Large Pairing Jahn-Teller Distortions Around Divacancies in Crystalline Silicon

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Ab initio atomic and electronic structures of neutral ($V_2{}^0$) and charged ($V_2{}^+, V_2{}^-, V_2{}^{2-}$) Si divacancies are investigated using bulk-terminated clusters with up to $\approx$320 Si atoms. For the first time, the relaxed structures for $V_2{}^+$, $V_2{}^0$, and $V_2{}^-$ are found to exhibit *large pairing* Jahn-Teller distortions consistent with electron paramagnetic resonance experiments. Atomic relaxations, Jahn-Teller and relaxation energies, and hyperfine parameters are calculated for various charge states and compared with available experimental data. The cluster size and the anisotropic nature of the relaxations play key roles in establishing the stability of the structures with large pairing distortions.

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Since the pioneering electron paramagnetic resonance (EPR) studies of Watkins and Corbett [1], there have been controversies about the electronic and atomic structures of the divacancy V_2 in crystalline Si. These controversies have revolved around the exact nature of the symmetry-lowering Jahn-Teller (JT) distortions that split the degenerate deep levels. To date, the *sense and the magnitude* of these distortions, as inferred from the EPR data and theoretical calculations, have been at variance. This disagreement has created an ongoing debate for the ground state structures of V_2 in Si and presented a fundamental challenge to understanding this important semiconductor defect.

The ideal simple divacancy, which is created by removing two neighboring Si atoms, has a D_{3d} symmetry and two doubly degenerate deep levels, labeled e_u and e_g (Fig. 1). While the e_g level is empty, the lower e_u level is occupied by one, two, and three electrons for the positively charged ($V_2{}^+$), neutral ($V_2{}^0$), and negatively charged ($V_2{}^-$) divacancies, respectively. As a result of this degeneracy, the lattice distorts to gain electronic energy. Upon symmetry lowering to C_{2h}, each e level splits into levels labeled a and b. Of these four levels, a_g and b_u have amplitudes, while a_u and b_g have nodes on the mirror plane of the C_{2h} distortion that contains the vacant sites and atoms 3 and 6 in Fig. 1(a). The ordering of these four levels inside the band gap depends on the particular sense and magnitude of the distortion.

The EPR experiments of Watkins and Corbett indicated that $V_2{}^+$ and $V_2{}^-$ have the low symmetry of C_{2h}, and the highest occupied levels for both charge states have amplitudes on the mirror plane. They also established that the JT distortions occur in a *pairing* sense, which results in $d_{12} < d_{13} = d_{23}$, where d_{ij} is the distance between atoms i and j [Fig. 1(b)]. The JT energies E_{JT} were estimated to be 1.3 eV and 2.4 eV for $V_2{}^+$ and $V_2{}^-$, respectively. From these experimental findings, Watkins and Corbett concluded that the JT distortion had to be large enough for the a_g level split from the upper e_g level to be lowered below the a_u level, as shown in Fig. 1(b). This would give configurations of $V_2{}^+$:b_u^1 (or a_g^1) and $V_2{}^-$:$b_u^2 a_g^1$ (or $a_g^2 b_u^1$), explaining both the wave function character of the highest occupied level and the sense and the degree of the distortion. Indeed, a small pairing JT distortion [Fig. 1(c)] would not be consistent with the experimental findings, as

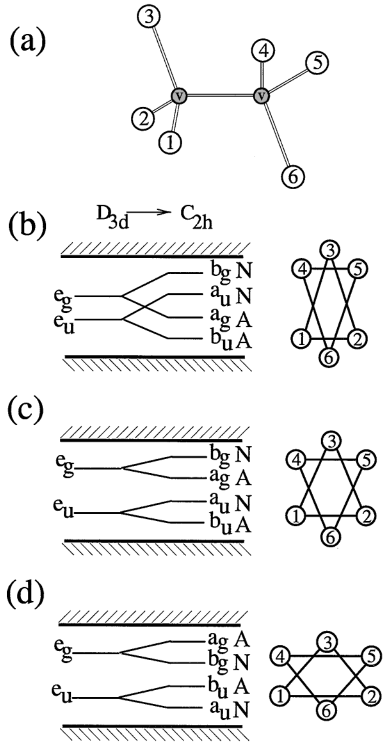

FIG. 1. (a) Atomic structure of the simple divacancy in crystalline Si with its six nearest neighbor atoms. The small shaded circles labeled by V represent the vacant sites. (b)–(d) Electronic structures, level symmetries, and the corresponding atomic structures viewed along the [111] divacancy axis for the case of (b) large pairing Jahn-Teller distortion, (c) small pairing Jahn-Teller distortion, and (d) resonant-bond configuration. The letters A and N next to the level symmetries represent whether the level has amplitude or node, respectively, on the mirror plane of the C_{2h} distortion.

it would imply V_2^{-}:$b_u^2 a_u^1$, for which the highest occupied level has a node on the mirror plane.

