

Resonant Bonds in Symmetry-Lowering Distortion around a Si Divacancy

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We propose a novel Jahn-Teller distortion for the negatively charged divacancy (V_2^-) in Si on the basis of the first-principles total-energy calculations. This distortion is *inverse* to the conventional pairing Jahn-Teller distortion and the origin of its energy gain is newly discovered *resonant bonds*. The proposed model successfully reproduces results of electron spin resonance.

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Vacancies in covalent semiconductors are accompanied by Jahn-Teller distortion of surrounding atoms in many cases: Removing atoms from the semiconductor causes several dangling bonds which induce partially occupied degenerate deep levels in the energy gap; the deep levels thus split upon symmetry-lowering Jahn-Teller distortion and hereby gain electronic energy. This picture was deduced from earlier electron spin resonance (ESR) experiments performed for vacancies in Si [1], and is supported by chemical intuition that pairing of the dangling bonds significantly gains energy through formation of *weak covalent bonds*. Recent *ab initio* total-energy calculations carried out for a Si monovacancy [2] along with calculations in the past [3] have indeed confirmed the picture. Yet the concept of this pairing Jahn-Teller distortion, we here argue, is insufficient to describe some important properties of vacancies in semiconductors.

An example that is scientifically typical and technologically important is the Si divacancy V_2 . Removing two adjacent Si atoms in a crystal causes six dangling bonds: Three of them close to each other are oriented to one vacant site and the other three to the other vacant site. This ideal (i.e., unrelaxed) divacancy of D_{3d} symmetry induces two doubly degenerate levels, labeled e_u and e_g , in a region of the energy gap [4–6]. The e_g level located 0.3–0.5 eV higher than the e_u level [6] is empty and the e_u level is partially occupied (i.e., V_2^+ : e_u^1 , V_2^0 : e_u^2 , and V_2^- : e_u^3). It is thus expected that symmetry-lowering lattice distortion takes place. Yet the symmetry-lowering distortion is not, by necessity, the pairing Jahn-Teller distortion since pairing among the three neighboring dangling bonds causes one isolated dangling bond with some frustration. Actually the conventional interpretation of the ESR data on the Si divacancy in terms of the pairing Jahn-Teller distortion model is in a dilemma: In the pioneer ESR measurements, Watkins and Corbett [4] found that the divacancy with either negative or positive charge has the low symmetry of C_{2h} ; they also found that the highest occupied level in both charge states has amplitude on the mirror plane of C_{2h} (i.e., the plane intersects the divacancy axis and nearest atoms 1 and 1' in Fig. 1); on the other hand, the e_u level splits into the lower

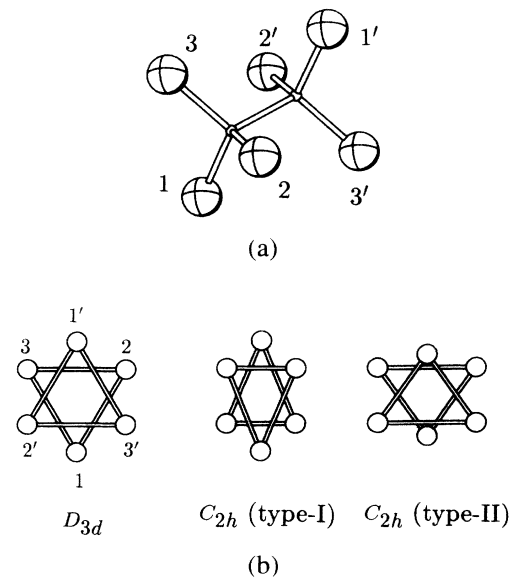


FIG. 1. (a) The atomic structure of the ideal divacancy with the six nearest neighbor atoms. (b) The view of the atomic structures along the divacancy axis ($\langle 111 \rangle$) of the high symmetry (D_{3d}) and of the low symmetry (C_{2h}) with the type I and type II Jahn-Teller distortions. In the type I (pairing) model, $l_{23} < l_{12}$, where l_{ij} indicates the distance between the i th and j th atoms. To the contrary, $l_{23} > l_{12}$ in the type II (resonant-bond) model.

b_u level and the upper a_u level in a simple pairing Jahn-Teller distortion model; this is inconsistent with the ESR observation described above since the highest occupied a_u level in V_2^- has a node on the mirror plane. To resolve this dilemma, Watkins and Corbett introduced a large pairing Jahn-Teller distortion model, in which the Jahn-Teller effect is so enormous that the a_g level splitting from the e_g level is located below the b_u level (i.e., V_2^+ : a_g^1 and V_2^- : $a_g^2 b_u^1$): The highest occupied level, either a_g or b_u , has amplitude on the mirror plane, consistent with the ESR data. Other data later obtained have been interpreted in terms of this model [7,8]. The large pairing-distortion model, however, seems to contradict the low energy barrier ~ 0.06 eV from one Jahn-Teller distortion direction

to another estimated from their own ESR measurement [4] and with small thermal broadening of the optical transition, $V_2^+ \rightarrow V_2^0 + h$ [9].

