Microscopic mechanism of atomic diffusion in Si under pressure

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We have performed the first-principles total-energy calculations on the atomic diffusion of group-V impurities in Si, and have revealed the pressure effect on the activation energy of the diffusion. For the vacancy mechanism, the activation energies for P, As, and Sb decrease with pressure. For the interstitial mechanism, on the other hand, the formation energy of the interstitial impurity shows a general tendency to increase with pressure. Combining the results with the experimental data, we have concluded that there is a dominant contribution of the vacancy mechanism for the As diffusion. The microscopic origin of the pressure dependence is clarified in terms of the local strain around the defects. The negative pressure dependence common to the group-V impurities for the vacancy-mediated diffusion is well explained by the peculiar nature of the isolated vacancy: (a) breathing distortion of the surrounding Si atoms toward the vacancy site, which gives rise to a tensile strain around the vacancy, and (b) the characters of the wave function and the lattice distortion originating from the vacancy, which cause the weak vacancy-impurity interaction. The positive pressure dependence for the interstitial-mediated diffusion is closely related to the atomic structures of the interstitial impurities which cause compressive strain to the surrounding Si-Si bonds.

I. INTRODUCTION

Atomic processes of impurity diffusion in Si are of great scientific and technological interest. In particular, the problem of identifying the dominant diffusion mechanism has attracted considerable attention.[1] The local-density calculations[2,3] show that several diffusion mechanisms (the vacancy mechanism, the interstitial mechanism, and the concerted exchange mechanism[4]) could contribute to the diffusion because they have comparable activation energies. Experimentally, the diffusion constant and other quantities have been extensively measured by changing various environments. Among them, the most commonly used approach is the oxidation of Si: The stress near the interface of Si and silicon oxides induces the interstitial Si (Si_i) atoms and thus the concentrations of Si_i and the vacancy (V) are changed from the equilibrium values in the Si substrate. Therefore, diffusion of the impurity atom is enhanced or retarded upon oxidation, depending on the chemical species of the impurity, which provides information on the mechanisms of the impurity diffusion. However, the oxidation techniques do not always give unambiguous results. For example, there are controversies for the diffusion of the As impurity: Fahey *et al.*[5] argued that both the vacancy and the interstitial mechanisms seem to give comparable contributions to the diffusion, whereas Nichols, Van de Walle, and Pantelides[3] concluded that the interstitial mechanism is dominant based on the local-density calculation.

In this context, we pay attention to an alternative approach, i.e., applying pressure. Study of the pressure effect seems to be promising: First, significant enhancement in the diffusion constant is observed for the Si self-diffusion[6] and the As diffusion[7]; second, the formation energies of the vacancy and the self-interstitial, which are closely related to the activation energies for the vacancy-mediated and the interstitial-mediated diffusions, respectively, were shown to exhibit opposite pressure dependence.[8] We thus expect that the identification of the diffusion mechanism is conveniently performed by comparing the experimental data with the calculated pressure dependence for each diffusion mechanism.[9] Our aim in this paper is to show the usefulness of this approach by presenting the systematic results for the diffusion of group-V impurities, and by clarifying the physics involved in the pressure effect.

In this paper, we perform first-principles total-energy calculations on the activation energy Q and its pressure coefficient. Fully relaxing all the atoms in a large supercell, carefully avoiding the effects due to the finite cell size, we calculate not only the formation energy E_f but also the migration energy E_m for the first time (note that the activation energy Q is given as a sum of E_f and E_m). In the calculation we use the norm-conserving pseudopotentials,[10] the Cerperley-Alder[11] exchange-correlation energy in the local-density approximation (LDA), the plane-wave basis set with the cutoff energy of, typically, 10 Ry, and the one special k point[12] in the Brillouin-zone integration.[13] The nonlocal part of the Si pseudopotential is treated by the Kleinman-Bylander procedure.[14] In order to avoid the influence of the so-called "ghost,"[15] the nonlocal terms for impurity atoms are exactly calculated using the Štich method.[16] The system is simulated by the supercell model which contains 64 atoms in a unit cell. Both the electronic and geometric degrees of freedom are optimized by the highly efficient conjugate gradient (CG) method.[9,17,18] Here we adopt the alternate optimization,[9] i.e., the optimization of the electronic degrees of freedom at a given geometry and then the succes-

sive geometry optimization, in contrast to the simultaneous optimization.[19] In the geometry optimization, all atoms are fully relaxed without restricting the symmetry.