In contrast with these experimental findings, theoretical calculations so far [2–8], which have mainly employed the *ab initio* plane-wave supercell technique with 64 atoms, have found a different JT distortion both in terms of the magnitude and the sense of the relaxation. For V_2^{-}, Saito and Oshiyama found the atomic displacements opposite to the experimental finding [4] resulting in $d_{12} > d_{13} = d_{23}$ [Fig. 1(d)]. This so-called "resonant-bond" (RB) configuration reverses the order of the a_u and b_u levels compared to the pairing JT distortion, so that the highest occupied level in V_2^{-}:$a_u^2 b_u^1$ has amplitude on the mirror plane. For V_2^{+}, they found a structure with a small pairing JT distortion. Also, Seong and Lewis found a RB configuration as the ground state structure for V_2^{0} [5]. Although these calculations can explain the wave function character of the highest occupied state, the sense of the distortion is in disagreement with the experimental finding of rebonding by pairs [6,7]. In addition, the calculated energy difference between the RB configuration and the pairing configuration for V_2^{-} was only 2.4 meV, much too small for a definite conclusion. Recently, 216-atom supercell calculations of Pesola *et al.* have suggested lower symmetry (S_2) "mixed" structures changing from more of a pairing type to more of a RB type in going from V_2^{+} to V_2^{-} [8].

Motivated by these discrepancies between theory and experiment, in this paper we investigate the atomic and electronic structures of divacancies in Si by performing large-scale *ab initio* total-energy calculations. Our calculations show, for the first time, that the ground state structures for V_2^{+}, V_2^{0}, and V_2^{-} do have *large pairing* JT distortions. We find that the distortions are large enough for the a_g level to be lowered below the a_u level, so that the highest occupied levels in V_2^{+}:b_u^1 and V_2^{-}:$b_u^2 a_g^1$ both have amplitudes on the mirror plane, consistent with EPR experiments. For the ground state structures, we present results for the calculated JT and relaxation energies and hyperfine parameters for various charge states and system sizes containing up to ≈320 Si atoms. We find that the highly anisotropic nature of the atomic relaxations and the size of the system simulating the crystalline defect are crucial to establishing the stability of the structures with large pairing distortions.

In our calculations we used the *ab initio* cluster method, where the bulk defect was simulated from first principles by bulk-terminated Si clusters. In the past, this method was used successfully to investigate the structural energetics of monovacancies in Si [9]. Our calculations were performed in real space using the higher-order finite difference pseudopotential method [10]. To model the divacancy, we used hydrogen-passivated clusters with $N_{\rm sh} = 4$ to 17 complete shells of Si atoms around the divacancy. In order to take into account the anisotropic nature of the relaxations without making the number of atoms prohibitively large, we also considered a prolate cluster with incomplete shells from $N_{\rm sh} = 13$ to 25, which included atoms along directions with the largest atomic relaxations. The atomic compositions and sizes of all clusters considered are given in Table I. Our calculations were performed within the local density approximation [11] using nonlocal pseudopotentials [12]. The grid spacing was chosen to be 0.75 a.u. Only Si atoms fully coordinated with other Si atoms were relaxed. The number of relaxed Si atoms is also given in Table I.

The size dependence of the relaxations in the first shell with a constrained D_{3d} symmetry (breathing mode distortions only) is shown in Fig. 2. For all charge states, the relaxations are inward (towards the vacant sites), and gradually increase in magnitude as the charge state changes from $(+)$ to $(2-)$. The size of the system is crucial to determining the magnitudes of the relaxations, which change by as much as 0.21 Å upon increasing $N_{\rm sh}$ from 4 to 17. We find the converged displacements ΔR_1 to be -0.26 Å, -0.28 Å, -0.31 Å, and -0.32 Å for V_2^{+}, V_2^{0}, V_2^{-}, and V_2^{2-}, respectively. The supercell calculations of Saito and Oshiyama [4] find $\Delta R_1 = -0.12$ Å for V_2^{-}, much smaller than our value. We believe that this discrepancy is largely due to the inadequacy of the 64-atom supercell in modeling the divacancy.

