Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

What is the Thermal Conductivity Limit of Silicon Germanium Alloys?

Yongjin Lee, Alexander J. Pak and Gyeong S. Hwang[#]

McKetta Department of Chemical Engineering, University of Texas, Austin, Texas 78712, USA

Computational Details

To calculate the κ values of each SiGe alloy at 300K, equilibrium molecular dynamics (EMD) was employed using LAMMPS. The interatomic interactions were described using the Stillinger-Weber potential function with parameters that were re-optimized using a force-matching method based on DFT calculations. At each composition studied, unit cells were first constructed with 2^{3N} atoms in which the Si and Ge sites were randomly distributed. The unit cell length along the <100> direction was determined by Vagard's law; the lattice parameter of $Si_{1-x}Ge_x$ (a_{SiGe}) was approximated using linear interpolation between the Si and Ge lattice constants (optimized from DFT-GGA calculations), i.e, $a_{SiGe} = (1–x)a_{Si} + xa_{Ge}$, where a_{Si} = 5.4571 Å and a_{Ge} = 5.7564 Å.

As shown in Fig. 1 of the main text, each supercell was constructed by repeating the unit cell (for $N < 5$) in the x, y, and z directions such that the final size was commensurate with the $N = 5$ case. Therefore, each $Si_{1-x}Ge_x$ system for EMD calculations contained 32768 atoms. By doing so, the finite size effect typical in EMD calculations was mitigated and the influence of repeating unit cell size on κ could be clearly compared. Periodic boundary conditions were applied in all three directions and a time step of 0.5 fs was used.

First, each system was equilibrated in the canonical ensemble (NVT) using a Nose-Hoover thermostat for 5×10^5 steps at 300 K. Then, heat fluxes were computed using the microcanonical ensemble (NVE) during the following 4×10^6 steps (2 ns). Quantum corrections were applied using

a Debye temperature (T_D) approximated for $Si_{1-x}Ge_x$ by $T_D(Si_{1-x}Ge_x) = (1–x)T_D(Si) + xT_D(Ge)$, where $T_D(Si) = 645$ K and $T_D(Ge) = 374$ K. All reported results for each composition were obtained from statistics averaged over 15 independent simulations for 3 different configurations (5 independent runs for each configuration).

The phonon relaxation time τ_i is obtained by fitting the autocorrelation function of the total energy $E_i(t)$ with an exponential ($e^{-t/\tau}$) and taking the time constant (τ) to be equal to the phonon relaxation time. $E_i(t)$ is calculated from

$$E_i(t) = \frac{A_i(t) \cdot A_i^*(t) \cdot \omega_i^2(t)}{2} + \frac{\dot{A}_i(t) \cdot \dot{A}_i^*(t)}{2} \quad \text{(Eq. S1)}$$

where

$$A_i(t) = \sum_{j=1}^{N_T} \sqrt{\frac{m_j}{N_T}} e(i,j) \cdot \vec{u}_j(t) \quad \text{(Eq. S2)}$$

$$\dot{A}_i(t) = \sum_{j=1}^{N_T} \sqrt{\frac{m_j}{N_T}} e(i,j) \cdot \vec{v}_j(t) \quad \text{(Eq. S3)}$$

$A_i(t)$ and $\dot{A}_i(t)$ are the potential and kinetic energy of mode *i*, respectively. ω_i is the angular frequency and * denotes the complex conjugate. N_T is the total number of atoms in a system, m_j is the mass of the *j*th atom, $\vec{u}_j(t)$ is the atomic displacement from equilibrium position (at t = 0), and $\vec{v}_j(t)$ is the atomic velocity at time *t*, and $e(i,j)$ is the polarization vector of *j*th atom for mode *i*. The eigenmodes and frequencies are obtained by direct diagonalization of the dynamical matrix, which was computed from finite differences of the atomic forces. $\vec{u}_j(t)$ and $\vec{v}_j(t)$ are obtained from the atomic trajectories generated by a microcanonical MD simulation 4 ns long. Effective group velocities ($v_{g,i}$) were calculated from least square fit by a quadratic function to dispersion

curves $\Delta\omega(q)$ within # Å^{-1} close to the Γ point. An effective mean free path of phonon mode *i* is defined by $\lambda_i = v_{g,i} \times \tau_i$. The examined composition is 50% Ge and the number of atoms in this calculation is 4096 for all samples.

