Vibrational Properties of Si Crystal with Vacancy: A Tight-Binding Study

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To analyze vibrational properties of Si crystal with a single charge-neutral vacancy, we perform large-scale simulations based on tight-binding molecular-dynamics method. Vibrational modes and frequencies are obtained by diagonalizing dynamical matrix within a harmonic approximation. Results indicate that there exist vibrational modes spatially localized around the vacancy and large frequency shifts associated with the localized modes contribute significantly to reduction of the vibrational free energy.

1. INTRODUCTION

Progress in wafer fabrication technology for semiconductor devices is made by the method to control defects in silicon crystal. Vacancy is representative of the defects and, in fact, vacancy-rich wafer are generally used in the device fabrication. Precise knowledge of the formation/migration energy of the Si vacancy has been a key to understanding of that. Despite a number of theoretical approaches have been attempted, the absolute values of those fundamental quantities for Si vacancy have not been precisely identified yet [1].

In experiment, a recent discovery of the elastic softening of Si crystals by ultrasonic measurements at cryogenic temperatures (< 10K) is expected to make progress in the study of vacancy in Si. Goto *et al*. [2] have proposed a mechanism of the softening based on an interaction between strain field and localized defect orbital. This mechanism has been well established in the *f*-electron systems such as rare-earth compounds [3]. In defective Si crystals, however, the presence of such an electronic state localized at the defect has not been quantitatively evidenced, at least, within theoretical treatments.

In this paper, vibrational properties of Si crystal with a single vacancy are investigated by using Tight-

Binding Molecular Dynamics (TBMD) simulations. Especially, localization of the vibrational mode, which appears due to the presence of the defect, and its contribution to the free energy are emphasized in the analyses.

2. METHODS

In the TB method, the total energy of a system is composed of the electronic band-structure energy and the repulsive energy. The electronic band-structure energy is expressed by

$$E_{elec} = 2\sum_{n=1}^{occ.}\varepsilon_n = 2\sum_{n=1}^{occ.}\mathbf{c}_n^{\dagger}\mathbf{H}\mathbf{c}_n \, ,$$

where $\mathbf{H}$ is the TB Hamiltonian matrix and $\mathbf{c}_n$ is its eigen-vector of n-th state. The repulsive energy is expressed by summation of classical interaction between atoms. For hopping parameters in Hamiltonian matrix elements and parameters in the repulsive potentials, we adopt the model proposed by Kwon *et al.*[4]. The number of Si atoms in the simulation cell is 511 (=512-1) and k-space integration is approximated by sampling only Γ-point.

MD simulations are performed via calculating interatomic forces by the Hellman-Feynman theorem. Initially, the defective system was prepared by removing a Si atom from the perfect crystal. We then performed TBMD run to obtain a relaxed configuration by quenching the system.

After the relaxed configuration is obtained, the dynamical matrix $D_{i\alpha j\beta}$ is diagonalized to calculate vibrational modes. Here i and j are indices of particles and α and β represent indices of coordinates (x,y,z). The dynamical matrix is calculated again through the Hellman-Feynmann theorem as

$$D_{i\alpha,j\beta} = \frac{\partial^2 E}{\partial r_{i\alpha}\partial r_{j\beta}} = \frac{\partial^2 E_{repul}}{\partial r_{i\alpha}\partial r_{j\beta}} + 2\sum_{n=1}^{occ.}\mathbf{c}_n^{\dagger}\frac{\partial^2 \mathbf{H}}{\partial r_{i\alpha}\partial r_{j\beta}}\mathbf{c}_n \, .$$

3. RESULTS

Figure 1 depicts the relaxed configuration viewed along a <111> direction. Before relaxation, Si atoms around the vacancy are kept at T_d symmetry. After relaxation, on the other hand, they moved to form D_{2d} symmetry due to the Jahn-Teller effect, which is well-known from many other theoretical analyses and simulations.
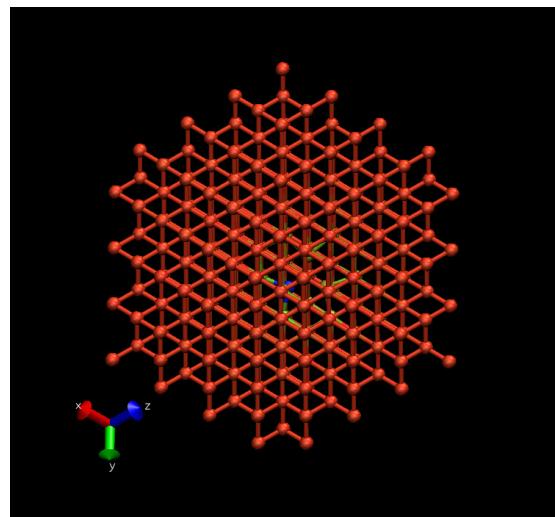

Fig. 1 Relaxed configuration of the 511-atom system of Si with a vacancy.

