Role of Nanostructures in Reducing Thermal Conductivity below Alloy Limit in Crystalline Solids

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Abstract

Atomic substitution in alloys can efficiently scatter phonons, thereby significantly reducing the thermal conductivity in crystalline solids to the "alloy limit". It has been difficult to beat the alloy limit without creating defects, dislocations, and voids, which also reduce electrical conductivity, making it ineffective for increasing the material's thermoelectric figure of merit. Using $In_{0.53}Ga_{0.47}As$ containing epitaxially embedded ErAs nanoislands a few nm in size, we demonstrate thermal conductivity reduction by almost a factor of two below the alloy limit, and corresponding increase in thermoelectric figure of merit by more than a factor of two. A theoretical model suggests that while point defects in alloys efficiently scatter short wavelength phonons, the ErAs nanoislands provides additional scattering mechanism for the mid to long wavelength phonon – the combination reduces the thermal conductivity below the alloy limit.

Introduction

The performance of thermoelectric energy conversion devices depends on the thermoelectric figure of merit (ZT) of a material, which is defined as $ZT = S^2\sigma T/k$ where S, σ, k, and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. Low thermal conductivity and high power factor ($S^2\sigma$) are essential for efficient operation of thermoelectric devices. Over the past five decades, it has been challenging to increase $ZT > 1$, since modifying one parameter in ZT affects the others due to their interdependence [1, 2]. Recent reports have shown, however, that it is possible to $ZT > 1$ by nanostructuring thermoelectric materials [3-5]. While the original goal for nanostructuring was to increase $S^2\sigma$ due to quantum confinement of carriers [6, 7], experiments [3-5] have shown that the key reason for $ZT > 1$ was the reduction of thermal conductivity. Yet, the fundamental reasons for how and why nanostructuring reduces thermal conductivity in crystalline materials are not fully understood. In this paper, we experimentally and theoretically show that it is possible to reduce thermal conductivity by a factor ~ 2 below the "alloy limit" in crystalline materials, thus laying down some principles of designing nanostructured thermoelectric materials.

Historically, it has been difficult to reduce the thermal conductivity of crystalline solids below that of an alloy without creating defects, dislocations, and voids – often called the "alloy limit" of thermal conductivity in crystalline solids. For example, thermal conductivity of pressure-sintered $Si_{0.8}Ge_{0.2}$ alloy was shown to be less than that of the crystalline alloy due to heavy point defects [8]. However, the figure of merit was not increased due to proportional reduction in electrical conductivity. There have been reports that the thermal conductivity of Si/Ge superlattice can be lower than that of Si_xGe_{1-x} alloy [9, 10]. However, because of the large lattice mismatch (~ 4%) between Si and Ge, the strain between Si and Ge in Si/Ge superlattices produces defects and dislocations when the layer thickness exceeds the critical value. Such approaches also have not led to $ZT > 1$, thus suggesting that the electrical conductivity also reduces proportionally. More recently, despite systematically increasing the interfacial acoustic impedance mismatch in Si/Si_xGe_{1-x} or $Si_yGe_{1-y}/Si_xGe_{1-x}$ superlattices, Huxtable *et al*. [11, 12] failed to reduce the thermal conductivity below that of Si_xGe_{1-x} alloy without creating significant defects in the superlattice.

There are very few instances, however, where the thermal conductivity was reduced below the alloy limit [13, 14], while maintaining the crystalline structure of the material. Using GaAs/AlAs superlattices, Capinski *et al*. [13] showed that only when the period thickness was in the range of a few nm, the cross – plane thermal conductivity was less than that of an $Al_{0.5}Ga_{0.5}As$ alloy. Venkatasubramanian [14] measured the cross – plane thermal conductivity of Bi_2Te_3/Sb_2Te_3 superlattices and found the lattice conductivity of short-period (a few nm) superlattices to be less than those of solid solution alloy. It has been theoretically proposed that the thermal conductivity in such periodic structures is reduced due to the formation of phonon bandgaps [15], akin to the formation of

bandgaps in periodic electronic and photonic structures. However, at present there is no direct proof of this for phonons in the GaAs/AlAs and Bi_2Te_3/Sb_2Te_3 systems. It is noteworthy, though, that the common feature in these two studies was the length scale a few nm of the superlattice period.

