The study of Si/Ge interdiffusion using molecular dynamics simulation

M V Bastrakova, K R Mukhamatchin, Yu M Kuznetsov, M V Dorokhin
Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, 603950, Russian Federation

Abstract. The coefficients of mutual diffusion of silicon into germanium (and vice-versa) at temperatures of 900-1300K were found based on molecular dynamics simulation. For the characteristic temperature $T_c=1100$ K, which is close to the melting point of Ge, we determined the thickness of the diffusing layer for each type of atom. It is shown that the depth of diffusing significantly depends on the sintering time, and silicon atoms penetrate 1.5 times deeper into bulk germanium than germanium into silicon.

1. Introduction
Various materials with pronounced thermoelectric properties are being actively studied. At the same time, one of the promising materials is Si/Ge solid solutions, which have high mechanical strength, low volatility, radiation and high temperature stability, which allows us to consider them as thermoelectric material of the future [1]. Such compounds are often obtained by a means of a solid state diffusion using the systems which trigger the diffusion by heating and applying the pressure [2, 3]. In this case, it is important to identify and study the diffusion processes of Ge and Si. Many theoretical and experimental studies have been done for diffusion bonding of different materials. However, investigation of diffusion bonding Si/Ge at atomic scale has yet to be carried out. The molecular dynamics (MD) simulation, which is not limited by sample preparation and testing condition and can be used to simulate various mechanical behaviors in nanoscales, is the most widely used numerical method in nanomechanics [4-5].

This work is aimed at the detailed investigation of interdiffusion of Ge and Si at the atomic scale. In this paper, the simulation of diffusion processes in the Si/Ge system was performed using the method of molecular dynamics (MD). The advantage of the MD method is a high spatial and temporal resolution which allows us to study both thermodynamic properties and time-dependent phenomena. In order to understand the structural property changes through the diffusion process in detail, we studied the radial distribution function between the sites of different Si/Ge atoms. The diffusion behaviors of atoms at the interface were presented and the thicknesses of the diffusion Si/Ge layer were also derived by the Arrhenius equation on the basis of diffusion coefficients for different system temperatures obtained by the MD simulation.

2. Simulation model and numerical results
In this paper, the MD simulation of the Si/Ge system was performed using the LAMMPS package [6]. The Tersoff potential was used to describe the interaction between Si and Ge atoms [7]. It was assumed that the initial thermal velocities of atoms are subject to the Gaussian distribution at room temperature, and it is also taken into account that the contacting surfaces are subjected to compression in the direction perpendicular to the weld of the contacting materials. For MD calculations, the system
relaxes during 100 ps with a microscopic (nve) ensemble from the loading temperature $T = 300$K to the set sintering temperature $T_c$. Then the system evolves 1000 ps at a given pressure $p = 7$ MPa and temperature $T_c$ (npt ensemble).

To identify the changes in crystal structure the radial distribution functions (RDFs) were carried out. The RDF $g(r)$ describes the fluctuations in density around a given atom [8], which can be thought as the average number of atoms found at a given distance in all directions. The number of atoms inside the shell region between $r$ and $r + dr$ for a given system can be expressed in term of RDF $g(r)$ as

$$dn(r) = \frac{N}{V} g(r) 4\pi r^2 dr,$$

where $N$ and $V$ represent the total number of atoms in the model and its volume, respectively. For our system that contains two kind of atoms Si and Ge, the RDF is referred to as partial radial distribution function, which means the density probability for the atoms of silicon to have a neighbor of the atoms germanium at given radial distance $r$. It can be computed according to the following equation:

$$g_{Si-Ge}(r) = \frac{V}{N_{Si}N_{Ge}} \frac{dn_{Si-Ge}(r)}{4\pi r^2 dr},$$

In Figure 1 shows the dependence of the RDF for different temperatures. As the temperature increases, we see the peaks widen due to the thermal movement of the atoms. Atoms for low temperatures (300-600) K are strongly restricted in their positions, the peaks are particularly sharp. This indicates that the crystal structure is preserved. The structure began to change at about 1000 K, and the RDF shows an amorphous structure due to an unordered interface at the material interface and the occurrence of structural defects. In this case, the solid phase is preserved, but the long-range order is noticeably weaker. For 2000 K the emergence of broad peaks in the RDF (Figure 1) shows that the structure has melted and is in liquid state.

![Figure 1. Radial distribution function (RDF) of interface Si\-Ge at different temperatures $T_c = 300$ K (red curve), 600 K (blue curve), 1000 K (green curve), 2000 K (black curve).](image)

At the next step, we numerically studied the mean square displacements (MSD) of Si and Ge atoms from their equilibrium positions at $T_c = 900$ K – 1300 K to study the diffusion processes

$$\text{MSD}_{Si,Ge} = \frac{1}{N_{Si,Ge}} \sum_{i} \left[ r_i(t) - r_i(t_0) \right]^2,$$
where \( r(t) \) represents the position \( i \) of the Si/Ge atom at time \( t \), and \( r(t_0) \) indicates the initial position of the corresponding atom; \( N_{Si,Ge} \) are the number of atoms.

\[
\frac{d \text{MSD}}{dt} = \frac{1}{2d} \lim_{t \to \infty} \frac{d}{dt} \text{MSD}_{Si,Ge},
\]

(4)