While the fully relaxed V_2^{2-} contains only breathing mode displacements, other charge states of V_2 undergo symmetry-lowering JT distortions. Performing a symmetry-unrestricted geometry optimization, we observe atomic relaxations of the *large pairing* type in the relaxed structures of V_2^{+}, V_2^{0}, and V_2^{-} with C_{2h} symmetry. The degree of the distortion increases in going from V_2^{+} to V_2^{-}, in which the paired atoms relax towards each other by ≈1.1 Å compared to the bulk positions. As a result, the a_g level dips below the a_u level, so that the highest occupied levels in both V_2^{+}:b_u^1 and V_2^{-}:$b_u^2 a_g^1$ have amplitudes on the mirror plane. Detailed structural information on various charge states of V_2 is given in Table II.

The cluster size is very important in establishing the stability of the large pairing JT distortions and the change in the ordering of the a_g and a_u levels. For example, we find $\rm Si_{206}H_{158}$ to be the smallest cluster in which the a_g level has dipped below the a_u level for V_2^{0}. In reducing

TABLE I. Sizes of H-passivated Si clusters simulating the bulk divacancy given in terms of the number of Si shells $N_{\rm sh}$, atomic composition, and diameters d. The origin of each cluster is midway between the two vacant sites. Also given are the number of relaxed Si atoms $N_{\rm re}$ for each cluster. For the prolate $\rm Si_{246}H_{186}$ cluster, the dimensions refer to smallest and largest values along different directions.

$N_{\rm sh}$	Composition	d (Å)	$N_{\rm re}$
4	$\rm Si_{36}H_{42}$	11.1	6
7	$\rm Si_{84}H_{78}$	14.5	30
9	$\rm Si_{128}H_{98}$	16.5	60
11	$\rm Si_{164}H_{122}$	18.2	78
13	$\rm Si_{206}H_{158}$	19.7	114
17	$\rm Si_{316}H_{198}$	22.5	188
13–25	$\rm Si_{246}H_{186}$	19.7–27.2	138

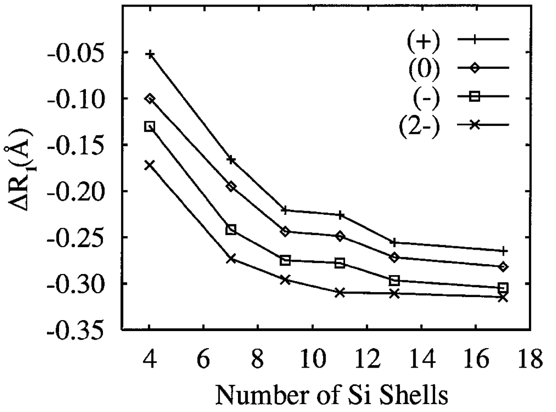

FIG. 2. Breathing mode displacements for the first shell of atoms around the divacancy as a function of the cluster size (given as the number of Si shells N_{sh} used in the calculation) for V_2^{+} (+), V_2^{0} (◇), V_2^{-} (□), and V_2^{2-} (×). Symmetry-lowering distortions are *not* allowed constraining the symmetry to D_{3d}. Negative sign means inward relaxation.

the size of the system further, the change in the ordering of the a_u and a_g ceases to exist in $\mathrm{Si}_{128}\mathrm{H}_{98}$ even for the case of V_2^{-}, which has larger JT distortions compared to V_2^{0}. Upon charging $\mathrm{Si}_{128}\mathrm{H}_{98}$ negatively, the extra electron goes into the node state a_u, and d_{12} slightly increases compared to V_2^{0}. This results in a structure with a small pairing JT distortion ($d_{12} = 3.19$ Å; $d_{13} = 3.38$ Å). If the extra electron is constrained to be placed into the a_g level corresponding to the configuration $V_2^{-}{:}b_u^2a_u^0a_g^1$, although the pairing distortion becomes large ($d_{12} = 2.90$ Å; $d_{13} = 3.37$ Å), the relaxed geometry is 0.27 eV higher in energy compared to the structure with the small pairing distortion. These are the same observations as those of Saito and Oshiyama [7] from their supercell calculations. Hence, the fact that they could not find an energetically stable structure with large pairing distortions for V_2^{-} should have been attributed to the use of a small 64-atom supercell, which does not allow long-ranged relaxations associated with large pairing distortions.

