Electronic Structure of the Jahn-Teller Distorted Vacancy in Silicon

N. O. Lipari, J. Bernholc, and S. T. Pantelides
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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This Letter reports self-consistent–field calculations of the electronic structure of the Jahn-Teller distorted vacancy in Si. With use of the tetragonal atomic displacements estimated by Watkins, it is found that the Jahn-Teller splitting of the sixfold-degenerate bound state in the gap is of the order of 0.5 eV. This, together with small breathing-mode displacements, results in a fully occupied doublet in the lower part of the band gap, in agreement with experimental observations.

The introduction of point defects such as vacancies and many chemical impurities in semiconductors gives rise to substantial rearrangements of the electron density and the atomic positions which are not well described by effective-mass and linear-response theories. The resulting localized states possess energy levels that lie deep in the forbidden energy gap and play an important role in determining many device properties through their influence on carrier lifetimes and impurity diffusion. Recently, the authors[1] and Baraff and Schlüter[2] independently reported the development of self-consistent Green's-function techniques which, for the first time, gave a detailed description of the electronic structure of the unrelaxed vacancy in Si at the same level of sophistication and accuracy characteristic of state-of-the-art electronic-structure calculations for bulk semiconductors, surfaces, and interfaces. However, that work did not take into account lattice distortions in the immediate vicinity of the vacancy. Such distortions, which are a manifestation of the Jahn-Teller effect, are known experimentally[3] to have a significant effect on the properties of the vacancy. The purpose of this paper is to provide a detailed theoretical picture of the consequences of Jahn-Teller distortions in terms of calculations which retain the level of accuracy achieved in the case of the undistorted vacancy.[1] We show that small, symmetry-breaking displacements of the nearest neighbors (of order a few tenths of an angstrom, as estimated by simple force models) have large effects on the electronic structure of the vacancy. In particular, they split the sixfold-degenerate bound state in the gap into a fully occupied doublet and an empty quadruplet. The splitting is large (of the order of half the band gap), so that the energy level of the occupied doublet is in the lower part of the band gap, in agreement with experimental observations.

From an analysis of electron-spin–resonance (ESR) data, Watkins[3] has concluded that the preferred distortion is tetragonal in nature, lowering the point symmetry from T_d to D_{2d}. Watkins also estimated the magnitudes of the displacements of the nearest neighbors with use of a simple force model. In addition to the symmetry-breaking displacements, the nearest neighbors can also move toward or away from the vacant site in the symmetric, so-called breathing mode, but no estimates of the corresponding displacements have been made.

Our calculations permit us to study the effects of symmetry-lowering and breathing distortions, independently, as well as simultaneously. The calculations were carried out using the method of Ref. 1,[4] the only difference being that the ionic contribution to the perturbation pseudopotential is now given by

$$U_i(\vec{r}) = -v_i(\vec{r}) - \sum_{\vec{R}} v_i(\vec{r}-\vec{R}) + \sum_{\vec{R}'} v_i(\vec{r}-\vec{R}'). \qquad (1)$$

Here $v_i(\vec{r})$ is a Si^{4+} ionic pseudopotential, $\vec{R}$ are the undistorted-lattice nearest-neighbor positions, and $\vec{R}'$ are the new nearest-neighbor positions. [In the case of the unrelaxed vacancy,[1] $U_i(\vec{r})$ contained only the first term in Eq. (1).] For each choice of the $\vec{R}'$, the potential arising from the change in the valence charge density is calculated self-consistently.

We find that a tetragonal distortion of the magnitude estimated by Watkins splits the sixfold-degenerate T_2 level, which in the undistorted case lies at $E_v + 0.7$ eV (where E_v is the valence-band edge), into a doublet B_2 at $E_v + 0.3$ eV and a quadruplet E at $E_v + 0.8$ eV. The doublet contains two electrons which maintain the neutrality of the defect and the quadruplet is empty. This result demonstrates explicitly that small symmetry-breaking displacements of the nearest neighbors of the vacancy can produce large level splittings.[5] Indeed, the calculated splitting, 0.5 eV, is of the order of half the band gap. Allowing for the pos-

