## Migration of interstitials in silicon

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We calculate total configurational energies for interstitial aluminum and silicon in silicon. The calculations, based on the self-consistent Green's-function technique, are done for a selective migration path along the "empty" channel in crystalline silicon. Short- and long-range structural distortions are found to be sizable and strongly varying along the migration path. Carrier capture is possible along the migration path, resulting in a drastic dependence of the migration barrier on the nominal charge-state of the defect. For aluminum migration in *p*-type silicon we find a barrier of  $V_B = (1.3 \pm 0.5)$  eV, which in *n*-type material can be lowered by  $\Delta V_B = (0.8 \pm 0.4)$  eV due to carrier capture. Both numbers agree well with experiment. Assuming a similar migration path for interstitial silicon the calculated values are  $V_B \approx (0.4 \pm 0.5)$  and  $(2.0 \pm 0.4)$  eV. In addition, the heat of tetrahedral formation of interstitial Si is evaluated to be  $\Delta H_I \approx 4.7$  eV.

## I. INTRODUCTION

The migration of interstitial atoms in semiconductors is a long-standing problem and is fundamental to most defect reactions.<sup>1-4</sup> In contrast to metallic systems, semiconductors exhibit the phenomenon of enhanced migration, which, in some way, represents a coupling to the migration process of the energy stored in electron-hole pairs. Enhanced migration has been recognized as an important feature of defect reactions and device degradation. In this paper we theoretically investigate the question of migration and enhancement processes for a particular system, i.e., interstitial aluminum in silicon. This system has been studied experimentally in much detail<sup>5</sup> and is therefore ideally suited for quantitative theoretical interpretations.

Recently, we proposed a novel mechanism for the enhancement process in this system.<sup>6</sup> We were able to calculate the *change* in the barrier against migration upon carrier capture without having to calculate the barriers themselves. In the present paper we calculate barriers by evaluating total-energy differences, and thus obtain a complete picture of the migration process of interstitial aluminum in silicon. We also extend our calculations and replace aluminum by silicon, thereby simulating a particular channel for self-diffusion. Unfortunately, and in contrast to aluminum, no confirmed, direct observations of self-interstitial migration exist.<sup>7</sup> Therefore, our siliconin-silicon results can only be gauged as being consistent with indirect observations (or the lack thereof).

The barriers are calculated by evaluating total configurational energies within the self-consistent Green'sfunction technique.<sup>8</sup> First, illustrative results using this technique have recently been proposed by us.<sup>9</sup> More detailed discussions of theoretical techniques and underlying fundamental issues will be published separately.<sup>10</sup> In Sec. II of this paper we briefly present the expressions used to evaluate the total energy, discuss chosen parameters, and give other details of the calculations. In Sec. III a variety of results for Al and Si in different interstitial positions will be given and available experimental observations will be interpreted. The paper is concluded in Sec. IV.

# **II. CALCULATIONS**

The defect energy we wish to calculate is the difference  $\Delta E$  between the total energies of the perfect and defect crystals. For the present study we are interested in the diffusion barrier, which we take to be the difference between two defect energies, one with the defect in its minimum-energy configuration, the other with the defect in the saddle-point state it passes through along the proposed diffusion path. Thus, we shall calculate the energy difference between two distinct defect configurations, each of which is characterized by a defect energy  $\Delta E$ .

We work within the local-density-functional formalism,<sup>11</sup> which allows us to express  $\Delta E$  as a functional of the self-consistent electronic charge densities  $\rho_{\rm el} = \rho_{\rm el}^0 + \Delta \rho_{\rm el}$  evaluated in the potential of a adiabatically moved ion cores

$$\rho_{\mathrm{ion}}(r) = \rho_{\mathrm{ion}}^{0}(r) + \Delta \dot{\rho}_{\mathrm{ion}} = \sum_{\{R_{\mathrm{ion}}\}} \rho_{\mathrm{ion}}(r - R_{\mathrm{ion}}) \; .$$

As derived in Refs. 9 and 10,  $\Delta E$  may be written as

$$\Delta E = \sum_{i=1}^{9} \Delta E_i - \mu n , \qquad (1)$$

where n is the nominal electronic charge of the defect and  $\mu$  is the energy of the donor or acceptors which supplied the n electrons needed to charge the defect. We write

$$\Delta E_1 = \sum_i n_i \epsilon_i - \sum_i n_i^0 \epsilon_i^0 ,$$

the change in one-electron energies, and

$$\Delta E_{2} = \frac{1}{2} \int \int dr \, dr' \frac{\left[\Delta \rho_{\rm ion}(r) \Delta \rho_{\rm ion}(r') - \Delta \rho_{\rm el}(r) \Delta \rho_{\rm el}(r')\right]}{|r - r'|}$$
  
$$\Delta E_{3} = \int \int dr \, dr' \frac{\left[\rho_{\rm ion}^{0}(r) + \rho_{\rm el}^{0}(r)\right] \Delta \rho_{\rm ion}(r')}{|r - r'|} ,$$

