P H Y S I C A L   R E V I E W   L E T T E R S

Thermal Conductivity Reduction and Thermoelectric Figure of Merit Increase by Embedding Nanoparticles in Crystalline Semiconductors

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Atomic substitution in alloys can efficiently scatter phonons, thereby reducing the thermal conductivity in crystalline solids to the "alloy limit." Using $In_{0.53}Ga_{0.47}As$ containing ErAs nanoparticles, we demonstrate thermal conductivity reduction by almost a factor of 2 below the alloy limit and a corresponding increase in the thermoelectric figure of merit by a factor of 2. A theoretical model suggests that while point defects in alloys efficiently scatter short-wavelength phonons, the ErAs nanoparticles provide an additional scattering mechanism for the mid-to-long-wavelength phonons.

The performance of thermoelectric energy conversion devices depends on the thermoelectric figure of merit (ZT) of a material 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 [1]. While $S^2\sigma$ can be maximized by doping, it is necessary to use a semiconductor with crystalline order to achieve high carrier mobility. The lowest thermal conductivity in crystalline solids is generally that of an alloy—often called the "alloy limit"—due to scattering of phonons by atomic substitutions. Historically, it has been challenging to increase $ZT > 1$ because of the difficulty of reducing thermal conductivity below the alloy limit. Recent reports have shown that ZT can be increased beyond unity by nanostructuring thermoelectric materials, and the key reason for increase in ZT was the reduction of thermal conductivity [2–4]. Yet, the fundamental reasons for how and why nanostructuring reduces thermal conductivity in crystalline materials are not fully understood. In this Letter, we experimentally and theoretically provide an explanation.

It has been difficult to beat the alloy limit in crystals without creating defects, dislocations, and voids. 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 [5]. However, ZT was not increased due to a proportional reduction in electrical conductivity. There have been reports that the thermal conductivity of a Si/Ge superlattice can be lower than that of a Si_xGe_{1-x} alloy [6,7]. However, because of the large lattice mismatch ($\sim 4\%$) between Si and Ge, the strain in Si/Ge superlattices produces defects and dislocations when the layer thickness exceeds a critical value. Such approaches also have not led to significant increases in ZT, thus suggesting that the electrical conductivity also reduces proportionally. More recently, despite systemati-

cally increasing the interfacial acoustic impedance mismatch in a $Si_yGe_{1-y}/Si_xGe_{1-x}$ superlattice, Huxtable *et al.* [8,9] failed to reduce the thermal conductivity below that of a 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 [10,11], while maintaining the crystalline structure of the material. Using GaAs/AlAs superlattices, Capinski *et al.* [10] showed that only when the period thickness was in the range of 1–4 nm, the cross-plane thermal conductivity was less than that of an $Al_{0.5}Ga_{0.5}As$ alloy. Venkatasubramanian [11] measured the cross-plane thermal conductivity of Bi_2Te_3/Sb_2Te_3 superlattices and found the lattice conductivity of only short-period (1–5 nm) superlattices to be less than that of a solid solution alloy. It has been proposed that the thermal conductivity in such periodic structures is reduced by phase-correlated phonon scattering, either by localization [11] or through the formation of phonon band gaps [12]. While this is certainly possible, at present there is no direct experimental evidence that correlated phonon scattering indeed reduces thermal conductivity.

In this Letter, we experimentally demonstrate and theoretically explain that it is possible to beat the alloy limit using uncorrelated phonon scattering. To do so, we use $In_{0.53}Ga_{0.47}As$ as the alloy, in which ErAs nanoparticles, few nanometers in diameter, are epitaxially embedded. In alloys such as $In_{0.53}Ga_{0.47}As$, atomic substitutions scatter phonons due to differences in mass and/or bond stiffness. In the Rayleigh scattering regime, the scattering cross section varies as $\sigma \sim b^6/\lambda^4$, where b is the size of the scattering particle and λ is the phonon wavelength. For atomic substitutions in alloys, $b \sim 1$ Å. The above relation suggests that short-wavelength or Brillouin zone edge phonons are scattered much more effectively than the mid-

and long-wavelength phonons. Hence, these latter phonons dominate heat conduction in alloys. By introducing ErAs nanoparticles of $b \sim 1$–4 nm in $In_{0.53}Ga_{0.47}As$, we hypothesize that the mid- and long-wavelength phonons are also scattered, which reduces the thermal conductivity below that of an alloy.