II. RESULTS AND DISCUSSION

A. Mechanisms of the diffusion

It is considered that impurities diffuse via the long-lived fast-diffusing intermediate species, i.e., the vacancy-impurity pair for the vacancy mechanism and the interstitial impurity for the interstitial mechanism. We assume that the concentration of the impurity is small and the quasiequilibrium is realized. In that case, the activation energy of the diffusion is simply given as a sum of the formation energy of the intermediate species (E_f) and its migration energy (E_m). The most laborious task is then to determine the migration path and the migration energy E_m. We indeed determine them for the first time from our first-principles calculations, as described below.

The migration process of the vacancy-impurity pair consists of two steps: First the impurity jumps to a neighboring vacancy site and second, the vacancy migrates around the impurity atoms to occupy a new neighboring site; repeating the two steps the pair migrates. It is conjectured that the vacancy migrates along a silicon hexagon to occupy the new neighboring site.[20,21] We have found that the calculated migration energy for the path is consistent with the experimental value (Table I), which supports the above migration path for the vacancy. In Fig. 1 the potential surface for the vacancy migration around the As impurity is shown. Relaxation of the surrounding atoms is fully taken into account in the figure. At the saddle point of the migration, the vacancy is located at the third-nearest-neighbor site of As. Contrary to the prevailed picture,[20,21] the shape of the potential surface near the saddle point is flat. This is a consequence of the local strain induced by the As impurity. The migration path of the interstitial impurity is obtained by a fitting procedure. In the fitting, we first put the As atom on the line that connects the stable position and symmetrical positions (bond-center site, hexagonal site, and split interstitial site). Then, fully relaxing Si atoms, we calculate the total energy. Gradually shifting the position of the As atom along the line, we repeat the total-energy calculation and fit the obtained total energies to plane-wave expansion. We have used 13 total energies and 305

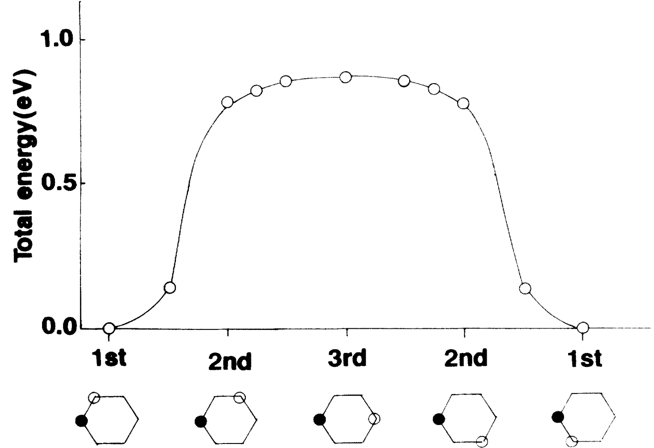

FIG. 1. The potential-energy surface for the vacancy (○) migration along the hexagon which contains the As atom (●). The open circles are the calculated values and the line is a guide for eyes. The charge state of the As-V pair is neutral.

TABLE I. The activation energy for the vacancy mechanism at zero pressure (Q) and its energy increase at $P=60$ kbar (ΔQ). We also show the migration energy of the impurity-vacancy pair (E_m) and the binding energy of the pair at the saddle-point configuration (E_b^s). The experimental data are parenthesized. All quantities are in eV and a neutral charge state is assumed.

Species	Q	ΔQ	E_m	E_b^s
P	4.2(3.5∼3.7[a])	−0.9	0.8(0.94[c])	0.3
As	3.9(4.1∼4.3[a])	−0.6 (−1.4[b])	0.9 (1.07[c])	0.7
Sb	3.9(3.9∼4.1[a])	−0.7	0.9(1.28[c])	0.7
Si	4.2(4.0∼5.1[a])	−1.1	0.2 (0.45[d])	

[a]Selected data by Ref. 1.
[b]Compiled value from Ref. 7.
[c]Reference 20 and 21.
[d]Reference 27.

