First-principles molecular dynamics simulations of structural phase transitions in Si

Tetsuya Morishita* and Shuichi Nosé
Department of Physics, Faculty of Science and Technology, Keio University

Constant-pressure first-principles molecular dynamics simulations were carried out to study structural phase transitions of silicon. In compression processes, two types of structural transformations were realized depending on transition pressures. One is the transition from the diamond to the simple hexagonal (sh) structure and another, from the diamond to the bcc structure. In a decompression process, the fcc structure was transformed to the sh one. Though our results are not entirely consistent with experimental results, phase transitions are well realized considering our small system size and crude electronic state calculations.

Introduction

Crystalline silicon has various structures according to pressure and/or temperature.[1)] The diamond structure is stable at room temperature and atmospheric pressure. However, at higher pressure, many other structures are observed in experiment. At 11 GPa, the diamond structure changes to the β-tin structure and at 16 GPa, β-tin changes to the simple hexagonal (sh) structure. At higher than 40 GPa, the hcp structure and than 80 GPa, the fcc structure is observed, respectively. It is considered that the electronic state plays an important role in structural transformations of Si.

In this report, structural transformations induced by pressure changes of crystalline Si are investigated via first-principles molecular dynamics (FP-MD) simulations at constant-pressure and constant-temperature. The electronic state is explicitly considered in FP-MD, so that structural transformations in covalent and metallic system will be realized in dynamical simulations. To carry out these simulations, we employed the combination of the Car-Parrinello (CP) method [2)] and the Parrinello-Rahman (PR) method.[3)]

Computational method

It is essential to employ the PR method for investigations of structural transformations in MD simulations. In the PR method, changes of shape of a simulation unit cell are allowed and three edge vectors of a unit cell are regarded as dynamical variables. We combine this method with the CP method (this is often referred to as the constant-pressure CP method.[4)]). Electronic wave functions for occupied valence states were only considered and expanded in a plane wave basis. The sampling point in the Brillouin zone is restricted to Γ point only. The electron-ion interaction was described by a norm-conserving pseudopotential[5)] with a separable form.[6)] The exchange and correlation energy was calculated within the local density approximation (LDA) and parameterized form by Perdew and Zunger [7)] was used. Our simulation cell contained 64 atoms and temperature of atoms was kept to 300 K throughout MD runs by a Nosé-Hoover thermostat.[8,9)]

* Present address: RIKEN (Institute of Physical and Chemical Research), WAKO, SAITAMA 351–0198, Japan, tetsuya-@atlas.riken.go.jp

Results

We report three simulation results of structural transformations. Two of them are in compression processes and one in a decompression process.

The simulation accompanying a compression process was started with the diamond structure. Cutoff energy E_{cut} of a plane wave basis was 20 Ry and external pressure was set to 0 GPa. At this pressure, we confirmed that the diamond structure was kept stable in our system. After equilibration in the diamond structure, pressure was raised to 14 GPa instantaneously. In experiment, a phase transition from diamond to the β-tin structure occurs around this pressure. However, no structural change was observed during the simulation. After $\sim$ 1ps from this compression, pressure was again raised up to 26 GPa. At the moment, the simulation cell began to deform and a structural phase transition occurred. We analyzed the transformed structure and found that it is almost the sh structure, but it contains a defect. Radial distribution function g(r) for this structure was calculated and this reveals clearly a characteristic feature of the sh structure. g(r) for the diamond structure (before compression) and for the transformed structure (after compression) are shown in Fig. 1. There is some difference between the transformed and ideal sh structures in g(r). This may be caused by a defect found in one hexagonal layer. From a detailed analysis, it is found that one particle is excessive to form the ideal sh in our simulation cell, and is located within a hexagonal layer accompanying distortion around the particle.

