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Atomistic structures of amorphous $Si_{1-x}Ge_x$ alloys: A molecular-dynamics study

Mitsuhiro Yamaguchi, Manabu Ishimaru* and Yoshihiko Hirotsu*
Department of Materials Science and Engineering, Osaka University, Osaka, Japan
Fax: +81-6-6879-8434, e-mail: m-yama22@sanken.osaka-u.ac.jp
*The Institute of Scientific and Industrial Research, Osaka University, Osaka, Japan
Fax: +81-6-6879-8434, e-mail: ishimaru@sanken.osaka-u.ac.jp

Structural characteristics of amorphous silicon-germanium (a-$Si_{1-x}Ge_x$) alloys have been examined by molecular-dynamics (MD) simulations using the Tersoff interatomic potential. The a-$Si_{1-x}Ge_x$ networks were generated by rapid quenching from liquid $Si_{1-x}Ge_x$ alloys. The present MD simulations reproduced well the amorphous structures of $Si_{1-x}Ge_x$ alloys obtained experimentally. This suggests that the MD calculations based on the Tersoff potential is sufficient for the structural analysis of a-$Si_{1-x}Ge_x$ alloys. The a-$Si_{1-x}Ge_x$ alloys showed complete chemical disorder for all compositions, suggesting that Si and Ge atoms are fully miscible in the a-$Si_{1-x}Ge_x$ networks. A weak composition dependence was observed in the bond length of Si-Si, Si-Ge and Ge-Ge pairs. The bond length and bond angle around Ge atoms have more distortion than those around Si atoms. This is attributed to the difference of the bond-stretching and bond-bending forces between Si and Ge.

Key words: silicon-germanium, molecular-dynamics, Tersoff interatomic potential, amorphous

1. Introduction

Amorphous semiconductors currently play an important role for electronic and optoelectronic device applications. It is known that the physical properties of an amorphous semiconductor strongly depend on atomic configurations, and therefore it is technologically important to understand the amorphous structures of these materials. Amorphous semiconductors consisting of IV and III-V elements possess tetrahedral networks with a covalent bonding. In the case of elemental amorphous semiconductors such as amorphous Si and amorphous Ge, we need to consider only topological disorder. Therefore, the structural model of the elemental amorphous semiconductors has been almost established. For the amorphous semiconductor alloys composed of different atomic species, on the other hand, not only topological disorder but also chemical disorder should be considered.

Amorphous silicon-germanium (a-$Si_{1-x}Ge_x$) alloys are one of the important semiconductor alloys. Their structural features have been investigated by extended x-ray absorption fine structure (EXAFS) [1-4]. The experimental results suggested that the random mixing of Si and Ge atoms at the first coordination shell and no (or a weak) composition dependence in the bond lengths of Si-Ge and Ge-Ge pairs. Kim et al. [5] and Ko et al. [6] have generated a-$Si_{1-x}Ge_x$ alloys by rapid quenching from melted $Si_{1-x}Ge_x$ with employing *ab initio* molecular-dynamics (MD) simulations. However, their results were not completely fit to those obtained experimentally. That is, the computer-generated amorphous networks contain Ge- and Si-rich regions, and the Ge-Ge (Si-Si) bond length decreases (increases) with increasing the Ge composition. This motivated us to study the amorphous structures of Si-Ge system.

Ab initio MD simulations are numerically so intensive that amorphous networks were prepared from the liquid state by rapid quenching with > 10^{14} K/s. To avoid this unrealistic quenching rate, the MD simulation using an empirical interatomic potential is an effective method. We have recently performed MD simulations using the Tersoff interatomic potential [7] in order to examine the validity of this potential for amorphous Si [8,9]. Bording [10] also generated amorphous Ge based on the Tersoff potential. Both results were in good agreement with those obtained experimentally, suggesting that MD calculations based on the Tersoff potential is useful for structural analysis of a-$Si_{1-x}Ge_x$ alloys. In this study, we performed MD simulations using the Tersoff interatomic potential in order to clarify the local structures of a-$Si_{1-x}Ge_x$ alloys.

