

## Fully relaxed point defects in crystalline silicon

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We have studied intrinsic point defects in crystalline silicon via a tight-binding molecular-dynamics scheme. The intrinsic defects studied in this work are the vacancy, the interstitial, the divacancy, the split divacancy, and the vacancy-interstitial complex. Fully relaxed geometries, gap states, and formation energies are investigated. It is shown that the relaxation effects cannot be neglected, in particular, in the peak position of band-gap states.

### I. INTRODUCTION

Intrinsic defects in silicon have been extensively investigated both experimentally and theoretically, since the understanding of the role of defects in silicon is essential to control the quality of semiconductor devices. Intrinsic point defects such as the vacancy ( $V$ ), the interstitial ( $I$ ), the divacancy ( $V_2$ ), the split divacancy ( $V_2^m$ ), and the vacancy-interstitial ( $V-I$ ) complex are introduced intentionally or unintentionally during the device fabrication.

The vacancy has been studied by electron-spin-resonance (ESR) measurements<sup>1,2</sup> and by *ab initio* calculations within the local-density approximation.<sup>3-5</sup> Since Corbett and Watkins<sup>6</sup> proved that divacancies could be produced by high-energy electron or neutron irradiation, independent of vacancy migration or congregation, a good model of divacancy with different charge states was suggested.<sup>7</sup> The energy levels in the forbidden gap introduced by divacancies have been studied by ESR experiments<sup>6,8</sup> and theories.<sup>9-13</sup> However, the formation energy has not been calculated yet, mainly because its electronic structures are severely distorted in the fully relaxed geometry.

Most intrinsic defects are studied theoretically by the first-principles calculations within the local density approximation. This method has been very fruitful for calculation of electronic structures, though the fully relaxed geometry is not fully incorporated in most of calculations. The advent of the *ab initio* molecular-dynamics (MD) method<sup>14</sup> removed this limitation. However, the *ab initio* MD method is computationally expensive for the dynamical calculation at the present stage and the application to large systems is still limited. Therefore it is necessary to introduce a scheme that retains the minimum accuracy of the *ab initio* method and at the same time retains the computational efficiency.

In this study we adopt the MD method combined with the universal tight-binding (TB) method introduced by Goodwin, Skinner, and Pettifor.<sup>15</sup> Since the electronic overlap integrals are parametrized, this method is very efficient. The parameters are fitted to the universal binding-energy curve of the first-principles calculations,

and this method is therefore very accurate and can be applied to large systems of defects. We will generate the fully relaxed defect geometries by the TB MD method and study the relaxation effects in the electronic energy levels in the forbidden gap and the formation energies of various point defects. These results are further compared to other theoretical and experimental works when possible.

### II. METHOD

We adopt the TB scheme developed by Goodwin, Skinner, and Pettifor<sup>15</sup> in our defect studies. This method simply uses Chadi's empirical tight-binding scheme.<sup>17</sup> However, since Chadi's scaling law of the positional dependence,  $1/r^2$ , is not transferable to different structures, a different scaling law with an exponential factor is introduced such that the new TB scheme can generate the universal total-binding-energy curve. Combining this new TB scheme with the MD simulation method, one may study complex systems such as liquid<sup>18</sup> and amorphous<sup>19</sup> silicon. The details of this method have been described by Goodwin, Skinner, and Pettifor.<sup>15</sup>

In order to find the equilibrium structures of different defects, we have run 2000 time steps (one time step =  $1.08 \times 10^{-15}$  s) at 300 K to equilibrate the structures. Then the system is slowly quenched to zero temperature by scaling velocities with the rate of 0.98 per every time step. Several runs are made in order to make sure the true ground-state configurations are obtained. We use the cubic supercell containing 64 silicon atoms, where the periodic boundary conditions are applied to all  $x, y, z$  directions to emulate the bulk silicon. For a single vacancy or interstitial complex, one atom is simply removed or added in the supercell. The cutoff distance 3.2 Å was chosen such that the first nearest neighbors are considered in the MD simulation.

### III. RESULTS AND DISCUSSION

Typical point defects that may be formed during the fabrication of devices are the vacancy, the interstitial, the divacancy, and possibly the  $V-I$  complex. In this study

we will discuss the fully relaxed geometries near defects, the formation energies, the electronic density of states, and the defect levels in the forbidden gap. These will be compared to other results.

