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The local atomic structures in $\text{Si}_{1-x}\text{Ge}_x$ and $\text{Si}_{1-x}\text{Sn}_x$ random solid solutions

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Abstract. Using molecular-dynamics method based on three-particle Tersoff's potential simulation we have studied the $\text{Si}_{1-x}\text{Ge}_x$ and $\text{Si}_{1-x}\text{Sn}_x$ random solid solutions. Bond lengths and strain energies of these alloys can be predicted. The calculated results are compared with those obtained from other theoretical calculations and experimental measurements.

Keywords: Tersoff's potential, first-neighbor bond lengths, second-neighbor bond lengths, Vegard's law.

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1. Introduction

$\text{Si}_{1-x}\text{Ge}_x$ is a complete solid solution system with the diamond-cubic structure. The 4.2 % difference in the lattice constants of the constituent Ge and Si atoms leads to various unique alloying effects on the electronic, optical, thermodynamic, and mechanical properties. Thus, $\text{Si}_{1-x}\text{Ge}_x$ alloys are important for microelectronics and optoelectronics in view of possibilities of bandgap engineering.

As a group-IV semiconductor alloy with variable biaxial strain, epitaxially grown $\text{Si}_{1-x}\text{Sn}_x$ alloy layers have attracted interest over the last few years [1 – 4]. Also the interest was aroused due to theoretical predictions that, in the case of a considerable content of Sn, this material might have a direct bandgap [5]. Until now, however, the successful synthesis of epitaxial $\text{Si}_{1-x}\text{Sn}_x$ has been reported only for Sn concentrations smaller than about 5 % grown on (001)-oriented Si [1].

Accurate knowledge of the local atomic structure in the context of the local strain relaxation is essential in order to clarify the origins of electronic, optical, thermodynamic, and mechanical properties and to utilize the device potential of $\text{Si}_{1-x}\text{Ge}_x$ and $\text{Si}_{1-x}\text{Sn}_x$ solid solutions. There has been some experimental studies of the local structural relaxation in $\text{Si}_{1-x}\text{Ge}_x$ alloys. H. Kajiyama *et al.* [6] probed the bond-length relaxation in crystalline $\text{Si}_{1-x}\text{Ge}_x$ alloys. L. Incoccia *et al.* [7] and Y. Nishino *et al.* [8] studied the local structure of hydrogenated amorphous Si-Ge alloys. M. Matsuura *et al.* [9] measured Ge-to-Si first-neighbor and second-neighbor distances of silicon-rich SiGe/Si (100) films. All these experimental results show a tendency for the

first-neighbor bond lengths in $\text{Si}_{1-x}\text{Ge}_x$ alloys to be almost independent of concentration and close to the respective lengths in pure materials and compounds. Nowadays, there aren't any empirical data of local atomic structure $\text{Si}_{1-x}\text{Sn}_x$ at all. But $\text{Si}_{1-x}\text{Ge}_x$ and $\text{Si}_{1-x}\text{Sn}_x$ belong to the same family of group-IV semiconductor alloys, it is intriguing to theoretically test the $\text{Si}_{1-x}\text{Sn}_x$ alloy similar to those in $\text{Si}_{1-x}\text{Ge}_x$ [10].

2. Calculations

For the calculations of local atomic structure of $\text{Si}_{1-x}\text{Ge}_x$ and $\text{Si}_{1-x}\text{Sn}_x$ alloys by the use of molecular dynamics (MD), we have to determine the potential model first. Among many empirical potentials, which have been suggested for tetrahedral semiconductors, the Tersoff three-particle potential turned out to be a most successful to investigate many properties of semiconductor compounds [11].

Interatomic potential interaction energy of two neighbor atoms i and j has the form:

$$V_{ij} = f_C(r_{ij})(a_{ij}f_R(r_{ij}) + b_{ij}f_A(r_{ij})), \quad (1)$$

where

$$f_R(r) = A \exp(-\lambda r), \quad (2)$$

$$f_A(r) = -B \exp(-\mu r), \quad (3)$$

$$f_C(r) = \begin{cases} 1, & r < R, \\ \frac{1}{2} + \frac{1}{2} \cos \left[\pi \frac{(r-R)}{(S-R)} \right], & R < r < S, \\ 0, & r > S, \end{cases} \quad (4)$$

