Effects of Electron Correlation and Electron-phonon Coupling on the quantum state of a Silicon Vacancy

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Recently, Goto *et al.* have discovered the anomalous elastic softening due to vacancy in crystalline silicon in the low-temperature ultrasonic measurements. To investigate the quantum state of the silicon vacancy, we introduce a cluster model which includes both the Coulomb interaction between electrons in the dangling bond and the coupling between the electrons and Jahn-Teller phonons. We solve the model by using the numerical diagonalization method and find that the V^+ state which has spin $S = 1/2$ is stable with the trigonal mode phonon while unstable with the tetragonal mode phonon. The obtained result is consistent with the newly observed experiment.

KEYWORDS: silicon vacancy, Jahn-Teller effect, electron-phonon coupling, nonadiabatic effect, electron correlation

1. Introduction

Lattice defect in crystalline silicon is one of the most influential factors to determine the quality of semiconductor devices. Although a void, which is a collection of vacancies, is observable, it is difficult to observe a single vacancy itself.

Recently, Goto *et al.* succeeded in the direct observation of the isolated vacancy in crystalline silicon using the ultrasonic measurement.[1)] They observed anomalous softening of elastic constants of the tetragonal (E) and trigonal (T) modes in non-doped and B-doped FZ silicon crystals at low temperature below 20K down to 20mK. which indicates that the vacancy with the triply degenerate states gives rise to the elastic softening. The widely spread orbital around the vacancy and the strong electron-lattice interaction enabled the direct observation of vacancies with extremely low concentrations. Remarkably, the softening in non-doped silicon is independent to the external magnetic field up to 16T but the softening in B-doped silicon disappears by 2T or more. Therefore it is inferred that the non-doped silicon has the V^0 vacancy state whose charge is neutral with spin $S = 0$ and B-doped silicon has the V^+ state whose valence is $+1$ with $S = 1/2$, respectively.

In early theoretical studies, Schlüter *et al.*[2,3)] 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 distortions within the adiabatic approximation. Additionally, the V^+ state was unstable; which is called the negative-effective U system. It seems to be inconsistent with the low-temperature elastic softening. However, the nonadiabatic effect of the Jahn-Teller distortions, which is thought to play crucial role at low temperature, was not considered there.

In our previous paper,[4)] 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 take account of the breathing and tetragonal mode phonons (E+B) as a simple extension to the previous model derived by Schlüter *et al.* for a silicon vacancy on the basis of the first-principle calculation.[2,3)] The result was that the degeneracy of the V^+ and V^0 states still remained against Jahn-Teller effect but the V^+ state was unstable like Schlüter's result. However, our model was not enough because it did not consider the trigonal mode (T) which shows larger softening than the tetragonal mode (E) in the experiment.[1)]

In this paper, we introduce a cluster model that take account of the all kinds of phonons (B+E+T) and investigate the silicon vacancy state.

The contents of this paper are as follows; In Sec. 2, we describe the model Hamiltonian for the silicon vacancy and the formulation used in this study. In Sec. 3, results of the calculation are presented. Finally, we summarize the results of the present work in Sec. 4.

2. Model and formulation

Our cluster model includes 6 orbitals: 4 orbitals ($i = 1-4$) of dangling bonds in the nearest neighbor atoms of the vacancy and 2 orbitals from the valence band ($i = 5$) and the conduction band ($i = 6$), respectively. The model Hamiltonian is given by;

$$\begin{aligned}\mathcal{H} &= \sum_{i=1}^{6}\sum_{j=1}^{6}\sum_{\sigma\pm1} t_{ij}(Q)a_{i\sigma}^{\dagger}a_{j\sigma} + U\sum_{i=1}^{4} a_{i\uparrow}^{\dagger}a_{i\uparrow}a_{i\downarrow}^{\dagger}a_{i\downarrow} \\ &+\frac{P_{\mathrm{B}}^2}{2M_{\mathrm{B}}} + \frac{P_{\mathrm{E}_1}^2 + P_{\mathrm{E}_2}^2}{2M_{\mathrm{E}}} + \frac{P_{\mathrm{T}_1}^2 + P_{\mathrm{T}_2}^2 + P_{\mathrm{T}_3}^2}{2M_{\mathrm{T}}} \\ &+\frac{1}{2}K_{\mathrm{B}}Q_{\mathrm{B}}^2 + \frac{1}{2}K_{\mathrm{E}}(Q_{\mathrm{E}_1}^2 + Q_{\mathrm{E}_2}^2) \\ &+\frac{1}{2}K_{\mathrm{T}}(Q_{\mathrm{T}_1}^2 + Q_{\mathrm{T}_2}^2 + Q_{\mathrm{T}_3}^2) - \beta' Q_{\mathrm{B}} \qquad (1)\end{aligned}$$

