Charge State Dependent Jahn-Teller Distortions of the *E*-Center Defect in Crystalline Si

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The atomic and electronic structures of a lattice vacancy trapped next to an As impurity (the *E*-center defect) in crystalline Si are investigated using *ab initio* pseudopotential total energy calculations. Jahn-Teller distortions and energies, reorientation barriers, defect wave function characters, and hyperfine coupling parameters associated with (−) and (0) charge states of the *E* center are calculated using a combination of real-space cluster and plane wave supercell methods. For the first time in the theoretical study of this defect, the senses of the Jahn-Teller distortions in the two charge states are found to be opposite, changing from a large pairing type in (0) to a large resonant-bond type distortion in the (−) charge state, in agreement with experimental data.

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A lattice vacancy (V) trapped next to an As dopant impurity is one of the most dominant and important defects produced by electron radiation of n-type crystalline Si. Labeled also as the E center, the As-V defect complex was first established in the mid-1960s via electron paramagnetic resonance (EPR) experiments [1]. Since then, the E center has been one of the most important benchmarks in understanding vacancy-impurity interactions, the vacancy-assisted diffusion of As in a Si lattice, as well as dopant and annealing dependence of conductivity in As-doped Si [2]. These are problems of both fundamental and current technological interest [3]. Over the last decade, increasing efforts in elucidation of doping limits in heavily As-doped Si have focused on complexes denoted by As_nV as the possible primary deactivating defect structure. The simplest of such defect complexes (corresponding to $n = 1$) is the E center. In spite of its importance and various electronic structure calculations carried out on this defect [4], its interesting ground-state atomic and electronic properties, in particular, the reversal of the Jahn-Teller distortions as a function of its charge state, as revealed by EPR and optical absorption experiments [1,5] have so far not been theoretically confirmed. In this Letter, we present, for the first time, results from large-scale first principles calculations on the atomic and electronic structures of the E center, which verify the experimental interpretations from nearly four decades ago.

In its ideal structure, the E center has a C_{3v} point group symmetry with the threefold axis along the As-V pair, as shown in Fig. 1. The highest occupied deep level inside the band gap is a doubly degenerate e state which can accommodate up to four electrons. Since this level is actually occupied by 1 and 2 electrons for the (0) and (−) charge states, respectively, the lattice Jahn-Teller (JT) distorts to assume a lower-symmetry structure and gains electronic energy. In the EPR and optical experiments of Watkins, Corbett, and Elkin, the E center was shown to produce a deep acceptor level at $E_c - 0.42$ eV observed by EPR in its neutral charge state. Both charge states were found to have the low symmetry of C_{1h}, and

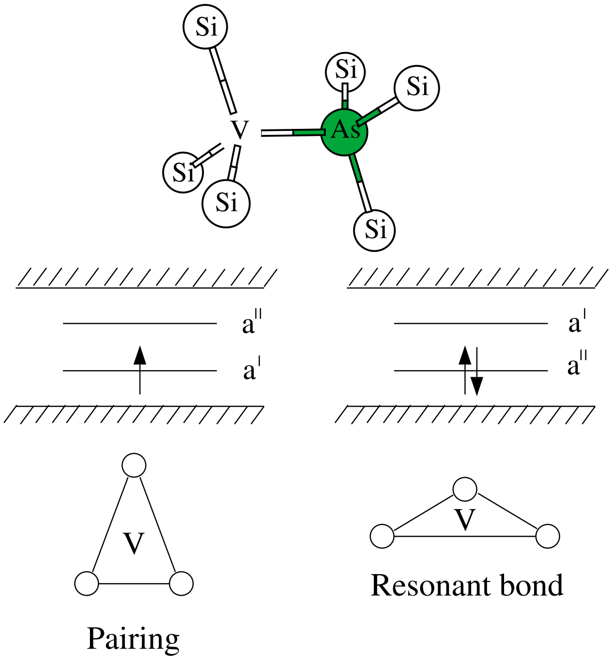

FIG. 1 (color online). Atomic structure of the ideal As-V pair (top), and electronic structure, level symmetries, and corresponding atomic structures viewed along the [111] As-V pair axis for large pairing distortions of the (0) charge state (bottom left) and large resonant bond distortions of the (−) charge state (bottom right).