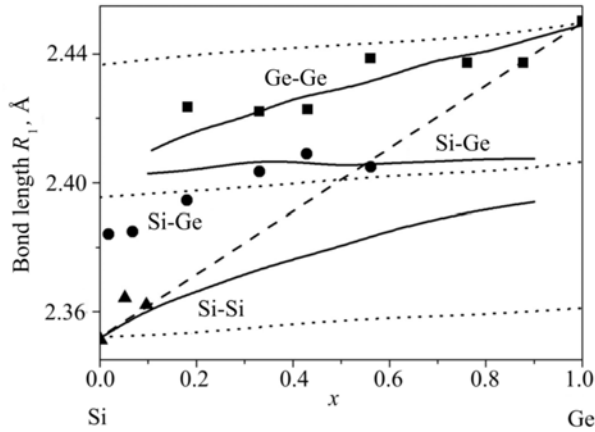


Fig. 1. First near-neighbor bond length in $\text{Si}_{1-x}\text{Ge}_x$ solid solutions vs composition x . Solid lines – our MD calculations; ■ – Ge-Ge bond length (X-ray absorption measurements [16]), ● – Si-Ge bond length (X-ray absorption measurements [16]), ▲ – Si-Si bond length (X-ray absorption measurements [16]); dotted lines – FDUC calculations [17]; dashed line – Vegard's law.

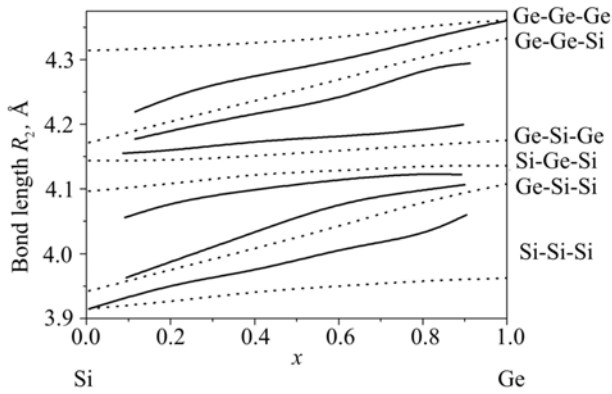


Fig. 2. Second near-neighbor bond lengths in $\text{Si}_{1-x}\text{Ge}_x$ solid solutions vs composition x . Solid lines are the calculated bond lengths from our MD model. Dotted lines – FDUC calculations [17].

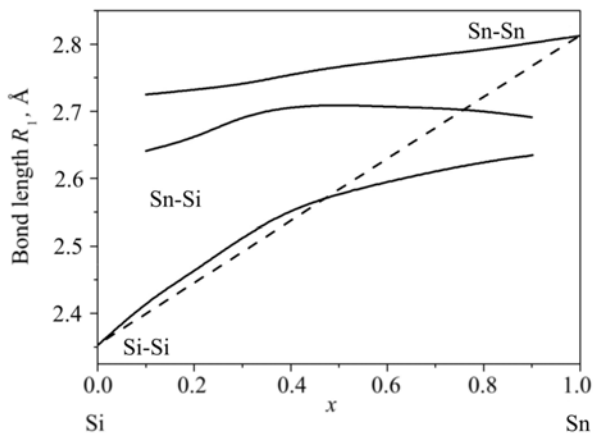


Fig. 3. First near-neighbor bond lengths in $\text{Si}_{1-x}\text{Sn}_x$ solid solutions vs composition x ; dashed line – Vegard's law.

b_{ij} is many-body-order parameter describing how the bond-formation energy is affected by the local atomic arrangement due to the presence of other neighboring atoms (the k -atoms). This many-body function of atomic positions i, j, k has the form

$$b_{ij} = \chi_{ij} \left(1 + \beta^n \zeta_{ij}^n\right)^{-1/2n}, \quad (5)$$

where

$$\zeta_{ij} = \sum_{k(\neq i, j)} f_C(r_{ik}) g(\theta_{ijk}) \exp(\lambda_3^3 (r_{ij} - r_{ik})^3), \quad (6)$$

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos \theta)^2}, \quad (7)$$

$$a_{ij} = \left(1 + \alpha^n \eta_{ij}^n\right)^{-1/2n}, \quad (8)$$

$$\eta_{ij} = \sum_{k(\neq i, j)} f_C(r_{ik}) \exp(\lambda_3^3 (r_{ij} - r_{ik})^3), \quad (9)$$

ζ_{ij} is an effective coordination number, $g(\theta)$ is a function of the angle between r_{ij} and r_{ik} , that has been fitted to stabilize the tetrahedral structure.

