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Cluster Model Calculations for Charge States of a Silicon Vacancy

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Abstract. To investigate the charge states of a silicon vacancy, we introduce a cluster model which includes both the Coulomb interaction $U$ between electrons in the dangling bond and the coupling $g$ between the electrons and Jahn-Teller phonons, and solve the model by using the numerical diagonalization method. It is found that, for $U > 0$ and $g = 0$, the ground state of the neutral charge state $V^0$ is spin singlet ($S = 0$) and orbital doublet. When $g$ is varied for a finite $U$, the ground state changes to the orbital triplet state with $S = 1$ at an intermediate coupling $g_1$, and finally changes to the orbital triplet state with $S = 0$ at a strong coupling $g_2$. The obtained result for $g > g_2$ is consistent with the low temperature elastic softening observed in non-doped crystalline silicon.

1. Introduction
Recent ultrasonic measurements have revealed that the elastic constant of non-doped crystalline silicon shows an anomalous softening at low temperature below 20K down to 20mK independent of the external magnetic field up to 16T \cite{1}. It is considered that the vacancy with the neutral charge state $V^0$ is responsible for the elastic softening. On the other hand, the softening of B-doped silicon disappears due to the external magnetic field at 2T or more, and it is considered that the charge state $V^+$ whose valence is +1 with $S = 1/2$ is consistent with the experimental results by taking into account of the spin orbit interaction \cite{2}. In early theoretical studies, Schlüter \textit{et al.} \cite{3, 4, 5} showed that the 3-fold orbital degeneracy in the ground state of a silicon vacancy is removed due to the tetragonal (E) mode Jahn-Teller distortion within the adiabatic approximation. In addition, when the chemical potential $\mu$ decreases, the vacancy state changes from $V^0$ state to $V^{++}$ state whose valence is +2 with $S = 0$ and then the $V^+$ state is unstable. These results seem to be inconsistent with the newly discovered elastic softening. Therefore, the nonadiabatic effect of the Jahn-Teller distortions, which was not considered in early theoretical studies, is thought to play crucial role for the low temperature elastic softening.

In our previous papers \cite{6, 7}, we investigated the silicon vacancy state, paying attention to the effect of the nonadiabatic Jahn-Teller distortions strongly coupled to electrons via the electron-phonon coupling, together with the correlation effect due to the electron-electron Coulomb interaction. For this purpose, we introduced a cluster model that takes account of the breathing, tetragonal and trigonal mode Jahn-Teller phonons (E+B+T) where the parameters were determined so as to reproduce the previous model derived by Schlüter \textit{et al.} for a silicon vacancy on the basis of the first-principle calculation \cite{3, 4}. What we found are; the $V^+$ state
becomes stable due to the strong coupling effect with the trigonal mode phonon (T) while unstable with the tetragonal mode phonon (E). In addition, the \( V^0 \) state shows the transition from \( S = 0 \) to \( S = 1 \) at a large \( g_T \) \[7\]. In this paper, we discuss the ground state of the \( V^0 \) in detail.

2. Model

Our cluster model includes 6 orbitals: 4 orbitals \((i = a \sim d)\) of dangling bonds in the nearest neighbor atoms of the vacancy and 2 orbitals from the valence band and the conduction band, respectively \[7\]. The model Hamiltonian is given by:

\[
\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_U + \mathcal{H}_Q + \mathcal{H}_{CV}. \tag{1}
\]

\(\mathcal{H}_0\) is a one-body term of electrons in the dangling bonds and \(\mathcal{H}_U\) is the Coulomb interaction term given by,

\[
\mathcal{H}_0 = \varepsilon \sum_{i=a}^{d} \sum_{\sigma=\pm1} a_{i\sigma}^\dagger a_{i\sigma} + t \sum_{i \neq j} \sum_{\sigma=\pm1} a_{i\sigma}^\dagger a_{j\sigma}, \tag{2}
\]

and

\[
\mathcal{H}_U = U \sum_{i=a}^{d} \sum_{\sigma=\pm1} a_{i\sigma}^\dagger a_{i\sigma} a_{i\sigma}^\dagger a_{i\sigma}, \tag{3}
\]

where \(a_{i\sigma}^\dagger\) and \(a_{i\sigma}\) are the creation and annihilation operators for an electron at site \(i\) with spin \(\sigma\), respectively. \(\varepsilon\) is a energy level of the dangling bonds and an electron in a dangling bond orbital transfers to another orbital via transfer integral \(t\). \(U\) is the on-site Coulomb interaction. \(\mathcal{H}_Q\) in Eq. (1) is an electron-lattice interaction term and is explicitly given as follows,

