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An Investigation of Temperature Dependence of Thermal Conductivity of Isotope Silicon

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Thermal conductivity of solid silicon as a function of the mole fraction of isotopes and temperature was investigated by molecular dynamics. We employed equilibrium molecular dynamics based on Green-Kubo's formula in which the autocorrelation function of heat flux was integrated as a function of duration time. The results of calculation showed that thermal conductivity of mixed isotope-silicon is smaller than that of pure isotope silicon. The results also showed that the thermal conductivity of isotope silicon decreased monotonically with increase in temperature within the temperature range from 300 to 1600K.
Key words: silicon, thermal conductivity, isotope, molecular dynamics

1. INTRODUCTION

Development of high-speed, large-scale integration circuits (LSIs) is important for realization of high-speed communication through information technology (IT). To enhance the operation speed of LSIs, a large amount of electric power must be supplied to the LSIs. Since the supply of a large amount of electric power would result in an increase in the temperature of the device, the heat generated by dissipation of the electric power must be removed efficiently from the device. For efficient removal of heat, heat transfer in the crystal must be enhanced. However, removal of heat from the device is limited by the thermal conductivity of a silicon crystal, which has been thought to a unique value of the crystal.

The thermal conductivity of a crystal is governed by lattice vibration or phonon propagation in the crystal. Therefore, if phonon propagation based on the lattice vibration can be controlled, it will be possible to change the thermal conductivity of a crystal. One of the governing parameters of thermal conductivity of a crystal is the mass of atoms in the crystal. Semiconductor crystals such as silicon, gallium nitride and gallium arsenide have several masses due to the existence of several isotopes of the materials in nature. Silicon has three different masses 28, 29 and 30, while gallium and arsene have two and three isotopes, respectively.

Studies on the effects of isotopes on thermal conductivity of semiconductors started about 50 years ago [1]. A pioneering work on the thermal conductivity of germanium indicated that the thermal conductivity could be modified by changing the mass ratio of the isotopes of germanium [2, 3]. Studies on the isotope effects on spin in semiconductors have also been developed within a couple of years due to development of idea of quantum computers [4-6].

Molecular dynamics simulation of thermal conductivity in crystals remains difficult due to limited computational power. The simulation domain should be in the order of one mean free path of phonon in order to estimate thermal conductivity precisely. Several hundreds million atoms must be taken into account to achieve such a condition. The results of MD simulation based on non-equilibrium or equilibrium conditions have been reported [7, 8]. Each method has both merits and demerits.
This paper reports calculated thermal conductivity as a function of the mole fraction of isotopes of silicon and temperature dependence of thermal conductivity of isotope silicon.

2. MOLECULAR DYNAMICS

We used a classical molecular dynamics technique, which gives a non-quantum description of system including an N-atom system. Newton's second law shown in eq. (1) describes the motion of atoms:

$$M\frac{d^2 r_i}{dt^2} = \sum_{j>i}^{N} F_{ij}, \tag{1}$$

where M, r_i, t and F_{ij} are mass and position of atoms, time, and force between atoms of i and j, respectively. The potential used in this study has two-body and three-body potentials based on Stillinger-Weber potential [9].

The temperature of the system was easily calculated from the velocity of each individual atom since the Boltzmann distribution function allows straightforward derivation of the mean kinetic energy in eq. (2):

$$\langle E \rangle = \frac{1}{2} M \sum_{i=1}^{N} v_i^2 = \frac{3}{2} N k_B T \tag{2}$$

where k_B is the Boltzmann constant. The temperature of the system was controlled by Nose's method [10] to

keep the temperature of the system constant.