Recently, Li *et al*. [16] measured the thermal conductivity of crystalline nanowires made of $Si/Si_{0.95}Ge_{0.05}$ superlattices and diameters in the range of 50-90 nm. Interestingly enough, they found the thermal conductivity of the superlattice nanowires to be lower than that of Si_xGe_{1-x} alloy, leading to the following hypothesis. According to Rayleigh criterion, the scattering cross section of phonons varies as $\sigma_{SC} \sim d^6/\lambda^4$, where d is the size of the scatterer and λ is the wavelength of the incident phonon. Since the defects in alloys are atomic in size, they are most effective in scattering short wavelength phonons, i.e. those near the Brillouin zone edge. However, mid to long wavelength phonons are scattered less effectively in alloys, and contribute to a large fraction of the thermal conductivity. By creating a nanowire, one introduces an additional length scale, which is used to scatter the mid-to-long wavelength phonons via boundary scattering. Hence, one introduces two spectrally-separated scattering mechanisms, which reduces thermal conductivity below the alloy limit. While this hypothesis provides a plausible explanation for the nanowire observations, it has so far not been verified, although the implications can be quite significant for designing thermoelectric materials. In this paper we explore this idea using a combined experimental and theoretical study of the thermal conductivity of $In_{0.53}Ga_{0.47}As$ containing epitaxially embedded ErAs nanoislands.

Experimental study

A detailed description of the growth method can be found in the literature[17, 18], and only a brief explanation will be provided here. All samples were grown on an InP substrate with a buffer layer of 100 nm InAlAs and 40 nm of n-type InGaAs using a molecular beam epitaxy (MBE) system at 490 ^oC to eliminate the effect of growth temperature on thermal conductivity. Two types of samples were grown: (i) containing ErAs nano-islands in a superlattice structure inside the InGaAs matrix; (ii) containing ErAs nano-islands that are randomly distributed in the three-dimensional InGaAs matrix. The total concentration of Er in randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$ is fixed at 0.3 %.

A silicon dioxide layer (~0.18 μm) was deposited on top of the samples at room temperature using plasma enhanced chemical vapor deposition for measurement purposes. The differential 3ω method [19] was used to measure thermal conductivity. Platinum (~ 380 nm in thickness and 30 μm wide) with chromium (~ 4 nm) as an adhesion layer was patterned on the top of the silicon dioxide layer for the heater and thermometer. Thermal conductivity measurements were performed in a cryostat at temperatures ranging from 40-800 K.

By incorporating ErAs nanoislands into $In_{0.53}Ga_{0.47}As$, we observed that the thermal conductivity is lower than that of pure $In_{0.53}Ga_{0.47}As$ alloy over a wide temperature range, with the largest reduction between 150 K and 450 K (see Figure 1). This agrees with the hypothesize that while alloy scattering in $In_{0.53}Ga_{0.47}As$ scatters the short wavelength phonons, the ErAs nanoislands preferentially scatters mid- to long wavelength phonons, which is described more in detail later in this paper. At temperatures above 600K, Umklapp phonon scattering dominates over other scattering processes, producing only marginal reduction over the thermal conductivity of $In_{0.53}Ga_{0.47}As$. Figure 1 plots the thermal conductivity of randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$. It is clear that this exhibits the lowest measured values compared to that of superlattice samples, which are shown as reference.

