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# THEORY OF THE SILICON VACANCY: AN "ANDERSON NEGATIVE U" SYSTEM

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We present a quantitative theory of the electron states associated with the silicon vacancy and propose a distortion model for the surrounding atoms that derives from self-consistent Green's function calculations for single particle states and from model calculations of elastic restoring forces. We find that the charge states $V^+$, $V^\circ$ and $V^{++}$ form an "Anderson Negative U System" and we predict two-electron transitions between $V^\circ$ and $V^{++}$.

## I. Introduction

Much of our present understanding of the charge states associated with the isolated single vacancy derives from Watkins' [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. Here we report calculations on a quantitative distortion model, using our Green's function technique [2] and a modified Keating model.[3] We obtain 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 the states $V^\circ$, $V^+$ and $V^{++}$ form an "Anderson negative U system" [4] so that $V^+$ is a metastable state, decaying either to $V^\circ$ or to $V^{++}$, depending on the Fermi level position. The calculated activation energies for charge transfer transitions are in quantitative agreement with DLTS measurements. For details we refer the reader to a complete discussion. [5] Here we only describe the essential physical features of the system.

## II. The Total Energy Functional

Consider the charge states $V^\circ$, $V^+$ and $V^{++}$ which are associated with tetragonal lattice distortions and important in p-type material. The states $V^-$ and $V^{--}$, associated with a trigonal lattice distortion, [1] are important in n-type material. The basic model for the states $V^\circ$, $V^+$, $V^{++}$ builds on the facts that self-consistent calculations of the electronic structure of the neutral <u>undistorted</u> vacancy reveal that a three-fold orbital degenerate level of $T_2$ symmetry resides in the gap.[2] Occupying that state with one or two electrons, yielding $V^+$ or $V^\circ$, 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 double degenerate level of E symmetry.

We choose as the two coordinates of our model Q, the linear displacement of a single atom in the tetragonal distortion, and $N_T$, the number of electrons (0, 1 or 2) occupying the lower $B_2$ 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 establish a Fermi energy in gap. We specify transfer energies as follows: $\mu$ is the energy to transfer an electron from the top of the valence band to the reservoir; $\varepsilon_1(Q)$, $\varepsilon_2(Q)$ are the energies to transfer an electron from the top of the valence band to the level when the level is initially empty, $\varepsilon_1$, or filled with one electron, $\varepsilon_2$. The total energy of the three states $V^{++}$, $V^{+}$ and $V^{\circ}$ can then be written as follows:

$$
\begin{aligned}
V^{++}: \quad & N_T = 0 \quad E_0(Q) = \tfrac{1}{2}kQ^2 \ , \\
V^{+}: \quad & N_T = 1 \quad E_1(Q) = \tfrac{1}{2}kQ^2 + \varepsilon_1(Q) - \mu \ , \\
V^{\circ}: \quad & N_T = 2 \quad E_2(Q) = \tfrac{1}{2}kQ^2 + \varepsilon_2(Q) - 2\mu \ . \qquad (1)
\end{aligned}
$$

The energies $E_i(Q)$ can be plotted on a configuration coordinate diagram . However, since Eq. (1) describes the transfer of electrons between the Fermi reservoir and the localized level, it involves the Fermi energy $\mu$. The state for which the system energy is lowest depends on $\mu$, as is illustrated in Figs. (1a), (1b). By plotting the minimum value $E_i(\mu)$ of each curve Fig. (1c), we can determine which $N_T$ is the ground state for any value of $\mu$ and thus determine the $\mu$ dependence of the equilibrium charge state of the vacancy.

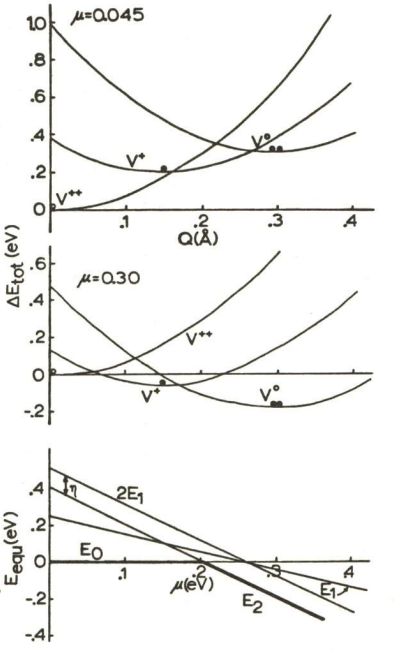


Fig. 1 Total energy of $V^{\circ}$, $V^{+}$, $V^{++}$ as a function of tetragonal distortion Q for two positions of Fermi-level: a) $\mu = 0.45$ eV (boron acceptors, $V^{++}$ ground state), b) $\mu = 0.30$ eV ($V^{\circ}$ ground state). Bottom panel c) equilibrium energies as a function of $\mu$. System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

