Silicon Vacancy: A Possible "Anderson Negative-U" System

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This Letter analyzes the electron states associated with the silicon vacancy and proposes a distortion model for the surrounding atoms that is derived from self-consistent calculations for single-particle states and from model calculations of elastic restoring forces. The predicted level structure is such that V^+ is, contrary to currently accepted ideas, a metastable state which decays either to V^0 or to V^{++}, depending on the Fermi energy.

Our present understanding of the charge states associated with the isolated single vacancy in silicon is incomplete. Much of what is know derives from Watkins's[1] EPR studies and observations of low-temperature radiation damage. These studies make it clear that Jahn-Teller distortions of atoms near the vacancy are important in determining the electronic structure of this particular point defect. Watkins has also devised a qualitative lattice distortion model which provides a framework in which to reason about the experimental results.

In this present work, we adopt many of Watkins's ideas about lattice distortion and build from them a quantitative model, using our Green's-function technique[2] to evaluate some of the parameters of the model and using a modified Keating model[3] to evaluate some of the others. What emerges is a level structure which differs from currently accepted interpretations in several interesting ways. First, for p-type silicon we predict the stability of V^{++}, a state which, being EPR invisible, has never been directly observed nor previously considered. Second, we find that states V^0, V^+, and V^{++} form an "Anderson negative-U system"[4] so that V^+ is a metastable state, decaying either to V^0 or to V^{++}, depending on the Fermi-level position, and implying that a change in Fermi level which takes the system between V^0 and V^{++} will cause release or capture of *two* electrons per vacancy. For p-type silicon the activation energy for decay of the metastable V^+ is 0.16 eV and consistent, within the precision of our calculations, with what Watkins has measured in EPR in indium-doped samples.

Watkins's model of the vacancy has assumed that it can support four charge states, V^+, V^0, V^-, and V^{--}. To these four, we propose to add V^{++}. Here, we consider only the states V^0, V^+, and V^{++} which are associated with tetragonal lattice distortions. The states V^- and V^{--}, associated with a trigonal lattice distortion,[1] are important in n-type material.

Our basic model for the states V^0, V^+, V^{++} builds on the fact that self-consistent calculations of the electronic structure of the neutral *undistorted* vacancy reveal that a threefold orbital degenerate level of T_2 symmetry resides in the gap.[2,5] Occupying that state with one or two electrons, yielding V^+ or V^0, produces a situation which is unstable with respect to Jahn-Teller distortion. This splits the T_2 level into a singly degenerate level of B_2 symmetry and a doubly degenerate level of E symmetry. The sense of the distortion is such as to lower the energy of the B_2 level.

We choose as the two coordinates of our model Q, the linear displacement of a single atom in the tetragonal distortions (i.e., *half* the usual normal *mode amplitude*), and N_T, the number of electrons (0, 1, or 2) occupying the B_2 level. The total-energy functional of the system will be expanded to second order in Q. *Equilibrium* transitions in which N_T changes involve addition or removal of an electron from the Fermi reservoir (partially filled acceptor levels) which establishes a Fermi energy in the gap. We specify transfer energies as follows: μ is the energy to transfer an electron from the top of the valence band to the reservoir, $\epsilon_1(Q)$ is the energy to transfer an electron from the top of the valence band to the B_2 level when the level is initially empty and the lattice distortion is Q, and $\epsilon_2(Q)$ is the energy required to transfer a second electron from the top of the valence band to the B_2 level. The zero of energy for the total system will be its energy in the reference state $Q=0$, $N_T=0$. Because the reference state is symmetric and the distortion Q is *purely* symmetry lowering, the linear term in the system energy is contributed only by ϵ_1

and ϵ_2. Thus, the total energy of the three states we are interested in can be written as follows:

$$V^{++}: N_T=0, \quad E_0(Q)=\tfrac{1}{2}kQ^2$$
$$V^{+}: N_T=1, \quad E_1(Q)=\tfrac{1}{2}kQ^2+\epsilon_1(Q)-\mu \qquad (1)$$
$$V^{0}: N_T=2, \quad E_2(Q)=\tfrac{1}{2}kQ^2+\epsilon_1(Q)+\epsilon_2(Q)-2\mu.$$

