

# First-principles study of the structure and energetics of neutral divacancies in silicon

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We report a first-principles study of the structure and energetics of the simple and split divacancies in silicon. The formation energies are estimated to be 4.63 and 5.90 eV, respectively. In both cases, relaxation proceeds inwards, and clearly is important, even though the relaxation energies amount to less than about 10% of the unrelaxed formation energies, enough to change the symmetry of the local structure. The binding energy of the divacancy is close to 2 eV. For the simple divacancy, we find the relaxed structure to be of the resonant-bond Jahn-Teller type. We also find, for both the divacancy and the split divacancy, the highest occupied states to lie close to the valence band maximum.

## I. INTRODUCTION

The structure and energetics of native defects in semiconductors have been the subject of much experimental and theoretical research effort over the years (cf., for instance, Ref. 1). In spite of this, a definite picture of even the simplest defects (vacancies, interstitials, and small complexes of them, such as divacancies), in the prototype semiconductor material (silicon), has not yet emerged. For example, in the case of interstitials in Si, the empirical Stillinger-Weber model<sup>2</sup> predicts that the hexagonal interstitial will relax into the tetrahedral position (i.e., there is no energy barrier between the two positions), whereas first-principles calculations yield the opposite result. Clearly, the energies of the two sites are similar and precise calculations are necessary in order to resolve such discrepancies. Likewise, detailed knowledge of formation energies is required for determining the relative population of defects in equilibrium, as well as for the accurate interpretation of calorimetric data.

The case of divacancies is of considerable interest: they are expected to be created in a relatively large number upon the irradiation of silicon by electrons, neutrons, or ions,<sup>3,4</sup> and, therefore, to play a role in the kinetics of relaxation of the irradiated material. The structure of the defect, however, remains controversial: Recently, Saito and Oshiyama proposed,<sup>5</sup> on the basis of first-principles calculations, a new Jahn-Teller distortion for the negatively charged divacancy, which the authors refer to as “resonant bond”; the positively charged divacancy exhibits the usual pairing configuration. The existence of the resonant-bond distortion has been disputed.<sup>6</sup>

The study of Saito and Oshiyama is, to our knowledge, the only one for divacancies where structural relaxation is fully taken into account *ab initio*. It is now well established, e.g., from first-principles calculations of simple point defects, that relaxation plays a significant role and cannot be ignored. Saito and Oshiyama have considered only the simple, nearest neighbor, divacancy in the negative and positive charge states, and have not examined in detail the relaxed configuration or the formation energies, including the effect of relaxation. In view of this, and in need of the accurate defect formation energies mentioned above, we have

carried out detailed first-principles calculations of the structure and energetics of neutral divacancies in silicon, rigorously and self-consistently taking into account the relaxation of the host lattice. We consider here the divacancy in both first-nearest-neighbor (“simple”) and second-nearest-neighbor (“split”) configurations, and also examine, for reference purposes, the monovacancy. A related study was given recently by Song and co-workers,<sup>7</sup> using a semiempirical tight-binding (TB) model<sup>8</sup> coupled with molecular dynamics (MD). In spite of the success of TB models, in describing the structural properties of various systems (Si and GaAs among others; see, for instance, Refs. 9–13), the method has its limitations and it is important to assess its validity.

We find the relaxed structure and formation energy of the monovacancy to be in agreement with other first-principles calculations. For the divacancies, the relaxed structures are only in fair agreement with the calculations of Song *et al.*: we find the TB model to overestimate somewhat (by a fraction of an eV) the formation energies; in addition, our first-principles calculations yield somewhat smaller relaxation displacements and energies than the TB model. The structure that we observe for the simple divacancy is of the resonant-bond type, as proposed by Saito and Oshiyama for the negatively charged divacancy. We find also that the divacancy is relatively tightly bound compared to independent vacancies, by almost 2 eV. Concerning the electronic structure of the defects, we observe, for both the divacancy and the split divacancy, the highest occupied states to lie close to the valence band maximum.

