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 $\mu$ 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 [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 $g_T$ [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:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_U + \mathcal{H}_Q + \mathcal{H}_{CV}. \quad (1)$$

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

$$\mathcal{H}_0 = \varepsilon \sum_{i,a} \sum_{\sigma = \pm 1} a_{i,a}^\dagger a_{i,\sigma} + t \sum_{i \neq j} \sum_{\sigma = \pm 1} a_{j,\sigma}^\dagger a_{j,\sigma}, \quad (2)$$

and

$$\mathcal{H}_U = U \sum_{i,a} \sum_{\sigma = \pm 1} a_{i,a}^\dagger a_{i,\sigma}^\dagger a_{i,\sigma}, \quad (3)$$

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

$$\mathcal{H}_Q = \sum_{i,j,a} \sum_{\sigma = \pm 1} \sum_{\nu} g_{i,j}^{\nu} Q_{\nu} a_{i,\sigma}^\dagger a_{j,\sigma} + \sum_{\nu} \left( \frac{P_{\nu}^2}{2M_{\nu}} + \frac{1}{2}K_{\nu}Q_{\nu}^2 \right) - \beta Q_B, \quad (4)$$

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. $g_{i,j}^{\nu}$ is the electron-lattice coupling constant [7]. Subscript $\nu$ represents the mode of the Jahn-Teller distortions: B (B : $x^2 - y^2$, 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, $Q_\nu = \sqrt{n/2M_\nu} \omega_\nu (b_\nu + b_\nu^\dagger)$ 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 $\nu$, respectively. $\mathcal{H}_{CV}$ in Eq. (1) is an effect of the conduction and valence band and is given as follows,

$$\mathcal{H}_{CV} = \sum_{\sigma = \pm 1} \left\{ \varepsilon_c a_{c,\sigma}^\dagger a_{c,\sigma} + \varepsilon_v a_{v,\sigma}^\dagger a_{v,\sigma} + \sum_{i=a}^d \left( t_c a_{i,\sigma}^\dagger a_{c,\sigma} + t_v a_{i,\sigma}^\dagger a_{v,\sigma} + \text{h.c.} \right) \right\}, \quad (5)$$

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 $\mathcal{H}_Q$ and $\mathcal{H}_{CV}$ 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 : $|s^0_i\rangle$, (3) two electrons are in different $T_2$ orbitals with spin triplet ($S = 1$) and orbital triplet : $|t^0_i\rangle$.

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

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

where $c_i^{\dagger}$ and $c_i$ 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 $|t^0_i\rangle$ is that with $(3/4)U$. As for the charge states $|s_i^i\rangle$ ($i = 1, 2, 3$), $\mathcal{H}_U$ 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 $A_1^2T_2^2$ and $A_1^0T_2^3$ 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          | $S = 0$ | $\sqrt{2} (|s^0_1\rangle + |s^0_2\rangle + |s^0_3\rangle)$ |
| $(5/4)U$    | 3          | $S = 0$ | $|s^0_1\rangle$ (i = 1, 2, 3) |
| $(3/4)U$    | 3 $\times$ 3 | $S = 1$ | $|t^{(2)}_{i}\rangle$ (i = 1, 2, 3; $S_z = 1, 0, -1$) |
| $(3/4)U$    | 2          | $S = 0$ | $\frac{1}{\sqrt{8}} (|s^2_1\rangle - |s^2_2\rangle)$ and $\frac{1}{\sqrt{6}} (-|s^2_1\rangle - |s^2_2\rangle + 2|s^2_3\rangle)$ |

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 $g^{cl}_t \sim 2.5$ [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 ground state of $V^0$ remains 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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