2. Simulation procedures

Cook and Clancy [11] have examined a solid-to-liquid phase transition by constant-pressure MD simulations using the Tersoff potential. They reported that the density of liquid Si is different from that obtained experimentally. Therefore, the present simulations were performed under constant-*NVT* conditions, i.e. constant-volume and constant-temperature conditions.

The Si and Ge atoms were at first placed randomly on the diamond lattice sites in a cubic MD cell with periodic boundary conditions. The size of the MD cell was chosen to be $4a_0 \times 4a_0 \times 4a_0$ for N = 512 and $5a_0 \times 5a_0 \times 5a_0$ for N = 1000, where a_0 is the equilibrium lattice parameter determined by Vegard's rule (a_0 = 5.431 Å for Si and a_0 = 5.658 Å for Ge). Then the system was heated up and quenched by rescaling the velocities of the particle. The Newtonian equations of

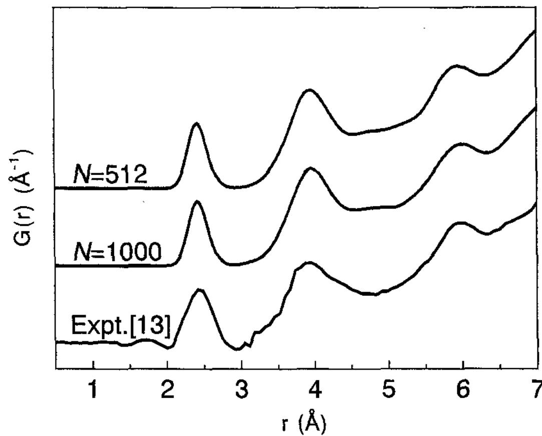

Fig. 1. Radial distribution functions $G(r)$ for the computer-generated atomic configurations with the composition of x = 0.5. An experimental result is also shown for reference [13].

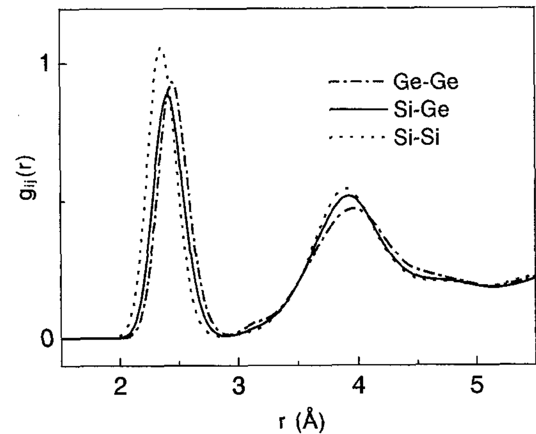

Fig. 2. Partial pair distribution functions $g_{ij}(r)$ of a-$Si_{0.5}Ge_{0.5}$ alloy.

motion were integrated using the velocity form of the Verlet algorithm with a time step of $\Delta t = 2 \times 10^{-3}$ ps.

The a-$Si_{1-x}Ge_x$ networks were generated by rapid quenching from liquid $Si_{1-x}Ge_x$ alloys. To generate the configurations of liquid state, the initial configuration was melted at 3500 K during 200 ps ($10^5 \Delta t$). Then the melted $Si_{1-x}Ge_x$ was cooled down to 300 K with a rate of 10^{12} K/s. This cooling rate corresponds to the upper limit achieved in laboratories to prepare amorphous silicon [12], so the defect concentration in the as-quenched sample is larger than the experimental value. In order to relax the amorphous structure, the as-quenched samples were annealed for 2000 ps ($10^6 \Delta t$) at 1500 K. After annealing, the samples were quenched to 300 K with a cooling rate of 10^{12} K/s before the final structural properties were examined.