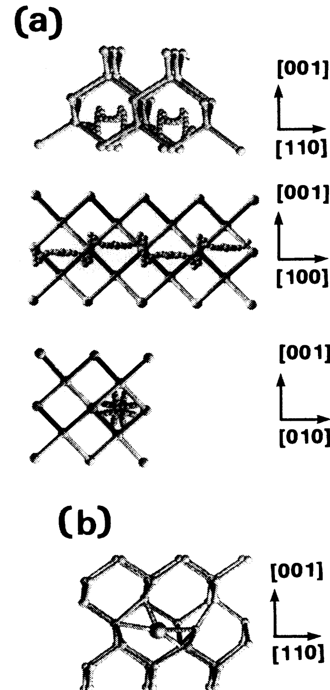

FIG. 2. (a) One of the favorable migration paths of the interstitial As impurity seen from three different directions. The relaxation of the surrounding Si atoms is fully taken into account in the calculation, but not shown in this figure. (b) The most stable interstitial structure for As. The charge state of the interstitial As is neutral.

plane waves. The error of the fitting is estimated to be about 0.1 eV. Although the 13 data points are not enough to fit the total-energy surfaces in the whole unit cell, we consider that this is satisfactory for the following two reasons. First, we have chosen the positions at which the total energy is considered to be low, so that the fitting is better in the important region. Second, the accuracy of the result is bound by the error in the total-energy calculation, which is estimated to be about 0.1 eV due to the local-density approximation and the finite supercell. In Fig. 2 we show one of the favorable migration paths and the most stable interstitial structure that we have obtained for As. The most stable structure has no symmetry and is accompanied by large lattice distortion. In this structure, one Si-Si bond is cut and the As atom is located between the bond-center site and the hexagonal site. Cutting nearby the Si-Si bond, the interstitial As migrates (Fig. 2).

We now discuss the activation energy for an impurity A. For the vacancy mechanism, Q is written as

$$Q=E(A-V^0)+\frac{1}{N}E(\text{bulk})-E(A_s^+)\ , \tag{1}$$

where the first term is the total energy of the impurity-vacancy pair at the saddle-point configuration, N the number of atoms in the supercell, and the third term the total energy of the positively charged substitutional impurity. Since the Fermi level is located at the middle of the energy gap (intrinsic case), the substitutional impurity is ionized. We assume that the impurity-vacancy pair is neutral.[20,22] Q can be rewritten as

$$Q=E(A-V^0)-E(A_s^0)+E(\text{bulk})-E(V^0)$$
$$+E(V^0)-\frac{N-1}{N}E(\text{bulk})+E(A_s^0)-E(A_s^+)\ . \tag{2}$$

The first four terms are the definition of the binding energy of the A-V pair at the saddle point $E_b^s(A-V^0)$, the fifth and sixth terms the formation energy of the neutral vacancy $E_f(V^0)$, and the last two terms the neutralization energy $E_n(A_s^+)$:

$$Q=-E_b^s(A-V^0)+E_f(V^0)+E_n(A_s^+)\ . \tag{3}$$

The neutralization energy is approximately half the energy gap for the intrinsic case. The experimental value for the energy gap is 1.1 eV, which we use in this paper. To avoid the effect due to the finite cell size, the formation energy of the vacancy is carefully obtained by summing the formation energy of the ideal vacancy and the relaxation energy. The formation energy of the ideal vacancy is calculated with the triply degenerate deep states (t_2 states) equally occupied: each state is occupied by $\frac{2}{3}$ electrons for the neutral charge state. The relaxation energy is calculated by the total-energy difference between the fully relaxed vacancy and the ideal vacancy with the lowest-energy deep state being occupied by two electrons. We use this complicated procedure for the following reasons. Due to the overlap of the wave function beyond the cell boundary, the deep level splits and possesses dispersion (0.65 eV). Thus, if only the lowest-energy state is occupied, the formation energy of the vacancy is underestimated. Since this situation is common to both the relaxed vacancy and the ideal vacancy, the relaxation energy is quite independent of the way of occupying electrons. The relaxation energy is thus conveniently obtained with the lowest-energy state occupied. On the other hand, the formation energy of the ideal vacancy is correctly obtained with the three equivalent deep states equally occupied. These are the reasons for adopting the above two-step procedure. The formation energy of the vacancy that is obtained by this procedure is equal to 4.0 eV. As for the interstitial mechanism, the activation energy is simply obtained by $Q=E_f+E_m+E_n(A_s^+)$, where

$$E_f=E(A_i^0)-\frac{1}{N}E(\text{bulk})-E(A_s^+)\ . \tag{4}$$

Here, the first term is the total energy of the interstitial impurity. Here we assume that the interstitial impurity is neutral in the diffusion process.

