8-2\mu_e$

B. Interstitial-mediated diffusion

1. Phosphorus-interstitial structures

The phosphorus interstitial pair was studied in configurations described as a substitutional phosphorus atom along with a T-site and H-site Ge self-interstitial; T- and H-sited phosphorus interstitials and $\langle 110\rangle$ and $\langle 100\rangle$ split interstitials. From all these initial structures, the neutral defect relaxed without barrier to a structure with the phosphorus atom lying between a hexagonal and a bond-centered site, which is labeled as P_{iX_2}. This structure was also the most stable in the singly negative charge state, while in the singly positive, the distorted bond center relaxes to a $\langle 100\rangle$ split interstitial with the P atom distorted toward an adjacent H site (P_{iS}). In the positive state, the P_{iS} structure is degenerate with the H-site phosphorus interstitial (P_{iH}) within the limits of the calculations. The stable structures are shown in Fig. 1 and their formation energies with respect to $\mathrm{P}_{\mathrm{Ge}}^{+}$ and energy levels are given in Table III. The nearest neighbor distances between P and adjacent Ge atoms are 2.44 Å (101% of the $\mathrm{P}_{\mathrm{Ge}}^{+}$-Ge distance) for the P_{iH}^{+}, 2.21 Å (91%) for the $\mathrm{P}_{iX_2}^{0}$, and 2.20 Å (91%) for the $\mathrm{P}_{iX_2}^{-}$ defects. In the P_{iS}^{+} defect, there is a separation of 2.18 Å (90%) between the P atom and the Ge that forms the other half of the split interstitial, 2.32 Å (96%) for the other two neighbors of the P atom, and 2.36 Å (97% of the bulk Ge-Ge separation) between the split-interstitial Ge and its neighboring Ge atoms. All of these structures are very similar to those previously published for silicon.[13] The binding energy for the dissociation of the P_{i}^{+} defect into $\mathrm{P}_{\mathrm{Ge}}^{+}$ and a neutral $\langle 110\rangle$ Ge self-interstitial was calculated within the supercell to be 0.7 eV. In a positively charged cluster, the total energy rose to 0.34, 0.54, 0.58, 0.70, and 0.77 eV above that of the stable bound defect as the component defects were moved from first to fifth nearest neighbor positions. The energy levels exhibit a normal level ordering within the band gap when calculated with the marker method and a possible negative-U behavior with the formation energy method. Using different markers leads to differences in the level positions of 0.2–0.3 eV. We do not have experimental results to compare for the PI defect, so it is not possible to determine which set of marker defects are more accurate. It will be seen, however, that the difference in energy calculated here has little effect on the diffusion properties of phosphorus.

2. Interstitial phosphorus migration paths

In the neutral and singly negative charge states, phosphorus diffusion was considered to take place by a combination of three movements relating to the six-membered ring when the defect is on: a movement of the phosphorus across the H-site to the Ge-Ge bond opposite the original location of the phosphorous (trans-H), a movement of the phosphorus atom around the six-membered ring from one Ge-Ge bond to the next (trans-S), and a rotation about the Ge-Ge bond the phosphorous atom interrupts to a different six-membered ring (rot). The trans-H and trans-S steps are shown in Fig. 2. In the positive charge state, the diffusion was considered to take place via exchange between the H-site and split-interstitial structures along with diffusion of the phosphorous

TABLE III. Formation energies relative to $\mathrm{P}_{\mathrm{Ge}}^{+}$ (E_f) and energy levels $[E(n-1/n)]$ in eV of the PI defect as calculated using neutral PI supercells and charged cluster calculations with different sets of markers (cluster Se/VO or SbV) or from the formation energies calculated for charged defects in the supercell (supercell).