3. Results and discussion

Figure 1 represents the radial distribution functions $G(r)$ of $Si_{0.5}Ge_{0.5}$ networks with N = 512 and 1000. These functions were obtained by averaging over 500 configurations during $500\Delta t$ (1 ps). Also shown in Fig.1 is the $G(r)$ obtained from x-ray diffraction experiment [13]. The $G(r)$ of N = 512 is almost the same as that of N = 1000, suggesting that this system size is sufficient for structural analysis of MD calculations. The first and second peaks locate at 2.43 and 3.94 Å, respectively. It should be noted that the third peak of crystalline $Si_{0.5}Ge_{0.5}$ (4.60 Å) is not observed. Good agreement was obtained between the simulated and experimentally measured $G(r)$ of a-$Si_{0.5}Ge_{0.5}$ alloy, though the adjustable parameters of the Tersoff potential are not fit to any liquid data. This indicates that the atomic configurations generated by the present MD simulations reproduce well those of the real a-$Si_{1-x}Ge_x$ alloys.

Figure 2 displays the partial pair distribution functions $g_{ij}(r)$ of a-$Si_{0.5}Ge_{0.5}$ alloy. The $g_{ij}(r)$ is the probability of finding j-atoms at a distance r from an i-atom. The obtained $g_{ij}(r)$ indicates that the first coordination shell consists of three subpeaks due to Si-Si, Si-Ge and Ge-Ge pairs: the simulated a-$Si_{1-x}Ge_x$ networks contain not only heteronuclear (Si-Ge) but also homonuclear (Si-Si and Ge-Ge) bonds. The first and second peaks locate at 2.45 and 3.97 Å for Ge-Ge, 2.41 and 3.93 Å for Si-Ge, and 2.36 and 3.90 Å for Si-Si correlation, respectively.

The bond lengths of Si-Si, Si-Ge and Ge-Ge pairs were determined from the first coordination distance in $g_{ij}(r)$. The bond lengths as a function of the Ge composition are shown in Fig. 3. The dotted line represents the least-square fit to the values obtained by the present MD simulations. Apparently, all bond lengths in the a-$Si_{1-x}Ge_x$ alloys increase with the Ge composition. It should be noted that a weaker compositional dependence is observed in the bond length of Si-Si and Si-Ge pairs. That is, the compositional dependence of bond lengths neither obeys Vegard [14,15] nor Bragg-Pauling [16,17] rule. This is attributed to the difference of the bond-stretching force between Si-Si (48.5 N/m) and Ge-Ge (38.7 N/m) [18]. According to the study of compositional dependence of a-$Si_{1-x}Ge_x$ alloys by Ridgway et al. [3], the bond length of Si-Ge pair shows a weaker compositional dependence

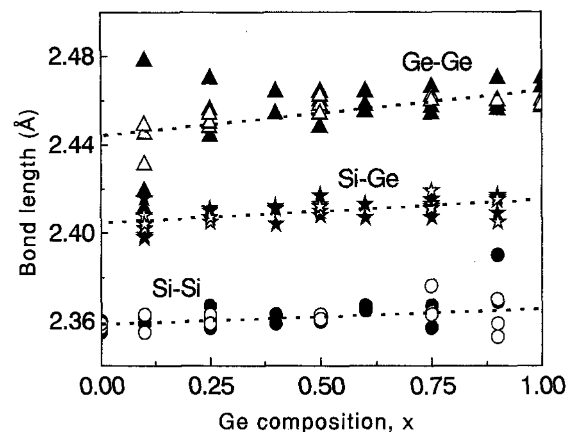

Fig. 3. The bond lengths of Si-Si, Si-Ge and Ge-Ge pairs as a function of the Ge composition. The solid (open) symbols denote N = 512 (N = 1000). The dotted line represents the least-square fit to the values obtained by the present MD simulations.

