

“Nanoparticle-in-Alloy” Approach to Efficient Thermoelectrics: Silicides in SiGe

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ABSTRACT

We present a “nanoparticle-in-alloy” material approach with silicide and germanide fillers leading to a potential 5-fold increase in the thermoelectric figure of merit of SiGe alloys at room temperature and 2.5 times increase at 900 K. Strong reductions in computed thermal conductivity are obtained for 17 different types of silicide nanoparticles. We predict the existence of an optimal nanoparticle size that minimizes the nanocomposite’s thermal conductivity. This thermal conductivity reduction is much stronger and strikingly less sensitive to nanoparticle size for an alloy matrix than for a single crystal one. At the same time, nanoparticles do not negatively affect the electronic conduction properties of the alloy. The proposed material can be monolithically integrated into Si technology, enabling an unprecedented potential for micro refrigeration on a chip. High figure-of-merit at high temperatures ($ZT \sim 1.7$ at 900 K) opens up new opportunities for thermoelectric power generation and waste heat recovery at large scale.

The “nanoparticle-in-alloy” approach to thermoelectric materials has been experimentally demonstrated in the concrete case of ErAs nanoparticles in InGaAs matrix, where nanoparticles led to a 50% reduction in thermal conductivity and a 2-fold increase in ZT .¹ The fundamental role of the nanoparticles in decreasing the thermal conductivity below that of the simple alloy was discussed in ref 2. It has also been argued that nanoparticles can enhance the power factor above that of the alloy via electron filtering.^{3,4} Experience with the aforementioned material suggests that it is essential that the nanoparticles blend well into the matrix lattice, without creating dislocations or defects. ErAs, a semimetal, is lattice matched with InGaAs.⁵

The following question thus arises: can we conceive other materials, based on nano-inclusions, which also lead to enhanced ZT ’s? This problem is far from trivial. From the materials science point of view, one needs to find a class of particles that can be grown into the matrix without creating dislocations. It also needs to be such that it scatters phonons efficiently but does not considerably shorten the electronic mean free path. We have found a wide class of materials suitable to be incorporated as nanoparticles in alloys of SiGe, leading to important enhancements in ZT . Use of silicon-compatible technology has the potential to lower the module manufacturing cost significantly. Major breakthroughs in

thermoelectric figure-of-merit $ZT > 1.5$ in the last 6–7 years were achieved using Te-based materials (Bi_2Te_3 , PbTe). Toxicity of these elements and material availability are major concerns. Here we propose an alternative SiGe-based material which could achieve similar performances without any of the toxicity or scarcity drawbacks.

Previously, some systems with quantum dot inclusions had been investigated for thermoelectric applications,^{6–9} but the importance of having an “alloy matrix” had not been clearly described. Here we show that an alloy matrix is much more interesting than a single crystalline one, both from scientific and technological standpoints. Our results are quite general and are not restricted to SiGe. Thus this paper illustrates a general strategy to search for new nanoparticle-in-alloy materials with enhanced thermoelectric properties.

Interest in enhancing the ZT of SiGe stems from the need to integrate room temperature thermoelectric devices into silicon technology at the micro and nanoscales. SiGe is ideal for integration, but it is very inefficient at room temperature ($ZT_{300} = 0.1$) and its ZT only approaches 1 at temperatures around 1000 K. Current room and intermediate temperature thermoelectrics are based on expensive and sometimes toxic materials, such as Bi_2Te_3 alloys, which cannot be so easily integrated into Si technology. Boettner and collaborators¹¹ were able to use sputtering and a silicon compatible microfabrication technology to build micro Bi_2Te_3 elements on silicon substrate and achieve outstanding cooling results exceeding 60 °C near room temperature. However, one still

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needs to make separate modules and integrate them on an IC chip later on. The additional thermal interface resistances due to the packaging reduce significantly their cooling power densities. In contrast, SiGe alloys can be integrated “monolithically” into Si devices, eliminating parasitic interface thermal resistances that considerably reduce thermoelectric energy conversion performance. It is known that having a room temperature ZT of 0.5 could make SiGe a material of choice for microelectronics spot cooling. Through the use of the 3D device geometry and heat spreading in the silicon substrate, even a modest ZT ~ 0.5 could provide localized cooling exceeding 1 kW/cm² and maximum cooling temperatures of 20–30 °C.^{5,10} Here we show that we can achieve the required performance by inserting nanoparticles into a SiGe matrix. The main question is the following: what are the right nanoparticles? This is a 2-fold question; the first challenge is to find the proper nanoparticle chemical composition. The second one is to determine the right nanoparticle sizes and concentrations that can increase ZT above 0.5 at room temperature and above 1 at higher temperatures.

We have found the answer to the first question in the form of silicides and germanides. Silicides (germanides) are a broad class of materials formed by the combination of a transition metal with Si(Ge).¹² Some silicides are metallic, and some are semiconducting. Some among them (for example NiSi₂) are closely lattice matched with Si and SiGe, making it possible to produce dislocation free embedded nanoparticle composites. In principle, by adjusting the concentration of Si and Ge, and including little amounts of C, it is possible to change the lattice parameter of the matrix to best match that of the nanoparticle alloy. A few examples of silicide nanoparticle growth on SiGe have been published in the literature.¹³ LITEN has also succeeded at synthesizing three-dimensional (3D) samples of embedded Ge nanodots into SiGe.¹⁴