### A. Fully relaxed geometry

A vacancy is formed simply by removing one atom from the 64-atom supercell. The fully relaxed geometry is obtained by slowly quenching the equilibrated structure at finite temperature ( $T=300$  K). The resultant geometry is illustrated in Fig. 1(a). Atoms 1 and 2 move away from the vacancy whereas atoms 3 and 4 are distorted toward the vacancy. Net displacements of neighboring silicon atoms range from 0.3 to 0.27 Å. As a result the relative distance between atoms 1 and 2 is 4.55 Å, larger than the ideal second-nearest-neighbor distance of 3.86 Å, while the relative distance between atoms 3 and 4 is equal to 3.25 Å.

Shown in Fig. 1(b) is the optimum geometry of the fully relaxed  $V_2$ , where two neighboring silicon atoms are removed. Unlike the single  $V$ , all the neighboring silicon atoms are distorted toward the vacancies along the axis connecting the two vacancies. Net displacements of neighboring atoms range from 0.6 to 0.45 Å, which is almost twice that in the case of a single vacancy, as expected. Thus the neighboring atoms near the vacancy form weak bonds with each other, as shown in Fig. 1(b). This configuration is consistent with the results from ESR experiment.<sup>6,7</sup>

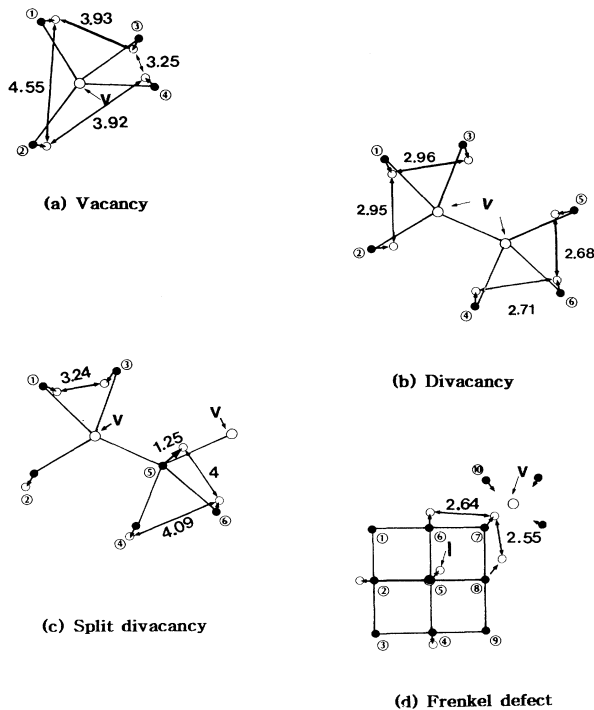


FIG. 1. The fully relaxed geometry of the (a) vacancy, (b) divacancy, (c) split divacancy, and (d) vacancy-interstitial complex. All units are in Å.

The split divacancy ( $V_1^m$ ) or Schottky defect is two vacancies at second-nearest-neighbor positions [see Fig. 1(c)]. This is an intermediate configuration between two separate vacancies and the paired vacancies  $V_2$ . The silicon atom 5 between two vacancies moves toward one of the vacancies by 1.25 Å, making new bonds to the neighbors of another vacancy. Atom 4 moves away from atom 5 by 0.5 Å, sustaining the distance of 4.09 Å between atoms 4 and 6. The net displacement of each atom in  $V_2^m$  varies from 0.35 to 1.25 Å.

A tetrahedral ( $T$ ) interstitial defect is formed by adding one extra silicon atom to a  $T$  site. It has four nearest neighbors at 2.36 Å and six second-nearest neighbors at 2.73 Å that form weak bonds with the  $T$  interstitial atom. Four nearest-neighbor atoms move outward the  $T$  interstitial atom by about 0.20 Å, whereas the second-nearest-neighbor atoms do not move appreciably. Shown in Fig. 1(d) is a  $V$ - $I$  complex or Frenkel defect. A vacancy is introduced near the interstitial defect. Atom 7, which is the first nearest neighbor of both the vacancy and the interstitial atom, moves toward the vacancy by 0.43 Å, which is the largest among displacements by neighboring atoms. In this case all neighboring atoms between the interstitial atom and the vacancy [atoms 5, 6, 7, and 8 in Fig. 1(d)] move toward the vacancy even though the net displacement is different from atom to atom.

### B. Formation energy

The formation energy of a defect is the variance of total energy of the system when a defect is introduced. Though the formation energy has not been studied well, it is an important parameter because it is related to the defect diffusion. In general the activation energy can be written

$$E_a = E_f + E_m, \quad (1)$$

where  $E_a$ ,  $E_f$ , and  $E_m$  are the activation energy, formation energy, and migration energy, respectively. With the activation energy  $E_a$  of each type of defect, one can write the diffusion constant as

$$D = D_0 \exp(-E_a/kT). \quad (2)$$

However, it is still difficult to determine  $E_f$  and  $E_m$ . Since our TB MD can provide the optimized geometries for various defects, we are able to calculate a reasonable formation energy and migration barrier.