where $a_{i\sigma}^{\dagger}$ is the creation operator for an electron at site i with spin σ and U is the on-site Coulomb interaction. Q_ν

is distortions with the effective mass M_ν together with the spring constant K_ν. β' shows the effect of pressure from surrounding atoms. Subscripts 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$_1$: zx, T$_1$: xy) show the breathing, tetragonal and trigonal modes respectively. In eq. (1), transfer integrals $t_{ij}(Q)$ are explicitly given by;

$$(t_{ij}) = \begin{pmatrix} \varepsilon & t_{a,b} & t_{a,c} & t_{a,d} & t_{\rm C} & t_{\rm V} \\ t_{a,b} & \varepsilon & t_{b,c} & t_{b,d} & t_{\rm C} & t_{\rm V} \\ t_{a,c} & t_{b,c} & \varepsilon & t_{c,d} & t_{\rm C} & t_{\rm V} \\ t_{a,d} & t_{b,d} & t_{c,d} & \varepsilon & t_{\rm C} & t_{\rm V} \\ t_{\rm C} & t_{\rm C} & t_{\rm C} & t_{\rm C} & \varepsilon_{\rm C} & 0 \\ t_{\rm V} & t_{\rm V} & t_{\rm V} & t_{\rm V} & 0 & \varepsilon_{\rm V} \end{pmatrix} \tag{2}$$

with

$$\begin{aligned}
t_{a,b} &= -t - g_{\rm B}Q_{\rm B} - \frac{g_{\rm E}}{\sqrt{3}}\left(+\frac{Q_{\rm E_1}}{\sqrt{2}} - \frac{Q_{\rm E_2}}{\sqrt{6}}\right) + \frac{g_{\rm T}}{\sqrt{3}}Q_{\rm T_1} \\
t_{c,d} &= -t - g_{\rm B}Q_{\rm B} - \frac{g_{\rm E}}{\sqrt{3}}\left(+\frac{Q_{\rm E_1}}{\sqrt{2}} - \frac{Q_{\rm E_2}}{\sqrt{6}}\right) - \frac{g_{\rm T}}{\sqrt{3}}Q_{\rm T_1} \\
t_{a,c} &= -t - g_{\rm B}Q_{\rm B} - \frac{g_{\rm E}}{\sqrt{3}}\left(-\frac{Q_{\rm E_1}}{\sqrt{2}} - \frac{Q_{\rm E_2}}{\sqrt{6}}\right) + \frac{g_{\rm T}}{\sqrt{3}}Q_{\rm T_2} \\
t_{b,d} &= -t - g_{\rm B}Q_{\rm B} - \frac{g_{\rm E}}{\sqrt{3}}\left(-\frac{Q_{\rm E_1}}{\sqrt{2}} - \frac{Q_{\rm E_2}}{\sqrt{6}}\right) - \frac{g_{\rm T}}{\sqrt{3}}Q_{\rm T_2} \\
t_{a,d} &= -t - g_{\rm B}Q_{\rm B} - \frac{g_{\rm E}}{\sqrt{3}}\left(+\frac{2}{\sqrt{6}}Q_{\rm E_2}\right) + \frac{g_{\rm T}}{\sqrt{3}}Q_{\rm T_3} \\
t_{b,c} &= -t - g_{\rm B}Q_{\rm B} - \frac{g_{\rm E}}{\sqrt{3}}\left(+\frac{2}{\sqrt{6}}Q_{\rm E_2}\right) - \frac{g_{\rm T}}{\sqrt{3}}Q_{\rm T_3}
\end{aligned} \tag{3}$$

where ε, $\varepsilon_{\rm C}$ and $\varepsilon_{\rm V}$ are energy levels of the dangling bonds, the bottom of conduction band and the top of valence band and t, $t_{\rm C}$ and $t_{\rm V}$ are transfers between the dangling bond to the dangling bond, to the conduction band and to the valence band, respectively. $g_{\rm E}$, $g_{\rm B}$ and $g_{\rm T}$ are the electron-lattice coupling constants for the breathing, tetragonal and trigonal mode, respectively. The parameters of this model are determined so as to reproduce the previous theoretical results[2,3] within the adiabatic approximation for the distortions together with the mean-field approximation for the Coulomb interaction.