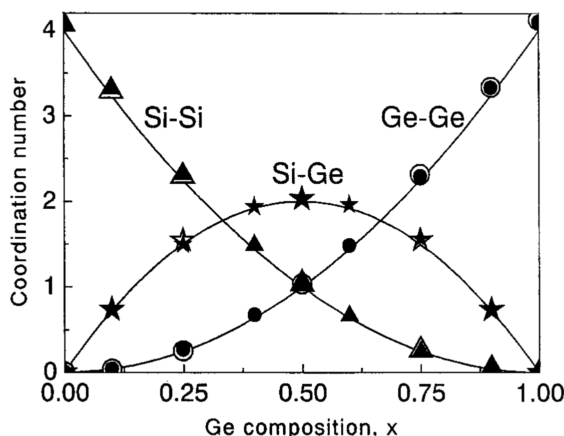

Fig. 4. The average coordination number as a function of the Ge composition. The solid (open) symbols denote $N = 512$ ($N = 1000$). The plots of the partial coordination numbers are along the functions of $4x^2$ (for Ge-Ge), $4(1\text{-}x)^2$ (for Si-Si) and $8x(1\text{-}x)$ (for Si-Ge).

than that of Ge-Ge pairs. Our present results support the validity of their experimental results.

In order to investigate the chemical disorder in the a-$Si_{1-x}Ge_x$ alloys, we plotted the average coordination number as a function of the Ge composition (Fig. 4). The average coordination number was determined by integrating $4\pi r^2 \rho g_{ij}(r)$ up to the first minimum in the $g_{ij}(r)$, where ρ is the average number density of atoms. The solid curve indicates the average coordination number in the case of complete chemical disorder: the number of Ge atoms surrounding a Ge atom follows a function of $4x^2$, Si atoms surrounding a Si atom $4(1\text{-}x)^2$, and Si atoms surrounding a Ge atom $8x(1\text{-}x)$. The calculated coordination number obtained by the present MD simulations corresponds to that of ideal chemical disorder, suggesting that Si and Ge atoms are fully miscible in the a-$Si_{1-x}Ge_x$ alloys. This result is in good agreement with that obtained by EXAFS [1].

Bond angle distributions provide useful information about local structure. With this profile, we can estimate the spatial atomic connectivity in the amorphous materials. Figure 5 shows the bond angle distribution function $g(\theta)$ of a-$Si_{0.5}Ge_{0.5}$ alloy with $N = 1000$. The distribution is an average over 500 configurations during $500\Delta\, t$ (1 ps). We chose the first minimum in the $g(r)$ as a cut-off distance. The average position and the standard deviation of bond angle are $\bar{\theta} = 108.7°$ and $\Delta\, \theta = 13.6°$, respectively. These results are in good agreement with those obtained experimentally [13]. For all compositions, it was found that the bond angle distribution peaks are nearly tetrahedral with $\Delta\, \theta = 13°\text{-}15°$.

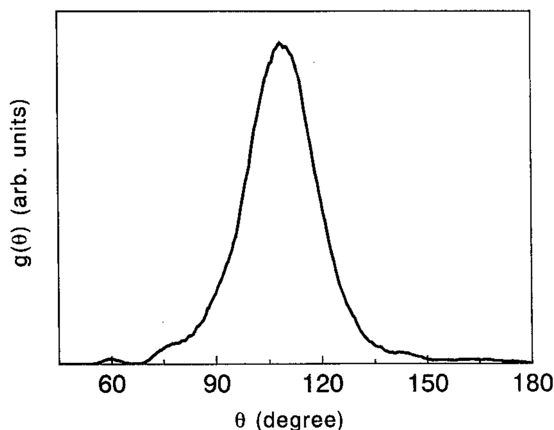

Fig. 5. Bond angle distribution function $g(\theta)$ of a-$Si_{0.5}Ge_{0.5}$ alloy with $N = 1000$.

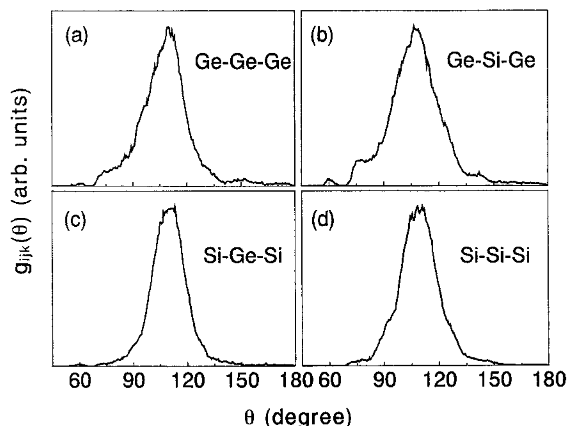

Fig. 6. Partial bond angle distribution functions $g_{ijk}(\theta)$ of a-$Si_{0.5}Ge_{0.5}$ alloy with $N = 1000$: (a) Ge-Ge-Ge, (b) Ge-Si-Ge, (c) Si-Ge-Si, and (d) Si-Si-Si combinations.