30 3460

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and

$$\Delta E_4 = -\int \int dr \, dr' \frac{[\Delta \rho_{\rm ion}(r) + \Delta \rho_{\rm el}(r)]\rho_{\rm el}^0(r')}{|r - r'|}$$

are electrostatic energies. The r' integration in  $\Delta E_4$  would, for a charged defect, diverge if carried over the infinite crystal. However, the actual integration is to be carried only over the volume  $\Omega_1$  in which the defect potential is allowed to be nonzero. The necessity and correctness of cutting off the potential have been already established.<sup>9,10</sup> The r integration of  $\Delta E_3$  gives rise to  $\Phi^0(r)$ , the electrostatic potential of the unperturbed crystal. Its average value is using arbitrary, but, having chosen it, the eigenvalues  $\epsilon_i$  and the energy  $\mu$  must be calculated using the same chosen value. We have

$$\Delta E_{3} = \int dr \{ \epsilon_{\rm xc}[\rho_{\rm el}(r)] - V_{\rm xc}[\rho_{\rm el}(r)] \} \rho_{\rm el}(r)$$
$$- \int dr \{ \epsilon_{\rm xc}[\rho_{\rm el}^{0}(r)] - V_{\rm xc}[\rho_{\rm el}^{0}(r)] \} \rho_{\rm el}^{0}(r)$$

the change in exchange-correlation energy, corrected for overcounting, and

$$\Delta E_6 = \int dr [\Delta V^{\text{out}}(r) - \Delta V^{\text{in}}(r)] \rho_{\text{el}}(r)$$

arises from replacing the kinetic energy by  $E_1$  and using Schrödinger's equation.  $\Delta V^{\text{in}}$  and  $\Delta V^{\text{out}}$  are the input and output total defect potentials of the last self-consistency iteration.  $\Delta E_6$  approaches zero as self-consistency is approached. We then write

$$\Delta E_7 = \sum_{\substack{\text{removed}\\\text{ions}}} E_{\text{self}}^{\text{ion}} - \sum_{\substack{\text{added}\\\text{ions}}} E_{\text{self}}^{\text{ion}} + \Delta E_{\text{overlap}}^{\text{ion}} ,$$

which removes spurious ion-core self-interaction and overlap terms which were introduced by using ion-core pseudopotentials in evaluating the ionic densities. Finally,

$$\Delta E_8 = -\Phi \int dr \rho_{\rm el}(r)$$

corrects for introducing a constant model potential  $\Phi$  in evaluating the self-consistent charge density  $\Delta \rho_{\rm el}(r)$  (see below). All integrals are evaluated over the finite volume  $\Omega_{\rm I}$  over which the defect potential  $\Delta V$  is allowed to be nonzero.

The changes in the electronic charge density  $\Delta \rho_{\rm el}(r)$  and in one-electron energies  $\Delta E_1$  are evaluated using selfconsistent Green's-function technique. As discussed in Refs. 9 and 10 this procedure requires the long-range Coulomb tails in the potential of charged defects to be cut off. The cutoff introduces two additional features. (i) A model potential

$$\Phi = \begin{cases} \text{const inside } \Omega_{\mathrm{I}} \\ 0 \text{ outside } \Omega_{\mathrm{I}} \end{cases}$$

must be added to the total defect potential  $\Delta V$  in order to obtain the correct amount of screening charge inside  $\Omega_{I}$ .  $\Phi$  simulates the effect of the long-range Coulomb tail for charged defects. Its value is determined by the macroscopic dielectric constant  $\epsilon_0$  of the semiconductor. The energy term  $\Delta E_8$  compensates for the effect of the model potential  $\Phi$  on the energy term  $\Delta E_1$ . (ii) In addition, any bound-state eigenvalue  $\epsilon_i$  in  $\Delta E_1$  has to be corrected for long-range Coulomb tails as discussed before.<sup>12</sup>