E_f				$E(n-1/n)$			
Charge	Supercell (eV)	Cluster		Level	Supercell (eV)	Cluster	
		Se/VO (eV)	SbV (eV)			Se/VO (eV)	SbV (eV)
+	2.88	3.12	2.90	(0/+)	$E_v+0.39$	$E_v+0.15$	$E_v+0.37$
0	$3.27-\mu_e$	$3.27-\mu_e$	$3.27-\mu_e$	(–/0)	$E_v+0.28$	$E_v+0.39$	$E_v+0.68$
–	$3.55-2\mu_e$	$3.66-2\mu_e$	$3.95-2\mu_e$				

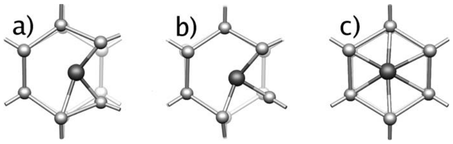

FIG. 1. Structures of the phosphorus interstitial complex, as viewed along a ⟨111⟩ direction. The smaller, lighter gray balls represent germanium atoms, and the larger, darker gray ball represents the phosphorus. Each structure has been superimposed on a lighter gray image of perfect germanium, as an aid to the reader. (a) The distorted bond-center structure P_{iX_2}. (b) The distorted ⟨100⟩ split interstitial P_{iS}. (c) The *H*-site phosphorus interstitial P_{iH}.

along 110 channels linking *H* sites. Therefore, diffusion steps between *H* sites (HH), between the P_{iS} structure and the adjacent *H*-site (short-SH) and an *H*-site one step removed from the initial position (long-SH), as well as the rotation of the P_{iS} structure into a different ⟨100⟩ direction (rot) were considered.

In the singly negative charge state, the rot step was calculated to have a small barrier of around 0.08 eV, with a saddle point with a bond-center structure distorted toward an adjacent tetragonal interstitial site ($P_{i\text{BC-T}}$). The trans-*S* step was then found to exhibit the lowest barrier of the translation steps, with a saddle point of the P_{iS} structure and a barrier of 0.80 eV. In the neutral charge state, the same path is followed, but the barrier for rot is a little more complex, and the trans-*S* barrier drops to 0.34 eV. In the singly positive charge state, the short-SH barrier is calculated to be 0.04 eV, the HH barrier 0.76 eV, and the rot barrier 0.42 eV. This suggests a diffusion path where the PI_S defect rotates with a saddle point of a split interstitial in the ⟨111⟩ direction (P_{i111}) and two lower barriers with ⟨110⟩ split-interstitial (P_{i110}) structures. The phosphorus atom then migrates across the adjacent hexagonal ring via the *H* site and rotates again. The barriers for all these paths are detailed in Fig. 3.

Combining these barriers with the formation energies for the P_i defect as calculated above, we find total diffusion barriers as reported in Table II. Again, the barrier depends on the position of μ_e and lies between 3.3 and 4.2 eV for a midgap Fermi level.

C. Correlated exchange

In the CE mechanism, two adjacent atoms rotate about their linking bond-center, exchanging positions without the involvement of any defect other than the dopant atom itself. The path was found to be essentially the same as that proposed by Pandey[18] for self-diffusion in silicon. The barrier for this process was calculated in the singly positive charge state, as this is the state that the substitutional phosphorus is expected to possess and is found to be 6.2 eV.

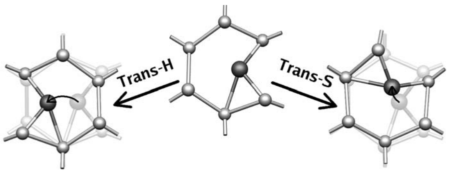

FIG. 2. Diffusion steps for the P_{iX_2} structure of the phosphorus interstitial. The smaller, light gray balls represent germanium atoms, and the larger, dark gray ball represents phosphorus. The central structure is a starting point, which is repeated behind the other two as an aid to the reader. To the left is the trans-*H* diffusion step, whereby the phosphorus atom moves across the adjacent *H* site, and to the right is the trans-*S* step, where the phosphorus moves around the six-membered ring.