A detailed description of the growth method can be found in the literature [13], 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 doped with 5×10^{18} cm^{-3} silicon using a molecular beam epitaxy system at 490 °C to eliminate the effect of growth temperature on thermal conductivity. The total thickness of $In_{0.53}Ga_{0.47}As$ film containing ErAs nanoparticles was either 1.2 or 1.6 μm. Two types of samples were grown, namely: (i) ErAs nanoparticles in a superlattice structure inside the $In_{0.53}Ga_{0.47}As$ matrix and (ii) ErAs nanoparticles that are randomly distributed in the three-dimensional $In_{0.53}Ga_{0.47}As$ matrix. The inset in Fig. 1(a) shows transmission electron microscope (TEM) images of a 0.4 monolayer (ML) ErAs/$In_{0.53}Ga_{0.47}As$ superlattice after thermal conductivity measurements up to 800 K. The black dots in the figure correspond to ErAs nanoparticles and the dark gray layer corresponds to $In_{0.53}Ga_{0.47}As$. As shown in Fig. 1(a), ErAs nanoparticles are epitaxially embedded in $In_{0.53}Ga_{0.47}As$.

For the purpose of thermal conductivity measurements, a silicon dioxide layer (~ 0.18 μm) was deposited on top of the samples at room temperature using plasma-enhanced chemical vapor deposition. The differential 3ω method [14] was used to measure thermal conductivity. A platinum (~ 380 nm thick and 30 μm wide) film with chromium (~ 4 nm thick) as an adhesion layer was deposited and patterned on top of the silicon dioxide layer for the heater and thermometer. Thermal conductivity measurements were performed in a cryostat. TEM images and the repeatability of the thermal conductivity measurements showed that material degradation did not occur over several temperature cycles, as shown in the inset in Fig. 1(a).

By incorporating ErAs nanoparticles 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 and 450 K [see Fig. 1(a)]. This supports our hypothesis that, in addition to alloy scattering of phonons, there must be additional phonon scattering due to the ErAs nanoparticles. At temperatures above 600 K, umklapp phonon scattering starts to dominate over other scattering processes, thus producing only marginal reduction over the thermal conductivity of $In_{0.53}Ga_{0.47}As$.

To explore the effects of ErAs particle size, the thermal conductivity of ErAs/$In_{0.53}Ga_{0.47}As$ was measured in the superlattice samples with a period thickness fixed at 40 nm [Fig. 1(a)]. Particle sizes are expressed in terms of ErAs deposition, which is given as the equivalent monolayer fraction if the ErAs grew as a complete film. ErAs grows in an island (Volmer-Weber) growth mode, and the island
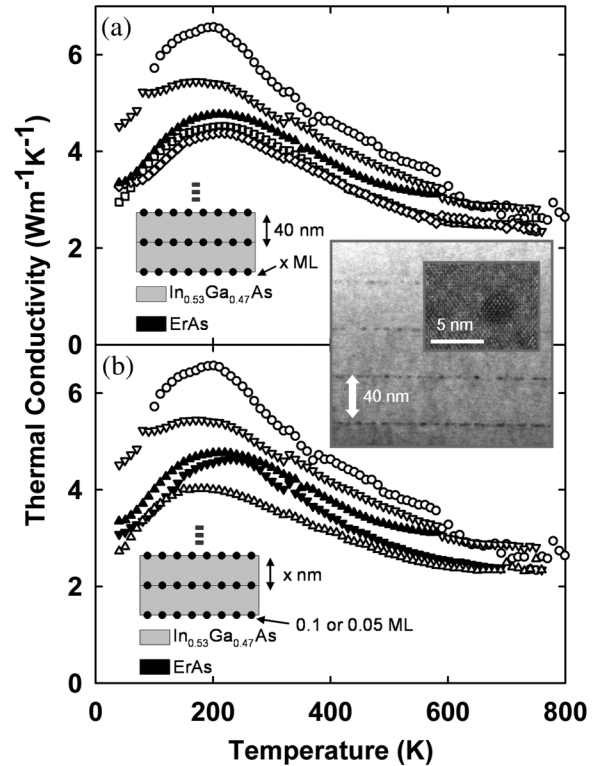

FIG. 1. (a) The effect of ML thickness on the thermal conductivity of a ErAs/$In_{0.53}Ga_{0.47}As$ superlattice. The thermal conductivity of $In_{0.53}Ga_{0.47}As$ (open circles) is shown as a comparison. ErAs deposition is varied from 0.05 ML (open downward triangles), 0.1 ML (solid upward triangles), 0.2 ML (open diamonds), to 0.4 ML (open squares). The inset shows TEM pictures of 0.4 ML with a 40 nm period thickness ErAs/$In_{0.53}Ga_{0.47}As$ superlattice. (b) The effect of superlattice period on the thermal conductivity of a ErAs/$In_{0.53}Ga_{0.47}As$ superlattice. Two different depositions are considered. One is 0.1 ML with 40 nm (solid upward triangles) and 10 nm (open upward triangles) and the other is 0.05 ML with 40 nm (open downward triangles) and 5 nm (solid downward triangles).