\[
\mathcal{H}_Q = \sum_{i,j=a}^{d} \sum_{\sigma=\pm1} \sum_\nu \sum_{\nu=1}^{\nu} Q_{\nu} a_{i\sigma}^\dagger a_{j\sigma} + \sum_\nu \left( \frac{P_{\nu}^2}{2M_{\nu}} + \frac{1}{2} K_{\nu} Q_{\nu}^2 \right) - \beta' Q_B, \tag{4}
\]

where \(Q_{\nu}\) and \(P_{\nu}\) are local distortion and the conjugate momentum with the effective mass \(M_{\nu}\) together with the spring constant \(K_{\nu}\), respectively. \(\beta'\) shows the effect of pressure from surrounding atoms. \(g_{ij}^{\nu}\) is the electron-lattice coupling constant \[7\]. Subscript \(\nu\) represents the mode of the Jahn-Teller distortions: B (B : \(x^2 + y^2 + z^2\)), E (E_1 : \(x^2 - y^2\), E_2 : \(3z^2 - r^2\)) and T (T_1 : \(yz\), T_2 : \(zx\), T_3 : \(xy\)) corresponding to the breathing, tetragonal and trigonal modes, respectively. Here, we replace the \(Q_{\nu}\) and \(P_{\nu}\) in Eq. (4) by the phonon operators, \(Q_{\nu} = \sqrt{\hbar/2M_{\nu} \omega_{\nu}} (b_{\nu} + b_{\nu}^\dagger)\) and \(P_{\nu} = i \sqrt{\hbar \omega_{\nu} / 2 (b_{\nu} - b_{\nu}^\dagger)}\), with \(\omega_{\nu} = \sqrt{K_{\nu}/M_{\nu}}\), for each mode \(\nu\), respectively. \(\mathcal{H}_{CV}\) in Eq. (1) is an effect of the conduction and valence band and is given as follows,

\[
\mathcal{H}_{CV} = \sum_{\sigma=\pm1} \left\{ \varepsilon_c a_{c\sigma}^\dagger a_{c\sigma} + \varepsilon_v a_{v\sigma}^\dagger a_{v\sigma} + \sum_{i=a}^{d} (t_c a_{i\sigma}^\dagger a_{c\sigma} + t_v a_{i\sigma}^\dagger a_{v\sigma} + \text{h.c.}) \right\}, \tag{5}
\]

where \(\varepsilon_c\) and \(\varepsilon_v\) are energy levels of the bottom of the conduction band and the top of the valence band, respectively. An electron in a dangling bond orbital transfers to the conduction band via \(t_c\) and to the valence band via \(t_v\), respectively. The parameters of this model are determined so as to reproduce the Schlüter’s results \[3, 4\] within the adiabatic approximation for the distortions together with the mean-field approximation for the Coulomb interaction.
3. Results
First, we examine the effect of the Coulomb interaction in the absence of \( H_Q \) and \( H_{CV} \) in Eq. (1). As shown in Fig. 1(a), the 4-fold degenerate dangling bond orbitals hybridize with each other to form the non-degenerate bonding orbital \((A_1)\) and the 3-fold degenerate anti-bonding orbitals \((T_2)\). In the case of the neutral charge state \( V^0 \) with \( A_1^2T_2^2 \) (see Fig. 1 (b)), 2 electrons are occupied in the \( A_1 \) orbital, and \( (1) \) two electrons are in the same \( T_2 \) orbital with spin singlet \((S = 0)\) and orbital triplet \(: |s^0_i\rangle\), \( (2) \) two electrons are in different \( T_2 \) orbitals with spin singlet \((S = 0)\) and orbital triplet \(: |s^0_j\rangle\), \( (3) \) two electrons are in different \( T_2 \) orbitals with spin triplet \((S = 1)\) and orbital triplet \(: |t_i^S\rangle\).

