Tuning thermal transport in crystalline solids using embedded nanoparticles

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Abstract. We theoretically predict that thermal transport in crystalline solids can be tuned using embedded nanoparticles, which we call “thermal doping”. We exploit the strong dependence of phonon scattering cross-section on nanoparticle size and phonon wavelength to achieve the tunability. By adjusting the size, size distribution and concentration of nanoparticles, we theoretically show that the thermal conductivity can be reduced by a factor of 4 below the alloy limit.

1. Introduction
During the last century, tuning of electrical conductivity of semiconductors by doping has received a lot of attention, and has now formed the foundation for semiconductor electronics and optoelectronics. However, there is still only limited tunability for thermal conductivity. Today, there are several examples where current technology is limited by the inability to adequately manipulate thermal transport. Heat dissipation in current microelectronics [1], data storage [2], optoelectronics [3], etc., and thermal isolation in thermoelectrics [4] are examples where there is a significant need for controllable thermal transport.

Alloying is known to be the best solution for tuning thermal transport in a crystalline solid. For example, thermal conductivity of silicon and germanium [5] at room temperature is around 140 Wm\textsuperscript{-1}K\textsuperscript{-1}, and 60 Wm\textsuperscript{-1}K\textsuperscript{-1}, respectively. However, thermal conductivity of Si\textsubscript{x}Ge\textsubscript{1-x} alloys [6] can be as low as 5-10 Wm\textsuperscript{-1}K\textsuperscript{-1} at room temperature. In such alloys, 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 $\lambda$ is the phonon wavelength. For atomic substitutions in alloys, $b$ is on the order of Angstrom. Thus the above relation suggests that short wavelength or Brillouin zone edge phonons are scattered much more effectively than the mid and long wavelength phonons.

In this study, we want to generalize the concept of impurity scattering as a way to manipulate thermal transport. In addition to atomic substitutions, if we can incorporate nanoparticles epitaxially in crystalline solids, which is routine growth technique nowadays [7,8], we could potentially have more...
control over the thermal transport, which we call “thermal doping”. When a temperature gradient is
imposed on a material (from left to right), the material can become either thermally resistive or
conductive depending on the ‘thermal doping’ process. Atomic-scale particles effectively scatter the
short wavelength phonons whereas nanoparticles whose sizes are comparable to the wavelength of
mid/long wavelength phonons effectively scatter mid/long wavelength phonons. Phonon transport can be
spectrally-selective scattered in this way. Therefore, thermal properties of the material can be tuned.
Whereas the electrical doping increases electrical conductivity, thermal doping decreases thermal
conductivity of a material. Depending on the size of nanoparticles, not only short wavelength phonons
but also mid to long wavelength phonons can undergo spectrally-selective scattering [9]. If one reduces
the nanoparticle size to atomic scale, one should reach the limiting case of alloys [9].

2. Theoretical analysis

Although we present theoretical analysis of thermal transport in a crystalline alloy material, the
implication of this study can be applied to any crystalline material of interest. We will assume that for
the sample containing randomly distributed nanoparticles, the thermal conductivity is isotropic and can
be compared to predictions of an isotropic model. The thermal conductivity of phonons is predicted
using Callaway’s model with relaxation time approximation [10]. Relaxation time of phonon scattering
due to nanoparticles, \( \tau_D \), is given by

\[
\tau_D^{-1} = \frac{\nu \sigma_{sc} (\chi)}{V}
\]

where \( \nu \) in equation (1) is the volume density of nanoparticles, \( \sigma_{sc} \) denotes scattering cross-section as a
function of \( \chi \), the size parameter and \( \nu \) is the phonon group velocity. The size parameter is defined as \( \chi = kR \) where \( k \) is the phonon wavevector, and \( R \) is the radius of the scattering particle. When \( \chi \ll 1 \), this
is the so called Rayleigh scattering regime. The other extreme, where \( \chi \to \infty \), is the geometrical scattering regime. Approximate analytical solutions for these two extremes have been derived [11] and
bridged with a simple formula for the intermediate values of \( \chi \). The combined scattering cross section valid over the entire size parameter relates these two extremes by \( \sigma_{total}^{-1} = \sigma_{Rayleigh}^{-1} + \sigma_{Geometric}^{-1} \). The effects of size distributions of phonon impurities are incorporated as a Gamma distribution [12]. Therefore, the scattering cross section in equation (1) is

\[
\sigma_{sc} = \int_{0}^{\infty} \sigma_{total} \left( \frac{R}{b} \right)^{a-1} e^{-\frac{R}{b}} \frac{dR}{b \Gamma(a)}
\]

where \( a \) is the shape parameter, \( b \) is the scale parameter, and \( \Gamma(a) \) is the gamma function. The mean is
equal to \( ab \) and the standard deviation is equal to \( a^{0.5} b \).