In this Letter, we present total-energy electronic-structure calculations within the local density approximation (LDA), which provide a natural reconciliation of the above dilemma. We first confirm that the pairing Jahn-Teller distortion [type I in Fig. 1(b) schematically], which is found to be metastable, leads to an electron configuration of $b_u^2 a_u^1$ for V_2^- with the highest occupied level having a node on the mirror plane. Instead, we find that a geometry accompanied by the novel Jahn-Teller distortion [type II in Fig. 1(b)] in which the displacement of the atoms is *inverse* to that in the pairing distortion is stable. The origin of the energy gain in this new distortion is the existence of newly discovered *resonant bonds* among dangling bonds, in contrast to the *weak covalent bonds* in the conventional pairing distortion. We also find that the type II distortion reverses the level ordering and leads to an electron configuration of $a_u^2 b_u^1$ for V_2^- , with the highest occupied level having amplitude on the mirror plane. For V_2^+ , we find that the type I and type II distortions have comparable total energies. We thus propose a new model in which the novel Jahn-Teller distortion with *resonant bonds* takes place for V_2^- , whereas the conventional pairing distortion does in V_2^+ : The common b_u representation in the highest occupied level for both charge states is consistent with the ESR data [4]. It is shown that the present model quantitatively explains the ESR [4] and electron nuclear double resonance (ENDOR) [8] data, which have been discussed in terms of the conventional pairing model for thirty years.

All calculations have been carried out by use of norm-conserving pseudopotentials [10] and LDA [11] combined with conjugate-gradient minimization technique as reported elsewhere [2,12]. Divacancy in an otherwise perfect Si is simulated by the repeating cubic supercell which contains 64 lattice sites. We use Γ point sampling for Brillouin zone integration and the 8-Ry cut-off energy in the plane wave basis set. The symmetry-unrestricted geometry optimization has been performed for all atoms in the supercell. The remaining forces acting on atoms are less than 2 meV/Å in the optimized geometries. We have examined calculational parameters, and then the calculated total-energy difference is estimated to have the accuracy within 0.1 eV or less.

We set out with a geometry of V_2^- with the restriction of D_{3d} symmetry [Fig. 1(b) schematically]. In the optimized geometry, each of the six nearest Si atoms around the vacant sites is displaced inwards from the crystal site by 0.12 Å and consequently the shortest distance among the six nearest Si atoms becomes shorter (3.64 Å) than that (3.84 Å) in the ideal divacancy. The deep level e_u is found to be occupied by three electrons as was concluded from the previous Green's-function calculation [6], while

the e_g gap level is found to be close to the conduction band bottom.

We next find that symmetry unrestricted optimization for V_2^- leads to the two (meta)stable geometries of C_{2h} symmetry. One is the pairing configuration (type I) and the other is the resonant-bond configuration (type II). In the resonant-bond configuration, the distance l_{ij} between the i th and the j th Si atoms near to a vacant site (see Fig. 1 and Table I for labeling) holds the relation, $l_{12}(=l_{13}) < l_{23}$. The obtained $l_{12} = 3.60$ Å is shorter than the corresponding value (3.64 Å) without the Jahn-Teller distortion, indicating that atom 1 forms weak bonds with atoms 2 and 3 by the Jahn-Teller effect. Figure 2 indeed shows that the charge density between atoms 1 and 2(3) is slightly higher than that between atoms 2 and 3. The coordination number of atom 1 is five (three covalent bonds and two weak bonds) and thus the two weak bonds are *resonant*. The electron configuration is found to be $a_u^2 b_u^1$, consistent with the experimental result of ESR: The highest occupied level has amplitude on the mirror plane of C_{2h} (Fig. 3 indeed shows that the b_u level has amplitude on the plane). The reason for the level ordering between the b_u and a_u levels is that the former and the latter have antibonding and nonbonding characters, respectively, for the weak resonant bonds; the b_u level has nodes on the resonant bond axes between atoms 1 and 2 or 3 and thus has higher energy (Fig. 3). The calculated energy difference between the two levels is 22 meV.