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estimates of the JT energy $E_{\rm JT}$ indicated large Jahn-Teller distortions. The energy per unit strain along the (second-nearest neighbor) Si-Si bond $M = (dE/d\varepsilon)_{\text{Si-Si}}$ was measured to be $M = +11$ eV and $M = -20$ eV for the (0) and $(-)$ charge states, respectively [5]. From the sign of M, it was suggested that the distortion occurred in a pairing sense for the (0) charge state, and a resonant-bond sense for the $(-)$ charge state (Fig. 1). This rather interesting and unexpected suggestion is actually possible within the "Mexican hat" potential in the e-mode space, where the lowest-energy distortion can have either sign depending on the higher order terms in the Jahn-Teller coupling or anharmonic restoring forces [5]. The electronic structures of the two distortions differ from each other by a reversal of the ordering of the a' and a'' levels, as shown in Fig. 1. Of these two levels, a' (a'') has amplitude (a node) on the mirror plane of the C_{1h} distortion.

Another important defect related to the E center is the divacancy V_2 in Si. The theoretical versus experimental controversy [6] over the atomic and electronic structures of V_2 was recently resolved by the authors using *ab initio* cluster calculations, which confirmed the experimental findings [7]. The key aspect of the calculations was related to large, anisotropic, and long-ranged atomic relaxations along the $[1\bar{1}0]$ zigzag chains. From symmetry, the E center with an ideal C_{3v} symmetry resembles V_2 with its ideal D_{3d} symmetry. As such, large relaxations along the same zigzag chains on the vacancy side can be expected for the E center as well.

Most of our calculations for the atomic and electronic structures were performed using an *ab initio* cluster method in real space on bulk terminated Si clusters with H passivation at the boundaries. The calculations were done using the higher order finite difference method [8] with Troullier-Martins pseudopotentials at a grid spacing of 0.6 a.u. We used three clusters of compositions $\text{AsSi}_{84}\text{H}_{78}$, $\text{AsSi}_{128}\text{H}_{98}$, and $\text{AsSi}_{206}\text{H}_{158}$ with 9, 11, and 13 shells around the central defect, respectively, to gauge the size dependence of results. The E center was also modeled using a plane wave supercell approach for an independent check of the results. These calculations were performed using a bulk supercell of 216 atoms with $q = 2$ $\mathbf{k}$-point sampling and ultrasoft pseudopotentials at a 155 eV cutoff energy [9].

The relaxations in the first shell for the lowest-energy structures of both charge states of E center are shown in Fig. 2. For the (0) charge state, the lowest-energy structure has C_{1h} symmetry and large pairing (LP) distortions on the vacancy side, in agreement with experiment, and almost purely breathing mode distortions on the As side. As in V_2, the relaxations are large along $[1\bar{1}0]$, as manifested by the large displacements of the paired atoms by 0.5 Å toward each other. For the $(-)$ charge state, the lowest-energy structure has the same C_{1h} symmetry, but large resonant-bond (RB) type distortions on the vacancy side, in agreement with experiment. The apex and base atoms (in the isosceles triangle formed by the three Si atoms near the vacant site) have moved toward each other mainly along $[11\bar{2}]$ by the large amounts of 0.77 and 0.43 Å, respectively. In this quite distorted atomic configuration, the apex atom is fivefold coordinated with relaxed bond lengths of 2.40, 2.51 (two of them), and 2.77 Å (two of them). The bond angles for the nearest neighbor atoms deviate significantly from the tetrahedral bond angle (109.47°) down to 90° and 95°. The largest relaxed bond length of 2.77 Å between the apex atom and the two base atoms (which were second-nearest neighbors at 3.84 Å in the ideal defect) is only 18% larger than the bulk Si-Si distance, indicating the formation of two relatively strong covalent bonds.

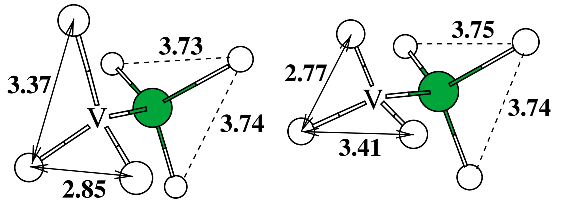

FIG. 2 (color online). Relaxed minimum-energy atomic structures in the first shell around the E center in its neutral (left) and negatively charged (right) states. Arsenic atom is represented by the gray circle. All distances between Si atoms are in Å. The second nearest neighbor distance in bulk Si is 3.84 Å. Both figures have a reflection symmetry with respect to the plane passing through the As-V axis and the apex Si atom.