B. The activation energies and the pressure coefficients

We now discuss the As diffusion. The calculated Q without the pressure is 3.9 eV for the vacancy mechanism, and 4.3 eV for the interstitial mechanism. Thus the vacancy mechanism seems to be more important than the interstitial mechanism. This argument is corroborated by the results under pressure. Namely, the two mechanisms show opposite pressure dependence: For the vacancy mechanism, the activation energy decreases by 0.6 eV when the pressure of 60 kbar is applied (i.e., $\Delta Q=-0.6$ eV), whereas for the interstitial mechanism $\Delta Q\geq 0.4$ eV (Tables I and II).[23] (On the basis of the calculated bulk modulus, the system under the pressure of 60 kbar is simulated by reducing the lattice constant by 2.0%.) On the other hand, the experiment of Nygren *et al.*[7] shows that Q decreases monotonically with $2.3\pm1.8\times10^{-2}$ eV/kbar. This corresponds to $\Delta Q=-1.4\pm1.1$ eV for $P=60$ kbar. Only for the vacancy mechanism is the pressure coefficient consistent with the experimental data. From this we argue that there is a major contribution from the vacancy mechanism for the As diffusion. We cannot rigorously exclude the possibility that the interstitial mechanism also contributes to the diffusion at zero pressure, because ΔQ could be negative when the vacancy mechanism quickly dominates the interstitial mechanism with increasing pressure. However, since the observed activation energy shows an approximately linear behavior at $P=0,20,30$ kbar,[7] it is natural that the vacancy mechanism gives a larger contribution to the diffusion even at

TABLE II. The formation and migration energy for the interstitial at zero pressure and their energy increase at $P=60$ kbar. All quantities are in eV and a neutral charge state is assumed.

Species	E_f	Q	ΔE_f	ΔQ
P	3.5		0.5	
As	3.4	4.3	0.7	≥ 0.4
Sb	3.9		0.1	

zero pressure.

Originally, Nygren *et al.*[7] concluded that the interstitial mechanism is dominant on the basis of the observed negative activation volume (-9 ± 4 Å^3). They considered that the activation volume V for the vacancy mechanism is not negative for the following reason. They first decomposed V into the relaxation volume (V_r) and the formation volume (V_0) of the ideal impurity-vacancy pair ($V=V_0+V_r$). Here, V_0 is approximately equal to the formation volume of the ideal vacancy (20 Å^3). They considered that, since the breathing relaxation does not seem to be so large, V_0 dominates, i.e., V is positive. But our calculation shows that the breathing distortion is indeed large (0.40 Å), and V is estimated to be -5 Å^3.[24] The dominance of the vacancy mechanism is thus consistent with the negative activation volume.

We next present calculated result for other group-V impurities. We find peculiar atomic size dependence for each mechanism. For the vacancy mechanism, the calculated activation energy for P is 4.2 eV, which is larger than the experimental values [3.5 ~ 3.7 (Ref. 1) by 0.5 ~ 0.7 eV]. On the other hand, the activation energy for Sb is 3.9 eV, which is within the range of the experimental data. This seems to show that the vacancy mechanism is a strong candidate for the Sb diffusion, but it is not for the P diffusion. The calculated activation energies of the group-V impurities exhibit negative pressure dependence, and the amount of the decrease is similar to each other: As shown in Table I, Q decreases by 0.9, 0.6, and 0.7 eV under 60 kbar for P, As, and Sb, respectively. For the interstitial mechanism, on the other hand, the formation energy of the interstitial impurity, E_f, shows a general tendency to increase with pressure. By applying a pressure of 60 kbar, E_f increases by 0.5, 0.7, and 0.1 eV for P, As, and Sb, respectively (Table II). Since the migration energy is rather small (0.3 eV for the As diffusion), E_m gives a minor contribution to the activation energy. This means that Q will increase or slightly decrease with pressure. Therefore, each mechanism exhibits different pressure dependence so that the dominant mechanism could be identified for the group-V impurities by performing the corresponding experiments.