## II. COMPUTATIONAL DETAILS

The present calculations were carried out within the framework of density-functional theory (DFT) in the local-density approximation (LDA). We use a nonlocal, norm-conserving pseudopotential;<sup>14</sup> this potential is *s* local, and *p* and *d* nonlocal, with a core radius of 1.8 Å. The electron exchange-correlation energy is given by the Ceperley-Alder form.<sup>15</sup> Models of the relaxed defects were constructed as follows: Starting with an ideal 64-atom crystal of Si (lattice parameter  $a = 5.395$  Å), atoms at appropriate positions were

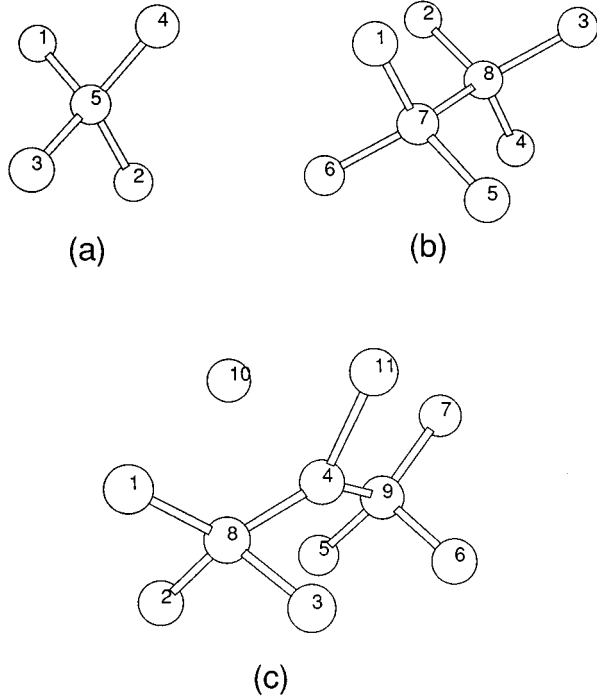


FIG. 1. Relaxed structure of (a) the monovacancy (empty site labeled 5), (b) the simple divacancy (empty sites labeled 7 and 8), and (c) the split divacancy (empty sites labeled 8 and 9).

removed to simulate the various defects. The models were then relaxed at zero temperature, using the conjugate-gradient program CASTEP (CAMbridge Serial Total Energy Package). In the case of the simple divacancy, we also used,

as starting point, the relaxed configuration from the TB calculation of Song *et al.*, and a configuration with pairing-mode symmetry, in order to test the robustness of our resonant-bond ground state. As we will see below, we find, in both cases, the same final configuration as when starting from the ideal-crystal structure. Only the  $\Gamma$  point was used for reciprocal-space sampling. The wave functions were expanded in a plane-wave basis, with an energy cutoff  $E_C$  of 8 Ry; in the case of the simple divacancy, a 10-Ry cutoff was also considered (see below). All defects were taken to be in their neutral charge state.

### III. RESULTS AND DISCUSSION

#### A. Relaxed configurations

We present, in Fig. 1, the fully relaxed geometries of the three defects considered here and give, in Tables I and II, details of the relaxation patterns of the neighbors. Concerning the divacancy, we show only the results obtained with the 8-Ry energy cutoff: we find the relaxed geometry not to depend significantly on  $E_C$  — displacements are the same to within about 0.02 Å for the two values of  $E_C$  considered — in agreement with Smargiassi’s findings<sup>16</sup> for the monovacancy. The relaxation vectors of the atoms, Table I, are expressed here in terms of the usual breathing and pairing modes.<sup>1</sup> In the case of divacancies, we assume the defects to consist each of two tetrahedra centered on the two vacant lattice sites and calculate the breathing and pairing modes of each atom with respect to the nearest-neighbor vacancy. Thus, for the simple divacancy, we have in total six-nearest neighbors, as depicted in Fig. 1(b). For the split divacancy, there are seven-nearest neighbors, but one atom [labeled “4”

TABLE I. Relaxation properties of the atoms neighboring the defects. Atoms are labeled as illustrated in Fig. 1; “Vac.” is the label of the nearest vacant site. Note that atom number 4 in the case of the split divacancy is common to the two tetrahedra. All distances are in Å.  $\Delta V/V_0 = (V - V_0)/V_0$  is the relative volume change of a defect upon relaxing from the ideal configuration, the volume of which is denoted  $V_0$ . For the breathing mode and the volume, + and – refer to outward and inward relaxation, respectively.