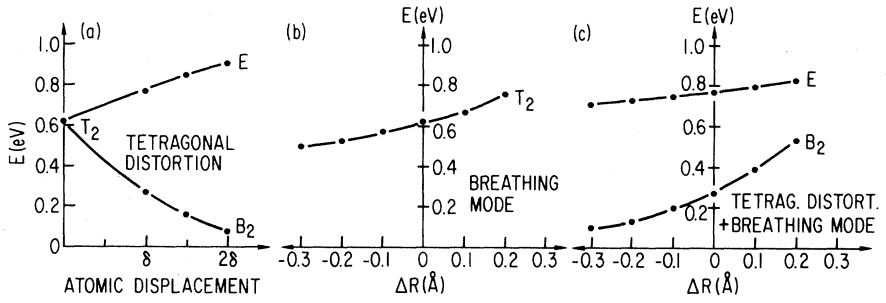

FIG. 1. (a) Jahn-Teller splitting of the T_2 vacancy level in the gap for various values of tetragonal displacements of the nearest neighbors. δ is equal to the value estimated by Watkins (Ref. 3). (b) The effect of breathing-mode displacements of the vacancy nearest neighbors on the T_2 vacancy level in the gap. Negative values correspond to inward displacements. (c) The combined effect of tetragonal displacements (as estimated by Watkins, Ref. 3) and various breathing-mode displacements of the vacancy nearest neighbors on the T_2 vacancy level in the gap. Negative values correspond to inward displacements.

sibility that Watkins's values of the displacements represent underestimates,[3] we repeated the calculation with larger displacements. The results are shown in Fig. 1(a).

In addition to symmetric-breaking displacements, we have investigated the effect of breathing-mode displacements of the nearest neighbors. The results, for several values of the atomic displacements, are shown in Fig. 1(b). As expected, no splitting occurs. The T_2 level simply moves up or down depending on whether the atoms move away from or toward the vacant site. We have also carried out calculations in which tetragonal distortions are combined with breathing-mode displacements. One set of results is shown in Fig. 1(c). In all cases, we find that inward breathing displacements lower the energies of both the doublet and the quadruplet, whereas outward breathing displacements raise both levels. Overall, the calculations indicate that a combination of tetragonal and breathing displacements can indeed place the energy level of the fully occupied doublet in the lower part of the gap, as found experimentally.[6] As Fig. 1(c) shows, this can be accomplished by combining Watkin's estimates for the tetragonal displacements with small inward breathing-mode displacements, or by combining larger tetragonal displacements with small outward breathing-mode displacements. The latter possibility is consistent with arguments suggesting that outward displacements, which strengthen the backbonds, are most likely to occur.[7] If that is indeed the case, our calculations indicate that the preferred breathing-mode displacements actually raise the energy level of the fully occupied doublet. This rather surprising behavior is actually consistent with the fact that the bound states in the gap have a predominantly dangling-bond character (Fig. 2). Detailed understanding of this

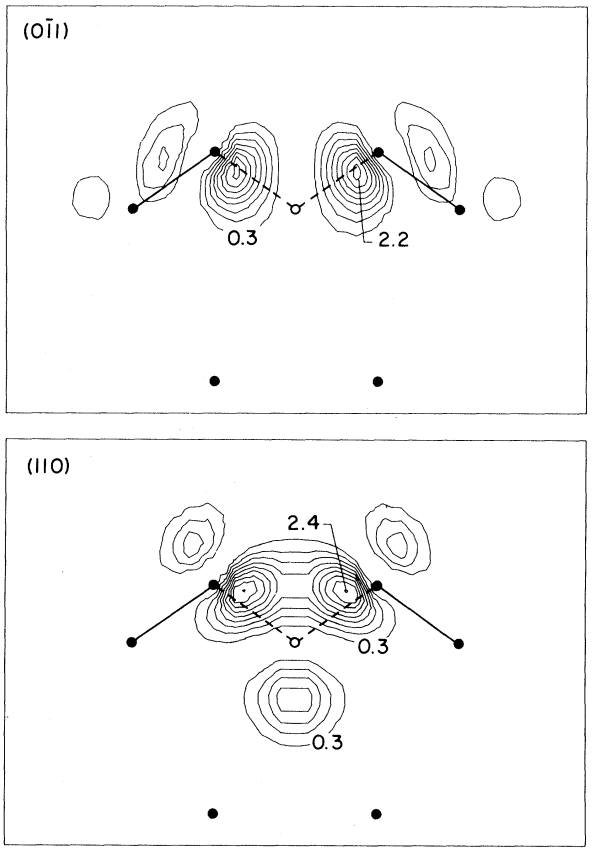

FIG. 2. The wave function of the B_2 bound state of the tertagonally distorted vacancy in Si in two inequivalent (110) planes.