The energies $E_i(Q)$ can be plotted on a configuration-coordinate diagram such as that used by Henry and Lang to discuss nonradiative transitions.[6] In such plots, the lowest minimum of the three curves indicates the ground state of the system, and the energy difference between the minimum of a particular curve and its crossing point with another curve is the activation energy out of that particular state. There is, however, one important difference between Henry and Lang's curves, which describe capture from a *band*, and our Eqs. (1), which describe the transfer of electrons between the *Fermi reservoir* and the localized level. Because Eq. (1) involves the Fermi energy μ, the state for which the system energy is lowest depends on μ, as is illustrated in Figs. 1(a) and 1(b). We let $E_i(\mu)$ ($i=0$, 1, 2) denote the minimum value of $E_i(Q)$ for a given μ. By plotting $E_i(\mu)$ as done in Fig. 1(c), we can determine which N_T is the ground state for any value of μ and thus determine the μ dependence of the equilibrium charge state of the vacancy. Used for activation energies, this prescription applies to direct transfer of an electron between vacancy and acceptor.

Because of e-e repulsion, we expect $\epsilon_2(Q) > \epsilon_1(Q)$. The spatial extent of the states we have calculated suggests that the difference is not strongly dependent on Q. Therefore, we shall put $\epsilon_2(Q)=\epsilon_1(Q)+U$, where U is a constant. Furthermore, over the range of distortions we have examined, $\epsilon_1(Q)$ is linear, so that $\epsilon_1(Q)=\epsilon_L-VQ$. These forms, combined with Eqs. (1), give us

$$E_0(\mu)=0, \quad E_1(\mu)=\epsilon_L-\mu-E_{JT}, \qquad (2)$$
$$E_2(\mu)=2E_1(\mu)-\eta,$$

where $E_{JT}=V^2/2k$ and $\eta=2E_{JT}-U$. As Fig. 1(c) reveals, for $\eta>0$, $E_0(\mu)$ or $E_2(\mu)$ is always the state of lowest energy, while $E_1(\mu)$ is always an excited state of the system. The condition for $\eta>0$ is that $E_{JT}>U/2$, which will be recognized as Anderson's condition for a negative effective U.[4]

The Fermi energy E_F for which the transition between V^0 and V^{++} occurs is that for which $E_0(\mu)=E_2(\mu)$, i.e., $E_F=\epsilon_L-2E_{JT}+U/2$. Stability of V^{++} requires that $E_F>0$. If E_{JT} is too large, the "negative-U" aspects will be enhanced, but V^{++} will not be stable at accessible values of μ in the gap.

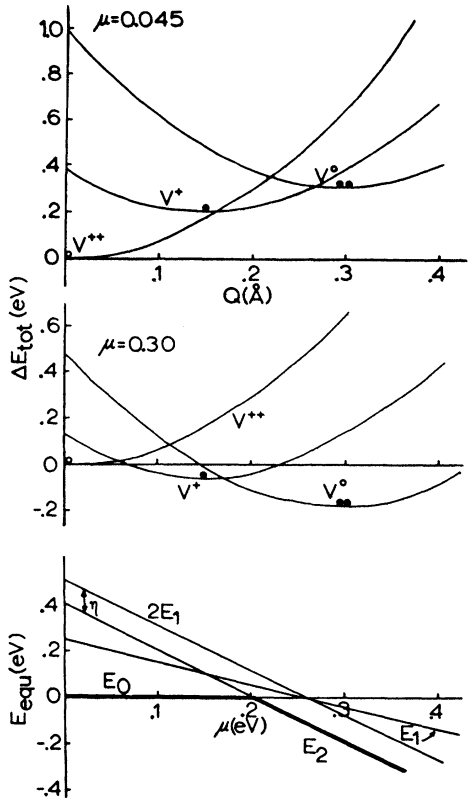

FIG. 1. Total energy of V^0, V^+, V^{++} as a function of tetragonal distortion Q for two positions of Fermi level: (a) $\mu=0.45$ eV (boron acceptors, V^{++} ground state), (b) $\mu=0.30$ eV (V^0 ground state). (c) Equilibrium energies as a function of μ. System ground state is indicated by heavy line.