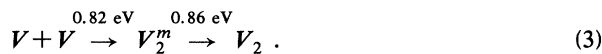
Shown in Table I are the formation energies of unrelaxed and relaxed configurations. The calculated formation energies of  $V$  and  $T$ -interstitial are within the observed values.<sup>16</sup> The relaxation energies of  $V$  and  $I$  are 1.42 and 2 eV, respectively, which are about 30% of the total formation energy. Thus the relaxation effect cannot be neglected even in the case of single point defects. The migration barrier for the vacancy is 1.0 eV, which is calculated by changing a position of a neighbor atom to the vacancy site for unrelaxed geometry. This value should be lower for fully relaxed geometry and hence gives better agreement with the observed values 0.3 eV.<sup>20</sup> With this rough estimation the activation energy should be

TABLE I. Formation energy and relaxation energy of various defects. The values in parentheses in the third column are the observed values in Ref. 20. The values in parentheses in the fourth column are the percentages of the total formation energies. All units are in eV.

Defect	Formation energy		Relaxation energy
	Unrelaxed	Relaxed	
Vacancy	5.10	3.68 (3.6–5.0)	1.42 (27%)
<i>T</i> -interstitial	6.30	4.3 (4.3–6.2)	2.0 (32%)
Divacancy	7.41	5.68	1.73 (23%)
Split divacancy	8.97	6.54	2.43 (27%)
Frenkel	10.44	6.55	3.89 (37%)

$E_a \leq 4.7$  eV, which is within the range of observed values. It is suggested<sup>21</sup> that the activation energy ranging from 4.1 to 5.1 eV was well-fitted to the high-temperature diffusion regime. The vacancy is therefore suitable for the high-temperature diffusion regime. Unlike the diffusion of the vacancy, the diffusion of the interstitial atom occurs along different interstitial sites. It has been suggested that the interstitial atom takes paths along different sites. In our neutral case, the *T* site is the minimum site and has migration barrier height 0.63 eV along hexagonal sites. The migration along different sites can occur athermally by exchanging charges as suggested in previous work.<sup>21</sup>

The formation energy of  $V_2$  is 5.68 eV with relaxation energy 1.73 eV, which is much less than that of two separated vacancies (2.84 eV), as expected. The relaxation energy of  $V_2^m$  is 2.43 eV, still less than that of two separated vacancies. All these relaxation energies are about 30% of the total formation energy, which clearly cannot be neglected. By comparing the formation energies of  $V_2$  and  $V_2^m$  with that of  $V$ , one may imagine the relationship



The binding energy of two vacancies is 1.68 eV. This suggests that  $V_2$  is very stable even at fairly high temperatures. However,  $V_2$  may be formed through the intermediate divacancy  $V_2^m$  since the binding energy is lower in the intermediate configuration, as shown in the above relationship, though the probability is low.

The formation energy of the unrelaxed Frenkel defect is 10.44 eV, fairly higher than the other defects. After relaxation, however, it becomes comparable to the values of other fully relaxed defects. The relaxation energy is about 37% of the total formation energy, which was expected from the large distortions of geometry where the atom between  $V$  and  $I$  gave maximum net displacement (1.25 Å). The probability of a Frenkel defect to be created during the defect-formation process is approximately equal to those of divacancies. For the  $V$ - $I$  complex to be a separate  $V$  and  $I$ , 1.43 eV is required,



This suggests that not only the  $V_2$  but also the  $V$ - $I$  com-

plex may be formed during the fabrication process of divacancies.

### C. Density of states near the band gap

The gap states introduced by defects play a crucial role in electrical and optical properties of silicon devices. Figure 2 illustrates the density of states near the band gap. The dotted line indicates an ideal configuration. For an ideal configuration, the band gap with an appropriate broadening factor is 1.24 eV, close to the experimental value 1.17 eV.