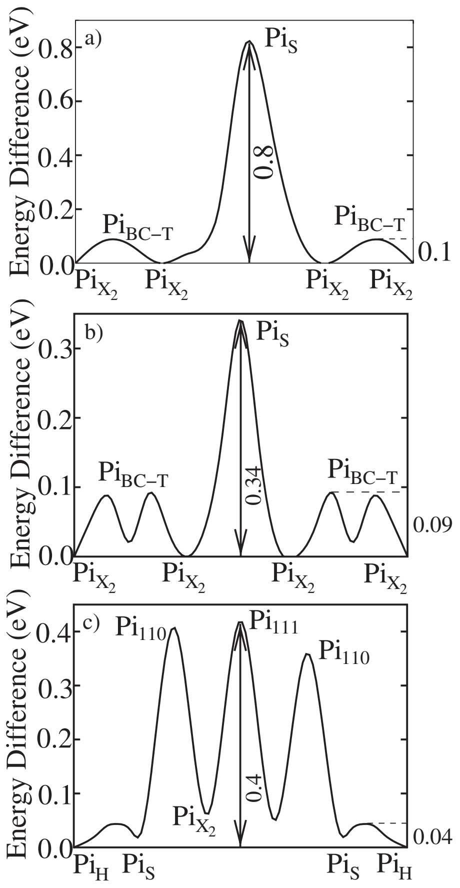

FIG. 3. Diffusion barriers for the P_i defect in various charge states, which are relative to the most stable P_i structure for that charge state. [(a) and (b)] Singly negative and neutral charge states, which show the trans-*S* diffusion step preceded and followed by a rot step. (c) Singly positive charge state diffusion, with the short-SH step preceding and following the rot step. In this case, the rot diffusion step consists of a series of three peaks as the defect moves through several different high-symmetry configurations during its motion.

IV. SUMMARY AND DISCUSSION

The CE mechanism is observed to have a very high diffusion barrier of 6.2 eV, suggesting that it is not an important process in the diffusion of phosphorus in germanium. The *PV* defect was examined in charge states ranging from the neutral to the doubly negative. Calculations give a donor level at $E_v+0.13$ eV and first and second acceptor levels at $E_v+0.43$ and 0.38 eV, respectively. Experimental values of $E_v+0.35$ and $E_c-0.23$ eV (Ref. 23) for the acceptor levels suggest that the cluster-based marker method is the most reliable method, and lacking experimental results for *PI* defects, we therefore take the marker method results as being

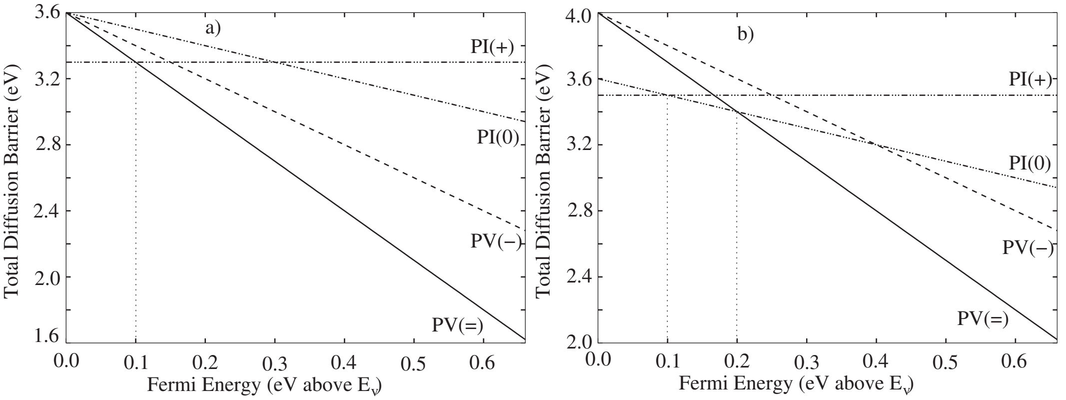

FIG. 4. Dependence of the diffusion energy, relative to P^+_{Ge}, on the Fermi level position for phosphorus complexes as calculated from (a) charged supercells and (b) energy levels found in a cluster using Se/VO as markers together with neutral defect formation energies found from supercells. Energies are given relative to singly positively charged substitutional phosphorus. Only the lowest barrier for each charge state is displayed, and the labels on the left of the graphs indicate the species and charge state corresponding to each line.

the most accurate. The binding energy between positively charged P^+_{Ge} and the double negative $V^=$ to form the singly negative PV^- defect was calculated in the supercell to be 0.6 eV. This agrees with the previous theoretical work using similar methods[24] but is not congruent with work in silicon. Similar annealing temperatures have been experimentally measured between the two materials,[25] but significantly higher binding energies of 1.1–1.3 eV have been calculated in Si.[24,26,27] Cluster calculations of the binding energy between P and V in germanium show moderate increase in the energy to 0.82 eV when the component defects are separated to the fourth-neighbor positions. This result is not converged with defect separation, but limited by the size of the cluster and would likely converge to a value close to the results for Si if sufficiently large clusters could be used. Additional Coulomb energies due to charged defects in the supercell[46] may explain the poor agreement of supercell-calculated energy levels with experiment in this work, and their inclusion in other studies should improve the reliability of their results.