A well-known shortcoming of the use of the localdensity approximation (LDA) is that it predicts band gaps considerably too small (e.g., 0.5 eV for Si).<sup>13</sup> This effect has recently been traced to the existence of a discontinuity in the exchange correlation potential for p- or n-type semiconductors.<sup>14</sup> As discussed earlier<sup>15</sup> we introduce into the perfect-crystal Hamiltonian  $H_0$  an energydependent nonlocal operator ("scissor operator")

$$M_E(r,r') = \Delta \sum_n \int d^3k \, \psi_n(k,r) \psi_n^*(k,r') \,, \qquad (2)$$

where *n* runs over conduction bands only, and where  $\Delta$  is an adjustable constant. This operator widens the band gap to the experimental value and represents a zerothorder approximation to the self-energy operator. Since  $M_E$  operates on the *perfect*-crystal wave functions it represents an implicit contribution beyond the LDA to defect ground-state energies when they are calculated within the Green's-function formalism. This contribution can be evaluated to first order as

$$\Delta E_{\text{scissor}} \approx \Delta \left[ \Delta N_{\text{el}} - \int \int \rho^0(r, r') \Delta \rho(r', r) dr dr' \right], \quad (3)$$

where  $\rho^0$  and  $\rho = \rho^0 + \Delta \rho$  are the single-particle density matrices for the perfect and defect crystals, respectively, and where  $\Delta N_{\rm el} = \int dr \,\Delta \rho_{\rm el}(r)$  is the number of electrons added to or subtracted from the system.  $\Delta E_{\rm scissor}$  obviously is the gap-correction energy  $\Delta$  times that amount of extra charge which derives from conduction states.

To account for long-range distortions beyond  $\Omega_I$ , the range of our Green's-function calculation, we evaluate an additional elastic energy,

$$\Delta E_9 = E_{\text{Keating}}(\{R_A\}_1) - E_{\text{Keating}}(\{R_A\}_2),$$

where  $E_{\text{Keating}}(\{R_A\})$  is the elastic energy evaluated, according to Keating, <sup>12,16</sup> of a set of atoms inside a volume  $\Omega_{\text{II}} \gg \Omega_{\text{I}}$ . The displacements in atom set  $\{R_A\}_2$  are identical to the ones determined by our Green's-function total-energy calculations, i.e., the displacements are limited to  $\Omega_{\text{I}}$ , while all atoms in  $\Omega_{\text{II}}$  are held fixed at their perfect-crystal positions. In set  $\{R_A\}_1$ , the nearby atoms are displaced as in set  $\{R_A\}_2$ , but, in addition, all other atoms within  $\Omega_{\text{II}}$  are allowed to relax freely so as to minimize the Keating elastic energy, which is determined by a bond-stretching constant  $\alpha$  and a bond-stretching constant  $\beta$ .  $\Delta E_9$  adds an effective "negative" spring which softens the elastic energies obtained in the short-range Green's-function treatment.

The actual calculations start with a self-consistent band structure for the perfect silicon crystal. Hamann-Schulter-Chiang-type ionic pseudopotentials are used,<sup>17</sup> with the Ceperley-Alder local potential for exchange and correlation.<sup>18</sup> As in earlier studies,<sup>6,12</sup> a Gaussian orbital set with decay constants of  $\alpha = 0.2$  and 0.6 a.u. and ten orbitals per decay constant ( $s,p,d,r^2$ ), is employed. The use of this basis with ionic pseudopotentials yields a good description of the ground state of Si.<sup>19</sup> The minimum optical gap, however, is found to be too small by  $\Delta \approx 0.3$  eV.

For the study of diffusion along the "charge-free" channels in silicon we consider two lattice centers: (i) the



FIG. 1. Atomic clusters used in expanding the Green's function for the interstitial  $T_d$  site (top) and  $D_{3d}$  site (bottom).

tetrahedral interstitial site ( $T_d$  symmetry), and (ii) the hexagonal interstitial site ( $D_{3d}$  symmetry). Around each site, finite-size clusters of atoms are selected for the evaluation of the Green's function. For  $T_d$ , 27 sites distributed over five shells of atoms are included. As shown in Fig. 1 (top) this includes all (4 + 6) atoms of the "cage" around the interstitial and all atoms bonded directly to the "cage" atoms. On each site the Green's function is expanded in the same orbital set as for the perfect crystal, which yields a space of 540 orbitals for the  $T_d$  Green's function. The use of symmetry reduces the largest matrix to rank 84.

The cluster used for the hexagonal site, shown in Fig. 1 (bottom), contains 19 sites distributed over four shells, including all atoms in the hexagonal ring around the interstitial center and every atom directly bonded to them. The orbital space contains 380 orbitals and yields matrices of rank up to 64 using  $D_{3d}$  symmetry. Note that the clusters used in the present work are somewhat larger than those used in our previous study of this problem.<sup>6</sup>

For both geometries  $(T_d \text{ and } D_{3d})$  only symmetrypreserving distortions were considered. For  $T_d$  symmetry, radial breathing modes of the four nearest and six next-nearest neighbors were allowed, while for  $D_{3d}$  symmetry, radial distortions of the nearest-neighbor hexagon was allowed as well as an axial change of the pucker of the hexagon. As discussed, all short-range relaxations are complemented by long-range relaxations derived from a Keating model.