Because of e-e repulsion, we set $\varepsilon_2(Q) = \varepsilon_1(Q) + U$, where U is a constant. Furthermore, over the range of distortions we have examined, $\varepsilon_1(Q)$ is linear, so that $\varepsilon_1(Q) = \varepsilon_L - VQ$. These forms, combined with Eq. (1), give us

$$
\begin{aligned}
E_0(\mu) &= 0 \ , \\
E_1(\mu) &= \varepsilon_L - \mu - E_{JT} \ , \\
E_2(\mu) &= 2E_1(\mu) - \eta \ , \qquad (2)
\end{aligned}
$$

where $E_{JT} = V^2/2k$ and $\eta = 2E_{JT} - U$. As Fig. (1c) 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 is Anderson's condition for a negative effective U. [4] Transitions involving transfer of an electron between the vacancy and the top of the valence band occur. Expressions for activation energies of these processes are given in [5].

## III. Calculations and Results

We have performed fully self-consistent local density functional calculations of the undistorted vacancy with the $T_2$ state occupied by 1, 2, and 3 electrons (i.e., charge state $V^+$, $V^0$, and $V^-$), using our self-consistent Green's function technique. In terms of Slater's transition state arguments, we identify $\varepsilon_1(Q = 0)$ with $\varepsilon_{T2}(n = \frac{1}{2})$ and $\varepsilon_2(Q = 0)$ with $\varepsilon_{T2}(n = \frac{2}{2})$. This treatment accounts for e-e repulsion within the local density functional formalism. Two small adjustments are added. First, we 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 ($\approx 0.15$ eV for $V^+$). Second, an outward breathing distortion of the neighbors nearest the vacancy occurs, caused by strengthening their backbonds. 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. A reasonable value of 0.2 Å outward breathing raises the eigenvalue of the $T_2$ bound state by $\lesssim 0.1$ eV. We thus obtain $\varepsilon_L = 0.42 \pm 0.1$ 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 $d\varepsilon/dQ = -2.25 \pm 0.2$ eV/Å, lowering the $B_2$ level upon atom pairing.

The calculations for the distorted vacancy require 40 LCAO bands in the Green's function rather than the 20 pseudopotential bands we had used earlier for the undistorted vacancy. 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 <u>follows</u> the motion of the atoms.

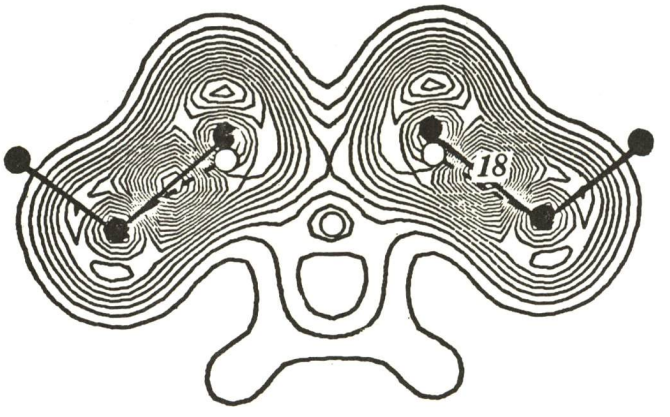


Fig. 2 Total valence charge distribution around the tetragonally distorted vacancy displayed in a (110) plane

To obtain the complete total energy, the spring constant k has been estimated from model calculations considering clusters of $\sim$ 100 atoms containing one vacancy. The calculations are done <u>exactly</u> 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. Since the local distortions around the vacancy contain many high Fourier components, we have here used parameters which describe compressibility and TA shear mode zone boundary frequencies correctly rather than $q \approx 0$ elastic modes. For tetragonal distortions we calculate $k = 14.8$ eV/Å$^2$ while for breathing distortions we find $k = 7.5$ eV/Å$^2$. These values are uncertain to about 10% due to 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 tetragonal equilibrium distortions of $Q = 0.15$ Å and $Q = 0.30$ Å for $V^+$ and $V^\circ$, respectively. The effective Anderson "U" = $U - 2E_{JT}$ is negative $\lesssim -0.1$ eV. This finding has been confirmed by very recent DLTS observations by Watkins and Troxell [6] who directly monitored the two-electron transition from $V^{++}$ to $V^\circ$. Furthermore, calculated activation energies to produce the metastable, but EPR visible $V^+$ are within 0.1 eV of experiment. A complete discussion is given in [5].

We have recently extended our calculations to include multiplet splittings of the localized levels.[7] The magnetic exchange splitting is calculated to be 0.35 eV for the undistorted neutral vacancy. However, combining multiplet and Jahn-Teller effects we find the ground state to be a singlet and dominated by Jahn-Teller distortions. The results for the negative U ground state thus remain essentially unaltered.

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7) M. Lannoo, G. A. Baraff and M. Schlüter, to be published.