Both charge states of the E center exhibit large, long-ranged, and anisotropic relaxation patterns (as in V_2) which involve atoms in the three zigzag chains of atoms passing through the vacant site. With the As-V pair axis pointing along [111], the (0) charge state with LP distortions has significant relaxations in the first, second, fifth, and eighth shells which contain atoms along the $[1\bar{1}0]$ zigzag chain containing the vacant site. Since the RB distortion of the $(-)$ charge state can be viewed as *two* LP distortions, significant relaxations in this case are observed in the same shells which contain atoms along the other *two* zigzag chains $[10\bar{1}]$ and $[01\bar{1}]$. In addition, since the distortions of the first shell atoms (especially the apex atom common to both zigzag chains) are quite drastic in the $(-)$ charge state, there are large relaxations in the third and sixth shells, resulting in a rather anisotropic relaxation pattern. The atomic relaxations calculated for the largest cluster considered ($\text{AsSi}_{206}\text{H}_{158}$) are in excellent agreement with results from supercell calculations, with almost all distortion amplitudes in the two different methods of calculation differing by not more than 0.02 Å. The largest difference of 0.05 Å is in the distortion amplitude of the apex atom in the $(-)$ charge state, which is found to be 0.72 Å in the plane wave supercell calculations.

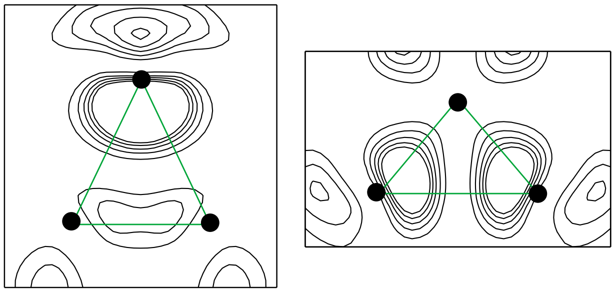

FIG. 3 (color online). Charge density contour plots for the highest occupied levels a' (left) and a'' (right) for the (0) and (−) charge states of the E center, respectively. The contour planes in both cases pass through the three Si atoms (filled circles) near the vacant site. Both figures are nearly to scale with respect to calculated interatomic distances.

TABLE I. Jahn-Teller energies for (0) and (−) charge states of the E center defect for structures with large pairing (LP) and resonant bond (RB) distortions along with experimental estimates from Refs. [1,5]. All energies are in eV. See the text for comparisons of theoretical values with experimental data.

Charge	LP	RB	Experiment
(0)	0.12	0.10	0.57
(−)	0.18	0.22	0.37

To verify the wave function characters of the highest occupied levels, we calculated charge density contour plots in the plane of the three Si atoms near the vacant site for both charge states (Fig. 3). For the (0) charge state, the highest occupied deep level is observed to have a' symmetry, which has amplitude in the mirror plane of the C_{1h} distortion in agreement with experiment. Most of the defect wave function is localized on the apex atom and in between the paired atoms giving rise to covalent bonds between second-nearest neighbors. We calculated the maximum value of the total charge density in between the paired atoms to be $0.38 e^-/\text{Å}^3$, which is $\approx 63\%$ of the maximum charge density along the Si-Si nearest neighbor bond [10]. For the (−) charge state, the highest occupied deep level is observed to have a'' symmetry with a node on the C_{1h} mirror plane. Most of the defect wave function is localized on the base atoms and in between the base atoms and the apex atom, again giving rise to two covalent bonds. In this case, the total charge density in between the apex and a base atom reaches a maximum value of $0.44 e^-/\text{Å}^3$, which is $\approx 73\%$ of the maximum Si-Si bond charge density, indicating a stronger covalency compared to the (0) charge state, as is evident from the shorter bond length.