In the pairing configuration (type I), $l_{23} < l_{12} = l_{13}$ (Table I). This indicates the formation of a *weak covalent bond* between atoms 2 and 3. Indeed, Fig. 2 shows that the charge density between atoms 2 and 3 is slightly higher than that between atoms 1 and 2(3). This pairing distortion is found to lead to the electron configuration of $b_u^2 a_u^1$; i.e., the energetical order of the two gap levels is reversed compared with that in the resonant-bond configuration. The energetical order of the two levels in the type I distortion is due to the fact that the a_u and b_u levels have the antibonding and bonding characters for the weak covalent bonds, respectively (Fig. 3). These characters are in contrast with the nonbonding (antibonding) character

TABLE I. Atomic geometries of V_2^+ and V_2^- . l_{ij} indicates the distance in Å between i th and j th atoms near to the vacancy site (see Fig. 1). θ is the angle of the back bond of the atom 1 and Δ is the amount of the displacement (Å) of atom 1 which is projected to the line from the crystal site to the nearest vacant site. The positive sign of Δ indicates inward displacement.

	V_2^+ (type I)	V_2^+ (type II)	V_2^- (type I)	V_2^- (type II)
l_{12}	3.75	3.68	3.65	3.60
l_{23}	3.61	3.78	3.55	3.69
θ	110.3	109.6	107.8	108.0
	110.3	109.6	107.8	108.0
	108.2	107.1	106.3	106.2
Δ	0.03	0.09	0.12	0.13

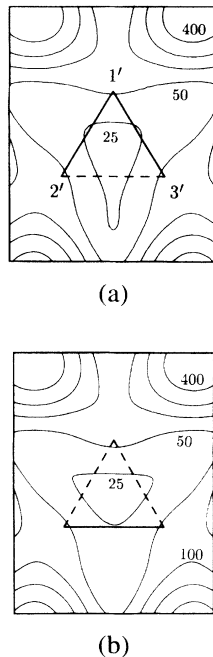


FIG. 2. The total electron density in V_2^- with the type II (a) and type I (b) distortions projected on the plane which is displaced inwards by 0.78 \AA along the $\langle 111 \rangle$ axis from the plane including atoms $1'$, $2'$, and $3'$. The vertices of the triangle correspond to the positions of the atoms (not on the plane) and the distance indicated by the solid line is shorter than that by the dashed line. The values of the contours are 25×2^n electrons/unit cell, where $n=0, 1, 2, 3$, or 4 .

of the a_u (b_u) level for the resonant bonds in the type II distortion. The obtained highest occupied level of a_u is inconsistent with the ESR data. (As Fig. 3 shows, the a_u level has the node on the symmetry plane.) This geometry is thus unlikely to be realized, although it is metastable. The a_g gap level, which was postulated to be located below the a_u level in the previous large pairing-distortion model [4], is found to be close to the conduction band bottom in the present calculation. It is emphasized that the large pairing-distortion geometry causing crossover of the a_g and a_u levels is found to be unstable; we actually choose some large pairing distortions for an initial geometry in the optimization process but finally reach the metastable geometry described above. Furthermore, we have performed tight-binding calculations [13] with sufficiently large unit cells containing up to 216 sites, and have obtained the same conclusion. The pairing Jahn-Teller model is therefore irrelevant for V_2^- .

The calculated total energy for the resonant-bond configuration (type II) is lower than that for the pairing configuration (type I) by 2.4 meV in V_2^- . This value is too small to conclude that the resonant-bond configuration is the stablest geometry. Considering the characters of the highest occupied levels in the two geometries as is stated above, however, we argue that the negatively charged divacancy V_2^- is accompanied by the resonant-bond distortion.

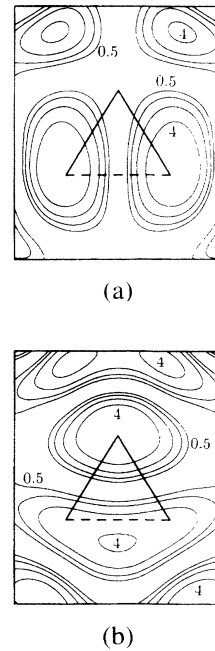


FIG. 3. The electron density in V_2^- with the type II distortion for the a_u (a) and b_u (b) levels. The plane in the figure is the same as in Fig. 2(a). The values of the contours are 0.5×2^n electrons/unit cell, where $n=0, 1, 2$, or 3 .