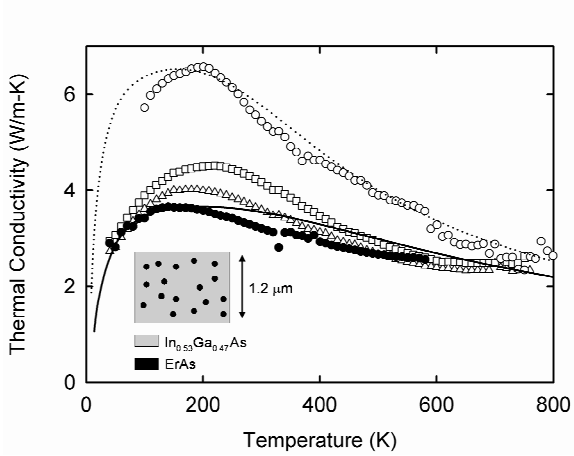

Figure 1: Temperature dependence of thermal conductivity of ErAs in $In_{0.53}Ga_{0.47}As$. Thermal conductivity of randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$ (solid circles) is shown clearly to be below that of $In_{0.53}Ga_{0.47}As$ alloy (open circles). Thermal conductivity of 0.4 ML with 40 nm period thickness (open squares) and 0.1 ML with 10 nm period thickness (open upward triangles) $ErAs/In_{0.53}Ga_{0.47}As$ superlattices are shown as references. Dotted and solid lines are based on theoretical analysis.

Theoretical study

We will assume that for the sample containing randomly distributed ErAs nanoislands (Figure 1), the thermal conductivity is isotropic and can be compared to predictions of an isotropic model. To understand the role of ErAs in reducing the thermal conductivity below the alloy limit, the thermal conductivity is predicted using Callaway's model [20] and shown as the dotted and solid lines in the Figure 1. The thermal conductivity is calculated as

$$\kappa = \frac{k_B}{2\pi^2 \upsilon}\left(\frac{k_B T}{\hbar}\right)^3 \times \left(\int_0^{\Theta/T} \frac{\tau_c x^4 e^x}{\left(e^x-1\right)^2} dx + \frac{\left[\int_0^{\Theta/T} \frac{\tau_c}{\tau_N} \frac{x^4 e^x}{\left(e^x-1\right)^2} dx\right]^2}{\int_0^{\Theta/T} \frac{1}{\tau_N}\left(1-\frac{\tau_c}{\tau_N}\right) \frac{x^4 e^x}{\left(e^x-1\right)^2} dx} \right) \quad (1)$$

where k_B is Boltzmann constant, $\hbar$ is Planck's constant divided by 2π, x as the normalized frequency, $\hbar\omega/k_BT$, and T as the absolute temperature, and υ and θ are the speed of

sound and Debye temperature of $In_{0.53}Ga_{0.47}As$, respectively. Here, τ_N is the relaxation time due to normal scattering, and τ_c is the combined relaxation time using Matthiessen's rule [21], given as

$$\tau_c^{-1} = \tau_B^{-1} + \tau_U^{-1} + \tau_N^{-1} + \tau_A^{-1} + \tau_{eph}^{-1} + \tau_D^{-1} \quad (2)$$

where it is composed of boundary scattering, τ_B, Umklapp scattering, τ_U, normal scattering, τ_N, and defect or alloy scattering, τ_A, electron-phonon scattering, τ_{eph}, and that due to ErAs nanoislands τ_D.

The values used for the prediction of $In_{0.53}Ga_{0.47}As$ thermal conductivity in Figure 1 are based mostly on those used in the literature [22]. Incorporating ErAs nanoparticles to $In_{0.53}Ga_{0.47}As$ has three effects on the thermal conductivity: (i) increase due to electronic contribution, since semimetallic ErAs nanoparticles act as dopants [17], (ii) decrease of phonon contribution due to electron-phonon scattering, and (iii) phonon scattering due to ErAs nanoislands. In the temperature range where thermal conductivity reduction due to ErAs is most evident, the predicted electronic contribution to thermal conductivity is marginal [23]. Furthermore, electron-phonon scattering contribution is also negligible [24]. Hence, τ_D plays a dominant role in thermal conduction when ErAs nanoislands are embedded. Assuming uncorrelated scattering by the nanoislands, we generalize the expression for defect scattering as

$$\tau_D^{-1}(\omega) = \frac{\upsilon}{V} \frac{\int_0^\infty \sigma(\omega, b)\phi(b)\,db}{\int_0^\infty \phi(b)\,db} \quad (3)$$