size is directly proportional to the amount deposited. For depositions greater than 0.1 ML, the dependence of thermal conductivity on ErAs particle size is less pronounced. However, the thermal conductivity of 0.05 ML is higher than those of other samples containing ErAs, although it is still less than that of $In_{0.53}Ga_{0.47}As$. By increasing the deposition beyond 0.1 ML, the average ErAs nanoparticle size also increases. However, there may be a sufficient number of scatterers for the mid-wavelength phonons that increasing the size has minimal effect on the thermal conductivity. Reducing the deposition to 0.05 ML reduces the average particle size, making it less effective in scattering the mid-wavelength phonons, thus producing a higher thermal conductivity.

The effect of period thickness over the thermal conductivity is shown in Fig. 1(b). It is evident that ErAs/$In_{0.53}Ga_{0.47}As$ superlattices with shorter period thickness have lower thermal conductivity. The fact that thermal conductivity is dependent upon period thickness of a few

tens of nanometers implies that the mean free path of a fraction of heat carrying phonons must be influenced and controlled by scattering from ErAs nanoparticles. Since short-wavelength phonons are scattered by the alloy atoms, this gives further evidence that mid-to-long-wavelength phonons are important in heat conduction in such materials. However, the thermal conductivity increases again as in the case of 0.05 ML with 5 nm period thickness even though it has short period. This could be explained using the results of Fig. 1(a). The size of ErAs in 0.05 ML is not large enough to effectively scatter the mid-wavelength phonons to reduce the thermal conductivity of $In_{0.53}Ga_{0.47}As$. One can, therefore, conclude that to reduce thermal conductivity below that of $In_{0.53}Ga_{0.47}As$, the size of ErAs nanoparticles should be sufficiently large that the scattering regime does not overlap with the Rayleigh scattering of the atomic scale defects in alloys.

The inset in Fig. 2(a) shows a TEM image of a sample where the ErAs nanoparticles are randomly distributed through the $In_{0.53}Ga_{0.47}As$ matrix. The total concentration of Er in randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$ is fixed at 0.3%. Figure 2(a) 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 those of superlattice samples, which are shown as reference. We will assume that, for the sample containing randomly distributed ErAs nanoparticles, 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 [15] and shown as the dotted and the solid lines in Fig. 2(a). The thermal conductivity is calculated as

$$k = \frac{k_B}{2\pi^2 v}\left(\frac{k_B T}{\hbar}\right)^3 \left\{\int_0^{\theta/T} \frac{\tau_c x^4 e^x}{(e^x - 1)^2}\, dx \right.$$
$$\left. + \frac{[\int_0^{\theta/T} \frac{\tau_c}{\tau_N} \frac{x^4 e^x}{(e^x-1)^2}\, dx]^2}{\int_0^{\theta/T} \frac{1}{\tau_N}(1 - \frac{\tau_c}{\tau_N})\frac{x^4 e^x}{(e^x-1)^2}\, dx}\right\}, \quad (1)$$

where k_B is Boltzmann constant, $\hbar$ is Planck's constant divided by 2π, x is the normalized frequency $\hbar\omega/k_B T$, T is the absolute temperature, and v 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 phonon-phonon scattering, and τ_c is the combined relaxation time using Matthiessen's rule, given as

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

where it is composed of boundary scattering τ_B, umklapp scattering τ_U, defect or alloy scattering τ_A, electron-phonon scattering $\tau_{e\text{-ph}}$, and that due to ErAs nanoparticles τ_D.

The values used for the prediction of $In_{0.53}Ga_{0.47}As$ thermal conductivity in Fig. 2(a) are based mostly on those used in the literature [16]. Incorporating ErAs nanopar-
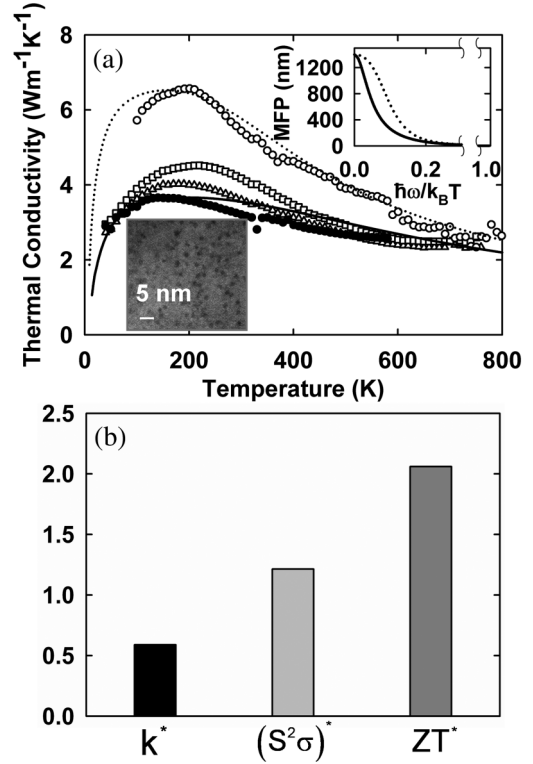

