

Thermal conductivity of epitaxial layers of dilute SiGe alloys

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The thermal conductivities of micron-thick epitaxial layers of dilute $\text{Si}_{1-x}\text{Ge}_x$ alloys, $2 \times 10^{-4} < x < 0.01$, are measured in the temperature range $297 < T < 550$ K using time-domain thermoreflectance. These new data are used to test competing models for the strength of phonon scattering by heavy impurity atoms. We find that the room temperature thermal conductivity of dilute SiGe alloys is adequately described by Abeles's theory of 1963. The change in the thermal conductivity with temperature, however, is less than predicted.

The thermal conductivity of a crystalline solid-solution is significantly smaller than the thermal conductivity of a pure crystals because high-frequency phonons are strongly scattered by deviations from the perfect periodicity of the crystal.¹ This property of semiconductor alloys has been applied for nearly 50 years in improving the efficiency of semiconductors used in thermoelectric cooling, heating, and power generation.² In modern high-speed and high-power electronics, however, the reductions in thermal conductivity created by mass-disorder are detrimental to the operation of the device: lattice matched and strained epitaxial alloys are essential for engineering the electronic structure of electronic devices but the small thermal conductivity of the alloys aggravates problems of thermal management.

The first theories of phonon scattering by point-defects are based on perturbation theory³ and the strength of the phonon scattering was shown to scale with the square of the difference between the mass of the substitutional atom and the average atomic mass. The dimensionless scattering strength Γ_1 is then

$$\Gamma_1 = \sum_i c_i \left(\frac{m_i - \bar{m}}{\bar{m}} \right)^2, \quad (1)$$

where c_i is the fractional concentration of the i th species, m_i is the atomic mass of the i th species, and \bar{m} is the average atomic mass. For Si, the naturally occurring isotope mixture gives $\Gamma_1 = 2.0 \times 10^{-4}$.

Since Eq. 1 was originally derived for weak scattering in the long wavelength limit, the reliability of this equation for describing phonon scattering by a heavy impurity atom can certainly be questioned. For example, the Ge atomic mass is 2.6 times the average atomic mass of the Si lattice and term in the parenthesis of Eq. 1 is significantly larger than unity; the Ge content of a dilute SiGe alloy increases the scattering strength by $\Delta\Gamma_1 = 2.5x$. Exact theoretical treatments of the lattice dynamics of one-dimensional chains⁴ and three-dimensional lattices⁵ support the use of Eq. 1 in the long wavelength, and while some of the experiments show discrepancies, in most cases, the low temperature thermal conductivities

of alkali halides doped with heavy impurity atoms^{5,6} typically agree quite well with modeling based on Eq. 1.

The main concern of this paper is the thermal conductivity of substitutional alloys near room temperature and above where most of the phonon modes of the crystal are thermally excited; therefore, we must consider scattering of all wavelengths of phonons, not only the long-wavelength limit. (Even for Si with a relatively high Debye temperature of 645 K, the heat capacity at room temperature is 80% of the classical limit.) An alternative to Eq. 1 has been discussed and applied in the analysis of thermal conductivity reductions created by heavy impurity atoms.⁷⁻⁹

$$\Gamma_2 = \sum_i c_i \left(\frac{m_i - \bar{m}}{m_i} \right)^2. \quad (2)$$

In this case, the mass difference is normalized by the impurity mass m_i rather than the average mass \bar{m} and the Ge content of a dilute SiGe increases the scattering strength by $\Delta\Gamma_2 = 0.38x$. For heavy impurity atoms, Eqs. 1 and 2 give very different predictions for the strength of the phonon scattering.

Our new contribution to this relatively mature topic is enabled by recent advances in materials and experimental techniques. Isotopically purified Si has been produced as bulk single crystals and epitaxial layers and a consensus has emerged¹⁰⁻¹² on the thermal resistance created by the naturally occurring isotope disorder of Si. Since the perturbation analysis for phonon scattering should have the greatest validity when the mass difference are small, these new data provide a rigorous constraint of the theory in the limit of weak scattering. The second advance is our development of an accurate technique for measuring the thermal conductivity of micron-thick layers of high thermal conductivity materials. In most cases, homogeneous single crystals of alloys are difficult to obtain by the methods employed in bulk crystal growth. Our new measurement technique enables us to study homogeneous epitaxial layers of semiconductor alloys grown by chemical vapor deposition or molecular beam epitaxy. The technique is based on time-domain thermoreflectance^{13,14}

