Thermal conductivity of epitaxial layers of dilute SiGe alloys

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The thermal conductivities of micron-thick epitaxial layers of dilute $Si_{1-x}Ge_x$ 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. Even though the mass difference between Ge and Si is much larger than the Si atomic mass, we find that the thermal conductivity of dilute SiGe alloys is adequately described by the scattering strength for point defects derived by perturbation theory by Klemens in 1955.

I. INTRODUCTION

The thermal conductivity of crystalline solid solutions is significantly smaller than the thermal conductivity of 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 semiconductor alloys aggravates problems of thermal management.

In Klemens's perturbation theory[3] for phonon scattering by point defects, the perturbation energy is proportional to the difference between the mass of the substitutional atom and the average atomic mass. The dimensionless scattering strength Γ_1 is then

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

where c_i is the fractional concentration of the ith species, m_i is the atomic mass of the ith species, and $\bar{m}$ is the average atomic mass. The relaxation time for a phonon mode of frequency ω and velocity v is $\tau^{-1} = A\omega^4$ with $A = \Omega\Gamma/(4\pi v^3)$ where Ω is the atomic volume. For Si, the naturally occurring isotope mixture gives $\Gamma_1 = 2.0 \times 10^{-4}$.

Since Eq. (1) is derived by perturbation theory for the limit of weak scattering, the reliability of this equation for describing phonon scattering by heavy impurity atoms can certainly be questioned. For example, the difference between the average atomic mass of Ge and the average atomic mass of Si is 1.58 times the average atomic mass of Si and the term in the parenthesis of Eq. (1) is significantly larger than unity. The Ge content of a dilute $Si_{1-x}Ge_x$ alloy increases the scattering strength by $\Delta\Gamma_1 = (1.58)^2 x = 2.5x$. Exact theoretical

treatments of the lattice dynamics of one-dimensional chains[4] and three-dimensional lattices[5] support the use of Eq. (1) in the long wavelength, and while some experiments show discrepancies, in most cases, the low temperature thermal conductivities of alkali halides doped with heavy impurity atoms[5,6] agree 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 of $3k_B$ per atom.) An alternative to Eq. (1) has been discussed and applied in the analysis of the reductions in thermal conductivity created by heavy impurity atoms:[7–11]

$$\Gamma_2 = \sum_i c_i \left(\frac{1/m_i - 1/\bar{m}}{1/\bar{m}} \right)^2. \tag{2}$$

This form of the scattering strength was derived by Tavernier using a perturbation energy that is proportional to the difference in the reciprocal of the atomic masses.[12] This form of the perturbation energy is based on the assumption that the momentum of the atomic vibrations is unchanged by the perturbation; this is in contrast to Klemens's theory[3] where the frequency of the atomic vibrations is unchanged by the perturbation. According to Eq. (2), the Ge content of a dilute $Si_{1-x}Ge_x$ 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.

We have omitted contributions to Γ_1 and Γ_2 from changes in the force constants and lengths of the Ge–Si bonds. The correct way to include these terms in the cross section for phonon scattering has been controversial for many years. Krumhansl[4] argues that terms linear in the mass difference and changes in force constant must be added first and then squared. Klemens[10] makes the same point concerning the changes in atomic radius. For the case we are considering,

Ge impurities in Si, the contribution to the scattering amplitude from the larger volume of the Ge atom, $\Delta V//V \approx 0.12$, is expected to enhance the scattering, while the contribution from the softening of the modulus $\Delta K/K \approx -0.23$ is expected to weaken the scattering. Therefore, the total correction to Γ_1, see Eq. (1), will be small. The total correction to Γ_2, see Eq. (2), might be significant, but given the large uncertainties in how to best evaluate those corrections, we have decided to omit them here.

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 emerged[13–15] on the thermal resistance created by the naturally occurring isotope mixture of Si. (The good agreement between theory[16] and experimental results for both bulk crystals[13,14] and epitaxial layers[15] lead us to discount other studies[17,18] of epitaxial layers that found much larger enhancements in the thermal conductivities of isotopically purified Si relative to natural Si.) Since the perturbation analysis for phonon scattering should have the greatest validity when the mass differences are small, these new data provide a rigorous constraint on 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[19,20] 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 approach and methods for data analysis are described in Refs. 15 and 21.

II. EXPERIMENTAL DETAILS

We previously reported data for two compositions of highly dilute $Si_{1-x}Ge_x$ alloys with $x=2.8\times10^{-4}$ and $x=1.3\times10^{-3}$ as a part of our study of the thermal conductivity of isotopically purified ^{28}Si.[15] The new data reported here are for compositions $x=2.0\times10^{-4}$ and $x=8.0\times10^{-4}$ at room temperature and $x=2.5\times10^{-3}$ and $x=0.010$ in the temperature range $297<T<550$ K. The epitaxial layers of $Si_{1-x}Ge_x$ alloys were grown using disilane and digermane precursors at a 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 to a precision of $\pm7\%$; the composition of the lower concentration samples were characterized to an accuracy of $\pm20\%$ by secondary ion mass spectrometry (SIMS) using the $x=0.010$ sample as a standard.