The interstitial geometry studied here contains an atom

which is far from where atoms sit in the perfect crystal. Extra orbitals are needed in the Green's function to give it sufficient flexibility to represent this extra atom. In our earlier study<sup>6</sup> we included extra orbitals by use of the cluster-extended Green's-function technique.<sup>20</sup> This simple and approximate method is sufficiently accurate to produce the eigenvalues and self-consistent potentials needed for a calculation of the barrier lowering by minority-carrier capture, the topic which was studied in the earlier work. However, here we are calculating the barrier height itself, and we need to evaluate the total energies for this. The approximation underlying the cluster-extended Green's function is not sufficiently accurate for this purpose, and so we now add the extra orbitals needed by using the ad-space method proposed by Williams et  $al.^{21}$  We have been able to recast this method in a form which makes it quite similar to the cluster-extended Green's-function technique, differing from it only by including a fixed (i.e., a given, not a self-consistent) term in the perturbation potential, as is explained in a separate paper which compares the two methods in full detail.<sup>22</sup> New computational features are the use of complex contour integration to obtain  $\Delta \rho_{\rm el}(r)$  and the use of an efficient Jacobian iteration scheme to reach self-consistency. About 30 different geometries and charge states were studied, each of which needed about 20 self-consistency iterations to obtain a well-converged total-energy value. A review of some other aspects of the method used here has recently been given elsewhere,<sup>23</sup> but these other aspects have been described in our earlier papers.8,12

### **III. RESULTS AND DISCUSSION**

It is instructive to first qualitatively study the electronic charge density and its changes induced by the insertion of interstitial atoms. Figure 2 shows the calculated charge density of the perfect Si crystal (top), as modeled by the Green's-function cluster, the density in the presence of an  $Al^{2+}$  tetrahedral interstitial (middle), and the difference density due to the defect (bottom). The contours are shown in a (100) plane intersecting the tetrahedral site. On this scale, the results for other charge states are very similar. Differences for Si interstitials will be discussed below.

The interstitial atom is fourfold coordinated and it attempts to establish tetrahedral bonds to its neighboring atoms, thereby slightly weakening their preexisting four bulklike bonds. This effect is somewhat more pronounced for the Si interstitial (see below). The difference defect density of the interstitial atom (Fig. 2, bottom) shows the tetrahedral symmetry and resembles qualitatively the negative of the vacancy defect density obtained in our earlier calculations.<sup>12</sup> Evidence for additional bond formation is obtained from comparing the breathing-mode stiffness of the four surrounding crystal atoms in the presence and absence of the interstitial atom. The interstitial atom increases local stiffness by about 40% (see Table I).

Figure 3 shows the calculated charge densities for  $Al^{2+}$ in the hexagonal interstitial site. The densities are shown in a (111) plane intersecting the interstitial. The plane does not intersect any perfect-crystal atoms, but intersects



FIG. 2. Calculated charge-density distribution for  $T_d$  interstitial Al<sup>2+</sup>. The unperturbed crystal density (top), the perturbed density (middle), and the defect difference density (bottom) are shown as contours in a (100) plane.

instead the midpoints of the six bonds in the hexagon. Insertion of an interstitial atom at the hexagonal site creates a local environment of high and remarkably constant electron density in the plane of the hexagon. This is even more pronounced for the silicon interstitial. Figure 4 shows the same densities as Fig. 3, but plotted in a (110) plane intersecting the hexagon at right angles. The formation of bridging charge across the hexagon is clearly visible. Again, results for Si are qualitatively similar. To

TABLE I. List of calculated structural parameters. The breathing distortion  $\Delta u$  is given in units of the nearest-neighbor distance.

	$\Delta u$ (%)	$K (eV/Å^2)$	$\Delta E$ (eV)
$T_d$ empty	<1	100	~0
T <sub>d</sub> Al,Si	< 1	140	< 0.1
$D_{3d}$ A1 <sup>+</sup>	≈6	61	0.5
$D_{3d}$ Si <sup>2+</sup>	≈7	69	0.8



FIG. 3. Charge-density distribution for  $D_{3d}$  interstitial Al<sup>2+</sup> shown in a (111) plane.

highlight the differences between the Al and Si interstitials, in Fig. 5 we show calculated charge densities for  $Si^{2+}$  in the tetrahedral site (top) and the hexagonal site (bottom). The results are qualitatively similar to those in Figs. 2 and 3. Quantitative differences, such as, e.g., the enhanced bond formation for silicon in the  $T_d$  site, are, however, clearly visible.