Presented in our previous works [13, 14] parameters for Ge and Si were taken from [11] and ones for Sn were derived from gray-tin cohesion energy adjustment equal to 3.12 eV per atom [12]. Simulation have been done for systems with $N = 216$ particles, the initial positions of which were taken in tetrahedral sites of cell, formed by $3 \times 3 \times 3$ unit cells of diamond type. The periodic boundary conditions were used. This method was based on solving the Newton equations set using the fast form of the Verlet algorithm [15], which being the self-starting, doesn't lead to roundoff errors accumulation. Simulation is started from an initial structure, in which two kinds of atoms are randomly placed on a diamond lattice. After the system passed to the equilibrium state with the step $\Delta t = 0.15 \cdot 10^{-15}$ s, we calculated the pair distribution function $g(r)$. When the substitutional solid solutions are formed, the first peak of pair distribution functions splits into three peaks corresponding to the Ge-Ge, Ge-Si and Si-Si for $\text{Si}_{1-x}\text{Ge}_x$ alloys or to the Sn-Sn, Sn-Si and Si-Si for $\text{Si}_{1-x}\text{Sn}_x$ alloys. At the same time, with the temperature increase, the pair distributions function peaks become something broader and displace a little, that means conservation of the tetrahedral crystal structure. Besides, the coordination number corresponding to the number of nearest neighbors was controlled in the modeling process. Such a behavior of the system is confirmed by the total energy as a function of the temperature.

3. Results and discussions

The purpose of this work is to study the structural properties of $\text{Ge}_x\text{Si}_{1-x}$ and $\text{Si}_{1-x}\text{Sn}_x$ solid solutions by using MD simulation. Fig. 1 shows the first near-neighbor lengths in $\text{Si}_{1-x}\text{Ge}_x$ solid solutions vs

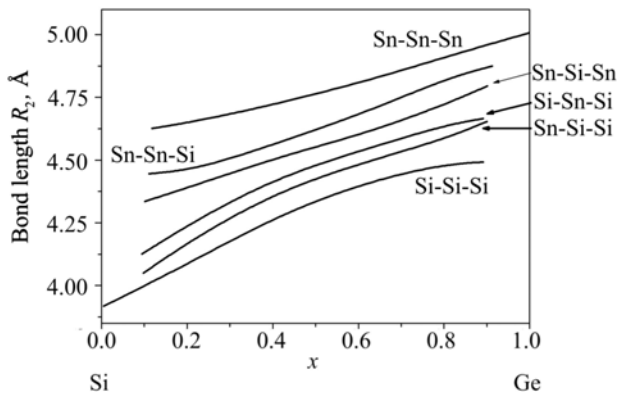


Fig. 4. Second near-neighbor bond length in $\text{Si}_{1-x}\text{Sn}_x$ solid solutions vs composition x .

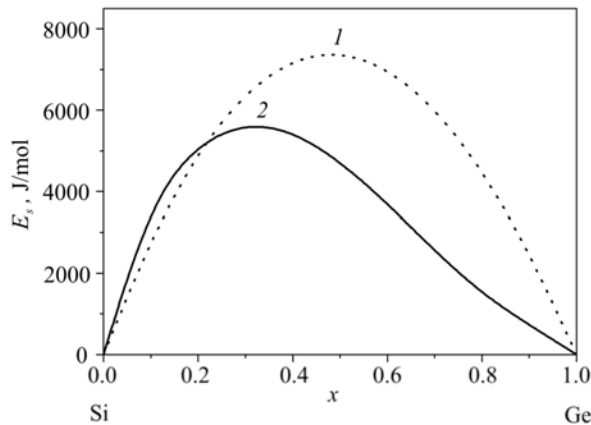


Fig. 5. Strain energy $\text{Si}_{1-x}\text{Ge}_x$ solid solutions vs composition x . 1 – Soma calculation [20]; 2 – our calculation.