Another type of a structural transformation is found in a compression process up to 38 GPa (0 GPa $\rightarrow$ 14 GPa $\rightarrow$ 38 GPa). This simulation was carried out employing 12 Ry E_{cut}. At 14 GPa, the diamond structure was still kept just as the previous result. However, when external pressure was raised up to 38 GPa, a drastic phase transition was observed. g(r) for the transformed structure is shown in Fig. 2. There is no defect in the transformed structure and this structure corresponds to the bcc structure almost perfectly. This bcc

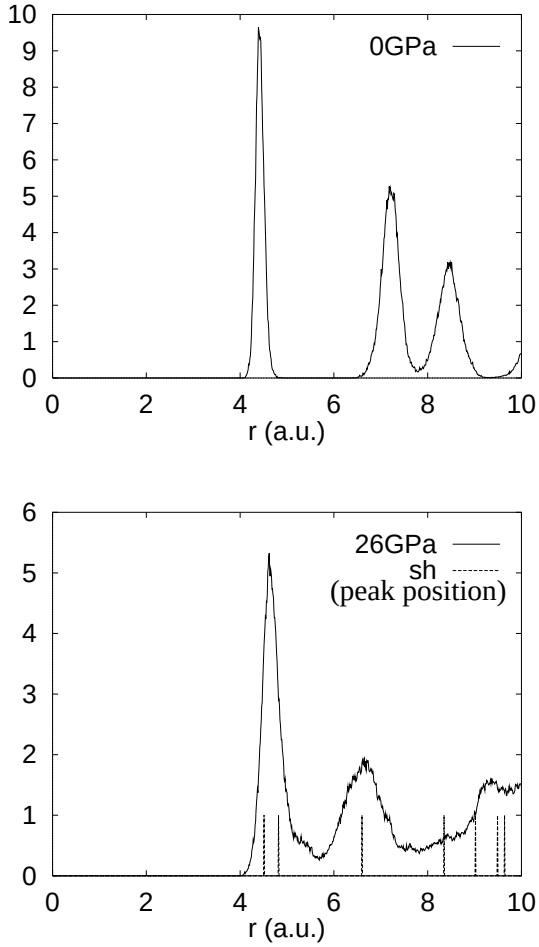

Fig. 1. Radial distribution function g(r) at 0 GPa in diamond (upper panel), and at 26 GPa in the transformed structure (lower panel) is shown, respectively. Peak positions expected from the ideal sh structure are shown by short vertical lines.

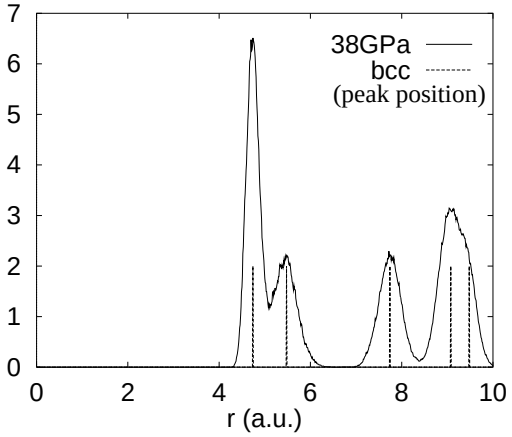

Fig. 2. g(r) obtained at 38 GPa. Peak positions expected from the ideal bcc structure are shown by short vertical lines.

structure is very stable though it is not observed in experiment.

A decompression simulation was started with the fcc structure at 90 GPa employing 12 Ry E_{cut}. It is confirmed that the