We also perform the total-energy calculations for the positively charged divacancy V_2^+ . Again, we find two (meta)stable geometries of C_{2h} symmetry: the pairing (type I) and the resonant-bond (type II) configurations (Table I). The electron configurations are $b_u^1 a_u^0$ and $a_u^1 b_u^0$ for type I and the type II, respectively. The ordering of the two levels in both types is the same as that in V_2^- , as is expected from the above discussion based on the bonding, nonbonding, and antibonding characters of the two levels. The calculated total energies for the two configurations are very similar to each other. We believe that the pairing configuration, in turn, is realized for the positively charged divacancy V_2^+ since the energy-level structure in the resonant-bond configuration is inconsistent with the ESR data [4]. It is therefore concluded that the pairing configuration is metastable (stable) in the negatively (positively) charged V_2 . In the pairing configuration, l_{12} (and l_{13}) in the negatively charged V_2 is smaller by 0.10 \AA than that in the positive charged case (Table I). This difference is expected to be the reason why the pairing configuration is metastable in the negatively charged V_2 : The shorter distance between atoms 1 and 2(3) gives some instability for the covalent bond between atoms 2 and 3. The decrease of l_{12} is enhanced by the larger inward displacement (Δ in Table I) of atom 1 and further the origin of the displacement is the larger electron population of the dangling bond as discussed later.

In order to corroborate our argument that V_2^- and V_2^+ are accompanied by the type II and type I distortions, respectively, we now compare the calculated wave functions

of the highest occupied level with the ESR [4,5] and the ENDOR [8] data: We focus on the amounts of the localization [usually labeled by $\eta^2(\%)$] and the s component [$\alpha^2(\%)$] for the wave function at each atomic site [14]. As is seen in Table II, the present model well reproduces the important features of the wave functions estimated from the experiment: The wave functions in both V_2^+ and V_2^- are very localized in atom 1, and the η^2 of the atom in V_2^- is slightly smaller than that in V_2^+ . Furthermore, the calculated α^2 in atom 1 for V_2^- is larger than that for V_2^+ , in good agreement with the experimental results.

The interesting feature that V_2^- has a larger value of α^2 at atom 1 than V_2^+ is attributed to the fact that atom 1 in V_2^- has the smaller bond angles with back-bond atoms (Table I); it is expected from a theory of chemical bonding [15] that, as the bond angle becomes smaller, α^2 increases because the s - p hybridization in the dangling bond is enhanced. The reasons for the smaller bond angles in V_2^- than those in V_2^+ are twofold. First, as the electron population of the dangling bond becomes large, the bond angles are likely to be small so that the dangling bond is stabilized by increase of its s component. The reduction of the bond angles is actually caused by the inward displacement (Δ); as Δ increases, the averaged bond angle becomes small, as seen in Table I [16]. Second, the inward displacement is affected by the Jahn-Teller effect: As seen in Table I, the inward displacement in the pairing configuration is smaller than that in the resonant-bond configuration for the positively charged divacancy. In the resonant-bond configuration, the formation of the resonant bonds is achieved mainly by the inward displacement of atom 1, reducing l_{12} and l_{13} . In the pairing distortion, however, the formation of the weak covalent bond with reduction of l_{23} enhances the inward displacements of atoms 2 and 3 but is irrelevant to the displacement of atom 1.

In conclusion, we perform the norm-conserving pseudopotential calculation based on the LDA, in order to clarify the atomic and electronic structures of the divacancy. We argue that V_2^+ is accompanied by the pairing Jahn-Teller distortion, whereas V_2^- is accompanied by the newly discovered resonant-bond distortion. The different types of Jahn-Teller distortions lead to the same representation (b_u) as the highest occupied level for the two charge

TABLE II. The wave function of the highest occupied level (b_u) in V_2^+ (type I) and V_2^- (type II). η^2 and α^2 are the amounts (%) of the localization and of the s component, respectively, at each atomic site.

			Theory	ENDOR	ESR
V_2^+ (type I)	atom 1	η^2	24.7	27.7	31
		α^2	14.3	11	11
	atom 2	η^2	4.9		2
V_2^- (type II)	atom 1	η^2	20.7	24.6	27
		α^2	21.7	17	17
	atom 2	η^2	6.3	3.0	3

states. This is a natural explanation of the puzzle that the wave functions of the highest occupied levels for V_2^+ and for V_2^- observed by the ESR and the ENDOR measurements are similar to each other. The detailed features of the wave functions calculated on the basis of the present model are in good agreement with the experiments.

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