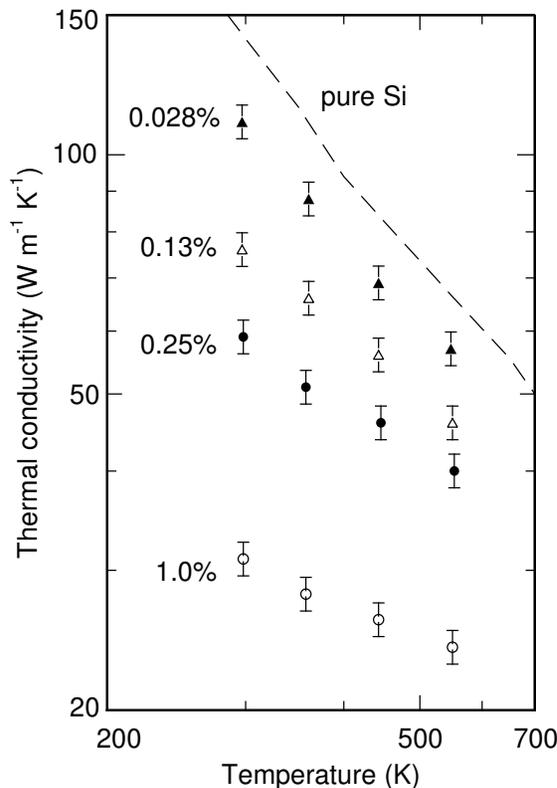


FIG. 1: Thermal conductivity of epitaxial SiGe layers as a function of temperature. The data points are labelled by the Ge concentration in atomic percent. Data for 0.028% and 0.13% are from Ref. 12. The error bars reflect an experimental uncertainty of $\pm 5\%$ in thermal conductivity. The dashed line is the thermal conductivity of pure Si from Ref. 16.

measurements of heat transport but we modify the analysis of the data to take advantage of the extra information contained in the out-of-phase component of the thermoreflectance signal. The details of our technique and methods for data analysis are described in Refs. 12 and 15.

We previously reported data for two compositions of highly dilute $\text{Si}_{1-x}\text{Ge}_x$ alloys with $x = 2.8 \times 10^{-4}$ and $x = 1.3 \times 10^{-3}$ as a part of our study of the thermal conductivity of isotopically purified Si.¹² The new data reported here are for compositions $x = 2.0 \times 10^{-4}$ and $x = 8.0 \times 10^{-4}$ at room temperature and $x = 2.5 \times 10^{-3}$ and $x = 0.010$ in the temperature range $297 < T < 550$ K. The new epitaxial layers of $\text{Si}_{1-x}\text{Ge}_x$ alloys were grown at the Seitz Materials Research Laboratory using disilane and digermane precursors at a growth temperature of 1073 K; the thickness of the $x = 0.010$ layers is 580 nm; the thickness of the other layers is 1.3 μm . The Ge content of the $x = 0.010$ sample was measured by Rutherford backscattering spectrometry; the composition of the lower concentration samples were characterized to an accuracy of $\pm 15\%$ by secondary ion mass spectrometry (SIMS) using the $x = 0.010$ sample as a standard.