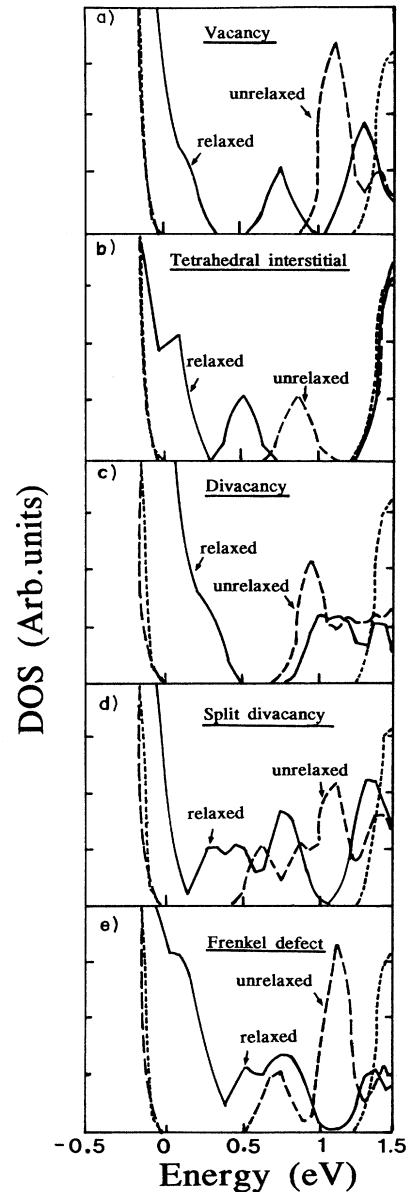


FIG. 2. The density of states near the band gap. The dotted line indicates an ideal crystal. The dashed line is for the unrelaxed configuration. The solid line is for the fully relaxed configuration. (a) Vacancy. (b) *T*-interstitial. (c) Divacancy. (d) Split divacancy. (e) Vacancy-interstitial complex.

TABLE II. Energy levels of various defects before and after relaxation. The observed values are from Ref. 22. All units are in eV.

Defect	Energy levels		Observed values
	Unrelaxed	Relaxed	
Vacancy	$E_v + 1.12$	$E_v + 0.76$	
T-interstitial	$E_v + 0.88$	$E_v + 0.52$ $E_v + 0.12$	
Divacancy	$E_v + 0.94$	$E_v + 1.00$ $E_v + 0.46$	$E_v + 0.94$ $E_v + 0.76$ $E_v + 0.42$
Split divacancy	$E_v + 1.12$	$E_v + 0.76$	
	$E_v + 0.88$	$E_v + 0.46$	
	$E_v + 0.64$	$E_v + 0.34$	
Frenkel	$E_v + 1.12$	$E_v + 0.76$	
	$E_v + 0.76$	$E_v + 0.52$	

Vacancy has a triplet ( $t_3$ ) degenerate level which gives a strong peak near the conduction-band tail ( $E_v + 1.12$  eV), where  $E_v$  is taken to be zero. However, this level splits into  $E_v + 0.76$  eV and other levels inside the conduction-band tails due to Jahn-Teller (JT) distortions. Furthermore, the valence-band tails are heavily developed. Similar behaviors in the case of  $I$  are shown in Fig. 2(b). There is a peak at  $E_v + 0.88$  eV. After the relaxation, the new peaks are developed near the valence-band tails,  $E_v + 0.12$  eV and  $E_v + 0.52$  eV, whereas the change in the conduction-band tails is negligible.

In the case of  $V_2$  there are two doublets ( $e_g, e_u$ ) at  $E_v + 0.94$  eV and one inside the conduction bands. Under the JT distortion these will be split into several singlets near  $E_v + 1.0$  eV,  $E_v + 0.46$  eV, and near the valence-band tails after the relaxation. In the case of  $V_2^m$

the energy levels near the conduction-band tails and in the middle of the band gap appear before the relaxation. These become shifted toward the valence-band tails. The energy levels are spread over the band gap (see Table II).

The gap states of the unrelaxed  $V-I$  complex are similar to the sum of those of respective defects. The  $V-I$  complex reveals both the JT distortion and relaxation. The triplet state splits into several singlets reproducing gap states near the center and the valence-band tails. The relaxation gives significant changes in the gap states, in particular, in the valence-band tails. One notes from the density of states of various defects that the valence-band tails are related to the formation of weak bonds, which was introduced by the relaxation near the defect sites.

#### IV. SUMMARY

We have studied the fully relaxed intrinsic point defects in crystalline silicon with a tight-binding molecular-dynamics methods. The details of fully relaxed geometry are generated by the TB MD method. The calculated formation energies of various defects enabled us to estimate the binding energy of the divacancy and the vacancy-interstitial complex. The binding energies of the divacancy and the vacancy-interstitial complex are 1.68 and 1.43 eV, respectively. These complexes are very stable even at fairly high temperatures. The changes in the density of states near the band gap of various defects are also discussed. It should be mentioned that the relaxation effect cannot be neglected in the study of defects, in particular, in the energy levels of the gap states.

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