With the divacancy pointing along the [111] direction, the general pattern of the relaxations can be described as an anisotropic and long-ranged propagation along the zigzag chains of atoms in the $[1\bar{1}0]$ direction, which decays along the [111] direction on either side of the vacant sites. The largest relaxations occur along the two zigzag chains, each of which contains the two paired atoms, e.g., atoms 1 and 2 in Fig. 1(a), and the vacant site nearest to them. Figure 3 shows for the case of V_2^{-} the strikingly large magnitude and long-ranged character of the relaxations along one of these two zigzag chains (relaxations along the other chain not shown are identical by symmetry). As seen in Fig. 3(a), the atoms with the same shell index in the upper chain relax mainly towards each other by 0.53 Å in the first shell decaying to 0.07 Å for atoms as far as ≈11.5 Å away from the vacant site. The two atoms not shown in this figure, which also have large displacements of 0.25 Å, are in the first shell around the divacancy [atoms 3 and 6 in Fig. 1(a)]. The atoms relax inward mainly along the $[11\bar{2}]$ direction. The relaxations for the lower zigzag chain of atoms, half of which are bonded to the upper chain atoms by bonds along the [111] direction (therefore, *not* on the same plane as the upper-chain atoms), are relatively smaller [Fig. 3(b)]. While almost all atoms relax inward, a few atoms such as the two atoms in the fourth shell relax outward by ≈0.05 Å. These observations suggest that the relaxations associated with the large pairing distortions in V_2 are very anisotropic and long ranged along particular directions. As such, a large system size, which should be preferably anisotropic in order not to make the number

TABLE II. Relaxed atomic geometries of V_2^{+}, V_2^{0}, V_2^{-}, and V_2^{2-}. d_{ij} is defined in the text with respect to Fig. 1, and d_{iv} is the distance of atom i to the nearest vacant site. α is the angle subtended by d_{12} at the atomic site 3. All distances are given in Å, and angles in degrees. In the unrelaxed geometry, $d_{12} = d_{13} = 3.84$ Å, $d_{1v} = d_{3v} = 2.35$ Å, and $\alpha = 60°$.

Charge state	d_{12}	d_{13}	α	d_{1v}	d_{3v}
(+)	2.98	3.43	51.6	1.97	2.20
(0)	2.85	3.37	50.1	1.92	2.15
(−)	2.76	3.30	49.1	1.89	2.10
(2−)	3.29	3.29	60.0	2.05	2.05

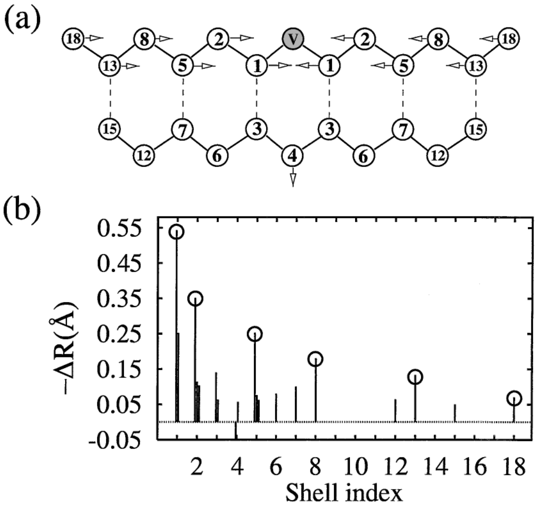

FIG. 3. (a) Two zigzag chains of atoms in the $[1\bar{1}0]$ direction (the upper containing one of the vacant sites labeled by V) along which the atoms relax considerably. The numbers labeling the atoms refer to the shell index (not to be confused with atom indices in Fig. 1). The largest relaxations occur along the upper chain with the atoms in the same shell relaxing mainly toward each other as shown by the arrows on the atoms. Half the atoms in the lower chain are bonded to atoms in the upper chain as shown by dotted lines. These bonds are in the [111] direction parallel to the divacancy axis. This means that the two chains are *not* on the same plane. The arrow on the fourth shell atom in the lower chain indicates that the atom relaxes outward from the vacant site. (b) Atomic relaxations as a function of the shell index for V_2^{-}. Only displacements more than 0.05 Å are shown. The distortion amplitudes marked with circles refer to the upper chain of atoms in (a), while the rest refer to the lower chain.