\[ \mathcal{H}_U = \frac{U}{4} \sum_{i,j=0,x,y,z} \left( c_{i\uparrow}^\dagger c_{j\uparrow} + c_{i\downarrow}^\dagger c_{j\downarrow} + c_{i\uparrow}^\dagger c_{j\downarrow}^\dagger c_{j\uparrow} c_{i\downarrow} + c_{i\downarrow}^\dagger c_{j\uparrow}^\dagger c_{j\downarrow} c_{i\uparrow} \right) + \sum_{i_1 \neq i_2 \neq i_3 \neq i_4} c_{i_1\uparrow}^\dagger c_{i_2\downarrow}^\dagger c_{i_3\downarrow}^\dagger c_{i_4\uparrow}^\dagger, \]  

where \( c_{i\sigma}^\dagger \) and \( c_{i\sigma} \) are the creation and annihilation operators for an electron at \( A_1 \) orbital \((i = 0)\) and \( T_2 \) orbitals \((i = x, y, z)\) with spin \( \sigma \), respectively. The charge state \(|s^0_i\rangle\) is an eigenstate of \( \mathcal{H}_U \) in Eq. (3) with eigenenergy \((5/4)U\), and \(|t_i^S\rangle\) is that with \((3/4)U\). As for the charge states \(|s^i_\uparrow\rangle\) \((i = 1, 2, 3)\), \( \mathcal{H}_U \) is written by the following matrix

\[ \begin{pmatrix} U & (1/4)U & (1/4)U \\ (1/4)U & U & (1/4)U \\ (1/4)U & (1/4)U & U \end{pmatrix}. \]  

The off diagonal term in the matrix (7) comes from the second term in the right-hand side of Eq. (6) and represents the transfer of a pair of \( \uparrow \) and \( \downarrow \) electrons between \( T_2 \) orbitals. Diagonalizing the matrix (7), we obtain the doubly degenerate eigenstates with eigenenergy \((3/4)U\) and non-degenerate one with \((3/2)U\), as previously obtained by Lannoo et al. [5] (see Table 1).

For large \( U \), we include the charge states \( A_1^4T_2^4 \) and \( A_0^4T_2^4 \) in addition to \( A_1^2T_2^2 \) and diagonalize the Hamiltonian by using the Householder method. Figure 2 shows the eigenenergies thus obtained as functions of \( U \). We find that the ground state of \( V^0 \) for \( U > 0 \) and \( g = 0 \) is spin singlet \((S = 0)\) and orbital doublet.

Finally, we also consider the effect of the electron-phonon interaction \( g \). We solve the Hamiltonian Eq. (1) by using the numerical diagonalization with the standard Lanczos
Table 1. Charge states of $V^0$ for $U > 0$ and $g = 0$

| Eigenenergy | Degeneracy | Spin | Eigenstate |
|-------------|------------|------|------------|
| $(3/2)U$    | 1          | $S = 0$ | $\frac{1}{\sqrt{3}} (|s_1^0\rangle + |s_2^0\rangle + |s_3^0\rangle)$ |
| $(5/4)U$    | 3          | $S = 0$ | $|s_i^0\rangle$ (i = 1, 2, 3) |
| $(3/4)U$    | 3 x 3      | $S = 1$ | $|t_{i}^{(z)}\rangle$ (i = 1, 2, 3; $S_z = 1, 0, -1$) |
| $(3/4)U$    | 2          | $S = 0$ | $\frac{1}{\sqrt{2}} (|s_1^0\rangle - |s_2^0\rangle)$ and $\frac{1}{\sqrt{6}} (-|s_1^0\rangle - |s_2^0\rangle + 2|s_3^0\rangle)$ |

Figure 2. Eigenenergies of $V^0$ versus Coulomb interaction $U$ for $g = 0$.

algorithm, where the cutoff of the phonon number is set to be 5 for breathing mode and 7 for trigonal (or tetragonal) mode. The ground state changes from orbital doublet state with $S = 0$ to the orbital triplet state with $S = 1$ at an intermediate coupling $g_{c1}^{T} \sim 2.5$ [eV/Å], and finally changes to the orbital triplet state with $S = 0$ at a strong coupling $g_{c2}^{T} \sim 8.5$ [eV/Å]. The calculated result for $g_{T} > g_{c2}^{T}$ is consistent with the ultrasonic experiments for the non-doped silicon [1]. We note that, in the strong coupling regime with tetragonal mode phonon instead of trigonal one, the grand state of $V^0$ remain orbital doublet with $S = 0$. Therefore, it is expected that the charge state at the silicon vacancy is in the strong coupling regime with trigonal mode phonon. The explicit and detailed results for $g > 0$ will be shown in a subsequent paper.

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