Here, we replace the distortion and the momentum 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.

Then, we take into account of both effects of the nonadiabatic electron-phonon coupling and the electron correlation by using the numerical diagnalization with the standard Lanczos algorithm for the Hamiltonian eq. (1) with eqs. (2), (3), where the cutoff of the phonon number is set to be 5 for each modes.

We calculate in case of both E+B and T+B. because the calculation that treat with the all kinds of phonons (B+E+T) is difficult due to the computational complexity.

3. Results and discussion

In Fig. 1, we carried out a calculation with the tetragonal and breathing mode phonons (E+B) and plot the energy difference $E(\alpha/\beta)$ between the occupancy states V^α and V^β of a silicon vacancy, where α and β show the number of valence of the vacancy site and the electron occupation number in the 4 orbitals of the dangling bonds are 2, 3, 4, 5 and 6 for the V^{++}, V^+, V^0, V^- and V^{--} states, respectively. When the chemical potential μ is varied, a transition between the occupancy states V^α and V^β takes place at $\mu = E(\alpha/\beta)$. The closed marks with solid lines represent boundaries separating the different stable occupancy states and open marks represent boundaries of unstable states. We note that the V^+ state is always unstable. It is consistent with the previous mean-field results.[2,3]

A calculation with the trigonal and breathing mode phonons (T+B) is carried out and $E(\alpha/\beta)$ are shown in Fig. 2. In this case, there is a region where the V^+ state is stable. This result is contrast to the result in the case of E+B which is above mentioned.

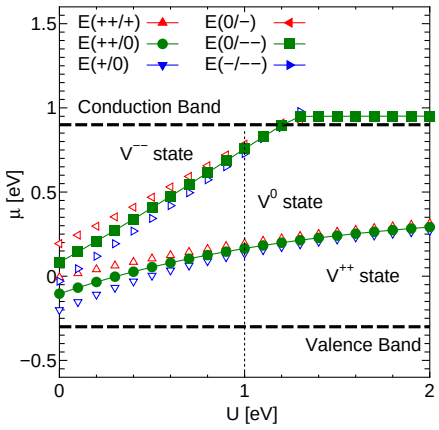

Fig. 1. Stable occupancy state of a silicon vacancy as a function of U and μ in the case of E+B. The vertical solid line shows the parameter corresponding to the Schlüter's result. The upper and the lower dashed horizontal lines represent ϵ_C and ϵ_V, respectively.

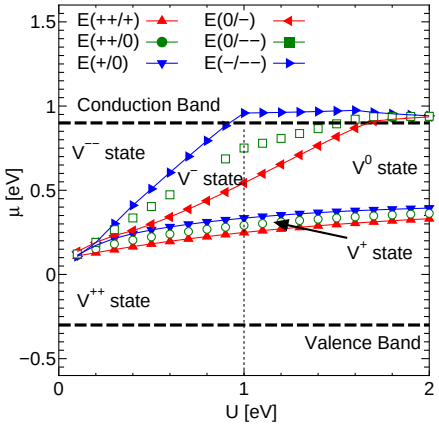

Fig. 2. Stable occupancy state of a silicon vacancy as a function of U and μ in the case of T+B.

Figures 3 (a) and (b) show fluctuations $\sqrt{\langle Q_{\rm E}^2\rangle - \langle Q_{\rm E}\rangle^2}$ and $\sqrt{\langle Q_{\rm T}^2\rangle - \langle Q_{\rm T}\rangle^2}$ as functions of the electron-lattice coupling constants $g_{\rm E}$ and $g_{\rm T}$ in the cases of E+B and T+B, respectively. These increase according to $g_{\rm E}$ and $g_{\rm T}$ in the V^0 and V^+ states, because of the orbital degeneracy and strong electron-phonon coupling due to the dynamical Jahn-Teller effects. On the other hand, the V^{++} state does not have orbital degeneracy so the fluctuations are almost invariable in

the change of $g_{\rm E}$ and $g_{\rm T}$. The jump of the V^0 state with large $g_{\rm T}$ means a change of state from $S = 0$ to $S = 1$.