System	$\Delta V/V_0$ (%)	Atom	Vac.	Breathing	Pairing 1	Pairing 2	Displacement
Monovacancy	–35	1	5	–0.30	–0.14	–0.24	0.41
		2	5	–0.29	–0.14	–0.24	0.40
		3	5	–0.29	–0.14	–0.24	0.40
		4	5	–0.30	–0.14	–0.24	0.41
Simple divacancy	–17	1	7	–0.27	+0.05	–0.10	0.29
		5	7	–0.11	+0.12	–0.01	0.17
		6	7	–0.11	–0.05	–0.11	0.17
		2	8	–0.11	+0.12	+0.01	0.17
		3	8	–0.11	–0.06	+0.11	0.17
		4	8	–0.27	+0.06	+0.10	0.29
Split divacancy	–28	1	8	–0.11	–0.02	–0.10	0.15
		2	8	–0.05	–0.02	–0.09	0.10
		3	8	–0.31	–0.05	–0.20	0.37
		4	8	–0.40	–0.09	–0.71	0.82
		4	9	–0.40	+0.66	–0.27	0.82
		5	9	–0.05	+0.09	–0.02	0.10
		6	9	–0.31	+0.20	–0.05	0.37
7	9	–0.11	+0.10	–0.03	0.15		

TABLE II. Distances (in Å) between the atoms neighboring the defects, which are second-nearest neighbors in the ideal crystal. Atoms are labeled as illustrated in Fig. 1; “Vac.” is the label of the nearest vacant site. In the perfect crystal, all distances are equal to 3.81 Å.

System	Vac.	Pair	$d$	Vac.	Pair	$d$
Monovacancy	5	1–2	3.53			
	5	1–3	3.53			
	5	1–4	3.00			
	5	2–3	3.03			
	5	2–4	3.53			
	5	3–4	3.53			
Simple divacancy	7	1–5	3.40	8	2–3	3.71
	7	1–6	3.40	8	2–4	3.40
	7	5–6	3.71	8	3–4	3.40
Split divacancy	8	1–2	3.58	9	4–5	3.85
	8	1–3	3.53	9	4–6	2.78
	8	1–4	3.85	9	4–7	3.61
	8	2–3	3.66	9	5–6	3.66
	8	2–4	3.61	9	5–7	3.58
	8	3–4	2.78	9	6–7	3.53

in Fig. 1(c)] is common to the two tetrahedra, and we calculate its relaxation vectors relative to both vacant sites. As a measure of the variation in open volume resulting from the relaxation of the defects, we also list, in Table I, the difference  $\Delta V/V_0 = (V - V_0)/V_0$ . For the monovacancy,  $V_0$  and  $V$  are the volumes of the tetrahedra formed by the four atoms near the vacant site, before and after relaxation, respectively. In the case of divacancies, we approximate the total volume  $V$  by the sum of the volumes of the two tetrahedra.

The structure of the monovacancy is well understood, from both experimental<sup>17</sup> and theoretical<sup>18</sup> viewpoints. In particular, its relaxed state has been studied from first principles by Smargiassi<sup>16</sup> and using a TB model by Song *et al.*<sup>7</sup> and Wang *et al.*<sup>19</sup> Our results agree quite well with both approaches. (There seems, however, to be a small disagreement between the two TB calculations, Refs. 7 and 19, which both use the Goodwin-Skinner-Pettifor TB parametrization:<sup>8</sup> the configuration found by Song *et al.* has lower symmetry than that found by Wang *et al.* This might be due to the different relaxation procedures used. Our relaxed configuration agrees precisely with Wang *et al.*) All four neighbors move inwards, i.e., towards the vacancy, by a substantial 0.4 Å. The pairing modes are nonzero, however, i.e., the tetrahedral symmetry is broken, leading to a Jahn-Teller distortion, such that the atoms pair up along the [110] axis; the resulting configuration has  $D_{2d}$  symmetry. Atom-atom distances in the relaxed configuration are in the range 3.00–3.53 Å (cf. Table II) and “bond” angles (between the vacancy and adjacent atoms; such bonds, of course, are virtual) are in the range 94–118°, to be compared to 3.81 Å and 109° for the ideal geometry. The open volume of the vacancy decreases by a very significant 35% during relaxation.

For the divacancy, we find the displacements of the neighboring atoms from their ideal-crystal positions to be relatively small compared to the monovacancy case—four atoms move by 0.17 Å and the other two by 0.29 Å—and the open

volume decreases by about 17%, as can be seen in Table I. Again here, all atoms move inwards, and the pairing-mode distortions are rather small, although significant enough to show the symmetry-lowering Jahn-Teller distortion from  $D_{3d}$  to  $C_{2h}$ . This is in qualitative agreement with the TB calculations of Song *et al.*, who also observe inward relaxation for all atoms; their model, however, predicts displacements in the range 0.45–0.60 Å, roughly twice as large as those observed in the TB relaxation of the monovacancy. The relaxed configuration of the divacancy, shown in Fig. 1(b), is characterized by atom-atom distances in the range 3.40–3.71 Å (cf. Table II), i.e., a bit smaller than in the perfect structure; bond angles are narrowly distributed about the ideal tetrahedral angle.

