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_{c1}, and finally changes to the orbital triplet state with $S = 0$ at a strong coupling g_{c2}. The obtained result for $g > g_{c2}$ 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 [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 [2]. In early theoretical studies, Schlüter *et al.* [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 μ 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 [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 *et al.* for a silicon vacancy on the basis of the first-principle calculation [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 $g_{\rm T}$ [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;

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_U + \mathcal{H}_Q + \mathcal{H}_{\rm CV}. \tag{1}$$

$\mathcal{H}_0$ 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

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

where $a_{i\sigma}^\dagger$ and $a_{i\sigma}$ are the creation and annihilation operators for an electron at site i with spin σ, respectively. ε 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,

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

where Q_ν and P_ν are local distortion and the conjugate momentum with the effective mass M_ν together with the spring constant K_ν, respectively. β' shows the effect of pressure from surrounding atoms. g_ν^{ij} is the electron-lattice coupling constant [7]. Subscript ν 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_ν and P_ν in Eq. (4) by the phonon operators, $Q_\nu = \sqrt{\hbar/2M_\nu\omega_\nu}(b_\nu + b_\nu^\dagger)$ and $P_\nu = i\sqrt{M_\nu\hbar\omega_\nu/2}(b_\nu - b_\nu^\dagger)$, with $\omega_\nu = \sqrt{K_\nu/M_\nu}$, for each mode ν, respectively. $\mathcal{H}_{\rm CV}$ in Eq. (1) is an effect of the conduction and valence band and is given as follows,

$$\mathcal{H}_{\rm CV} = \sum_{\sigma=\pm1} \left\{ \varepsilon_{\rm C} a_{{\rm C}\sigma}^\dagger a_{{\rm C}\sigma} + \varepsilon_{\rm V} a_{{\rm V}\sigma}^\dagger a_{{\rm V}\sigma} + \sum_{i=a}^{d} \left(t_{\rm C} a_{i\sigma}^\dagger a_{{\rm C}\sigma} + t_{\rm V} a_{i\sigma}^\dagger a_{{\rm V}\sigma} + {\rm h.c.} \right) \right\}, \tag{5}$$

where $\varepsilon_{\rm C}$ and $\varepsilon_{\rm V}$ 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 $t_{\rm C}$ and to the valence band via $t_{\rm V}$, 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 $\mathcal{H}_Q$ and $\mathcal{H}_{\rm CV}$ 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

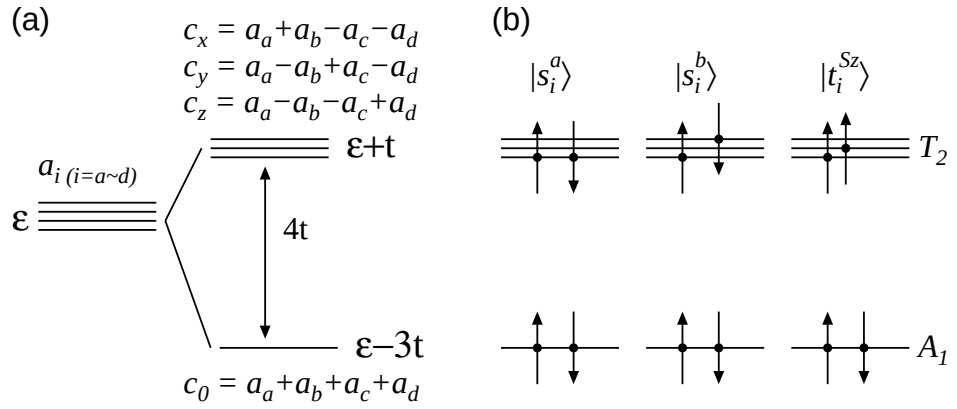

Figure 1. Energy level splitting due to the transfer integral t (a) and $A_1^2T_2^2$ configurations of the neutral charge state V^0 (b).

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 : $|s_i^a\rangle$, (2) two electrons are in different T_2 orbitals with spin singlet ($S=0$) and orbital triplet : $|s_i^b\rangle$, (3) two electrons are in different T_2 orbitals with spin triplet ($S=1$) and orbital triplet : $|t_i^{Sz}\rangle$.

$\mathcal{H}_U$ in Eq. (3) can be rewritten as

$$\mathcal{H}_U = \frac{U}{4}\left[\sum_{i,j=0,x,y,z}\left(c_{i\uparrow}^\dagger c_{i\uparrow}c_{j\downarrow}^\dagger c_{j\downarrow} + c_{i\uparrow}^\dagger c_{j\uparrow}c_{i\downarrow}^\dagger c_{j\downarrow} + c_{i\uparrow}^\dagger c_{j\uparrow}c_{j\downarrow}^\dagger c_{i\downarrow}\right) + \sum_{i_1\neq i_2\neq i_3\neq i_4} c_{i_1\uparrow}^\dagger c_{i_2\uparrow}c_{i_3\downarrow}^\dagger c_{i_4\downarrow}\right], \quad (6)$$

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 σ, respectively. The charge state $|s_i^b\rangle$ is an eigenstate of $\mathcal{H}_U$ in Eq. (3) with eigenenergy $(5/4)U$, and $|t_i^{Sz}\rangle$ is that with $(3/4)U$. As for the charge states $|s_i^a\rangle$ ($i=1,2,3$), $\mathcal{H}_U$ is written by the following matrix

$$\begin{pmatrix} U & (1/4)U & (1/4)U \\ (1/4)U & U & (1/4)U \\ (1/4)U & (1/4)U & U \end{pmatrix}. \quad (7)$$

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 $A_1^1T_2^3$ and $A_1^0T_2^4$ 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	$S = 0$	$\frac{1}{\sqrt{3}}(\|s_1^a\rangle + \|s_2^a\rangle + \|s_3^a\rangle)$
$(5/4)U$	3	$S = 0$	$\|s_i^b\rangle \quad (i = 1, 2, 3)$
$(3/4)U$	3×3	$S = 1$	$\|t_i^{Sz}\rangle \quad (i = 1, 2, 3;\ S_z = 1, 0, -1)$
$(3/4)U$	2	$S = 0$	$\frac{1}{\sqrt{2}}(\|s_1^a\rangle - \|s_2^a\rangle)$ and $\frac{1}{\sqrt{6}}(-\|s_1^a\rangle - \|s_2^a\rangle + 2\|s_3^a\rangle)$

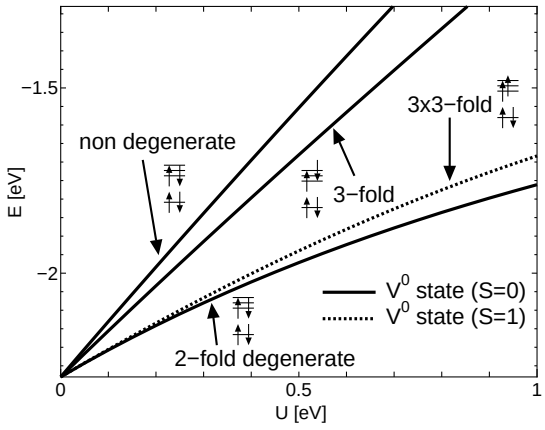

Figure 2. Eigenenergies of V^0 versus Coulomb interaction U for $g = 0$.

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 $g_{\rm T}^{c1} \sim 2.5$ [eV/Å], and finally changes to the orbital triplet state with $S = 0$ at a strong coupling $g_{\rm T}^{c2} \sim 8.5$ [eV/Å]. The calculated result for $g_{\rm T} > g_{\rm T}^{c2}$ 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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