The phosphorus-interstitial structures found here are in excellent agreement with those previously calculated in silicon.[13] In the neutral and negative charge states, the defect lies in a highly distorted bond-center configuration (P_{iX_2}), while in the positive charge state, the defect rearranges to a distorted $\langle 100\rangle$ split interstitial (P_{iS}) or a hexagonal interstitial (P_{iH}), with degenerate formation energies. The energy levels were found to depend on the method used to calculate them. The cluster calculations give a donor level at $E_v+0.15$ or 0.37 eV and an acceptor level at $E_v+0.39$ or 0.68 eV depending on the marker used. The errors in the method are worse in this case than normal. We do not have experimental results to compare these, but the behavior is not dissimilar to the P_{Si}-interstitial carbon defect in Si, with donor and acceptor levels at $E_v+0.48$ and $E_c-0.38$ eV, respectively. The binding energy between the neutral $\langle 110\rangle$ Ge self-interstitial and P^+_{Ge} to form the stable form of P^+_i was calculated in the supercell to be 0.7 and 0.77 eV in the cluster calculation, when the component defects were moved to fifth-neighbor positions. In contrast to the vacancy case, this is quite close to the supercell value and seems that it may be nearly converged by this distance, but cluster size restrictions prevent further tests.

The total barriers obtained depend on the method used to calculate the formation energies of the complex defects. Figure 4 compares the barriers obtained from formation energies as calculated from charged supercells with those calculated using neutral phosphorus defects and marker method calculated energy levels using Se/VO for the interstitial defects. Using the SbV marker for the interstitial defects lowers the total energy for PI(+) diffusion, such that it is the most favorable diffusion path up to $\mu_e=0.2$ eV. This is the only difference to the diffusion paths, and since P-doped material is unlikely to be *p* type, it does not make a significant difference to the diffusion of P.

These results suggest that, for $\mu_e \lesssim E_v+0.2$ eV, it is more favorable for phosphorus diffusion to proceed via an interstitial-mediated mechanism. This would proceed in the positive or neutral charge states depending on μ_e and the energy level positions for the PI defect. For $\mu_e \gtrsim E_v+0.2$ eV, it is more favorable for the diffusion to proceed through a vacancy-mediated mechanism in the doubly negative charge state with a barrier of $4.0\ \text{eV}-3\mu_e$.

For a μ_e of 0.5–0.6 eV, a diffusion barrier of ~2.2–2.5 eV is calculated, which is in agreement with previous experimental data giving diffusion barriers ranging from 2.07 to 2.85 eV.[19–22] The charge state of the diffusing PV defect is also in agreement with the experimental studies that suggest a doubly negatively charged diffusing species and that it can be enhanced by a supersaturation of interstitial or vacancy defects.[21] Comparing our results to those suggesting a singly negative diffusing species and a diffusion barrier of 2.85 eV,[22] it is interesting to note that this barrier is in good agreement with our results for diffusion via PV^- in highly *n*-doped regions.

The phosphorus-interstitial results are very similar to previous modeling work performed on phosphorus interstitial defects in Si, with similar structures and diffusion energies calculated.[12,13] Finally, comparing the results calculated here to those previously calculated by the authors for boron diffusion in Ge, we find that the diffusion barrier for phosphorus is ~1 eV lower than that for boron.[45]

V. CONCLUSIONS

Phosphorus diffusion in germanium was studied through a number of paths using *ab initio* methods. The results suggest that the mobile species during phosphorus diffusion under equilibrium conditions is the phosphorus-vacancy pair, likely in a doubly negative charge state with a barrier of 4.0 eV $-3\mu_e$. The charge state and diffusion barrier is in agreement with some previous experimental work,[19–21] but other work suggests a single-negative diffusing species.[22]

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