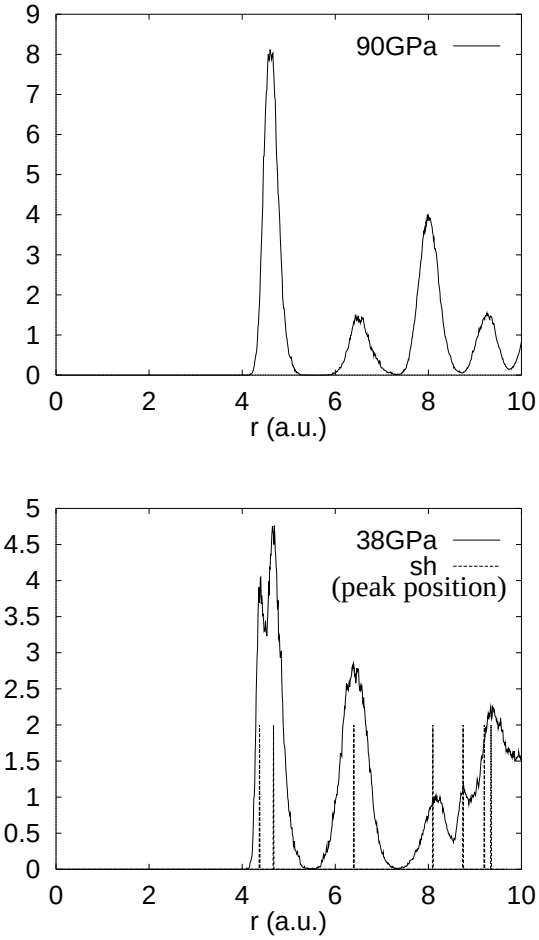

Fig. 3. g(r) obtained in the decompression simulation. g(r) at 90 GPa in fcc (upper panel), and at 38 GPa in the transformed structure (lower panel) is shown, respectively. Peak positions expected from the ideal sh structure are shown by short vertical lines.

fcc structure was stable at 90 GPa. After equilibration in fcc, pressure was reduced to 38 GPa instantaneously and a structural transformation was observed. We analyzed this transformed structure in detail and found that it is the sh structure accompanying slight deformation. g(r) for the fcc structure (before decompression) and for the transformed structure (after decompression) are shown in Fig. 3. g(r) for the latter corresponds to the sh structure almost perfectly, though small displacement is found in stacking of hexagonal layers.

Discussion and conclusion

The results of three simulations with structural transformations were reported. In two compression processes, different transformed structures were obtained depending on the transition pressures (26 and 38 GPa, respectively). In the transformed structure obtained at 26 GPa, the ideal sh structure can be found by excluding an interstitial defect particle. In our preliminary calculation, total energy of this structure is lowered about 2 mRy/atom by excluding the defect particle. The transition from the diamond to bcc structure at 38 GPa was also observed in another simulation. The bcc structure is not observed in experiment and more accurate electronic calculations show that the energy of bcc is higher than that of sh and hcp around 40 GPa. Therefore, we consider that

this transition is primarily caused by our poor electronic state calculations. In the decompression process, the fcc was transformed to sh structure. In this transformed structure, hexagonal layers are stacked just as sh but with small displacement.

These results show that the mechanism of FP-MD combined with the PR method worked well. Considering our small system size and crude electronic state calculations, we conclude that structural phase transitions were well realized by constant-pressure FP-MD. The discrepancy between simulations and experimental results will be reduced by electronic state calculations with higher accuracy.

References

1) J. Z. Hu, D. Merlcle, C. S. Menoni, and I. L. Spain: Phys. Rev. B **34**, 4679 (1986).
2) R. Car and M. Parrinello: Phys. Rev. Lett. **55**, 2471 (1985).
3) M. Parrinello and A. Rahman: Phys. Rev. Lett. **45**, 1196 (1980).
4) P. Focher et al.: Europhys. Lett. **26**, 345 (1994).
5) G. B. Bachelet, D. R. Hamann, and M. Schlüter: Phys. Rev. B **26**, 4199 (1982).
6) L. Kleinman and D. M. Bylander: Phys. Rev. Lett. **48**, 1425 (1982).
7) J. Perdew and A. Zunger: Phys. Rev. B **23**, 5048 (1981).
8) S. Nosé: Mol. Phys. **52**, 255 (1984); W. G. Hoover: Phys. Rev. A **31**, 1695 (1985).
9) T. Morishita and S. Nosé: Phys. Rev. B **59**, 15126 (1999).