C. Origin of the pressure dependence

We are now in a position to investigate the origin of the pressure dependence. For the vacancy mechanism, the major origin of the negative pressure dependence is the nature of the isolated vacancy. The formation energy of the isolated neutral vacancy, $E_f(V^0)$, decreases by 1.0 eV when the pressure $P=60$ kbar is applied. The breathing relaxation is 0.30 Å toward the vacancy site at zero pressure and at $P=60$ kbar it is 0.52 Å. On the other hand, when we do not allow the breathing relaxation, i.e., for the ideal vacancy, the pressure effect is significantly reduced; $\Delta E_f(V^0)$ is -0.2 eV. Thus, most of the pressure dependence of $E_f(V^0)$ comes from the breathing distortion. Since the electronic level structure is unchanged within about 0.03 eV under the pressure of 60 kbar, the pressure dependence is not due to a change of the electronic structure. We argue that the strain that is stored in the surrounding Si-Si bonds is the origin of the pressure dependence. The breathing distortion causes long-range lattice relaxation: Along the zigzag chain of atoms in {110} planes, the bonds are elongated by 0.16, 0.09, and 0.06 Å at zero pressure so that tensile strain is caused by the distortion. Due to the tensile strain, the amount of work performed by the applied pressure is negative. Therefore, the energy around the vacancy is reduced when the pressure is applied. In fact, the elongation is reduced to 0.12, 0.05 and 0.03 Å along the chain at $P=60$ kbar, showing that the strain is released by the applied pressure. It is thus likely that the negative pressure dependence of Q is ascribed to the strain due to the breathing distortion. (We consider that further quantitative discussion is possible if we use the stress field theory of Nielsen and Martin[25,26], which enables us to calculate local strain in an arbitrary region in the cell.)

For the formation energy of the vacancy *at the third-nearest-neighbor site* of the impurity (the saddle-point configuration), namely Q, the breathing distortion is also found to be important; i.e., the pressure dependence is small if we do not allow for the breathing distortion, and the pressure effect on the electronic structure is small. The breathing distortions around the vacancy located at the saddle point of the impurities are close to that for the isolated vacancy both at $P=0$ and 60 kbar (Table III), and the distortions induce the elongation of the bond length that is positive and roughly the same as that of the isolated vacancy. (The bond lengths near the impurity atom are affected by the impurity atom.) This explains why the pressure dependence of Q is common among the different impurities ($\Delta Q=-0.6$ to -0.9 eV) and why it is comparable to the ΔE_f of the isolated vacancy (-1.0 eV). Yet there is a minor tendency that the breathing distortion is larger for atoms with larger radii. For example, the breathing distortions for Sb (atomic radius = 1.59 Å) and for P (atomic radius = 1.28 Å) are larger than the distortion of the isolated vacancy (atomic radius of Si = 1.32 Å) by 0.14 and 0.03 Å, respectively. We consider that this is due to the local compressive strain caused by the impurity atom: i.e., the volume of the vacancy is reduced by increasing the breathing distortion so as to compensate for the local strain by the impurity atom. This effect is also an important factor for the weak atomic-size dependence of ΔQ.

The slight atomic-size dependence of the breathing distortion is explained by the nature of the interaction between the vacancy and impurity that weakly binds the

TABLE III. The amount of the breathing relaxation of the vacancy which is located at the third-neighbor site from the impurity atom. For the convenience of the discussion, we add the calculated bond length between the substitutional impurity and the Si atom.

Species	$P=0$ kbar	$P=60$ kbar	Bond length
P	0.33 Å	0.47 Å	2.35 Å
As	0.40 Å	0.54 Å	2.43 Å
Sb	0.44 Å	0.55 Å	2.55 Å
Si	0.30 Å	0.52 Å	2.34 Å