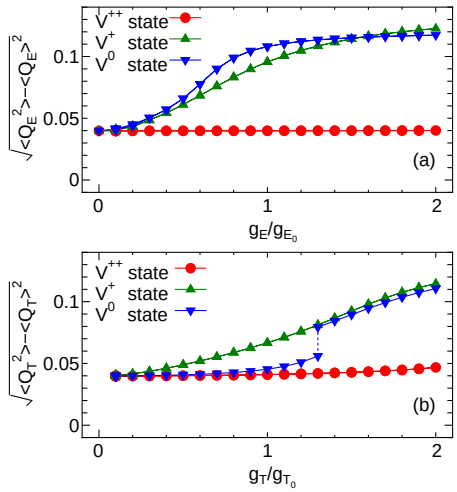

Fig. 3. Fluctuation of tetragonal distortion $\sqrt{\langle Q_{\rm E}^2\rangle - \langle Q_{\rm E}\rangle^2}$ for the V^{++}, V^{+} and V^{0} states as functions of $g_{\rm E}$ in the case of E+B (a) and Fluctuation of trigonal distortion $\sqrt{\langle Q_{\rm T}^2\rangle - \langle Q_{\rm T}\rangle^2}$ as functions of $g_{\rm T}$ in the case of T+B (b).

Figures 4 (a) and (b) show phonon spectra as functions of $g_{\rm E}$ and $g_{\rm T}$ in the cases of E+B and T+B, respectively. The spectra with $\hbar\omega = 0$ and phonon softening appear in the V^0 and V^+ states but the spectra are almost invariable in the V^{++} state.

4. Summary

We introduce the cluster model which includes both the electron-phonon coupling together with the electron-electron correlation and investigate the quantum state of the silicon vacancy by using the numerical diagonalization method.

We found that; the V^{++} state has no degeneracy and shows no anomaly. the V^+ and V^0 states still have orbital degeneracy against the Jahn-Teller effect because of the strong quantum fluctuation due to the nonadiabatic coupling between electrons and Jahn-Teller distortions. They have large fluctuations and show softening. the V^+ state is stable in the case of T+B but unstable in the case of E+B. These obtained results are striking contrasts to the previous theoretical results within the adiabatic approximation[2,3] and are consistent with the experimental result.[1]

At this stage, two questions still remain. The one of this is the mechanism of the external magnetic field dependency of the softening in B-doped silicon. It should meet a requirement that it solves the degeneracy of the orbit by solving the degeneracy of spin $S = 1/2$, and the $\vec{L}\cdot\vec{S}$ interaction is thought as a candidate. The another one is the V^0 state. The parameters of trigonal mode are not shown in the previous study, so we assumed that they are equal to the tetragonal ones though this state is sensitive to those. What is the ground state of the V^0 state with a realistic value of $g_{\rm T}$? It will be reported in a subsequent paper.

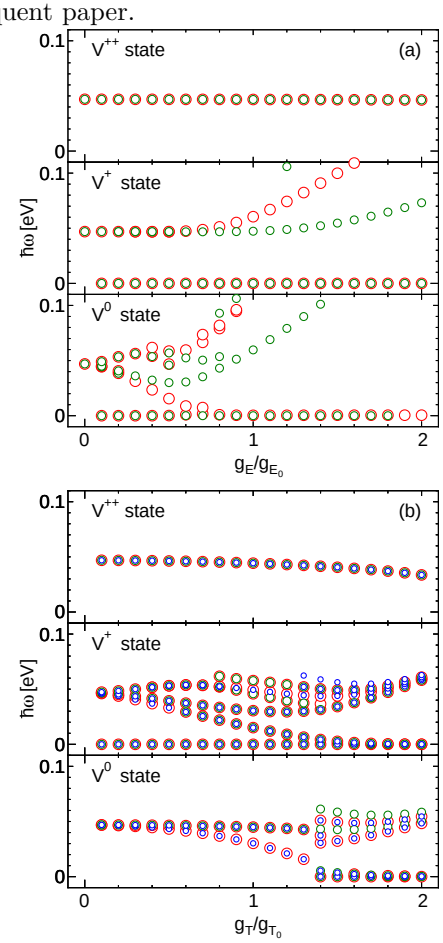

Fig. 4. Tetragonal mode phonon spectra for the V^{++}, V^{+} and V^{0} states as functions of $g_{\rm E}$ in the case of E+B (a) and as functions of $g_{\rm T}$ in the case of T+B (b).

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