We selected equilibrium molecular dynamics simulation based on Green-Kubo's formulation [11, 12]. The thermal conductivity can be expressed by eq. (3), which is the integral over time t of the heat flux autocorrelation function (HAF) based on the formula:

$$\lambda = \frac{1}{3Vk_BT^2}\int_0^\infty \langle J(t)\cdot J(0)\rangle dt, \quad (3)$$

where V is the volume of the system, and T is the temperature of the sample. The angular brackets denote an ensemble average. The heat flux vector $J(t)$ is estimated by the following equation:

$$J(t) = \frac{1}{V}\frac{d}{dt}\sum_i r_i E_i, \quad (4)$$

where E_i is the particle energy. When expressing E_i in terms of atomic kinetic and potential energies (Φ_{ij}), eq. (4) becomes the following equation:

$$J(t) = \frac{1}{V}\left[\sum_{i=1}^{N}\left(v_i E_i + \frac{1}{2}\sum_{j=1,j\neq i}^{N} r_{ij}\cdot\left(F_{ij}\cdot v_i\right)\right)\right], \quad (5)$$

where v_i is the velocity of the ith atom. The first term on the right-hand side is related to local particle shifts typically occurring in liquid, while the second term describes thermal energy dissipated between atoms, which are dominant in solids.

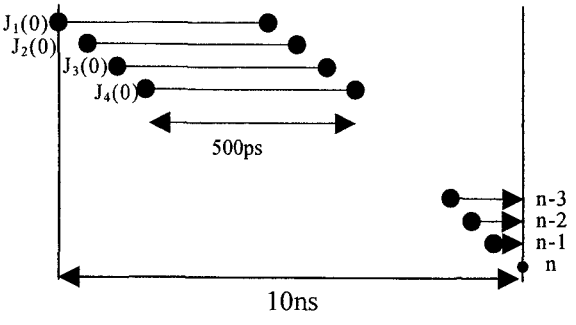

Fig. 1 Calculation scheme to obtain the average of the heat-flux autocorrelation function. The average of H. A. F. can be obtained by using $J_n(0)$ (n=1,n). Each H. A. F. has duration of 50ns. Total calculation time is 10 ns, which corresponds to $2x10^7$ steps.

We numerically obtained thermal conductivity of the system by integrating the ensemble average of $\langle J(0)\cdot J(t)\rangle$ as a function of time. Figure 1 shows the sequence of averaging process to develop statistics of the calculated data used in the present calculation. The time duration for the average of the autocorrelation function was selected to be 500 ps, which is longer than that of the typical phonon lifetime 76 ps [14]. We obtained the H. A. F. of $J(0)\cdot J(t)$ by averaging the sequence of $J_1(0)\cdot J_1(t)$, $J_2(0)\cdot J_2(t)$,.... Thus, total calculation time was set to 10 ns, which corresponds to $2x10^7$ steps shown in Fig. 1. We used the NVT ensemble with constraints of constant number of atoms and constant volume and temperature of the system. The time step was set to 0.5 fs with a total number of atoms of 64 to 1000. The temperature of the system was controlled by Nose's algorithm. We used the velocity Verlet method to calculate the H. A. F. with a long duration, since we need long duration to obtain sufficient statistics for calculation of thermal conductivity. When we calculate thermal conductivity as a function of isotope concentration, the isotopes of ^{28}Si, ^{29}Si and ^{30}Si are randomly set in the initial stage of calculation using random numbers.

3. RESULTS and DISCUSSION

3. 1 Temperature dependence

Figure 2 shows typical thermal conductivity as a function of time calculated by using eqs. (3), (4) and (5). Variation of the calculated thermal conductivity is almost saturated within the first 60 ps. The composition of isotopes was set to that of natural silicon (^{nat}Si), which contains ^{28}Si, ^{29}Si and ^{30}Si of concentration of 92.1%, 4.7% and 3.1%, respectively. Temperature and total number of atoms were set to 300 K and 512, respectively. The reported thermal conductivity of natural silicon is 156 W/mK [6], which is close to the calculated value shown in Fig. 2.

