On the elastic softening due to a vacancy in Si

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Abstract. Recently, an elastic softening at low temperatures has been observed in Si by an ultrasonic measurement. By assuming that an intrinsic defect of vacancy causes this softening, which is suggested by the experiment, the effects of monovacancy on the elastic properties have been theoretically studied. The primal concern of this paper is to survey existence of a low-energy excitation, which would be expected commonly for such an abnormal behavior. Although the static ground-state of monovacancy is stiff owing to the strong Jahn-Teller distortion, it is found that a low-energy excitation really exists in the motion of the neighboring Si atoms surrounding the vacancy.

1. Introduction
In an ultrasonic measurement conducted by Goto, it has recently observed that the elastic constant of Si is slightly but definitely decreased at low temperatures, less than 20 K [1], contrary to the normal behavior. The softening was observed for OH impurity in alkali halides [2], and other systems [3, 4], but it is the first time it is observed in semiconductors. By examining this elastic softening for specimens of various preparation conditions, these authors conclude that the softening is caused by monovacancy. Vacancies are intrinsically incorporated in Si wafers at some level. This effect could have a potential to use for quantitative detection of vacancy.

It is known that the vacancy (V) of silicon causes Jahn-Teller (JT) distortion depending on the charged state [5, 6, 7]. Furthermore, it also exhibits a negative U in the electronic system. The JT distortion in this system is significant. The energy gain by this distortion, $E_{JT}$ is estimated to be 0.17 eV, by Baraff et al [8]. Goto et al analyzed their ultrasonic data, and estimated the energy gain ($\Delta_{JT}$ in their notation) of the JT distortion to be 0.2 mK. There is a large discrepancy between these two. Besides this discrepancy, Goto et al stated that the tetrahedral symmetry around the vacancy is not broken down to 20 mK, which is also contradict with the previously established understanding. In this way, there are a number of issues to be studied further.

In this paper, the effect of vacancy on the elastic constant of silicon is studied by first-principles calculations. First, we re-examined the JT distortion, because the study of Baraff et al was so old, that the state-of-art calculation method might yield a different answer quantitatively or qualitatively. Second, in order to study the dynamic effect, which we believe to be important for understanding this phenomenon, MD simulations are performed. The underlying idea is that the observed transition temperature about 20 K could be a sign of a transition of the JT distortion to a high-symmetry configuration.
2. Calculation method
First-principles (FP) pseudopotential method with local-density approximation is used in this study. The used code is our own “Osaka2k” code [9]. It is generally believed that the concentration of vacancy is less than $10^{15} \text{cm}^{-3}$. Such a concentration is hopelessly low for the supercell method to simulate. What can be done by the supercell method is to calculate the elastic properties of a high concentration limit and to guess those of low-concentrations by interpolation. We use 64-atoms super cell. The plane-wave expansion was used with the cutoff energy of 21 Ry.

Even for the current status FP calculations, it is difficult to know the exact structure of the vacancy. Change in the calculation conditions yields a different conclusion. Puska et al report that the symmetry type of distortion ($D_{2d}$ etc) as well as the formation energy is varied by changing the $k$ point sampling and the cell size up to 256-atoms cell [10]. According to a recent study [11], the dependence of the size of supercell exists up to about 1000 atoms.

We are not aware of this problem too much. For the present purpose, the existence of JT distortion itself is important, while details of distortion type are not so important. For 64-atoms supercell, we have chosen $\Gamma$ point for the $k$ sampling throughout this study, just because this condition leads to $D_{2d}$ distortion for $V^0$, which is experimentally found.

3. Result and discussion
3.1. Adiabatic potentials
First, we examined the adiabatic potential of vacancy. The starting point is the doubly charged state $V^{2+}$: there is no electron in the degenerate $T_2$ orbital, so that no JT distortion occurs. The total energy of this state is expressed by $E_0(Q)$ as a function of the atom displacement $Q$. For the singly charged state $V^+$, the total energy is expressed by $E_1(Q)$. Similarly, $E_2(Q)$ is used for the neutral state $V^0$.

Baraff et al [8] modeled the adiabatic potential form by simple relationships

$$E_0(Q) = \frac{1}{2} kQ^2$$
$$E_1(Q) = \frac{1}{2} kQ^2 + \varepsilon_1(Q) - \mu$$
$$E_2(Q) = \frac{1}{2} kQ^2 + 2\varepsilon_1(Q) + U - 2\mu,$$

where $k$ is the force constant and $\mu$ is the chemical potential of electron. In these expressions, a one-electron level $\varepsilon_1$ appears, which is assumed to be $\varepsilon_1(Q) = \varepsilon_L - VQ$. The constant $V$ is the force causing JT distortion. In Eq. (1c), $U$ is a repulsive energy when one more electron is added. Nowadays, calculation of adiabatic potential $E(Q)$ is a quite standard in FP calculation, and we do that.

Expressions (1) are physically appealing, but a little bit trouble arises when we fit the actual potential curve with these forms. According to Eq. (1), the energy minima of various charge state $q$ appear with an equal spacing of $Q = V/k$, and the energy gain $E_{JT}$ by JT distortion is constant $E_{JT} = V^2/2k$ independent of $q$. Of course, in actual potential curves, neither of these properties hold.