Figure 2 shows that the slope coefficients of the MSD curve with increasing temperature for both Si and Ge. Thus the diffusion coefficients of Si and Ge atoms at the interface can be derived from the slopes of MSD profiles after a longer delay time by the Einstein equation:

\[
D_{Si,Ge} = \frac{1}{2d} \lim_{t \to \infty} \frac{d}{dt} \text{MSD}_{Si,Ge},
\]

where \( d = 3 \) is the dimension of space. Based on the numerical calculation data presented in Figure 1, we found the diffusion coefficients \( D_{Si,Ge} \) for various temperatures \( T_c \) by the least squares method. Applying the Arrhenius equation [9] to the calculated numerical data, one can obtain the temperature dependences of the diffusion coefficients \( D_{Si} \) and \( D_{Ge} \) and reveal the activation energy: \( Q_{Si} = 0.25 \text{ eV} \) and \( Q_{Ge} = 0.33 \text{ eV} \) (see details in [10]), which in order of magnitude smaller than the data from [11]. The latter is attributed to the experimental conditions including the application of the external pressure. The classical diffusion theory demonstrates that the diffusion coefficient keeps invariable under isothermal condition. So, though our MD simulations only last for 1000 ps, we have good reasons to extrapolate the duration of the diffusion with a constant diffusion coefficient.

In order to get deeper understanding of the diffusion in Si/Ge, we try to calculate the thickness of the diffusion layer by means of a hybrid method. Under isothermal condition, when the system achieves equilibrium, the regular diffusion process of Si and Ge should meet the classical diffusion equation which can be expressed as

\[
\frac{\partial n}{\partial t} = D \nabla^2 n,
\]

(5)

where \( n \) is the atom concentration, \( t \) is the diffusion time, and \( D \) is the diffusion coefficient. One of its conventional solutions is
\[ n(z,t) = \frac{N}{2\sqrt{\pi Dt}} e^{-\frac{z^2}{4Dt}} \]

where \( N \) is the quantity of the diffusion matter, and \( z \) is the diffusion distance. Obviously, it is a Gaussian distribution function, and we can calculate the thickness of the diffusion layer \( L \) by

\[ L = L_{Si} + L_{Ge} = 3\sqrt{2D_{Si}t} + 3\sqrt{2D_{Ge}t} \]  \hspace{1cm} (6)

Information about the position (coordinates) of atoms can be obtained from the LAMMPS program files. Using this data, you can also get the thickness of the diffusion layer. The numerical results were compared with the calculated ones using the Eq. (6). Figure 3 shows that these two types of results have the same values and the same trend over the actual simulation time. Therefore Eq. (6) can be used to extrapolate to real time of the diffusion experiments which usually takes at least several seconds. This way for a characteristic temperature \( T_c = 1100 \) K and a time of 15 min, the width of the diffusion layer is \( L_{Si} \sim 4.3 \) μm and \( L_{Ge} \sim 1 \) μm.

![Figure 3. The thicknesses of the diffusion layer, where solid curves obtained by Eq. (6) and dots – the LAMMPS simulations for different temperatures \( T_c = 900 \) K (red curve), 1000 K (black curve), 1100 K (blue curve), 1200 K (green curve), 1300 K (gray curve).](image)

3. Conclusion

We investigated the inter-diffusion of Si and Ge atoms at the interface Si/Ge using numerical simulation based on classical molecular dynamics methods. Based on the radial distribution function between the sites of various Si/Ge atoms, we studied changes in structural properties during diffusion. It was found that significant changes begin to occur at temperatures of 1000 K, which is associated with the rate of diffusion processes and the formation of a large number of defects at the interface. Using the mean square atomic displacement, the coefficients of mutual diffusion of Si in Ge and vice-versa were found at sintering temperatures of 900–1300 K. The thickness of the diffusion layer was calculated numerically and based on the classical theory and the simulation results were extrapolated to a minute scale for a qualitative comparison with the real diffusion experiments, and it was shown that the diffusion depth significantly depends on the sintering time, while silicon atoms penetrate 1.5 times deeper into bulk germanium than germanium into silicon, which consistent with experiments.

Acknowledgments

This work was supported by a grant from the Russian Science Foundation № 17-79-20173.
References
[1] Gayner C, Kar K 2016 Prog. Mat. Science 83 330.
[2] Usenko A., Moskovskikh D., KorotitskiyA. et.al. 2016 J. of Electronic. Mater. 45(7) 3427.
[3] Dorokhin M V, Demina P B, Erofeeva I V et.al. 2019 Semiconductors 53(9) 1158.
[4] Smagina J V, Novikov P L, Armbrister V A et.al. 2009 Physica B 404 4712.
[5] Ji P, Zhang Y, Yang Mo 2013 J. Appl. Phys. 114 234905.
[6] LAMMPS download site: lammps.sandia.gov.
[7] Heermann D W 1990 Computer simulation methods in theoretical physics (Berlin: Springer) p. 664
[8] Laidler K J 1987 Chemical Kinetics (Third ed. Harper & Row) p. 272.
[9] Kuznetsov Yu M, Bastrakova M V, Dorokhin M V et.al. 2020 AIP Advances: in press
[10] Volodin V, Gatskevich E I, Dvurechenskii AV et.al. 2003 Semiconductors 37(11) 1315.