where $\sigma(\omega, b)$ is the scattering cross-section based on acoustic Mie theory [25] as a function of phonon frequency, ω, and ErAs nanoisland diameter, b, and $\phi(b)$ is the size-distribution of ErAs islands. Phonon scattering by the ErAs was found to be more dependent on the differences in bond stiffness with respect to $In_{0.53}Ga_{0.47}As$ as opposed to mass differences [26]. Here, V denotes a volume containing one ErAs particle, which is fixed considering the total concentration of Er is 0.3 % in randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$. Based on the TEM picture [24], the mean diameter, $\bar{b}$, of the ErAs islands was found to be 2.4 nm. The only adjustable parameter in this analysis is the standard deviation of distribution. To fit the maximum thermal conductivity, a value of 0.975 nm was chosen, and this was used to predict the thermal conductivity over the whole temperature range. Given the image in the references [18, 24] and the lack of control over the size of ErAs during growth process in randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$, such a value seems reasonable. The excellent agreement between predictions and experimental data suggests that we can now explain how and why nanoislands reduce the thermal conductivity below the alloy limit. In contrast to previous work [13, 14], we have shown the alloy limit can be beaten with non-periodic structures, and that phonon bandgap formation and other forms of correlated scattering may not be necessary for achieving this. This may simplify the manufacturing of such materials for thermoelectric applications since periodic structures require more stringent control.

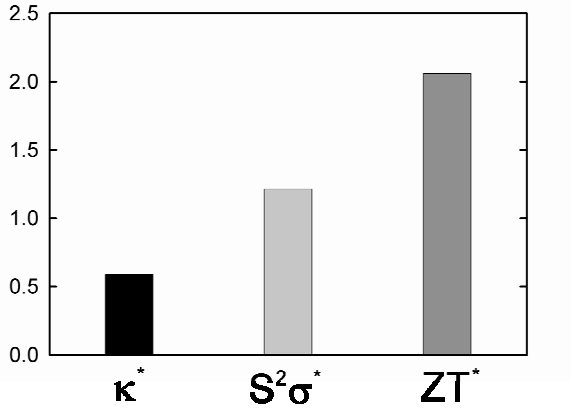

Figure 2: Resulting enhancement of the thermoelectric figure of merit. Thermal conductivity, power factor and the figure of merit, ZT, of randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$ are normalized as those of $In_{0.53}Ga_{0.47}As$.

Figure 2 explains how the thermoelectric properties changes due to incorporating ErAs nanoislands. Thermal conductivity, power factor and the thermoelectric figure of merit of randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$ are normalized as those of $In_{0.53}Ga_{0.47}As$. Certainly almost factor of two reductions in thermal conductivity at room temperature is shown. Incorporating ErAs does not degrade the power factor. In fact, power factor of randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$ [18] is even higher than that of $In_{0.53}Ga_{0.47}As$ [27]. The enhancement in power factor could be attributed to selective filtering of hot electrons by using heterostructure thermionic emission [28]. Comparing the figure of merit of those two, incorporating ErAs nanoislands clearly enhanced the efficiency by more than a factor of two. Not only thermal conductivity has been reduced below alloy limit, but also there is increase in power factor by incorporating nanoislands. Certainly the implication of this work can be utilized and extened for designing other thermoelectric materials.

Conclusions

In summary, by epitaxially incorporating nanoislands of ErAs in an alloy of $In_{0.53}Ga_{0.47}As$, a significant reduction in thermal conductivity over that of $In_{0.53}Ga_{0.47}As$ was observed over a 40-800K temperature range. Corresponding increases in thermoelectric figure of merit was more than a factor of two. Theoretical analysis revealed ErAs nanoislands scatter mid-to-long wavelength phonons, while the atomic scale defects in $In_{0.53}Ga_{0.47}As$ effectively scatter the Brillouin zone edge phonons. In the case of randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$, there is large size distribution of ErAs which effectively scatters a wide phonon spectrum. While the absolute value of the figure of merit of ErAs/ $In_{0.53}Ga_{0.47}As$ is not as high compared to that of Bi or Pb-based nanostructured materials, what we have uncovered here are some principles of designing nanostructured thermoelectric materials with high ZT.

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