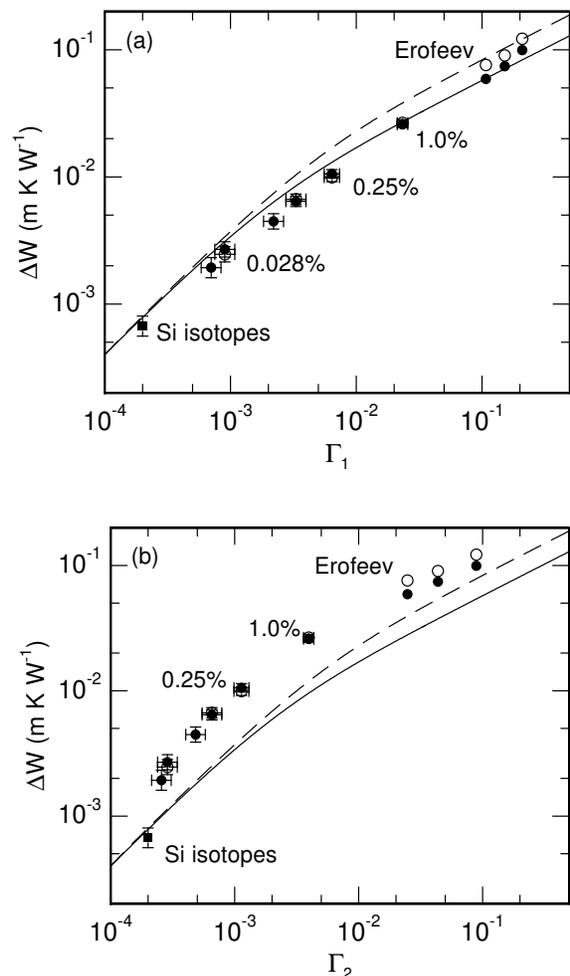


FIG. 2: Increase in the thermal resistance ΔW generated by mass-disorder phonon scattering in Si at 297 K (solid symbols) and 550 K (open symbols). In the upper figure (a), the dimensionless strength of phonon scattering is evaluated using Eq. 1; the bottom figure (b) uses Eq. 2. Selected points for dilute Ge alloys (filled and open circles) are labeled by the Ge concentration in atomic percent; the six data points labelled “Erofeev” are for alloys with 5, 8.5, and 15% Ge concentrations from Ref. 17. The solid square is for the thermal resistance created by the naturally occurring isotope disorder in Si from Ref. 11. The data for 297 K and 550 K nearly overlap for Ge concentrations of 0.028, 0.13, 0.25, and 1.0 atomic percent. The solid and dashed lines are the evaluation of Abeles’s theory, see Ref. 18, for 297 and 550 K respectively with $\alpha = 2$.

The thermal conductivity of $\text{Si}_{1-x}\text{Ge}_x$ is plotted as a function of temperature and composition in Fig. 1. The thermal conductivity of Si is decreased by a factor of ≈ 2 for a Ge concentration of 0.13 atomic percent. The temperature dependence of the data becomes progressively less pronounced with increasing Ge content.

In Fig. 2, we plot the increase in thermal resistance ΔW of Si created by mass-disorder using the measured thermal conductivity of ^{28}Si from Ref. 11 as the baseline. The x-axis of the upper and lower plots differ: for the

upper plot, the x-axis is evaluated using Eq. 1 and for the lower plot, the x-axis is evaluated using Eq. 2. As we have noted previously¹², the use of Eq. 1 to describe the phonon scattering strength Γ_1 produces a smooth connection between the the thermal resistance created by isotope disorder and the thermal resistance created by low concentrations of Ge. If we instead use Eq. 2 and plot the data as a function of Γ_2 , the thermal resistance increases sharply for low concentrations of Ge, see Fig. 2b.

The solid and dashed lines are our evaluation of the theory developed by Abeles¹⁸ in 1963 to describe the high temperature thermal conductivity of $\text{Si}_{1-x}\text{Ge}_x$ alloys with much higher concentrations Ge, $x > 0.2$. Since we are mostly interested in low Ge concentrations, we do not include the virtual crystal approximations of the original theory that are needed to describe the entire range $0 < x < 1$. The theory has one free parameter: α , the ratio of the normal to umklapp three-phonon relaxation rates. In the original analysis, Abeles found $\alpha = 2.5$. We find that $\alpha = 2.0$ produces a better match between theory and data at low concentrations, see Fig. 2a. The agreement between theory and experiment is remarkably good when the strength of the mass-disorder scattering

is calculated using Eq. 1, see Fig. 2a.

On close inspection however, we note that the theory over-predicts the temperature dependence of the thermal resistance. For example, the thermal resistance with $x = 0.01$ is the same at $T = 297$ and $T = 500$ K to within the uncertainties of our measurement while the theory predicts an increase in the thermal resistance of a factor of $(550/297)^{0.5} = 1.36$. Presumably, this discrepancy results from the simplifications used in developing the theory¹⁸—e.g., the use of the Debye model model to describe the lattice dynamics. More sophisticated models of the lattice dynamics will be required to make a truly quantitative theory of the thermal conductivity of semiconductor alloys.

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