We also calculated JT energies for structures with LP and RB distortions in both charge states, as shown in Table I. For the neutral defect, the structure with LP distortion is slightly more favorable than the structure with RB distortion, as indicated by the larger E_{JT} in the former. The E_{JT} value of 0.12 eV is smaller than the experimental estimate of 0.57 eV due to size effect (increasing the system size not only increases E_{JT} but also the difference between LP and RB distortions in V_2 [7]) and overestimate of experimental values. This overestimate of E_{JT} is typical for a system with long-ranged strain, since external stress assists in the motion of all $[1\bar{1}0]$ chain atoms, while the experimental E_{JT} is estimated by projecting out stress components for the first shell only [11]. In addition, the small energy difference of 0.02 eV between LP and RB bond distortions is consistent with small reorientation barriers between (three) symmetry-equivalent pairing configurations estimated to be 0.06 eV from low-temperature reorientation lifetime studies [1]. For the (−) charge state, on the other hand, the structure with RB distortion is more favorable than the structure with LP distortions by 0.04 eV. The E_{JT} value of 0.22 eV is in better agreement with estimates from experimental data. The data in this case are the optical absorption bands, in particular, the 6000 cm^{-1} absorption band, which has been identified by Watkins and Corbett as coming from electronic transitions from filled to empty molecular orbitals [5]. Ignoring off-diagonal coupling between the two upper a' states, this energy should roughly correspond to $2E_{\text{JT}}$. Since the experiment does not involve external stress in this case, the small discrepancy between experiment and theory is most likely due to size effects.

For further comparisons with experimental data, we calculated the hyperfine coupling parameters [12] for the E center defect in its EPR-visible neutral charge state. The calculated isotropic (a) and anisotropic (b) hyperfine parameters and wave function localization amounts η^2 along with the available experimental data are presented in Table II. Since most of the wave function in the (0) charge state is localized on the apex atom [Si(1)], the value of a at this site is quite large, as is also clear from the large wave function localization amount (55%). The agreement between theoretical and experimental values is very good, giving additional proof that the theoretically calculated structure with LP distortions in the neutral state indeed corresponds to the experimentally observed

TABLE II. Isotropic (a) and anisotropic (b) hyperfine parameters and wave function localization amounts (η^2). Si(1) and Si(23) refer to apex and base Si atoms in Fig. 1, respectively. The values in parentheses are experimental data [1].

Site	a (MHz)	b (MHz)	η^2
Si(1)	394	47	0.55
	(348)	(51)	(0.59)
As	59	1	0.01
	(43)	(2)	(0.01)
Si(23)	57	6	0.07

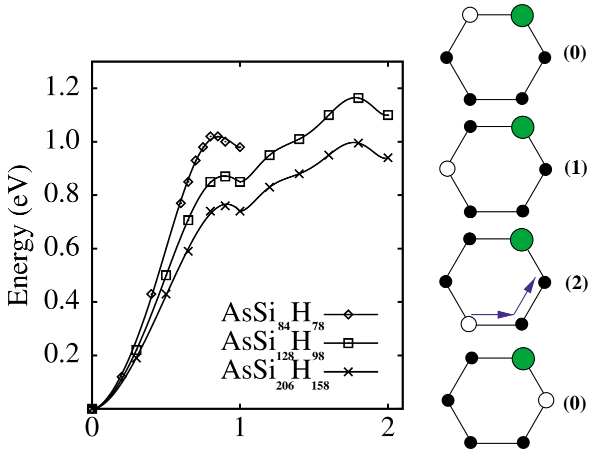

FIG. 4 (color online). Reorientation barrier calculations (left) for the As-V axis via vacancy migration through the sixfold ring of the Si lattice (right). The points (◇, □, ×) correspond to actual calculations for three cluster sizes fitted to smooth curves. The smallest cluster does not allow full relaxations along the (1) → (2) path, due to not allowing H-passivated Si atoms to move. The solid, gray, and open circles correspond to Si, As atoms, and the vacant site, respectively.

structure. Clearly, the structure with RB distortions in the (0) cannot be compatible with experimental hyperfine data, since the unpaired electron in this case is in the a'' state with a node at the Si(1) site, which would result in a vanishing isotropic hyperfine parameter.

Finally, we calculated the barrier for the reorientation of the As-V axis from a particular [111] direction to another one and compared the calculated values with experimental results from high temperature stress studies. The calculations were performed for the reorientation path suggested by Watkins and Corbett, which is a symmetric four-step jump of the vacancy along a sixfold ring of the Si lattice. Figure 4 shows the energy profile of the vacancy migration along the ring for three different cluster sizes. All atoms other than the relevant Si atom were allowed to relax in the calculations. Not too surprisingly, the results show a somewhat considerable size dependence of the reorientation barrier. The value we get for the largest cluster considered is 1.0 eV, in excellent agreement with the experimental value of 1.07 ± 0.08 eV [1] and other theoretical calculations [4].

In summary, the above theoretical calculations show for the first time the interesting reversal of the sense of the Jahn-Teller distortion as a function of the charge state of the As-V pair defect in Si, confirming the experimental ground-state structures and properties proposed by Watkins, Corbett, and Elkin.

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