In order to make sure that the relaxed configuration of the divacancy shown in Fig. 1 is not a local minimum of the total-energy surface, we have repeated the structural relaxation using, as starting point, the TB-relaxed configuration of Song *et al.*<sup>7</sup> We found exactly the same configuration as when starting from the ideal crystal, indicating that, indeed, the geometry that we obtain corresponds to the ground state of the defect.

As mentioned in the Introduction, Saito and Oshiyama have recently proposed a “resonant-bond,” Jahn-Teller distortion for the negatively charged divacancy in Si;<sup>5</sup> the positively charged divacancy, in contrast, exhibits the conventional pairing pattern, and both have the  $C_{2h}$  symmetry. In the resonant-bond Jahn-Teller configuration, one of the distances between the three atoms (taken in pairs) neighboring either empty lattice sites is longer than the other two, while the opposite is true in the pairing distortion. Our calculations indicate, as can be seen in Table II, that the neutral Si divacancy also exhibits the  $C_{2h}$  resonant-bond distortion. The question of whether or not this distortion is relevant to the interpretation of experimental data is under discussion.<sup>6</sup> It is interesting to note that the resonant-bond distortion has very recently been observed at the As end of the divacancy in GaAs.<sup>20</sup>

For the negatively charged divacancy, Saito and Oshiyama actually observed, using a very similar computational framework, a bistable situation between resonant-bond and pairing-mode distortions;<sup>5</sup> the difference in energy between the two states is very small—2.4 meV, within the accuracy of the calculation. We looked for this possible bistability in the case of the neutral divacancy, by starting the relaxation process from a pairing-mode-distorted initial configuration. This was found to be unstable: the system, again, relaxed into the resonant-bond configuration, thereby confirming the resonant-bond nature of the ground state. Our calculations indicate, however, that the total-energy surface between the two states is very flat. It cannot be excluded that a more accurate model will lead to a small barrier, and therefore bistability.

The situation is quite different in the case of the split divacancy ( $D_{2d}$  symmetry in the ideal configuration), where some atoms undergo a large relaxation, as demonstrated in Table I. In particular, atom 4, which is shared by the two vacancies, moves by a sizeable 0.82 Å (and the 8–4–9 angle increases to 135°), almost breaking the bond with one of its original neighbors, labeled 10 in Fig. 1 (the relaxed 4–10 distance is 2.78 Å; the equilibrium bond length is 2.35 Å).

TABLE III. Formation energies ( $\Omega_u$ : unrelaxed;  $\Omega_r$ : relaxed) and relaxation energies ( $\Delta\Omega = \Omega_u - \Omega_r$ ) of the defects, all in eV. The relaxation energies are also given, in parentheses, as a percentage of the unrelaxed formation energy.

System	$\Omega_u$	$\Omega_r$	$\Delta\Omega$
Monovacancy	3.65	3.29	0.36 (10.0%)
Simple divacancy - $E_C = 8$ Ry	4.87	4.63	0.23 (4.8%)
Simple divacancy - $E_C = 10$ Ry	4.59	4.32	0.28 (6.0%)
Split divacancy	6.47	5.90	0.59 (8.9%)

Atom 10, in fact, does not rebond: it relaxes by approximately 0.3 Å, and retains one bond dangling. The displacements from the ideal structure range from 0.10 to 0.82 Å (including atom 4), and again here these are substantially smaller than the values calculated within the TB model by Song *et al.* (0.35 to 1.25 Å). Atom-atom distances range from 2.78 to 3.85 Å (again including atom 4; cf. Table II), so that, in fact, some second-neighbor atom pairs now are weakly bonded (e.g., the pairs 3–4 and 4–6). The bond angles, of course, also are severely distorted and lie in the range 85–112°. Overall, the volume of this defect decreases by ~28% upon relaxing, which is larger than for the simple divacancy, and almost as large as in the case of the monovacancy, as could be expected.