For further analysis of bond angle, the partial bond angle distribution functions $g_{ijk}(\theta)$ of a-$Si_{1-x}Ge_x$ alloys were calculated. The resulting $g_{ijk}(\theta)$ of a-$Si_{0.5}Ge_{0.5}$ alloy are displayed in Fig. 6. The average position and the standard deviation of bond angle are 108.0° and 13.9° for Ge-Ge-Ge, 107.7° and 16.0° for Ge-Si-Ge, 109.9° and 11.8° for Si-Ge-Si, and 109.2° and 12.0° for Si-Si-Si combinations. Besides the main peak of tetrahedral angle, two peaks exist at 60° and 75° in Figs. 6(a) and 6(b). These peaks originate from fivefold coordinated atoms [9]. This indicates that the bond angle around Ge

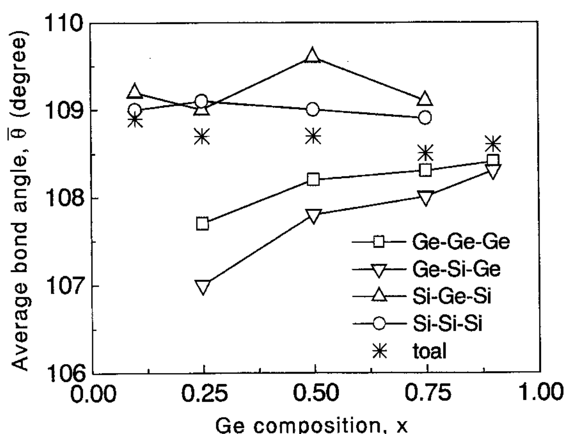

Fig. 7. The average bond angle for each combination as a function of Ge composition is plotted in figure 7. The bond angles were averaged for the structure of $N = 1000$. The star denotes the total average bond angle.

atoms have more distortion than that around Si atoms.

The average bond angle for each combination of atoms as a function of the Ge composition is plotted in Fig. 7. The bond angles were averaged for the structure of $N = 1000$. The average bond angles of Ge-Ge-Ge and Ge-Si-Ge are smaller than those of Si-Ge-Si and Si-Si-Si for all compositions. In other words, the bond angle surrounding Ge atom is more distorted for all compositions. Also it was found that the standard deviation surrounding Ge atom (Ge-Ge-Ge and Ge-Si-Ge) is larger than others for all compositions (not shown). This is attributed to the difference of the bond-bending force between Si-Si (13.8 N/m) and Ge-Ge (11.4 N/m) [18].

4. Conclusions

Amorphous structures of Si-Ge system have been examined by MD simulations using the Tersoff potential. The following results were obtained:

(1) The structural properties of a-$Si_{1-x}Ge_x$ alloys generated by the Tersoff interatomic potential are in good agreement with those obtained experimentally. This represents that the MD calculations based on the Tersoff potential is sufficient for the structural analysis of a-$Si_{1-x}Ge_x$ alloys.

(2) The average bond lengths of Si-Si, Si-Ge and Ge-Ge pairs become slightly longer with increasing the Ge compositions. A weaker compositional dependence is observed in the bond lengths of Si-Si and Si-Ge pairs.

(3) The a-$Si_{1-x}Ge_x$ alloys show complete chemical disorder for all compositions, suggesting that Si and Ge atoms are fully miscible in the a-$Si_{1-x}Ge_x$ alloys.

(4) Partial pair-correlation functions and partial bond angle distribution functions suggest that the Ge-Ge bond length and the average bond angle surrounding Ge atom is more distorted. This is attributed to the difference of the bond-stretching and bond-bending force between Si and Ge.

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