The spectral changes incurred by the insertion of an  $Al^{2+}$  interstitial atom are shown in Fig. 6 for the tetrahedral site (left) and the hexagonal site (right). Only important representations are shown. A "hyperdeep" state of  $A_1$  symmetry appears below the valence band. Its  $(T_d)$  charge density is shown in Fig. 7 (bottom). It is the lowest bound state in the locally attractive defect potential due to 4 + 1 atoms. The features playing key roles in the electronic diffusion enhancement are located near the optical gap. For  $T_d$  these are an  $A_1$  bound state near the top of the valence band (which becomes a strong resonance below the valence-band edge for  $Si^{2+}$ ) and a  $T_2$  resonance near the bottom of the conduction band (which for  $Si^{2+}$  just drops below the conduction-band edge). When the interstitial is moved into the  $D_{3d}$  site, the  $A_1$  bound state rises somewhat higher in the gap. The important



FIG. 4. Same as Fig. 3, but shown in a (110) plane.

feature is the splitting of the threefold-degenerate  $T_2$  resonance into a twofold  $\Gamma_6$  resonance which moves higher into the conduction band and into a onefold  $\Gamma_4$  bound state which drops into the gap.

These states near the gap are predominantly nonbonding in character, with some antibonding admixture. The  $A_1$  state is shown in Fig. 7 (top). Its character remains rather similar after moving to the hexagonal site (Fig. 8, bottom).

For the hexagonal case the two  $\Gamma_6$ -resonance states are quantized in the hexagonal layer, thus raising their energy making them slightly more antibonding. The split-off  $\Gamma_4$ bound state is quantized perpendicular to the hexagon and, due to the absence of nearby neighbors, the state becomes more nonbonding (see Fig. 8, top) and drops in energy.

The distribution of levels near the gap is summarized in Fig. 9. Here we have plotted the Slater-transition-state values,<sup>23</sup> interpolating between two charge states and correcting for Coulomb effects as discussed in Sec. I. The values refer to the distorted defect equilibrium configurations. The calculated deformation potentials for the levels are small ( $\approx 0.5-1.5 \text{ eV/Å}$ ), which is consistent with the predominantly nonbonding character of the states.



FIG. 5. Calculated charge density for interstitial Si<sup>2+</sup>, in the  $T_d$  site (top) and the  $D_{3d}$  site (bottom).

We now discuss the results for the total configurational energies. In *p*-type silicon the unrelaxed barrier for aluminum migration is calculated according to Eq. (1) as  $V_B(Al^{2+}/Al^{3+}) = (1.8\pm0.5)$  eV. This barrier involves a change in charge state (2 + to 3 +) as the atom migrates from  $T_d$  to  $D_{3d}$  symmetry (see Fig. 9). The theoretical  $Al^+$  barrier without change in charge state would be about 1.9 eV, which is about 50% larger than the value obtained from recent cluster-MNDO (where MNDO denotes mutual neglect of differential overlap) calculations.<sup>24</sup>

Virtually no radial relaxations (outwards < 1%) are calculated to occur for the tetrahedral site. For the hexago-



FIG. 6. Spectral changes in the valence and conduction bands of silicon for interstitial  $Al^+$  in the  $T_d$  site (left) and  $D_{3d}$  site (right). The spectra are broken down into irreducible representations.





FIG. 7. Charge-density distribution for the hyperdeep (bottom) and deep (top)  $A_1$  states of interstitial Al<sup>+</sup> in the  $T_d$  site.



FIG. 8. Charge-density distribution for the deep  $\Gamma_1$  (bottom) and  $\Gamma_4$  (top) states of interstitial Al<sup>+</sup> in the  $D_{3d}$  site.



FIG. 9. Calculated electrical level structure for interstitial Si (top) and Al (bottom) for tetrahedral  $(T_d)$  and hexagonal  $(D_{3d})$  symmetry.

nal site, a small increase in pucker ( $\approx 1\%$ ) and a sizable radial outward distortion ( $\approx 3\%$ ) are predicted by the Green's-function treatment for interstitial Al. This will lower the barrier to  $V_B(Al^{2+}/Al^{3+})=(1.5\pm0.5)$  eV. The outward relaxation will generate a long-range displacement field, which has been calculated according to Sec. II using a Keating model. We use the modified Keating parameters  $\alpha = 51$  a.u. and  $\beta = 4$  a.u., as for our Si-vacancy studies,12 to account for the anomalous flatness of the TA-phonon branch in silicon. The long-range relaxations increase the outward breathing to  $\approx 6\%$  and lower the barrier to  $V_B(Al^{2+}/Al^{3+}) = (1.3 \pm 0.5)$  eV. Similarly, they soften the breathing spring constant from  $\approx 98$  to  $\approx 61 \text{ eV/Å}^2$ . In *n*-type silicon the nominal charge states are Al<sup>+</sup>/Al<sup>-</sup>, and the relaxed barrier is calculated to be  $V_B(Al^+/Al^-) = (0.5 \pm 0.5)$  eV. To obtain this barrier we can also use the p-type value and consult Fig. 9 for the population of deep levels.