Transitions involving transfer of an electron between the vacancy and the top of the valence band can also occur. Activation energy for these processes is given as before, by calculating the difference between the minimum and the crossing, but with two differences. First, μ, the energy of the reservoir which supplies electrons to the vacancy in Eqs. (1), must be set equal to zero. Second, the energy μ, required to create the hole needed to permit the hole-capture process to take place, must be added to the hole-capture activation energy. This gives

$$(V^+\rightarrow V^0)_{act}=\left(1-\frac{\epsilon_L+U}{2E_{JT}}\right)^2\times E_{JT} \qquad (3a)$$

$$(V^+\rightarrow V^{++})_{act}=\left(1-\frac{\epsilon_L}{2E_{JT}}\right)^2\times E_{JT}+\mu. \qquad (3b)$$

[Corresponding formulas for the activation ener-

gy of the direct processes omit the μ in Eq. (3b) and replace ϵ_L by $\epsilon_L - \mu$ in both equations above.]

We have performed fully self-consistent, local-density–functional calculations of the *undistorted* vacancy with the T_2 state occupied by one, two, and three electrons (i.e., charge states V^+, V^0, and V^-), using our self-consistent Green's-function technique. We obtain the eigenvalues $\epsilon_{T_2}(n)$ for $n = 1$, 2, and 3. In terms of Slater's transition-state arguments,[7] we identify $\epsilon_1(Q=0)$ with $\epsilon_{T_2}(n=\frac{1}{2})$ and $\epsilon_2(Q=0)$ with $\epsilon_{T_2}(n=\frac{3}{2})$. This treatment accounts for e-e repulsion within the local-density–functional formalism. Two small adjustments are added. The first adjustment arises from the fact that the Green's-function technique is inherently unable to deal with $1/r$ potentials. We therefore cut off the $1/r$ tail at $R_c \approx 7$ a.u. and estimate the correction to the eigenvalue using first-order perturbation theory (≈ 0.15 eV for V^+). The second correction arises from the outward breathing distortion of the neighbors nearest the vacancy, caused by strengthening their back-bonds. We expect that this energy correction will be weakly dependent on N_T and thus enter our total energy model only as a small additive constant. (Our self-consistent calculations on V^0 yield $d\epsilon_{T_2}/dQ_b = 0.5 \pm 0.2$ eV/Å for the T_2 bound state, increasing its energy with outward breathing. A reasonable value of $Q_b \approx 0.2$ Å, in accord with experimentally deduced surface relaxation values,[8] raises the eigenvalue of the T_2 bound state by only 0.1 eV.) Allowing the full 0.1-eV rise, we obtain $\epsilon_L = 0.42 \pm 0.1$ eV and $U = 0.25 \pm 0.05$ eV.

For the purpose of calculating the force V, we have studied distortions which move the four atoms nearest the vacancy together in pairs. Our self-consistent calculations for the tetragonally distorted V^0 give $d\epsilon_{B_2}/dQ = 2.25 \pm 0.2$ eV/Å, lowering the level upon atom pairing and raising the doubly degenerate E states by exactly half that amount. Test calculations for atom depairing show a sign reversal of the B_2-E splitting, which checks the assumption of linearity for atomic motions ≤ 0.3 Å. Bernholc, Lipari, and Pantelides[9] have informed us that they obtained $d\epsilon/dQ$ values within 50% of ours while Jaros, Rodriquez, and Brand[10] have reported $d\epsilon/dQ$ values quite different from these.

There is also a contribution to V from the screening of the B_2 bound state. Using a homogeneous-medium approximation, we estimate this effect to be less than a 20% reduction of V. This should be about compensated by the increase in V caused by displacement of more distant neighbors which we have neglected in our estimate. We therefore take $V = d\epsilon_{B_2}/dQ$.