III. RESULTS AND DISCUSSION

The thermal conductivity of $Si_{1-x}Ge_x$ is plotted as a function of temperature and composition x in Fig. 1. The thermal
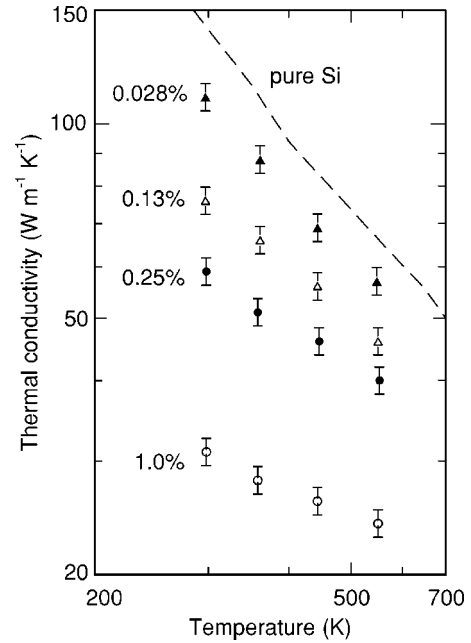

FIG. 1. Thermal conductivity of epitaxial SiGe layers as a function of temperature. The data points are labeled by the Ge concentration in atomic percent. Data for 0.028% and 0.13% are from Ref. 15. The error bars reflect an experimental uncertainty of $\pm5\%$ in thermal conductivity. The dashed line is the thermal conductivity of pure Si from Ref. 22.

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 the thermal resistance of Si created by mass-disorder ΔW as a function of the scattering strength Γ. For room temperature data, we use the measured thermal conductivity of ^{28}Si as the baseline;[14] the thermal resistance created by isotope scattering reported in Ref. 14, $\Delta W=6.4\pm1.0\times10^{-4}$ m K W^{-1}, is comparable to the average of the other two reliable measurements.[13,15] Our prior measurements of the thermal conductivity of ^{28}Si at elevated temperatures were not precise enough to determine ΔW for isotope scattering at $T=550$ K; therefore, we analyze ΔW at $T=550$ K only for cases where ΔW created by Ge impurities is at least an order of magnitude larger than ΔW created Si isotopes; this is true for Ge concentrations $>0.13\%$.

The horizontal axis of the upper and lower plots in Fig. 2 differ: for the upper plot, the horizontal axis is evaluated using Eq. (1) and, for the lower plot, the horizontal axis is evaluated using Eq. (2). As we have noted previously,[15] the use of Eq. (1) to describe the phonon scattering strength 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. 2(b).

The solid and dashed lines are our evaluation of the theory developed independently by Abeles[24] and by Parrott[25] to describe the high temperature thermal conductivity of
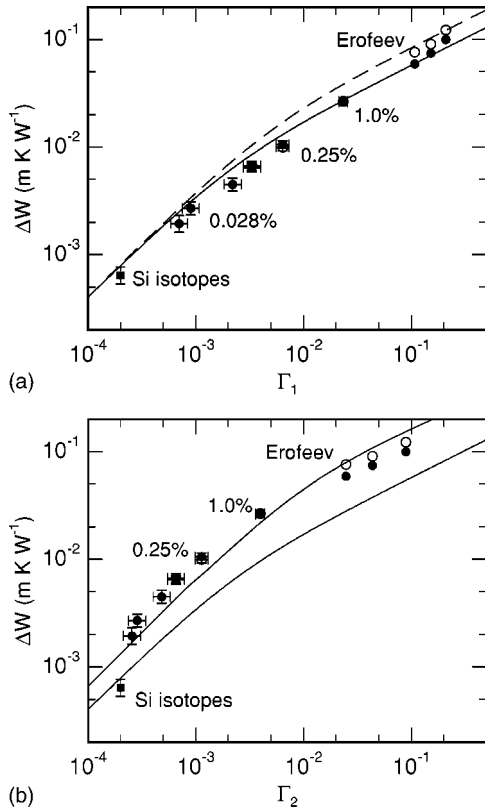
FIG. 2. Increase in the thermal resistance ΔW generated by mass-disorder phonon scattering in Si at $T=297$ K (solid symbols) and 550 K (open symbols). In the upper figure (a), the dimensionless strength of phonon scattering is evaluated using Eq. (1); the bottom figure (b) uses Eq. (2). Selected points for dilute Ge alloys (filled and open circles) are labeled by the Ge concentration in atomic percent; the six data points labeled "Erofeev" are for alloys with 5, 8.5, and 15% Ge concentrations from Ref. 23. The solid square is the thermal resistance at room temperature created by the naturally occurring isotope disorder in Si from Ref. 14. Data for 297 K and 550 K nearly overlap for Ge concentrations of 0.13, 0.25, and 1.0 atomic percent. In (a), the solid and dashed lines are our evaluation of Abeles's theory, see Ref. 24, for 297 and 550 K respectively with $\alpha=2$. In (b), the upper and lower solids lines are evaluations of Abeles's theory at $T=297$ K using $\alpha=20$ and $\alpha=2$, respectively.

