DESIGNING Si/Si$_{1-x}$Ge$_x$ SUPERLATTICES WITH TAILORED THERMAL TRANSPORT PROPERTIES

E. S. Landry and A.J.H. McGaughey
Department of Mechanical Engineering
Carnegie Mellon University
Pittsburgh, Pennsylvania 15213-3890

INTRODUCTION

Si/Si$_{1-x}$Ge$_x$ superlattices are promising candidates for thermoelectric energy conversion applications [1, 2], as the phonon transport through them can be inhibited while maintaining desirable electrical transport properties. No comprehensive experimental study has been performed to map the thermal conductivity design space accessible by Si/Ge nanocomposites. By using atomistic modeling tools, interesting areas of the design space can be identified and then further explored experimentally.

In this work, we use molecular dynamics (MD) simulations and the direct method to predict the thermal conductivity of bulk Si, bulk Ge, Si$_{1-x}$Ge$_x$ alloys, Si/Ge superlattices (with equal Si and Ge layer thicknesses), and Si/Si$_{0.7}$Ge$_{0.3}$ superlattices (with the Si layer being twice as thick as the alloy layer). The predictions are compared to experimental data.

PROCEDURE

The atomic interactions are modeled using the Stillinger-Weber interatomic potential [3–5]. The velocity Verlet algorithm is used to integrate the Newtonian equations of motion with a time step of 0.55 fs. The thermal conductivity predictions are made at a temperature of 500 K, where quantum effects are expected to be negligible. The 24 × 24 Si/Ge superlattice (i.e., a superlattice whose unit cell contains 24 monolayers of silicon and 24 monolayers of germanium) is shown in Fig. 1. The interfaces between the species are parallel to the (001) crystallographic plane, and unless otherwise noted, are perfect with no species mixing or defects. In all of the samples, the mass of each atom is randomly assigned according to the natural isotope abundance for each species [6]. All of the thermal conductivity predictions are made using relaxed, zero-stress, symmetrically strained samples.

The thermal conductivity is predicted using the direct method [7]. In this method, a known heat flux $q$ is applied across...
the sample and the resulting temperature gradient is measured. The thermal conductivity is then determined using the Fourier law. A schematic of the direct method simulation cell is shown in Fig. 2. The system consists of a sample bordered by hot and cold reservoirs (which have the same composition as the sample) and fixed boundaries in the z-direction (to prevent the sublimation of the reservoir atoms). Periodic boundary conditions are imposed in the x- and y-directions. We account for simulation cell size effects using the method suggested by Schelling et al. [7].

RESULTS

The thermal conductivity predictions for all of the structures are plotted in Fig. 3 against the atomic fraction of Ge in the sample. We predict the thermal conductivities of bulk Si and bulk Ge to be 103±21 W/m-K and 61±12 W/m-K, 35% and 80% greater than the experimental values of 76.2 W/m-K and 33.8 W/m-K. [6] The predicted value for bulk Si is within the measurement uncertainty of the value of 119±40 W/m-K predicted by Schelling et al. for isotopically pure Si [7].

For the Si$_{1-x}$Ge$_x$ alloys, the thermal conductivity initially decreases with increasing Ge concentration until $x \approx 0.375$, beyond which the thermal conductivity increases with increasing Ge concentration. To our knowledge, the thermal conductivity of undoped Si$_{1-x}$Ge$_x$ alloys at a temperature of 500 K has only been measured experimentally for $x \approx 0.3$ and $x \approx 0.7$ [8]. At these Ge concentrations, the MD-predicted thermal conductivities are approximately 50% and 30% less than the experimental measurements of $\sim$5-6 W/m-K [8].

Experimental data for the thermal conductivity of Si/Si$_{0.7}$Ge$_{0.3}$ and Si/Ge superlattices is available only up to a temperature of $\sim$300 K [9, 10]. The superlattice thermal conductivity, however, is experimentally observed to be independent of temperature above $\sim$200 K. Therefore, we can compare our MD predictions to the experimental room temperature measurements, assuming that the thermal conductivity remains temperature-independent up to a temperature of 500 K. Based on experimental thermal conductivity data for the Si$_{1-x}$Ge$_x$ alloy (which has a similar dependence on temperature as the superlattices) [8–10], we believe that the difference between the superlattice thermal conductivities at temperatures of 300 K and 500 K will be less than 25%.

We predict the thermal conductivity of the Si/Si$_{0.7}$Ge$_{0.3}$ superlattices to decrease with decreasing period length until a period length of 6.55 nm (the 32×16 superlattice), beyond which there is a slight increase in the thermal conductivity. Due to the prediction uncertainty (estimated to be $\pm$20%), however, we cannot conclude that a minimum exists in the Si/Si$_{0.7}$Ge$_{0.3}$ superlattice thermal conductivity as a function of period length. We note that thermal conductivity is observed to decrease monotonically with decreasing period length in the experiments [9]. This trend is expected when phonon transport is incoherent across the interfaces due to increasing interface density. For the entire period length range, the MD predictions are a factor of $\sim$2-3 below the experimental values. The MD predictions are in qualitative agreement with the experiment result that the superlattice thermal conductivity is greater than an alloy of similar composition (here, the Si$_{0.1}$Ge$_{0.9}$ alloy).