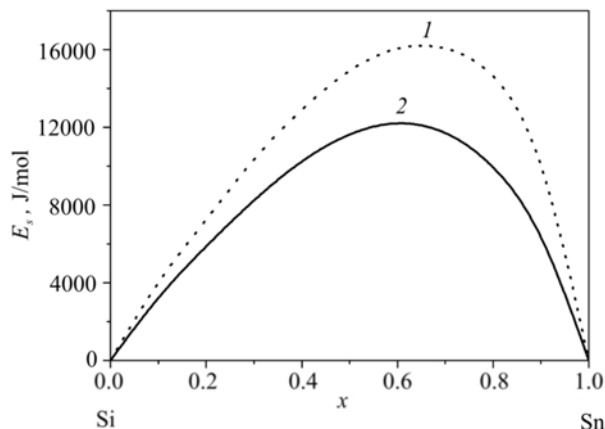


Fig. 6. Strain energy $\text{Si}_{1-x}\text{Sn}_x$ solid solutions vs compositions x . 1 – Soma calculation [20]; 2 – our calculation.

compositions x . The solid lines are values calculated from our model, the symbols are the X-ray absorption measurements by I. Yonenaga *et al.* [16]. For

comparison, Fig. 1 also shows the values calculated from FDUC model by Wu Zhonghua *et al.* [17] in the form of dotted lines. It can be seen that the first-neighbor bond lengths are in a good agreement with the experimental data of the X-ray absorption measurements. Fig. 2 displays the second near-neighbor bond length in $\text{Si}_{1-x}\text{Ge}_x$ solid solutions vs compositions x . All the first- and second-neighbor bond lengths vary almost linearly with compositions. Our theoretical investigations can predict the state of bond lengths, the agreement between our predictions and Wu Zhonghua calculations [17] are not very well. Nowadays, we haven't any experimental data for the second-neighbor bond lengths in $\text{Si}_{1-x}\text{Ge}_x$ solid solutions that can be used. For $\text{Si}_{1-x}\text{Ge}_x$ alloys, the MD model predicts an excellent agreement with experimentally observed Vegard's law for the first-neighbor bond lengths. The relative slopes of the second-neighbor bond lengths of Ge-Ge-Ge, Si-Si-Si normalized to the second-neighbor Vegard law are about 0.37, and about 0.185 for Ge-Si-Ge and Si-Ge-Si, and about 0.296 for Ge-Ge-Si and Si-Si-Ge.

The first- and second-neighbor bond lengths of $\text{Si}_{1-x}\text{Sn}_x$ solid solutions are shown in Figs 3 and 4, respectively. The Sn-Si and Si-Si first-neighbor bond lengths not vary linearly with compositions. But Sn-Sn bond length slightly depends vs compositions, that is in a good agreement with experimentally determined fact of tendency to surface segregation and insolubility of Sn in solid solutions [18]. The relative slopes of second-neighbor bond lengths of Sn-Sn-Sn, Si-Si-Si normalized to second-neighbor Vegard's law are about 0.365 and 0.56, respectively, and about 0.5 for Sn-Si-Sn and Si-Sn-Si. For second-neighbor bond lengths of Sn-Sn-Si and Si-Si-Sn the relative slopes are about 0.52 and 0.706, respectively.

Our calculations predicted that for $\text{Si}_{1-x}\text{Ge}_x$ six second-neighbor bond lengths vary linearly vs composition keeping the same slope, and the order from the large length to the small one is as follows: Ge-Ge-Ge, Ge-Ge-Si, Si-Ge-Si, Ge-Si-Ge, Ge-Si-Si, and Si-Si-Si. But six second-neighbor bond lengths of $\text{Si}_{1-x}\text{Sn}_x$ alloys have the weaker linear dependence on the composition, and the order from the large to small lengths is: Sn-Sn-Sn, Sn-Sn-Si, Si-Sn-Si, Sn-Si-Sn, Sn-Si-Si, and Si-Si-Si. The six second-neighbor bond lengths can be divided into two groups that share one set of the zincblende-type cell. The averaged bond length of Ge-Si-Ge(Sn-Si-Sn) is always larger than that of Si-Ge-Si(Si-Sn-Si), this is because the possibility to find Si-Ge-Si(Si-Sn-Si) bond lengths is less and Ge-Si-Ge(Sn-Si-Sn) ones is larger in $\text{Ge}[\text{Si}_{1-x}\text{Ge}_x]$ ($\text{Sn}[\text{Si}_{1-x}\text{Sn}_x]$) than in $\text{Si}[\text{Si}_{1-x}\text{Ge}_x]$ ($\text{Si}[\text{Si}_{1-x}\text{Sn}_x]$). In these notations, the first symbol respects to the central atom in unit cell.