Corrections  $\Delta E_{scissor}$  [Eq. (3)] due to LDA insufficiencies are less than 0.1 eV for all barriers. The barrier lowering from *p*- to *n*-type material is calculated to be  $\Delta V_B \approx (0.8 \pm 0.4)$  eV, which is close to the value of 0.9 eV we previously reported.<sup>6</sup> Since  $\Delta V_B$  involves four different charge states, uncertainties in bound-state positions add up to rather large uncertainties in barrier-height differences. These shortcomings can partially be circumvented by reformulating  $\Delta E$  in Eq. (1) using the kinetic-energy operator rather than eigenvalues. Investigations in this direction are currently underway. The various results sults obtained from the total-energy calculations are summarized in Table II.

In Table III we list some individual terms contributing to the barrier height of unrelaxed  $Al^+$  ( $V_B = 1.9$  eV). The first column shows the change in eigenvalues, i.e.,  $\Delta E_1$ , the second column shows the sum of all electrostatic

TABLE II. List of migration barriers for interstitial Al and Si in silicon calculated with the self-consistent Green's-function technique and a long-range Keating model.  $V_B = \Delta E(D_{3d})$  $-\Delta E(T_d)$  in eV.

	$V_B$ unrelaxed	$V_B$ short- and long-range relaxed
Al		
p type	$1.8 \pm 0.5$	$1.3 \pm 0.5$
n type	$1.0 \pm 0.5$	$0.5 {\pm} 0.5$
Si		
p type	$1.2 \pm 0.5$	$0.4 \pm 0.5$
n type	$-1.1\pm0.5$	$-1.6\pm0.5$

terms plus the self-consistent correction, i.e.,  $\Delta E_2$  $+\Delta E_3 + \Delta E_4 + \Delta E_6$ , and the third column contains the change in exchange-correlation energy, i.e.,  $\Delta E_5$ . Terms arising from  $\Delta E_7$  and  $\Delta E_8$  are small ( $\leq 0.1$  eV) and not listed. We see a strong cancellation between the eigenvalue term and the electrostatic energies. The exchangecorrelation energy, though smaller, remains an important factor in determining the barrier. Recently, Penetta and Baldereschi<sup>25</sup> discussed the migration of point charges and small interstitial ions in silicon. They explicitly evaluated  $\Delta E_3$  for point charges and remarked upon its sensitivity to a correct description of the unperturbed charge density  $\rho_{el}^0$  along the channels. We find an overall small (~0.0 eV for Al<sup>3+</sup> and 0.25 eV for Si<sup>4+</sup>) contribution of  $\Delta E_3$  to  $V_B$ . The sensitivity to  $\rho_{el}^0$  is, however, as claimed, sizable. We find  $\Delta E_3$  increasing by ~0.4 eV when going from a 500-plane-wave representation of  $\rho_{el}^{0}(r)$ to a 1500-plane-wave representation. A rather larger overall uncertainty to  $\pm 0.5$  eV in the total calculated barrier heights should conservatively be assumed due to the use of finite and different clusters for  $T_d$  and  $D_{3d}$  symmetries.

We now consider the experimental situation. For tetrahedral Al, the (+ + / +) level, calculated at  $\approx (E_v + 0.2)$  eV, is in good agreement with deep-level transient-spectroscopy (DLTS) measurements by Troxell *et al.*<sup>5</sup> They identified the so-called H3 level, observed at  $(E_v + 0.17)$  eV, with the second donor state Al<sup>+</sup>/Al<sup>2+</sup> of interstitial aluminum, and, via EPR measurements, confirmed the tetrahedral symmetry of the state. Troxel *et al.* also studied the temperature-dependent recovery rate of this defect in *p*-type material. In the absence of free electrons, the annealing process of interstitial A1 re-

TABLE III. Individual energy contributions to the unrelaxed barriers (in eV).

	$\frac{\Delta E}{\text{one}}$ electron	$\Delta E$ electrostatic	Δ <i>E</i> exchange correlation	$\Delta E$ total
Al <sup>+</sup>	6.0	-4.3	0.1	1.8
Si <sup>2+</sup>	24.9	-24.0	0.3	1.2



FIG. 10. Experimental temperature dependence of the recovery rate of the interstitial Al defect in *p*-type silicon. Two curves are shown: with no free carriers present  $(\bigtriangledown)$ , and with tree carriers present, either injected is a junction ( $\Box$  and  $\circ$ , respectively), or by laser light ( $\triangle$ ). (From Ref. 5.)