FIG. 2. (a) Thermal conductivity of randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$ (solid circles). Thermal conductivity of a $In_{0.53}Ga_{0.47}As$ alloy (open circles), 0.4 ML with a 40 nm period thickness ErAs/$In_{0.53}Ga_{0.47}As$ superlattice (open squares) and 0.1 ML with a 10 nm period thickness ErAs/$In_{0.53}Ga_{0.47}As$ superlattice (open upward triangles) are shown as references. Dotted and solid lines are based on theoretical analysis. The inset shows TEM pictures of randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$. Another inset shows the phonon mean free path (MFP) versus normalized frequency at 300 K. (b) Resulting enhancement of the thermoelectric figure of merit at 300 K. Thermal conductivity, power factor, and the figure of merit ZT of randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$ are normalized by the corresponding values of $In_{0.53}Ga_{0.47}As$.

ticles in $In_{0.53}Ga_{0.47}As$ has three effects on the thermal conductivity: (i) increase due to electronic contribution, since semimetallic ErAs nanoparticles act as dopants [13], (ii) decrease of phonon contribution due to electron-phonon scattering, and (iii) phonon scattering due to ErAs nanoparticles. In the temperature range where thermal conductivity reduction due to ErAs is most evident, the predicted electronic contribution to thermal conductivity is marginal [17]. Furthermore, the electron-phonon scattering contribution is also negligible [18]. Hence, τ_D plays a dominant role in thermal conduction when ErAs nanoparticles are embedded. Assuming uncorrelated scattering by the nanoparticles, we generalize the expression for defect scattering as [19]

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

where $\sigma(\omega, b)$ is the scattering cross section as a function of phonon frequency ω and ErAs nanoparticle diameter b, and $\varphi(b)$ is the size distribution of ErAs nanoparticles. Here $1/V$ is the volume density of ErAs particles, 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 image in Fig. 2(a), the mean diameter $\bar{b}$ of the ErAs nanoparticles was found to be 2.4 nm. The only assumption in this analysis is that the probability distribution is chosen to be a gamma function [20]. To fit the maximum thermal conductivity, a value of 1.9 nm was chosen for the standard deviation. This value was used to predict the thermal conductivity over the whole temperature range. Given the TEM image in Fig. 2(a) 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 agreement between predictions and experimental data suggests that we have a possible explanation of how and why nanoparticles reduce the thermal conductivity below the alloy limit. In contrast to previous work [10,11], we have shown the alloy limit can be beaten with nonperiodic structures [21]. This may considerably simplify the manufacturing of such materials for thermoelectric applications, since periodic structures require more stringent control and are more time consuming.

The inset in Fig. 2(a) shows the phonon mean free path versus normalized frequency at 300 K. The dotted line corresponds to the mean free path of $In_{0.53}Ga_{0.47}As$, and the solid line denotes that of randomly distributed ErAs nanoparticles in $In_{0.53}Ga_{0.47}As$. This theoretical analysis clearly demonstrates that ErAs nanoparticles scatters the low and intermediate phonon spectrum.

It should be noted that ErAs is a semimetal that can act as an electron donor in $In_{0.53}Ga_{0.47}As$, which should increase the electrical conductivity and reduce the thermopower in $In_{0.53}Ga_{0.47}As$. The room-temperature thermal conductivity, power factor ($S^2\sigma$), and the thermoelectric figure of merit (ZT) of randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$ are normalized by the corresponding values of $In_{0.53}Ga_{0.47}As$ and shown in Fig. 2(b). The power factor of randomly distributed ErAs in $In_{0.53}Ga_{0.47}As$ [13] is slightly higher than that of $In_{0.53}Ga_{0.47}As$ [22], and yet thermal conductivity reduction is by almost a factor of 2 below the alloy limit. The resulting ZT is increased more than a factor of 2, mostly due to reduction of the thermal conductivity.

In summary, by epitaxially incorporating nanoparticles 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. A corresponding increase in ZT by more than a factor of 2 was also observed. Theoretical analysis revealed ErAs nanoparticles scatter mid-to-long-wavelength phonons, while 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 a large size distribution of ErAs nanoparticles, which effectively scatters a wide phonon spectrum.

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