The lattice parameters of $\text{Si}_{1-x}\text{Ge}_x$ and $\text{Si}_{1-x}\text{Sn}_x$ solid solutions present the positive deviations from Vegard's law (Figs 1 and 3). But these deviations are smaller in their absolute magnitude for $\text{Si}_{1-x}\text{Ge}_x$ but larger for $\text{Si}_{1-x}\text{Sn}_x$ alloys. If we take $a_{A-B} < (a_A + a_B) / 2$, it means that the interactions between heterogeneous atoms are

somewhat stronger than those between identical atoms. On the contrary, when $a_{A-B} > (a_A + a_B) / 2$, the interactions between different atoms are somewhat weaker than those between identical atoms. Therefore, we can conclude that the positive deviation from Vegard's law in $\text{Si}_{1-x}\text{Ge}_x$ and $\text{Si}_{1-x}\text{Sn}_x$ solid solutions occurs because the interactions between heterogeneous atoms is somewhat weaker than those between the same atoms.

Our work shows the microscopical distorted configuration in the studied diamond-like solid solutions. Strictly speaking, the bond lengths in these alloys do not vary linearly with compositions, furthermore, the deviations of bond $\text{Si}_{1-x}\text{Ge}_x$ alloys are small and ones of $\text{Si}_{1-x}\text{Sn}_x$ alloys are considerable. The local distorted configuration is helpful to understand the properties of these solid solutions.

Based on the local atomic structures, the diamond-like structure consists of two zinclende-type ones. Although the atoms in diamond-like solid solutions deviate from the ideal lattice positions, but the long-range order is still preserved and the local structure distortions does not destroy long-range periodicity.

The binary solid solutions of IV group are not ideal [19]. This is predicted by the calculated strain-energy E_s vs composition (Fig. 5 – $\text{Si}_{1-x}\text{Ge}_x$ and Fig. 6 – $\text{Si}_{1-x}\text{Sn}_x$). Strain energy has the shape of parabola. Calculated in our work maximum of $E_s(x)$ isn't about $x = 0.5$ as shown in Figs 5, 6. This fact is clime that used in our model the three-particle Tersoff's potential better represents the nature of alloys than other two-particle ones. The magnitude of strain energy of $\text{Si}_{1-x}\text{Sn}_x$ are higher than that of $\text{Si}_{1-x}\text{Ge}_x$. This fact is in a good agreement with the theoretically confirmed fact of slight instability of $\text{Si}_{1-x}\text{Sn}_x$ alloys [1 – 3].

The MD model requires only the knowledge of the lattice and Tersoff's potential parameters of pure Si, Ge and Sn atoms. It can predict both the first- and second-neighbor equilibrium bond lengths and strain energy for any composition in diamond-like solid solutions. The obtained results are in a good agreement with those from experiments. Generally speaking, the diamond-like solid solutions can be regarded as the mixture of two zinclende-type solid solutions on the basis of local atomic structures. Summarizing the results, it can be concluded that MD model is reasonable and effective to describe the local structures of diamond-like solid solutions.

4. Conclusion

In this paper, we investigated the local atomic structures of diamond-like $\text{Si}_{1-x}\text{Ge}_x$ and $\text{Si}_{1-x}\text{Sn}_x$ solid solutions. The obtained results demonstrate an excellent agreement with those obtained from X-ray absorption measurements [16] for $\text{Si}_{1-x}\text{Ge}_x$ alloys. The relative slopes of second-neighbor bond lengths of Ge-Ge-Ge, Si-Si-Si normalized to second-neighbor Vegard's law are about 0.37, and about 0.185 for Ge-Si-Ge and Si-Ge-Si, and

about 0.296 for Ge-Ge-Si and Si-Si-Ge. The relative slopes of the second-neighbor bond lengths of Sn-Sn-Sn, Si-Si-Si normalized to the second-neighbor Vegard law are about 0.365 and 0.56, and about 0.5 for Sn-Si-Sn and Si-Sn-Si. For the second-neighbor bond lengths of Sn-Sn-Si and Si-Si-Sn the relative slopes are about 0.52 and 0.706. The deviation from Vegard's law for the lattice parameter in $\text{Si}_{1-x}\text{Ge}_x$ and $\text{Si}_{1-x}\text{Sn}_x$ solid solutions takes place because of the somewhat weaker interactions between the different atoms than those between the same atoms. Generally speaking, Ge(Sn) and Si do not form the ideal solid solutions that was also confirmed by the calculated strain energy E_s vs composition x of $\text{Si}_{1-x}\text{Ge}_x$ and $\text{Si}_{1-x}\text{Sn}_x$ alloys.

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