To resolve this problem, we extend the model to include $Q$ dependence on $\varepsilon_1$ and $U$; $\varepsilon_1(Q) = (1/2)aQ^2 - VQ$ and $U(Q) = (1/2)cQ^2 - DQ + U_0$. These parameters have dependence on the distortion type, breathing ($b$) or $E$-type distortion ($E$). The obtained parameters are listed in Table 1. In the table, the force constants obtained by the valence-force (VF) model are compared, by assuming only the nearest-neighbor interactions.

The force constant of $E$ mode is four times as large as that of $b$ mode. At the first glance, this might be curious, because usually the breathing mode infers the stretching deformation of bond
Table 1. Comparison of the parameters of adiabatic potentials of the breathing ($b$) and $E$-type distortions. In VF model, the zone center optic mode is expressed by $(8/3)k_r$, with the force constant for the bond stretching mode $k_r = 10.35$ eV/Å$^2$.

|       | $k_b$ eV/Å$^2$ | $k_E$ eV/Å$^2$ | $V_b$ eV/Å | $V_E$ eV/Å | $U$ eV |
|-------|----------------|----------------|-------------|-------------|-------|
| present | 2.53           | 10.86          | 0.5         | 2.24        | 0.25  |
| BKS[8] | 7.5            | 14.8           |             |             |       |
| VF model | $(1/3)k_r$  | $(4/3)k_r$  |                  |              |       |
| $a_b$      | 0.37           | $a_E$         | 0.53        | 1.38        |       |
| $c_b$      | −0.012         | $c_E$         | 0.35        | 0.063       | 0.068 |

length resulting in the strongest restoring force. But, in the tetrahedral configuration, $E$-type deformation behaves more likely as stretching deformation than $b$ mode does. This is illustrated in the effective force constants $k_E = 4k_b$ in VF model.

We obtained $Q_E = 0.18$ Å in our adiabatic potential and $E_{JT} = 0.10$ eV (0.17). Here and hereafter, the value in the parentheses indicates that of [8]. From these values, we estimate $U_{eff} = −0.14$ eV (−0.09), that is, negative $U$. We have reached essentially the same conclusion as Baraff [8]. The JT energy $E_{JT}$ is of the order of 0.1 eV, which is sufficiently larger than the thermal energy at room temperature. Since the JT distortion of vacancy is so strong, it is unlikely that the transition about 20 K observed in the ultrasonic measurement corresponds to the recovery of a high-symmetry configuration from the JT distortion.

We have evaluated the elastic constants of the supercell containing a vacancy. The elastic constants $C_{11}$ is larger for $E$ distortion than for $b$ distortion. This is consistent with the fact that $E$ mode is stable over $b$ distortion. Therefore, we again ensure that the recovery of larger elastic constant with increasing temperature cannot be a sign of transition from $E$ to $b$ distortion.

3.2. MD simulation
In static calculation, we see that the JT distortion is quite stable. However, we further persuade possibility of the instability of $E$-type distortion by taking dynamic effect into account. With this motivation in mind, we performed MD simulation. The $E$ distortion causes a tetragonal distortion to the tetrahedron composed of the four nearest-neighboring Si atoms around the vacancy. There are three equivalent tetragonal distortions, namely, those of $x$, $y$, and $z$ direction. By using a $z$ distortion as the initial configuration, MD simulation is performed. As usual, the initial temperature $T_0$ is provided by giving initial velocities chosen randomly. We compare the results between $T_0 = 10$ K and 600 K. In Fig. 1, time evolution of the six bonds of the nearest-neighbor tetrahedron are compared. For tetragonal distortion, two bonds have the same bond length, whereas the remaining four bonds have another length.

We found a characteristic frequency about 77 cm$^{-1}$ in these figures. This is a quite low frequency. This is an unexpected result, because $E$ mode is expected to have a higher frequency as described in the previous section. By analyzing the eigenvector, we found that this 77 cm$^{-1}$ mode really has $E$ character in the neighboring tetrahedral unit.

Now, we see a significant change between $T_0 = 10$ and 600 K. For the low temperature, two groups of bonds, which characterize the direction of $E$ distortion, are moved independently. However, for the high temperature, two groups are interchanged each other. This implies that
all the three polarizations of $E$ mode are mixed. While the energy barrier between $E$ and $b$ distortions is high, the energy barrier among three polarizations of $E$ mode is sufficiently low, so that even at room temperature the tetrahedral unit easily overrides the barrier to deform to other direction of distortion. It is highly likely that the low-temperature transition observed experimentally is related to this low-frequency excitation.

4. Summary
The effects of monovacancy on the elastic properties have been investigated by the first-principles method. The static properties of monovacancy are qualitatively the same as those obtained by Baraff et al. The distortion of $E$ symmetry is stable against the $b$ type. However, different polarizations of $E$ distortion are quite easily interchanged at finite temperatures. This may cause the low-temperature transition observed in the ultrasonic measurement.

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