Calculations for the distorted vacancy required more bands and more orbitals per unit cell in constructing G_0, the Green's function for the perfect crystal, than did those for the undistorted vacancy. We used ten s-, p-, and d-like wave functions, and two decay constants ($\alpha = 0.2$ and 0.6 a.u.) giving 40 LCAO bands in the Green's function rather than the 20 pseudopotential bands we had used earlier. Some measure of the degree of convergence this yields can be obtained from Fig. 2 which shows the total charge density in the neighborhood of the distorted defect. Notice how the density at the atom center and at the bond maximum follows the motion of the atoms.

In the absence of quantitative total-energy calculations, the spring constant k has to be estimated from model calculations. This has been done in the past with widely differing results.[11] We have therefore recalculated k by considering clusters of ~ 100 atoms containing one vacancy. The calculations are done *exactly* within a two-parameter Keating[3] force-constant model allowing all atoms in the cluster to relax in response to an imposed distortion of four nearest-neighbor atoms. The choice of bond-bending and bond-stretching parameters in the Keating model is of special importance because of the model's inability to describe Si phonon spectra correctly in all parts of the Brillouin zone (BZ). Since the local distortions around the vacancy contain Fourier components from the entire BZ with approximately uniform weighting, we have here used parameters which fit the softest phonon frequency over a large volume of the BZ. This volume does not include the small volume near $q = 0$. The parameters were chosen by fitting the compressibility

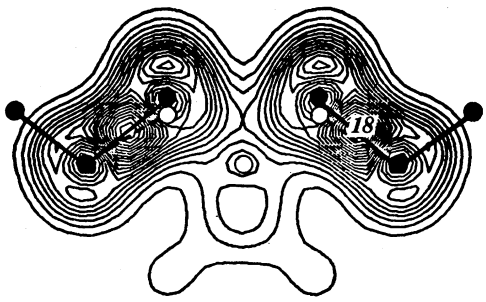

FIG. 2. Total valence charge distribution around the tetragonally distorted vacancy displayed in a (110) plane.

and the TA shear-mode zone-boundary frequencies correctly rather than $q \approx 0$ modes as Martin[12] had done. For tetragonal distortions we calculate $k = 14.8$ eV/Å^2. Test calculations show this value to be uncertain to about $\pm 10\%$ because of changes in the valence force field induced both by changes in N_T and by deviations from perfect crystal bond parameters. From the values of $V = 2.25$ eV/Å and $k = 14.8$ eV/Å^2, we get $E_{JT} = 0.17$ eV and equilibrium distortions of $Q = 0.15$ Å and $Q = 0.30$ Å for V^+ and V^0, respectively.

The Fermi energy E_F for transition from V^{++} to V^0 as the ground state is 0.20 eV. Watkins's measurement of the V^+-related EPR signal decay was in In-doped Si for which $\mu = 0.16$ eV, close to this transition energy. Thus, within the precision of our calculations, decay could be either $V^+ \rightarrow V^0$ or $V^+ \rightarrow V^{++}$. Activation energies for both decays turn out to be about equal, about 0.16 eV, which is close to Watkins's measured 0.06 eV.[1]

From the strength of the equilibrium V^+ EPR signal, Watkins[1] infers an energy difference of only 0.006 eV between V^+ and the ground state for boron-doped material. Our calculations yield a $V^{++} \rightarrow V^+$ difference of 0.20 eV. Although improving these estimates requires more precision than our calculations presently allow, other experiments might be used to refine the parameters of our model. In particular, the V^+ decay rate in heavily doped p-type material will be governed by direct transfer between the vacancy and the acceptor if their separation is comparable to the acceptor-state radius and the activation energy is lower than for hole emission. The direct-transfer activation energy is μ dependent and, for the parameters we have estimated here, very small. Thus, the activation energy for V^+ decay, measured in highly doped p-type material, should depend on the acceptor and should help to establish several of the parameters of the vacancy system.

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