$\mathrm{Si}_{1-x}\mathrm{Ge}_x$ alloys with much higher concentrations of Ge, $0.2 < x < 0.8$. In this theory, the Callaway transport equations are solved analytically in the high temperature limit for a Debye density of states and relaxation times of the phonons determined by the combination of point-defect scattering, and umklapp (U) and normal (N) three-phonon processes. The strength of the N processes is assumed to have the same form as the strength of U processes, $\tau_N^{-1}=B_N\omega^2 T$ and $\tau_U^{-1}=B_U\omega^2 T$. Since we are mostly interested in low Ge concentrations, we do not include the virtual crystal approximations[24] that are needed to describe the entire range of concentrations $0 < x < 1$. The theory has one free parameter: α, the ratio of the normal to umklapp three-phonon relaxation rates, i.e., $\alpha = B_N/B_U$. In the original analysis, Abeles found $\alpha=2.5$. We find that $\alpha=2.0$ produces a better match between the theory and the data at low concentrations; see Fig. 2(a). When the

strength of the mass-disorder scattering is calculated using Eq. (1), see Fig. 2(a), the agreement between theory and experiment is remarkably accurate. When the strength of the scattering is calculated using Eq. (2), see Fig. 2(b), we cannot simultaneously fit ΔW created by isotope scattering and ΔW for dilute SiGe alloys. Furthermore, use of Eq. (2) requires a very large value of the parameter, $\alpha=20$, to fit ΔW for SiGe alloys.

While the theory using Eq. (1) adequately describes the data, we note, however, that the theory overpredicts the temperature dependence of ΔW. For example, ΔW for $x=0.010$ is the same at $T=297$ K and 550 K to within the uncertainties of our measurement while the theory predicts an increase in ΔW by a factor of $\sqrt{550/297}=1.36$. Presumably, this discrepancy results from the simplifications used in developing the theory[24]—e.g., the use of the high temperature limit of the transport equations, and the use of the Debye model with a single phonon polarization to describe the lattice dynamics.

To examine the temperature dependence of ΔW in more detail, we follow the approach of Morelli and co-workers[16] and evaluate the Callaway transport equations numerically for a model that treats longitudinal and transverse modes separately. In this approach, dispersion of the phonon velocities is incorporated in an average sense by introducing a cutoff frequency for each mode that is equal to the phonon frequency at the zone boundary. We find that the low-temperature form of the N-process relaxation rate used in Ref. 16 produces too strong of a temperature dependence for ΔW. We therefore substitute a high temperature form for the N-process relaxation rate $\tau_N^{-1}=B_N\omega^2 T$. The relative strengths of B_U and B_N for transverse and longitudinal phonons is fixed by ratios of the mode velocities, Grüneisen constants, and cutoff frequencies. A fit to the room temperature thermal conductivity of ^{28}Si and natural Si is sufficient to constrain the remaining parameters of the theory; we find $(B_U)^T=1.2$, $(B_U)^L=0.8$, $(B_N)^T=2.2$, and $(B_N)^L=2.4$, all in units of 10^{-19} s K^{-1}. We have confirmed that this model is in agreement with the room temperature thermal conductivity of Si
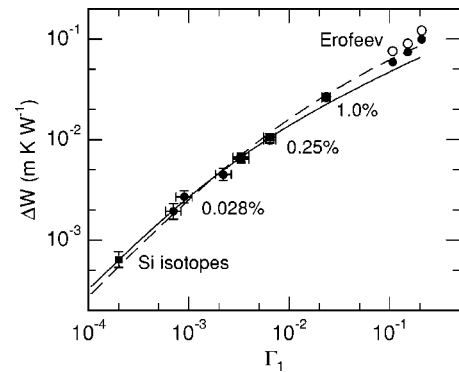

FIG. 3. Data for the thermal resistance ΔW generated by mass-disorder phonon scattering in Si at $T=297$ K (solid symbols) and 550 K (open symbols), as in Fig. 2(a), with comparisons to the more refined thermal conductivity model described in the text. Data for 297 K and 550 K nearly overlap for Ge concentrations of 0.13, 0.25, and 1.0 atomic percent. The solid and dashed lines are evaluations of the thermal conductivity model for 297 and 550 K, respectively.

nanowires[26] with diameters d between $37 < d < 115$ nm.

This more refined analysis predicts a smaller temperature dependence of ΔW than the original theories: the predicted change in ΔW is 24% between $T = 297$ K and 550 K for $x = 0.010$; see Fig. 3. This prediction is in better agreement with our data—we measure an increase of $4 \pm 5\%$ at $x = 0.010$—but still lies outside the experimental uncertainties.

In summary, we find that the strength of phonon scattering by heavy impurity atoms is well described by the perturbation theory of Klemens,[3] see Eq. (1), and that the strength of phonon scattering is poorly described by the perturbation theory of Tavernier;[12] see Eq. (2). The experimentally observed temperature dependence of the thermal resistance created by mass disorder is smaller than the temperature dependence predicted by the Callaway transport equations. More sophisticated models of the lattice dynamics will be required to develop a predictive theory of the thermal conductivity of semiconductor alloys that is accurate to better than 20%.

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