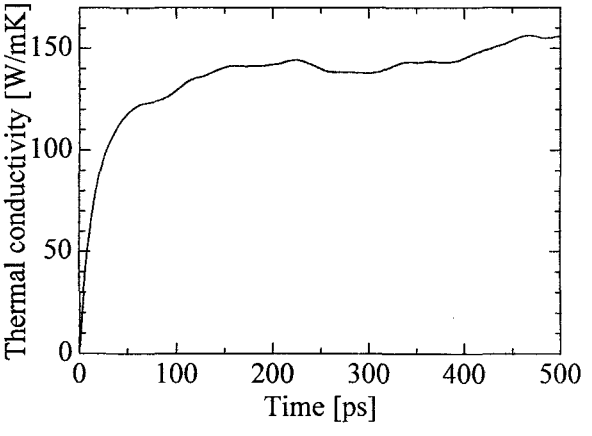

Fig. 2 Calculated thermal conductivity of natural silicon containing ^{28}Si, ^{29}Si and ^{30}Si at concentrations of 92.1%, 4.7% and 3.1%, respectively.

Figure 3 shows temperature dependence of the calculated thermal conductivity of silicon as a function of isotope concentration within the temperature range of

200 to 1685 K. Experimental data for natural silicon and the data on thermal conductivity of pure ^{28}Si reported by Volz et al. [13] are also shown in the figure.

The present calculation revealed that the values of natural silicon and purified isotope of ^{28}Si are monotonically decreased as a function of temperature. Although the thermal conductivity with enriched ^{28}Si is not shown in the temperature range from 1100 to the melting point (1685 K), we can estimate that the values with enriched ^{28}Si are higher than that of natural silicon.

Moreover, it can be seen that the values of silicon containing ^{28}Si, ^{29}Si and ^{30}Si at concentrations of 99.0%, 0.6% and 0.4% indicated by open triangles are higher than that with ^{28}Si, ^{29}Si and ^{30}Si at concentrations of 92.1%, 4.7% and 3.1% which corresponds to the concentration of natural silicon indicated by closed squares. Furthermore, silicon containing ^{28}Si, ^{29}Si and ^{30}Si at concentrations of 92.1%, 4.7% and 3.1% showed higher thermal conductivity than that with ^{28}Si, ^{29}Si and ^{30}Si at concentrations of 85.0%, 9.0% and 6.0% indicated by crosses.

The results show that degradation of the thermal conductivity depends on the isotope concentrations of ^{29}Si and ^{30}Si in ^{28}Si crystals.

The values of enriched ^{28}Si crystal denoted by open triangle calculated in the present study are slightly higher than those of experimental value indicated by closed triangle in the temperature range of 400 to 500 K. This may be based on the effects of periodic boundary condition on lifetime of phonon in the calculating system.

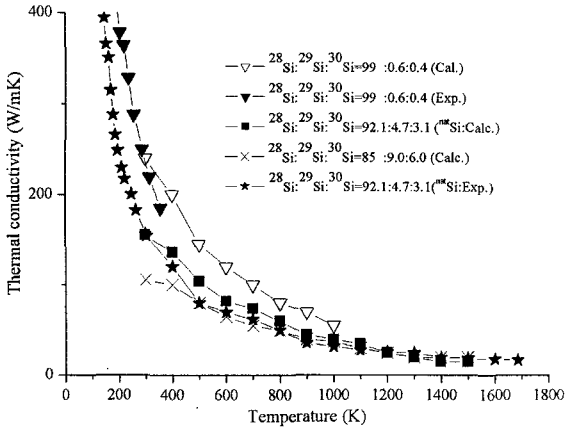

Fig. 3 Temperature dependence of thermal conductivity of isotope silicon. Open and closed triangles show the calculated and experimental values of silicon containing ^{28}Si, ^{29}Si and ^{30}Si at concentrations of 99.0%, 0.6% and 0.4%, respectively. Closed squares and stars show the calculated and experimental values of natural silicon, respectively. Crosses show calculated values of silicon containing ^{28}Si, ^{29}Si and ^{30}Si at concentrations of 85.0%, 9.0% and 6.0%, respectively.