pair. The binding energy of the impurity and the vacancy is indeed small, 0.3–0.7 eV (Table I). Moreover, the interaction of the pair is mainly the Coulombic interaction: The non-Coulombic interaction that accompanies distortion or formation of chemical bonds does not participate. In fact, the binding energy of the P and vacancy is 0.3 eV for the neutral charge state, but it vanishes for the positive charge state. In both charge states, the charge density near the P atom is almost the same as that of the substitutional P, and only the charge density near the vacancy is different (see Fig. 3). This indicates that the interaction that binds the pair is mainly the Coulombic interaction, i.e., the interaction between the positive charge around the P atom (P^+) and the negative charge around the vacancy (V^-) binds the pair. This is due to the peculiar nature of the vacancy. The wave function and the lattice distortion originating from the vacancy extend preferentially along the zigzag chain of atoms in {110} planes.[28,8,29] Since the impurity atom is off the chain in the saddle-point configuration, the impurity atom will be weakly perturbed by the presence of the vacancy, and vice versa.

For the interstitial mechanism, the formation energy of the interstitial impurity increases with pressure. It is not possible to clearly decompose the origin of the pressure dependence into factors as we have done above for the vacancy mechanism, but we find that the interstitial impurities cause compressive strain to surrounding Si-Si bonds, which contributes to increase the formation energy under pressure. In this system, the neighboring Si-Si bonds of the interstitial impurity atom are shorter than the equilibrium bond length. For example, all the bonds that are about 2–3 Å apart from the impurity are reduced by 0.05–0.1 Å. (The nearer bonds are more affected by the impurity atom so that the shrinkage of the bond lengths varies with position.) This indicates that compressive strain is generated in this system. The amount of the increase is found to be different (Table II): it is larger for P and As ($\simeq$0.7 eV) and smaller for Sb ($=$0.1 eV). The different pressure dependence is also related to the different amounts of strain caused by different atomic structures of the interstitial impurity (Fig. 4). The P and As interstitials have similar structure at zero pressure. But, when the pressure $P=60$ kbar is applied, although the structure of the P interstitial remains essentially the same, the As interstitial changes the structure: The Si atom, denoted as atom A in Fig. 5, is pushed toward the Si atom B by 0.4 Å, and makes an approximately symmetric structure, i.e., the bond lengths A-B and As-C are approximately the same, 2.7 Å, which is 0.3 Å longer than the equilibrium bond length. We call this structure the double interstitial. For the Sb interstitial, the atomic structure is similar to the double interstitial structure at zero pressure, and with the applied pressure the Si atom A further approaches the tetrahedral site by 0.1 Å. Thus, applying pressure and increasing atomic size produce a similar effect on the structure, i.e., the Si atom A is pushed toward the interstitial region. By this change of the structure, the compressive strain tends to be reduced. For example, under the pressure of 60 kbar, the shrinkage of the bond lengths is smaller for the Sb interstitial than for the P interstitial by about 0.03 Å for the bonds that are located about 2–3 Å apart from

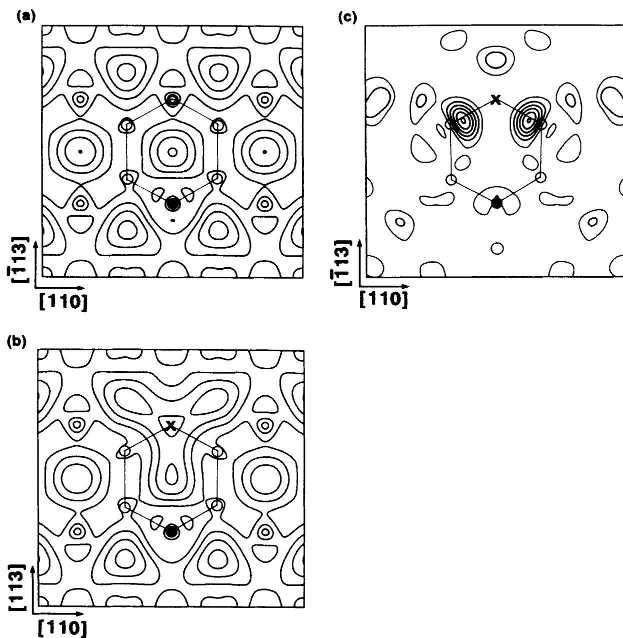

FIG. 3. (a) Charge density of the substitutional phosphorus. (b) Charge density of the P-V^0 pair at the saddle-point configuration of migration: $\rho(P\text{-}V^0)$. (c) The difference of charge density between the neutral pair and the ionized pair (P-V^+): $\rho(P\text{-}V^0)-\rho(P\text{-}V^+)$. The maximum value of the plot is 6.0 ($Å^{-3}$) for (a) and (b) and 8.7×10^{-2} ($Å^{-3}$) for (c). The subsequent contour lines differ by a factor of 2 for (a) and (b); they differ by 0.8×10^{-2} ($Å^{-3}$) for (c). The vacancy ($\times$) and P atom (●) are located at the top and the bottom of the hexagon, respectively. Open circles refer to Si atoms.