While our theoretical model is general, our test case is based on the thermal conductivity of
crystalline In\(_{0.53}\)Ga\(_{0.47}\)As containing ErAs nanoparticles (ErAs:InGaAs).

3. Results and discussions

Figure 1(a) shows effects of size distributions of nanoparticles on lattice thermal conductivity of
ErAs:InGaAs. The total concentration of ErAs in In\(_{0.53}\)Ga\(_{0.47}\)As is fixed as 0.3 %. The mean diameter of
ErAs is fixed as 2.4 nm. Experimental data and theoretical analysis of InGaAs and ErAs:InGaAs are
based on the author’s other publication[9]. In this calculation, the effect of electron–phonon scattering
has been considered, since ErAs nanoparticles introduces charges in In\(_{0.53}\)Ga\(_{0.47}\)As [8]. However the
effect of electron–phonon scattering turns out to be almost negligible [9]. Since ErAs nanoparticles
work as phonon impurities in In\(_{0.53}\)Ga\(_{0.47}\)As, the reduction is most evident near the thermal conductivity
maximum. As shown in the figure, a large standard deviation of the mean diameter of ErAs
nanoparticles results in a significant reduction in thermal conductivity. This is because thermal
conductivity is based on a broad band of phonon energy distribution, thus a larger range of scattering
leads to lower thermal conductivity. In the growth of crystalline solids containing nanoparticles, it probably would be easier to grow poly-dispersed than mono-dispersed ones. By adjusting growth temperature and/or rate to control size distribution of nanoparticles, the thermal properties of material can be tuned.

Figure 1 Thermal doping: Effects of (a) size distributions (standard deviations, $\sigma$); (b) total concentration; (c) size (mean diameter, $d_M$) of nanoparticles on thermal conductivity of ErAs:InGaAs.

Figure 1(b) shows the effects of total concentration of nanoparticles on thermal conductivity. The mean diameter and standard deviation of ErAs nanoparticles are fixed as 2.4 nm and 1.5 nm, respectively. Even though ErAs concentration increased from 0.25 % to 3.0 %, we assume that there is no change in phonon dispersion. As expected, larger concentrations of nanoparticles results in reduced thermal conductivity. Increasing total concentration of ErAs nanoparticles means decreasing mean spacing among ErAs nanoparticles. Therefore, phonon mean free path due to the ErAs nanoparticles
decreases. However, one needs to be careful when tuning the thermal transport by increasing total concentration of nanoparticles, because continually increasing nanoparticle concentration eventually would lead to change in the phonon dispersion [13], and to change in electronic band-structure. Therefore, it is suggested that, in thermal doping process, one would want to maintain small concentration of nanoparticles yet vary the size distributions of nanoparticles.

Figure 1(c) shows the effects of mean diameter of nanoparticles on the thermal conductivity. The concentration and standard deviation of ErAs nanoparticles are fixed as 0.3 % and 1.9 nm, respectively. At a fixed concentration of nanoparticles, a decrease in the mean diameter affects the phonon mean free path in two ways: (i) decreases the scattering cross-section, which increases the phonon mean free path; (ii) decreases the mean spacing among nanoparticles, which decreases the phonon mean free path. As shown in the figure, a small mean diameter results in reduced thermal conductivity, which indicates that the latter effect dominates the former.

4. Conclusions
In summary, we propose in this study that thermal doping using nanoparticles in crystalline solids leads to control over thermal transport in these solids. This method stems from alloying, which has by far been the best way to tune thermal transport in crystalline solid. We have shown that by varying size, size distributions and total concentration of nanoparticles, one can tune thermal transport in solids.

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