Distribution of the calculated mode frequencies is shown in Fig. 2, and is compared to that of crystal. A broadening of the mode frequency is observed, for instance, in the vicinity of 700 cm^{-1}. There are no sharply defined peaks in the frequency range. Similar tendency has been reported for a 63-atom simulation based on the density functional theory [5].
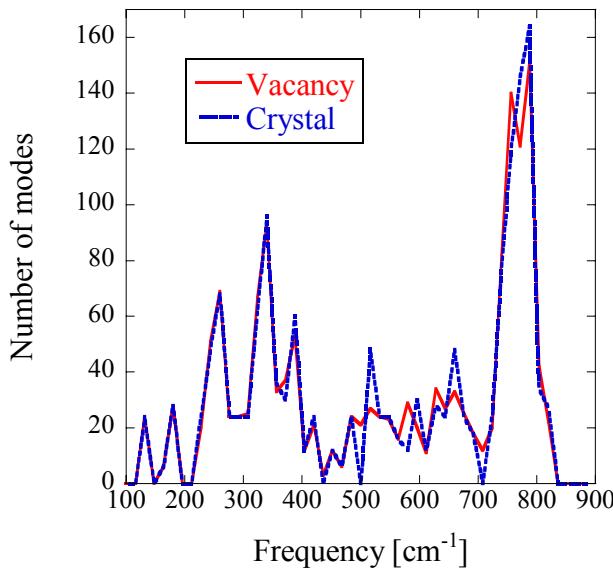
Fig. 2. Density distribution of vibrational mode in the defective system and that in the perfect crystal as functions of mode frequency.

Fig. 3. Localization index R and frequency shift from crystal vs. mode number.

We observe relative localization of the vibrational modes via a "localization index", R. $R(n)$ is defined as a mean square of the elements of the n-th eigen-vectors at neighboring sites of the vacancy. $d\omega_n = \omega_n^{(v)} - \omega_n^{(c)}$ defines the change of n-th mode frequency, where $\omega_n^{(v)}$ and $\omega_n^{(c)}$ are n-th eigen-frequencies of the system with and without vacancy, respectively. Figure 3 shows R and frequency shift from the crystal as functions of the mode number. The magnitudes of peaks of the localization index and the shift of mode frequency are different, but the positions of these peaks have good agreement. This coincidence between the peak positions indicates a close relationship between the frequency shift due to the presence of the vacancy and the localization of vibrational states.

Figure 4 shows the free energy contribution of each mode and the change of mode frequencies as functions of the mode number. This shows that the change of the vibrational free energy is directly relate to the shift of mode frequency.
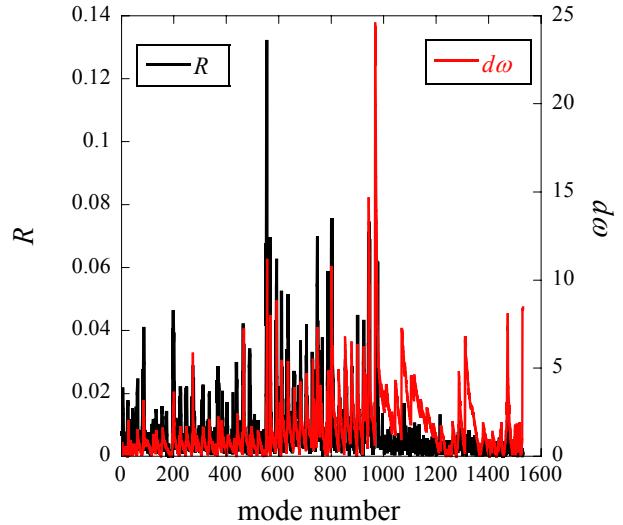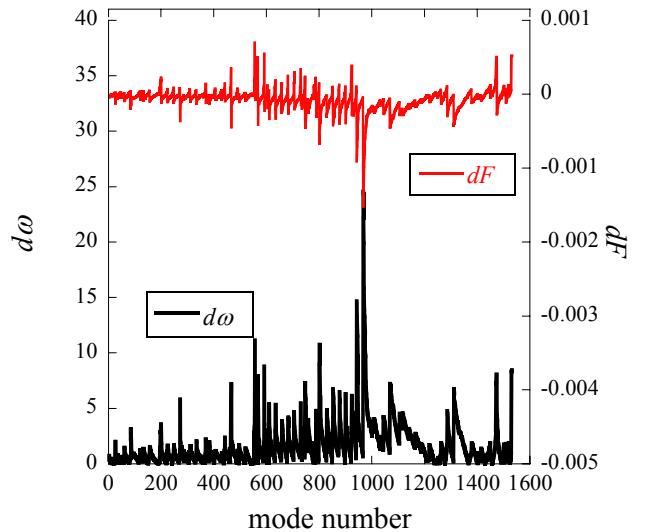

Fig. 4. Vibrational free energy and frequency shift as functions of mode number.

4. CONCLUSION

We have investigated the vibrational properties in Si crystal with a single vacancy via normal mode analyses based on the TB method. The obtained normal modes show the shift of mode frequencies relative to the case of crystal. They are related to the locally induced lattice vibrations and contribute directly to reduction of the vibrational free energy of the defective Si system.

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