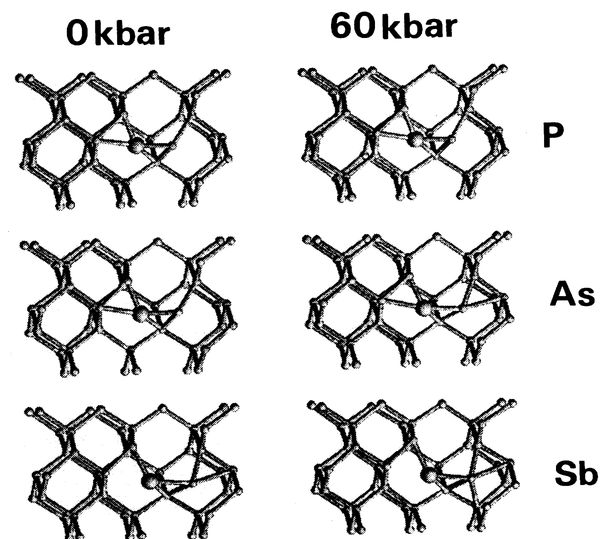

FIG. 4. The most stable interstitial structure of impurity atoms (P, As, and Sb) at $P=0$ and 60 kbar. The charge state of the interstitial impurity atom is neutral.

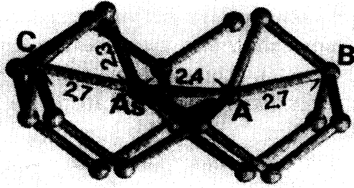

FIG. 5. The most stable interstitial structure for As at $P=60$ kbar. The bond lengths in unit of Å are shown in the figure.

the impurity. We consider that this is closely related to the tendency of the pressure dependence of E_f that is small for atoms with large atomic radii.

III. SUMMARY

In this paper, we have performed first-principle total-energy calculations on the activation energy Q and its pressure coefficient. Using a large cell of 64 sites, fully relaxing all the atoms in the cell, carefully avoiding the effects due to the finite cell size, the total energies are obtained in the calculations. Owing to the large cell size, it is possible to calculate not only the formation energy E_f but also the migration energy E_m for the first time. The obtained activation energies are consistent with the experimental data available. The result for the As diffusion in Si shows that Q decreases for the vacancy mechanism and increases for the interstitial mechanism. Comparing the result with the experimental data of Nygren *et al.*, we have concluded that the vacancy mechanism dominantly contributes to the As diffusion.

Then we have studied the pressure dependence for other group-V impurities (P and Sb), and have clarified the origin of the pressure dependence. For the vacancy mechanism, the activation energies for P, As, and Sb decrease with pressure by 0.6–0.9 eV. This means that the formation energy of the impurity-vacancy pair (in the saddle-point configuration) is decreased by 0.6–0.9 eV. We find that the results can be systematically explained by the following two features of the vacancy: (a) the breathing distortion of the surrounding Si atoms toward the vacancy gives rise to a tensile strain around the vacancy; and (b) the wave function and the lattice distortion originating from the vacancy, which preferentially extend along the zigzag chain of atoms in $\{110\}$ planes, result in the weak vacancy-impurity interaction. First, the negative pressure dependence can be ascribed to the breathing distortion. Owing to the breathing distortion, the surrounding Si-Si bonds are elongated, which causes tensile strain around the vacancy site. Due to the tensile strain, the amount of work performed by the applied pressure is negative, i.e., the internal energy around the vacancy is reduced by the applied pressure. The energy required to create the impurity-vacancy pair, or the activation energy, is also reduced under pressure. This effect is found to be the most important. Second, the weak atomic-size dependence of ΔQ (the pressure dependence of Q) is ascribed to the weak impurity-vacancy interaction that originates from the peculiar extension of the wave function and the lattice relaxation. Indeed, the amounts of the breathing distortions around the vacancy for P-V, As-V, and Sb-V pairs are close to each other and are similar to that for the isolated vacancy, reflecting the weak interaction. The similar breathing distortions produce the strain field which gives rise to similar ΔQ. Another factor which is important for the weak atomic-size dependence is the trend that the amount of the breathing distortion is larger for impurities with larger atomic size, which compensates the strain due to the impurities.