We predict the thermal conductivity of the Si/Ge superlattices to decrease with increasing period length and then reach a constant value of $\sim$12 W/m-K for period lengths between 6.64 nm and 11.07 nm (the 24×24, 32×32, and 40×40 superlattices). The decreasing thermal conductivity trend with increasing period length is indicative of coherent phonon transport (i.e., the phonons in the Si layer are coherently correlated to phonons in the Ge layer) and is a result of decreases in the average phonon group velocity [11–13]. We note that this trend is also observed in the experimental data of Borca-Tasciuc et al. [10]. The magnitude of the predicted thermal conductivity, however, is a factor of $\sim$4 greater than the experimental measurements. A major qualitative difference is observed between the MD predictions and experimental measurements as well. We predict the Si/Ge superlattice thermal conductivities to be greater than that of the Si$_{0.5}$Ge$_{0.5}$ alloy, while experimentally, the opposite trend is observed.

The differences between the MD predictions and experimental measurements observed for the Si/Ge superlattices is likely due to differences in the sample quality (e.g., interfacial species
mixing, strain-induced misfit dislocations). To test this hypothesis, we examine the effect of interfacial species mixing on the thermal conductivity of the $16 \times 16$ Si/Ge superlattice. We model the species mixing by randomly assigning the species of each atom in the interface region according to a distribution given by

$$x(z) = x_L + \frac{1}{2} (x_R - x_L) \left[ 1 + \tanh \left( \frac{4z}{D} \right) \right],$$

(1)

where $D$ is the interface thickness (i.e., the thickness of the species mixing region), $z$ is measured relative to the closest interface, and $x_L$ and $x_R$ are the desired Ge concentrations on the left ($z < 0$) and right ($z > 0$) sides of the interface ($x_L$ and $x_R$ are either 0 or 1 for the Si/Ge superlattices). As shown in Fig. 3, the thermal conductivity of the $16 \times 16$ Si/Ge superlattice decreases with increasing interface thickness between interface thickness values of 2-6 monolayers. The interfacial species mixing decreases the thermal conductivity by a factor of 3-5 relative to the structure with perfect interfaces. This reduction is due to diffuse phonon scattering at the interfaces, leading to decreased ability for phonons to travel coherently through the structure. The thermal conductivity of the superlattices with interfacial species mixing, however, is still greater than the value for the Si$_{0.5}$Ge$_{0.5}$ alloy. We note that interfacial species mixing has a negligible effect on the thermal conductivity of a $32 \times 16$ Si/Si$_{10.7}$Ge$_{0.3}$ superlattice, a structure where the phonon transport is already incoherent.

**DISCUSSION AND CONCLUSIONS**

Molecular dynamics simulations and the direct method have been used to predict the thermal conductivity of bulk Si, bulk Ge, Si$_{1-x}$Ge$_x$ alloys, and Si/Si$_{0.7}$Ge$_{0.3}$ and Si/Ge superlattices at a temperature of 500 K. Experimental data exists for all of the samples considered in this study, which allowed for the direct comparison between the experimental measurements and the MD predictions.

Although quantitative differences are observed, the predicted thermal conductivity trends for bulk Si, bulk Ge, the Si$_{1-x}$Ge$_x$ alloys, and the Si/Si$_{0.7}$Ge$_{0.3}$ superlattices are in qualitative agreement with the available experimental data. We attribute the quantitative differences to the accuracy of the Stillinger-Weber potential. We note that any exact agreement would be fortuitous due to the known differences in the Stillinger-Weber potential and experimental measured phonon dispersion (and thus, phonon group velocities) for Si and Ge [4, 14]. The qualitative agreement in the thermal conductivity trends, however, indicates that the Stillinger-Weber potential can be used to guide the design of Si- and Ge-based nanocomposites for desired thermal properties (e.g., low thermal conductivity).

We predict the thermal conductivities of the Si/Ge superlattices to be greater than an alloy with identical Ge concentration, while experimentally, the opposite trend is observed. Interfacial species mixing was found to decrease the thermal conductivity of a $16 \times 16$ Si/Ge superlattice relative to the value predicted for a structure with perfect interfaces. The reduction in the thermal conductivity, however, is not sufficient to reduce the superlattice thermal conductivity below the alloy value. We believe that additional phonon scattering in the experimental samples that results from defects not present in the MD model (e.g., strain-induced misfit dislocations) may explain the observed discrepancy.

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**REFERENCES**