behavior can be obtained in terms of a simple tight-binding model,[8] according to which both the T_2 bound state and the A_1 resonance at approximately $E_v - 0.7$ eV (Ref. 1) are basically linear combinations of the sp^3 dangling hybrids on the nearest neighbors, and the T_2-A_1 splitting is determined by the interaction V between dangling hybrids. When the atoms move in or out, two changes occur: First, the hybrid energy changes because its composition is no longer pure sp.[3] This dehybridization energy E_d can be estimated,[9] and, in fact, is found to lower the dangling-hybrid energy when the nearest neighbors move toward the vacancy. The second change occurs in the value of V. When the atoms move toward the vacancy, V is enhanced and the T_2-A_1 splitting increases. Thus, we conclude[10] that inward motion would result in a lowering of the A_1 resonance and an increase in the T_2-A_1 splitting. The T_2 level could move either way depending on the ratio of E_d and V. The opposite effects would be produced by outward motion. These simple predictions are confirmed by our self-consistent results (Fig. 3).

The present calculations also yield detailed information about individual wave functions and charge-density changes. In Figs. 2 and 4 we show some results in the case of a pure tetragonal distortion with use of Watkin's estimates of the atomic displacements. In Fig. 2 we show contour plots of the wave function of the occupied B_2 bound state in the gap. The two plots correspond to two inequivalent (110) planes, demonstrating a strong anisotropy of the wave function induced by the distortion. In Fig. 4 we show the total *change* in the charge density. The two plots correspond to the same two inequivalent (110) planes used in Fig. 2. We again observe a substantial amount of anisotropy caused by the tetragonal distortion. We also note that the change now extends beyond the cavity defined by the nearest neighbors. The nature of these charge-density changes depends on the type of assumed reconstruction and, in general, can be understood in terms of simple physical pictures. A detailed discussion will be given

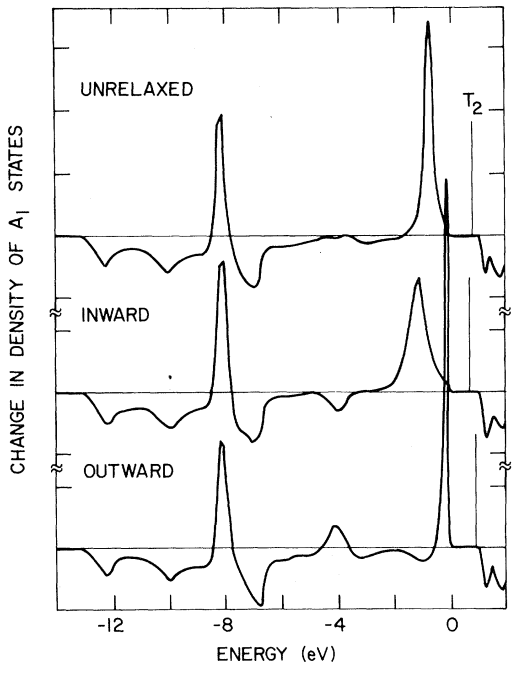

FIG. 3. The changes in the density of A_1 states within the band continua and the position of the T_2 bound state in the gap for the unrelaxed vacancy in Si, and for inward and outward breathing-mode displacement of the nearest neighbors.

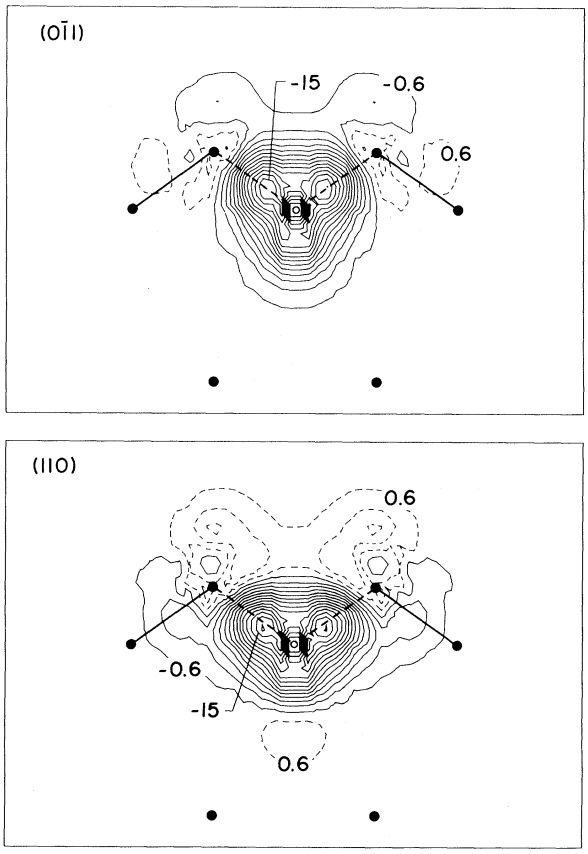

FIG. 4. The total change in the charge density in the case of the tetragonally distorted vacancy in Si in the same two inequivalent (110) planes as in Fig. 2. Solid lines correspond to removal of charge and dashed lines to addition of charge.

elsewhere.