### B. Formation energies

The formation energies of the defects, in their unrelaxed and relaxed states,  $\Omega_u$  and  $\Omega_r$ , respectively, are listed in Table III. The formation energy of a defect is defined as the difference in total energies of the system with and without the defect at constant number of particles. Here the number of particles varies, but we may write, equivalently,  $\Omega = E_D[N] - N\mu$ , where  $E_D[N]$  is the total energy of the defective system containing  $N$  atoms, and  $\mu$  is the atomic chemical potential of the host crystal, which we take to be, approximately, the total energy per atom of a silicon crystal ( $\mu = -107.007$  and  $-107.417$  eV, for  $E_C = 8$  and 10 Ry, respectively). We also show in Table III the relaxation energies, i.e., the difference in energies between unrelaxed and relaxed states,  $\Delta\Omega = \Omega_u - \Omega_r$ .

As mentioned earlier there is, to our knowledge, only one other estimate of the formation energies of divacancies in Si, based on a TB approach.<sup>7</sup> In contrast, there exist many calculations of the formation energy of the monovacancy. The value we obtain—3.29 eV—is consistent with other DFT/LDA calculations, which are in the range 3.0–5.0 eV,<sup>21</sup> depending on relaxation and on the particular choice of model parameters, especially the energy cutoff: for a model equivalent to ours, Smargiassi has found  $\Omega_r$  to decrease from 3.88 to 3.28 to 2.96 eV, upon increasing  $E_C$  from 6 to 8 to 10 Ry. Some first-principles models, also, do not allow, or partially allow for, neighboring-atom relaxation. This leads to higher formation energies, which should be compared, rather, with  $\Omega_u$ . Our result for  $\Omega_r$  for the monovacancy is also consistent with the TB value of 3.67, using a 64-atom supercell;<sup>7,19</sup> the energy of the monovacancy is, however, found to converge to about 4.12 eV upon increasing the size of the system to 512 atoms. Since increasing  $E_C$  causes the formation energy

to decrease, while increasing the system size does the opposite, by roughly the same amount, leading to substantial cancellation of errors, we conclude from this that our calculations are close to convergence, with respect to these two parameters taken together. Smargiassi has found, in addition, that  $\Gamma$ -point-only sampling gives formation energies for the monovacancy converged to better than 10%. It is quite likely, therefore, that a similar error bar applies to the case of divacancies.

Turning to divacancies, now, we find a relaxed formation energy for the simple divacancy of 4.63 eV, substantially larger than that for the monovacancy, as expected. We note that  $\Omega_r$  decreases to 4.32 eV ( $-0.31$  eV, or  $-6.7\%$ ), upon increasing  $E_C$  to 10 Ry; this, it turns out, is in excellent agreement with the corresponding variation reported by Smargiassi for the monovacancy ( $-0.32$  eV) discussed above. For the split divacancy, we obtain  $\Omega_r = 5.90$  eV, quite a bit more than for the simple divacancy, and almost twice as much as for the monovacancy. The formation energies, for the fully relaxed configurations that we obtain, are in fair agreement with the corresponding TB values of Song *et al.*—5.68 and 6.54 eV for the simple and split divacancy, respectively. Our results, further, differ with the TB values in one important aspect: relaxation energies, i.e., the energy difference between relaxed and unrelaxed states. While, in the TB-MD model of Song *et al.*, the relaxation energies amount to a very large fraction of the unrelaxed energies; in the range 23–27%, they are much less in our case, certainly no more than 10%, consistent with the smaller displacements observed in our calculations upon relaxing.

As a final point, we note that the energy required to form two monovacancies separated by an infinite distance (in an otherwise perfect crystal) is 6.58 eV, more than the cost of a split divacancy (5.90 eV) or of a simple divacancy (4.63 eV). Vacancies, therefore, may lower their energy, by as much as 1.95 eV, by combining first into split divacancies ( $-0.68$  eV), then into simple divacancies ( $-1.27$  eV). Divacancies, evidently, are quite stable; this is consistent with the fact that they are easily formed by electron irradiation at room temperature, and are persistent.<sup>3,4</sup>

### C. Band structure

The band structure of the Si divacancy has been the object of a lot of debate, ever since the publication of the pioneering work of Watkins and Corbett on this defect in various states of charge.<sup>3,22–25</sup> As discussed above, the negatively charged divacancy has been found by Saito and Oshiyama, on the basis of LDA calculations, to exhibit the resonant-bond Jahn-Teller distortion,<sup>5</sup> for which the highest occupied state has  $(a_u)^2 b_u^1$  symmetry. In contrast, for the conventional pairing mechanism, electron spin resonance measurements indicate that the highest occupied state is  $(a_g)^2$  (Refs. 3,6). The structure we find for the neutral divacancy, as we have seen, agrees with the result of Saito and Oshiyama for the negative divacancy; since it has one fewer electron, it follows that it must possess  $(a_u)^2$  symmetry. In the following, we report our results for the position in energy of the levels in the gap.