For the interstitial mechanism, on the other hand, opposite pressure dependence has been found: The formation energy of the interstitial impurity shows a general tendency to increase with pressure. More precisely, the amount of the increase is different; it is larger for P and As ($\simeq 0.7$ eV) and smaller for Sb(0.1 eV) at 60 kbar. The atomic structures of the interstitial impurities cause compressive strain to the surrounding Si-Si bonds, which is a possible origin of the positive pressure dependence. Applying pressure and increasing the atomic size of the impurity atom cause common changes of the atomic structure in which one Si atom is pushed toward the interstitial region. The amount of the strain in the surrounding Si-Si bonds tends to be reduced by the structural change, which is the reason for the smaller pressure dependence for impurities with larger atomic radii.

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metric atomic configuration). We have carefully checked, using a vacancy system, that the one-special-point calculation is enough to obtain converged formation energies and that the error that is caused by using the Γ-point-optimized geometry is about 0.1 eV or less.

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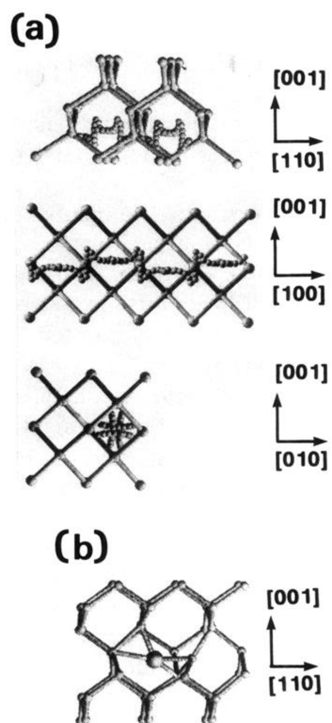

FIG. 2. (a) One of the favorable migration paths of the interstitial As impurity seen from three different directions. The relaxation of the surrounding Si atoms is fully taken into account in the calculation, but not shown in this figure. (b) The most stable interstitial structure for As. The charge state of the interstitial As is neutral.

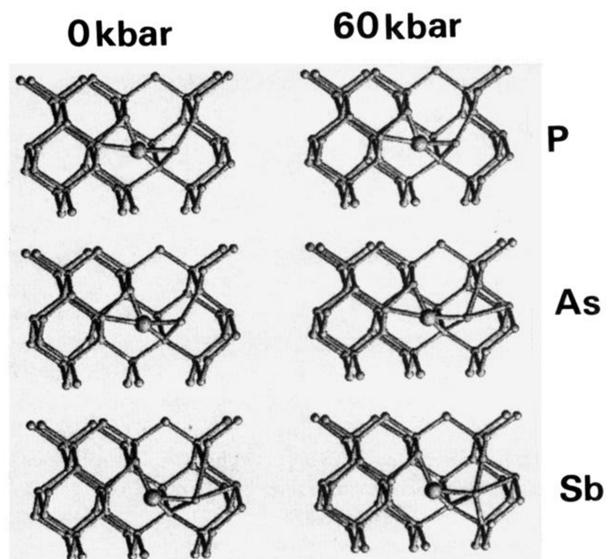

FIG. 4. The most stable interstitial structure of impurity atoms (P, As, and Sb) at $P=0$ and 60 kbar. The charge state of the interstitial impurity atom is neutral.

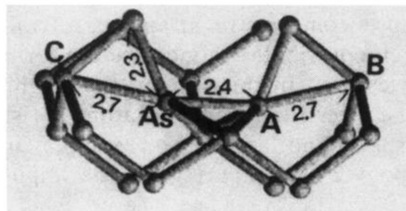

FIG. 5. The most stable interstitial structure for As at $P=60$ kbar. The bond lengths in unit of Å are shown in the figure.