In conclusion, we have used self-consistent-field calculations to study the effect of both symmetry-lowering and symmetry-preserving lattice distortions on the electronic structure of an isolated neutral vacancy in Si. We find that distortions of reasonable magnitude are very important and bring the bound-state energy to within the range of experimental measurements.

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[1]J. Bernholc, N. O. Lipari, and S. T. Pantelides, Phys. Rev. Lett. 41, 895 (1978).

[2]G. A. Baraff and M. Schlüter, Phys. Rev. Lett. 41, 892 (1978).

[3]G. D. Watkins, in *Lattice Defects in Semiconductors —1974*, The Institute of Physics Conference Proceedings No. 23, edited by F. A. Huntley (The Institute of Physics, Bristol and London, 1975), p. 1.

[4]The calculations were carried out using the ten-orbitals–per-atom basis of Ref. 1 and repeated with additional orbitals at sites 0.5 Å from the ideal nearest-neighbor positions in order to ensure convergence.

[5]Similar results have been obtained by the authors of Ref. 2 (private communication). Baraff, Kane, and Schlüter further adopted a phenomenological model for elastic forces and estimated the atomic displacements for various charge states of the vacancy.

[6]Experimentally, G. D. Watkins, J. R. Troxell, and A. P. Chatterjee [In, *Defects and Radiation Effects in Semiconductors—1978*, The Institute of Physics Conference Proceedings No. 46, edited by J. H. Albany, The Institute of Physics, Bristol and London, 1979), p. 16] identify a level at $E_v + 0.13$ eV, which they assign to either the $V^- \rightarrow V^0$ or the $V^0 \rightarrow V^+$ transition (see their Fig. 5). The energy level of the neutral vacancy is thus deduced to lie between $E_v + 0.04$ and $E_v + 0.04$ eV.

[7]The main argument is based on Pauling's bond-order/bond-length relation. For a summary of all arguments, see J. A. Van Vechten, Phys. Rev. 10, 1482 (1974). Semiempirical cluster calculations [e.g., R. P. Messmer and G. D. Watkins, Phys. Rev. B 7, 2568 (1973); K. L. Yip, Phys. Status Solidi (b) 66, 619 (1974)] have arrived at the same conclusion. Our calculations show that the backbond charge decreases when the nearest neighbors are moved toward the vacant site and increases in the opposite case. This result is consistent with a similar finding for surfaces [see, e.g., J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 31, 106 (1973), and Phys. Rev. B 8, 1777 (1973)]. See also the discussion by S. G. Louie, M. Schlüter, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B 13, 1654 (1976).

[8]J. Bernholc and S. T. Pantelides, Phys. Rev. B 18, 1780 (1978). See also J. Bernholc, N. O. Lipari, and S. T. Pantelides, to be published, and compare with the defect-molecule model, first introduced by C. A. Coulson and M. J. Kearsley, Proc. Roy. Soc. London, Ser. A 241, 433 (1957).

[9]See, e.g., W. A. Harrison, Surf. Sci. 55, 1 (1976).

[10]A more detailed discussion of these arguments will be given elsewhere.

[11]See Messmer and Watkins, Ref. 7.

Field-Induced Resistance Minimum in Palladium with Lattice Defects

G. Bergmann

Institut für Festkörperforschung, Kernforschungsanlage Jülich, D-5170 Jülich, West Germany

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Pd quench condensed onto a quartz plate in ultrahigh vacuum exhibits a pronounced resistance minimum in an external field. This anomaly has a two-dimensional origin but is not caused by the free surface atoms. A superposition with a small fraction of a Ni or Fe layer causes a similar anomaly as the magnetic field. The two effects are not additive. I suggest that a thin Pd sheet below the surface shows two-dimensional band ferromagnetism.

Low-temperature anomalies in the resistivity of metallic systems can indicate interesting physical phenomena such as ordering processes, phase transitions, formation of bound states, etc. A particularly interesting example is the occurrence of resistance minima in different metals, such as Kondo systems and metallic glasses. These systems respond differently to a magnetic field. An external magnetic field reduces the Kondo minimum but leaves the metallic-glass minimum unchanged.[1]

I will describe an experiment where an applied magnetic field builds up a pronounced resistance minimum. The subject of this investigation is