veals a diffusion potential barrier of  $V_B \approx 1.3$  eV (see Fig. 10). Our calculated value of  $V_B = (1.3 \pm 0.5)$  eV is in excellent agreement with this measurement. In the presence of free electrons, either laser-generated or junctioninjected, this diffusion barrier was lowered to  $V_B \approx 0.27$ eV (see Fig. 10). Interstitial Al in p-type Si thus shows enhanced migration with an effective barrier lowering of  $\Delta V_B \approx 0.93$  eV upon minority-carrier (electron) injection (see Fig. 10). We calculate a lowering of  $\Delta V_B = (0.8 \pm 0.4)$ eV, again in excellent agreement with experiment. Interestingly, the H3 hole trap at  $(E_v + 0.17)$  eV was found to saturate at low injection current ( $\sim 10^{-13} \text{ A cm}^{-2}$ ), while the enhanced diffusion saturated only for injection currents of  $\sim 1 \text{ A cm}^{-2}$ . It was therefore concluded<sup>5</sup> that the observed  $A1^+/A1^{2+}$  second donor state was not involved in the enhancement of the migration, and that an unobserved state must be responsible.

In our earlier study<sup>6</sup> of the problem we proposed a new model for the enhanced migration of interstitial aluminum which is confirmed and reinforced by our present calculations and which is consistent with all reported experimental findings. The migration path for Al originates at a stable tetrahedral site and lies along the nearlycharge-free channels, while the hexagonal site is a saddle



FIG. 11. Configuration-coordinate diagram for the totalenergy variation of Al diffusing along the channel in silicon. The lower curve corresponds to the diffusion of Al<sup>+</sup> without free carriers present. The upper curve, shifted by  $E_G$ , and by  $2E_G$ , respectively, correspond to Al<sup>+</sup> plus free electrons and holes. The shallow state for the tetrahedral site (*T*), Al<sup>0</sup> becomes a deep state for the hexagonal site (*H*). Upon thermal vibration, a second electron can be captured into the deep state, resulting in Al<sup>-</sup>. The set of curves corresponds to the calculated barrier values.

point on this path. There is a sizable energy barrier (measured as 1.2 eV and calculated as 1.3 eV in *p*-type Si) associated with unassisted migration (see lowest curve in Fig. 11). This barrier results mainly from the drastic changes in bonding configuration as illustrated by the changes in the local charge density, but it is reduced by about 25% by site-dependent short- and long-range elastic distortions.

Under electron injection, all the tetrahedral Al<sup>2+</sup> converts to Al<sup>+</sup> at low currents,<sup>5</sup> which according to our calculations, leaves the barrier unchanged. The positively charged Al<sup>+</sup> can bind another electron in a shallow effective-mass-like state Al<sup>0</sup>. Because of the Coulomb attraction similar to that binding Al<sup>+</sup>, this process should also saturate at comparably low currents. The strong  $T_2$ resonance near the conduction-band minimum drops into the gap as the Al vibrates thermally from the tetrahedral position towards the hexagonal one. This allows the effective-mass-like electron to be localized in the vicinity of the Al interstitial, lowering the barrier by about 0.6 eV. A second electron can be trapped, leading temporarily to Al<sup>-</sup> and a further barrier lowering of 0.2 eV. Our calculations show that the shallow-deep transition of these two electrons acts as a driving mechanism to help move the Al atom along the tetrahedral-hexagonal path (see Fig. 11). The participation of two electrons in the enhancement

process contradicts the commonly held belief that the maximum energy available for enhancement is equal to the gap  $E_G$ . The cross section for this process should, at anything but the lowest injection currents, resemble that of an ordinary one-electron process because one of the donor electrons is, at injection currents greater than those destroying the  $Al^{2+}$  EPR signal, already bound by Coulomb forces. Because the resonance is so close to the bottom of the band when the  $Al^0$  is at the equilibrium position, the activation energy to capture the next electron should be small. It would, however, be interesting to test the two-electron model and search for some superlinear enhancement cross section for very low injection currents. Furthermore, the study of counterdoped *n*-type material should give additional insight.

Apart from the remarkably large barrier lowering, which according to our model is due to the participation of two electrons, a drastic drop in the preexponential factor for the recovery rate of the defect has also been observed (see Fig. 10). In fact, the factor drops from  $3 \times 10^9$  to 70 sec<sup>-1</sup>. The value of  $3 \times 10^9$  sec<sup>-1</sup> is typical for a thermal process, i.e., the lattice-vibrational frequency ( $\sim 10^{13}$  sec<sup>-1</sup>) divided by the number of migrational jumps required before the defect becomes trapped ( $\sim 10^4$ ). The value 70 sec<sup>-1</sup> indicates that many more jumps are required before the defect is trapped. Presumably, the negatively charged one.