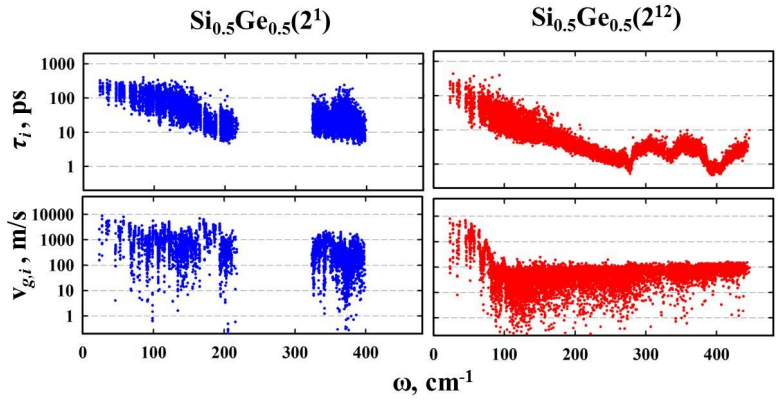

Figure S1. The phonon relaxation time(τ_i) and group velocity ($v_{g,i}$) of $Si_{0.5}Ge_{0.5}$ (2^1) and $Si_{0.5}Ge_{0.5}$ (2^{12}) as a function of frequency.

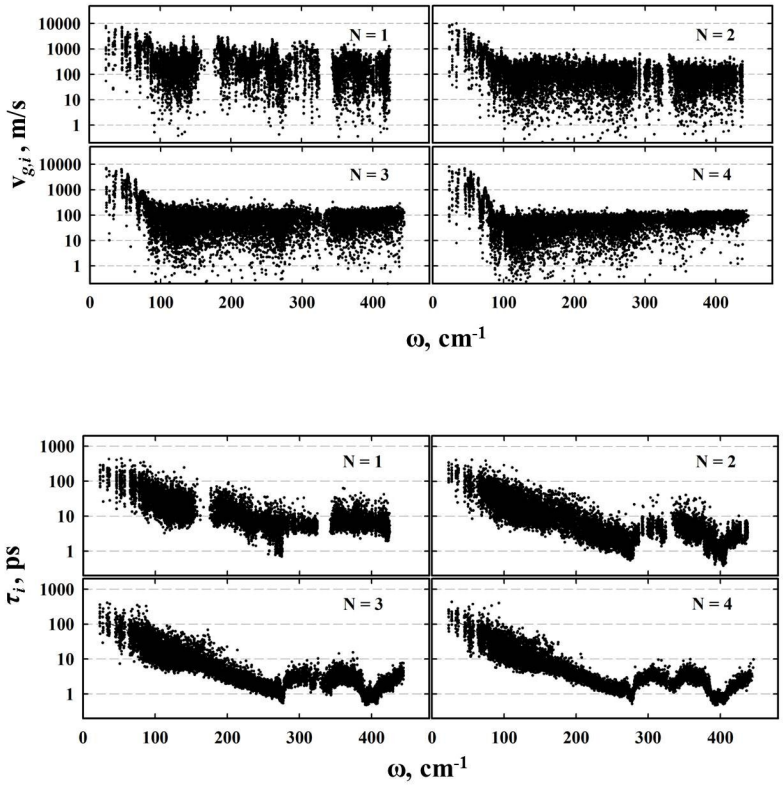

Figure S2. The phonon relaxation time(τ_i) and group velocity ($v_{g,i}$) of $Si_{0.5}Ge_{0.5}$ (2^{3N}) from $N = 1$ to 4 as a function of frequency.