The thermal conductivity versus temperature measured for various isotopic concentrations are displayed as log-log plots in Fig. 4. The overall feature of the curves displayed in Fig. 4 are those found for defect-free insulators: a maximum resulting of normal and Umklapp phonon processes which lead to a 1/T dependence above 100K. Although there are free electrons due to intrinsic carrier in the temperature range from 1200K to 1685K, the results shows that thermal conduction is not enhanced by the free carrier.

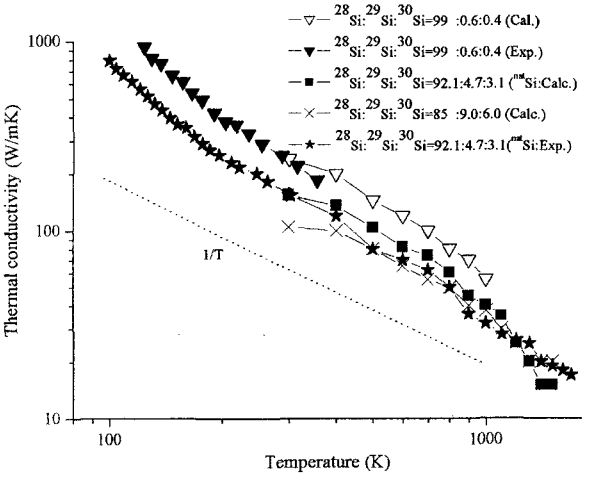

Fig. 4 Semi-logarithmic plot of thermal conductivity vs. T in the temperature range from 0 to 1685K.

3. 2 Isotope concentration

The effects of isotope concentration on thermal conductivity are shown in Fig. 5. The abscissa shows the concentration of $^{28}Si_x(^{29}Si_{4.7}{}^{30}Si_{3.1})_{1-x}$. The circle is the value of natural silicon with concentrations of $^{28}Si_{92.1}$, $^{29}Si_{4.7}$ and $^{30}Si_{3.1}$ [5].

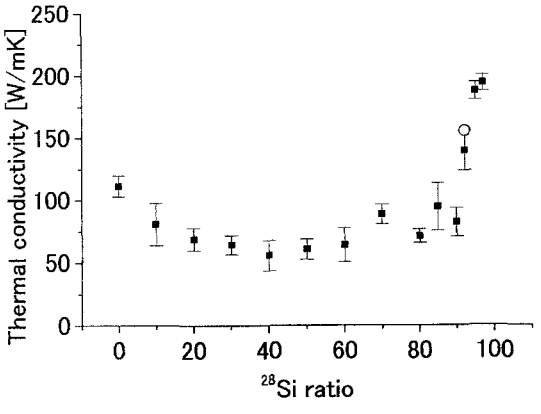

Fig. 5 Calculated thermal conductivity of $^{28}Si_x(^{29}Si_{30.1}{}^{30}Si_{19.9})_{1-x}$. The circles and open squares are the values of natural silicon with concentrations of $^{28}Si_{92.1}$, $^{29}Si_{4.7}$ and $^{30}Si_{3.1}$ and purified ^{28}Si-rich silicon [4, 5], respectively. The right end shows pure ^{28}Si, while the other end shows a mixture of ^{29}Si and ^{30}Si with a ratio of 4.7: 3.1.

The right end corresponds to pure ^{28}Si, while the other end shows a mixture of ^{29}Si and ^{30}Si. The results show that a binary isotope has greater thermal conductivity than that of a ternary isotope, while a pure isotope has much greater thermal conductivity. It has been demonstrated that mixing of isotopes results in the degradation of the thermal conductivity of silicon.

4. SUMMARY

Our numerical results obtained by using equilibrium molecular dynamics showed that the concentration of a mixed isotope affects the thermal conductivity of silicon. It was also clarified that thermal conductivities of natural and purified ^{28}Si decreased monotonically by increase of temperature of the system.

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