It is instructive to use the model for the Al diffusion to speculate on the silicon self-interstitial problem. If we repeat our Green's-function calculations for Si, a level structure as shown in Fig. 9 is obtained. The calculations show no deep  $A_1$  level in the gap and a 2 + charge state for Si in the tetrahedral interstitial site. The  $T_2$  state (a resonance for Al<sup>+</sup>) becomes slightly bound and drops below the conduction-band edge. Tetrahedral interstitial silicon would therefore most likely elude DLTS and/or EPR detection. A qualitatively similar finding has also been reported by Pantelides et al.<sup>26</sup> The calculated barriers for Si moving along the silicon channels are listed in Table II. p-type silicon the unrelaxed silicon barrier For  $V_B(\mathrm{Si}^{2+}/\mathrm{Si}^{2+}) \approx (1.2\pm0.5)$  eV is somewhat smaller than that found for aluminum. Here, this value is in close agreement with recent MNDO results (1.2 eV),<sup>24</sup> but it is about 0.6 eV lower than recent pseudopotential supercell calculations.<sup>27</sup> Short- and long-range relaxation contributions are somewhat larger than those obtained for aluminum, which lowers the barrier in p-type material to  $V_B(\text{Si}^{2+}/\text{Si}^{2+}) \approx (0.4 \pm 0.5)$  eV. For *n*-type material the barrier is drastically changed, in accord with the level structure in Fig. 9. The barrier lowering is about  $\Delta V_B = (2.3 \pm 0.4)$  eV, shifting the minimum from the tetrahedral to the hexagonal site. Provided the migration path is along the channels, this could produce athermal recombination-enhanced diffusion (Corbett-Bourgointype) which would make Si interstitials very mobile even at low temperatures, provided carriers are present. These are speculations, however, since no direct experimental data are available to indicate that the channel is the correct migration path. In fact, other theoretical studies seem to favor an entirely different migration path for interstitial Si, namely weaving through Si bonds<sup>28,29</sup> rather than along the nearly-charge-free channels—a conjecture recently opposed by some pseudopotential supercell studies.<sup>27</sup> In addition, more extended, fully bonded selfinterstitial complexes have been proposed. It has been pointed out<sup>26</sup> that both mechanisms may be correct at low and high temperatures, respectively.

Our Si interstitial calculations also allow us to estimate the formation energy  $\Delta H_f$  of self-interstitials in the tetrahedral site. We define  $\Delta H_{I}$  as the difference between  $\Delta E$ , evaluated for the interstitial atom according to Eq. (1), and the total energy of a perfectly bonded crystal atom (i.e., half of the unit-cell energy). For intrinsic silicon we find  $\Delta H_{\rm I} = (4.7 \pm 0.5)$  eV for tetrahedral Si<sup>2+</sup>, assuming that the two charge-compensating electrons are placed midgap. This includes a  $\Delta E_{scissor} \approx 0.9$  eV due to the gap correction. The value  $\Delta H_I$  is almost identical to the vacancy-formation energy  $\Delta H_v$ .<sup>30</sup> The two values are related to the threshold energy  $E_{\rm FP}$  for Frenkel-pair pro-~21 eV. We may write  $E_{\rm FP} = \Delta H_v + \Delta H_{\rm I} + E_L$ , where  $E_L$  denotes the lattice distortion and bond-breaking energy at the saddle point of the Frenkel-pair-formation process. Comparing our calculations to the experimental threshold,  $E_L \ge 4$  eV, a reasonable value. We add that the calculated value  $\Delta H_{\rm I}$  = 4.7 eV is about 50% smaller than an empirical estimate by Van Vechten.<sup>32</sup> As mentioned above, no direct low-temperature data on  $\Delta H_{\rm I}$  (for tetrahedral Si) are available. High-temperature-diffusion data<sup>33</sup> suggest a value of  $\Delta \hat{H}_{I} \approx 2.8$  eV which is presumably associated with a different (equilibrium) interstitial configuration.

#### **IV. CONCLUSIONS**

In this paper we present calculations of total configurational energies evaluated within the Green's-function for-

malism. The calculations focus on the diffusion of Al in silicon for which detailed experimental information is available. From these calculations emerges a consistent picture which is qualitatively able to describe the experimental situation. The main results are (i) the existence of large short- and long-range lattice distortions significantly lowering (up to 25%) the rigid barriers obtained from electronic energy differences, and (ii) the existence of a barrier-lowering mechanism associated with the charging of defects. This latter effect is unique to semiconductors and insulators. However, we believe that the particular shallow-deep alternation mechanism proposed here for the enhanced migration of interstitial Al is a quite common phenomenon in defect migration. The mechanism has some similarities with the "electron excitation" mechanism invoked for the photostimulated F-center production in KCL,<sup>3</sup> but it differs from the "common" models for enhanced migration in semiconductors, i.e., the chargestate mechanism, the saddle-point mechanism, or the energy-release mechanism.5,34

Note added in proof. In a recent letter [R. Car, P. J. Kelley, A. Oskigama, and S. T. Pantelides, Phys. Rev. Lett. 52, 1814 (1984)] the diffusion of Si in silicon was considered. Their results are similar to those reported here.

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