of atoms much too large, is needed to simulate V_2. The prolate $Si_{246}H_{186}$ divacancy cluster is one such cluster generated from $Si_{206}H_{158}$ with atoms added along the two zigzag chains shown in Fig. 3. Upon addition of atoms along these chains, the energetic stability of the structure is enhanced, and displacements can increase by as much as 0.1 Å. In contrast, we find that the relaxations for ${V_2}^-$ with a RB distortion are not only relatively small (largest $\Delta R = -0.36$ Å in the first shell) but also decay much faster away from the divacancy.

We also calculated relaxation energies E_r and Jahn-Teller energies E_{JT} for all charge states of V_2. We find $E_r = 0.75$ eV, 1.1 eV, 1.05 eV, and 1.35 eV for ${V_2}^+$, ${V_2}^0$, ${V_2}^-$, and ${V_2}^{2-}$, respectively, which are larger than the values reported in Ref. [8]. As for E_{JT}, we find values of 0.10 eV, 0.22 eV, and 0.15 eV for ${V_2}^+$, ${V_2}^0$, and ${V_2}^-$, respectively. Although the values of E_{JT} for ${V_2}^+$ and ${V_2}^-$ are smaller than the experimental values of 1.3 and 2.4 eV, the discrepancy is most likely due to a combination of (i) size effect and (ii) overestimate of the experimental values, which is common when estimating force constants and the linear JT coupling coefficients by stress-induced defect alignment [6]. In contrast, we calculated the E_{JT} values for RB-type distortions in ${V_2}^0$ and ${V_2}^-$ to be only 0.10 eV and 0.03 eV, respectively.

For additional comparisons with experiment, we calculated the hyperfine coupling parameters of ${V_2}^+$ and ${V_2}^-$ using the scheme of Van de Walle and Blöchl [13]. The calculated isotropic parameter a, anisotropic parameter b, wave function localization (η^2), and s-component (α^2) amounts at the first shell atomic sites are given for ${V_2}^+$ and ${V_2}^-$ in Table III along with the experimental data [1,14]. In general, the agreement between experimental and theoretical hyperfine parameters and wave function characters is very good. Instead, our calculations for the isotropic hyperfine parameters of ${V_2}^-$ with a relaxed RB distortion yield $a = 289$ and 85 MHz at atomic sites 1 and 2, respectively, which are much too large compared to the experimental values of 195 and 32 MHz. These observations, along with the JT energies, provide further evidence that the calculated structures with large pairing distortions indeed correspond to the experimentally observed ground state structures.

In summary, we investigated the atomic and electronic structures of various charge states of the divacancy in crystalline Si from first principles using large-scale cluster calculations. For the first time in a theoretical study of this defect, we find that the relaxed geometries for ${V_2}^+$, ${V_2}^0$, and ${V_2}^-$ exhibit large pairing JT distortions in agreement with EPR experiments. These structures are energetically stabilized upon using large system sizes to accommodate the long-ranged and anisotropic pattern of the relaxations. The calculated JT energies, wave function characters, and hyperfine parameters are found to be in good agreement with experiment. Hence, our study resolves the theoretical controversy regarding the atomic and electronic structures of the divacancies in Si and confirms the experimental interpretations of Watkins and Corbett from nearly 35 years ago.

TABLE III. Hyperfine parameters (a and b), and wave function localization (η^2) and s-component (α^2) amounts at the atomic sites in the first shell for ${V_2}^+$ and ${V_2}^-$. The values in parentheses are experimental data [1,14].

	Atomic site	a (MHz)	b (MHz)	η^2 (%)	α^2 (%)
${V_2}^+$	1	167.3	23.9	27.0	14.9
		(147.7)	(27.7)	(27.7, 31.0)	(11.7)
	2 or 3	31.4	1.2	2.0	39.5
		(22.5)	(1.93)	(2.0)	(22.0, 25.0)
${V_2}^-$	1	239.5	17.2	22.1	25.8
		(195.2)	(23.3)	(24.6, 27.0)	(17.0)
	2 or 3	39.0	3.9	4.8	20.1
		(31.5)	(2.2)	(3.0)	(25.6)

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