We discuss first the electronic structure of the well-documented monovacancy. In its unrelaxed state, which is of

$T_d$  symmetry, we find the highest occupied level of the defect to be triply degenerate and to lie 0.61 eV above the valence band maximum (VBM). Upon relaxing, as we have seen above, the Jahn-Teller distortion causes the symmetry to decrease to  $D_{2d}$ ,<sup>26</sup> and the highest occupied level, now a singlet, occurs at 0.23 eV. This is in qualitative agreement with the self-consistent field calculations of Lipari *et al.*,<sup>27</sup> which give the highest occupied state as a triplet at 0.7 and a singlet at 0.3 eV, before and after relaxation, respectively.

For the unrelaxed simple divacancy now, which is of  $D_{3d}$  symmetry, we find the highest occupied state to be a doublet at about 0.1 eV above the VBM. After relaxation, the symmetry is lowered to  $C_{2h}$  and the highest occupied state lies just above the VBM, at 0.04 eV. This result is for a cutoff in energy of 8 Ry. If we increase the cutoff to 10 Ry, we find the highest occupied level to lie in the valence band. This agrees, in fact, with a calculation by Lee and McGill, based of the extended Huckel theory, frequently used to interpret experimental data.<sup>24</sup> In view of the error bar of our calculations ( $\sim 0.1$  eV), therefore, we cannot definitely conclude that the divacancy leads to levels in the gap.

Yet, other calculations give rather different results: In a self-consistent, parameter-free, Green's function calculation, Sugino and Oshiyama<sup>22</sup> found the the highest occupied state (doubly degenerate) to be at 0.31 eV before relaxation; after relaxation with a valence-force model, the level splits into two levels, 80 meV apart, close to each other, and still in the band gap. In contrast, a cluster-method Green's function calculation by Kirton *et al.*<sup>25</sup> yields the highest occupied state (a doublet) to lie in the middle of the gap before relaxation and a small Jahn-Teller distortion splits the degenerate states. In their TB study, Song *et al.* find, before relaxation, the highest occupied state to be a doublet at 0.94 eV above the VBM, and, after relaxation, one occupied level at 0.46 eV and one unoccupied level at 1.00 eV. Here also, therefore, the highest occupied state moves towards the VBM after relaxation. Evidently, the precise positions of defect-induced gap states are sensitive to the particular model used, while all calculations seem to agree that the highest occupied level moves towards the VBM upon relaxing the structure. It should be noted, as a final point, that single-electron energy levels are distinct from ionization levels, i.e., values of the electron chemical potential at which a change in the charge state of the defect

takes place.<sup>18</sup> For instance, the observed values quoted in Ref. 7 correspond to successive ionizations of the divacancy from + to 2-, not to single-electron states.

For the split divacancy, we find the highest occupied state, before relaxation, to be a doublet at 0.37 eV above the VBM. Structural relaxation pulls down this level very close to the VBM, at 0.08 eV. This is only in fair agreement with the TB results of Song *et al.*, who also find relaxation to shift the defect states towards the valence band; in their case, however, the levels remain deep in the gap. To our knowledge, there exists no experimental electronic structure data for the split divacancy, and no other first-principles calculations.

#### IV. CONCLUDING REMARKS

We have presented a first-principles study of the structure and energetics of divacancies in silicon, within the framework of density-functional theory, with emphasis on relaxation and its consequences. We estimate the formation energies to be 4.63 and 5.90 eV for the simple and split divacancies, respectively. In both cases, relaxation proceeds inwards, clearly is significant, and therefore cannot be ignored, even though the relaxation energies amount to less than about 10% of the unrelaxed formation energies. The binding energy of divacancies is close to 2 eV, which indicates that they are stable, and explains that they are easily formed by electron irradiation at room temperature.<sup>3,4</sup>

We observe, for both the divacancy and the split divacancy, the highest occupied states to lie close to the valence band maximum. For the simple divacancy, we find the relaxed structure to be of the resonant-bond Jahn-Teller type. This implies that the highest occupied level has  $(a_u)^2$  symmetry, in agreement with recent calculations for the negative divacancy,<sup>5</sup> at odds with electron spin resonance measurements, which suggest that the symmetry is  $(a_g)^2$  (Refs. 3,6). Clearly, further studies are needed to resolve this controversy.

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