Let us now discuss the quantitative aspects of the nanoparticle-in-alloy approach. This approach was introduced for ErAs in InGaAs in ref 1, and the effect of the nanoparticles on the thermal conductivity has been analyzed in ref 2. An early suggestion to enhance ZT via embedded microparticles had been sketched in ref 15. A simple explanation of how nanoparticles can reduce the thermal conductivity below that of the alloy is the following. At low frequencies, the phonon scattering cross section of a sphere in a medium of different density is proportional to the square of its total extra mass, $\sigma = q^4(\delta M)^2/(4\pi D^2)$ (see eq 6.2.2 of ref 16), where q is the wave vector, D is the medium density, and δM is the total extra mass on the sphere. This means that N impurity atoms clustered together scatter low frequency phonons at a rate proportional to N^2 , that is, N times more strongly than if they were acting separately. On the other hand, at high frequencies the scattering cross section is proportional to the geometrical cross section of the sphere, πR^2 , where R is the sphere’s radius. Thus at high frequency, for a cluster composed of N impurity atoms, $\sigma \propto N^{2/3}$, whereas if the impurities were separated from each other their total cross section would depend roughly as $\propto N$. This means that N

independent atoms scatter high frequency phonons $N^{1/3}$ times more strongly than if they were clustered together as a nanoparticle. The inverse phonon mean free path is given by the addition of the different types of scatterers according to Mathiessen’s rule: $l^{-1} = l_a^{-1} + l_b^{-1}$. The mean free path is related to the cross section, σ , as $l_a^{-1} = n_a\sigma_a$, where n_a is the density of scatterers of type a in the medium. So if we have coexistence of scattering by individual atoms and also larger nanoparticles, their combined effect is an effective mean free path smaller than the smaller of the two, that is, large both at high and low frequencies. In this way, the resulting thermal conductivity is lower than the minimum one could obtain using an alloy with individual atomic size scatterers.

We now present a quantitative calculation of the thermal conductivity of nanoparticle in alloy matrix composites. In a frequency dependent relaxation time approximation, the thermal conductivity of the material can be expressed as an integral over frequency¹⁷

$$\kappa(T) = \int_0^\infty \mathcal{F}(\omega) \frac{\hbar\omega}{2\pi} \frac{df_B}{dT} d\omega \quad (1)$$

with $f_B = 1/(e^{\hbar\omega/k_B T} - 1)$. \mathcal{F} is a function calculated from the phonon dispersion and lifetimes. To a good approximation the phonon dispersion can be considered linear, and the relaxation time may be taken as solely dependent on frequency to yield

$$\mathcal{F}(\omega) = \tau(\omega) \frac{1}{2\pi} \omega^2 \sum_{i=1}^3 \Theta(\omega - \omega_i^c) 1/c_i \quad (2)$$

where Θ is the step function and ω_i^c are the branch cutoff frequencies, roughly corresponding to the maximum frequencies in the transverse and longitudinal acoustic branches. Since these parametric cutoffs are not precisely defined, a good approximation is to substitute them by an adjustable average cutoff, ω_c . When inserted into eq 1, this yields the Callaway formula.¹⁷ It is known that the Debye frequency cutoff originally employed by Callaway yields incorrect results for nanostructured systems. On the contrary, very good results are obtained when using the correct cutoff, ω_c , which in the case of Si was found to be 42 THz.¹⁷ For SiGe a good approximation is $\omega_c = \omega_c^{\text{Si}} c_{\text{SiGe}}/c_{\text{Si}}$, where $c_{\text{SiGe}}/c_{\text{Si}}$ is the ratio of the branch averaged speeds of sound in SiGe and Si.

The total relaxation time is a sum of anharmonic (a), alloy disorder (d), and nano particle (np) scattering contributions

$$\tau^{-1} = \tau_a^{-1} + \tau_d^{-1} + \tau_{\text{np}}^{-1} \quad (3)$$

The anharmonic contribution is well described by¹⁷

$$\tau_a^{-1} = B T \omega^2 e^{-CT} \quad (4)$$

Parameters B and C for bulk Si and Ge were obtained by fitting the experimental thermal conductivity of bulk crystals.¹⁷ For a Si _{x} Ge _{$1-x$} alloy, we take the weighted average parameters: $B = xB_{\text{Si}} + (1-x)B_{\text{Ge}}$, and similarly for C .

The alloy disorder contribution from the Si and Ge atoms is well accounted for by the effective medium approach originally employed by Abeles.¹⁸ In this approximation, the Rayleigh scattering rate of a Si or Ge atom is computed for the atom embedded in an effective medium with properties

averaged between those of pure Si and pure Ge, according to their relative volume fractions in the alloy. This yields

$$\tau_d^{-1} = x(1-x)A\omega^4 \quad (5)$$

where $A = ((M_{Ge} - M_{Si})/M)^2 \delta^3 / (4\pi c_{SiGe}^3)$, and δ^3 is the volume around one atom in the lattice. Alloy disorder scattering becomes 0 for the pure Si or pure Ge cases. This approach correctly reproduces the composition dependence of the thermal conductivity of SiGe alloys at room temperature and above.¹⁸

We include the nanoparticle contribution of the nanoparticles to the frequency dependent mean free path, using a Mathiessen type interpolation between the long and short wavelength scattering regimes^{2,19}

$$\tau_{np}^{-1} = \nu(\sigma_s^{-1} + \sigma_l^{-1})^{-1} \rho \quad (6)$$

where ρ is the density of nanoparticles, and the cross section limits are given by^{2,16}

$$\sigma_s = 2\pi R^2 \quad (7)$$

$$\sigma_l = \pi R^2 \frac{4}{9} (\Delta D/D)^2 (\omega R/\nu)^4 \quad (8)$$

Here ΔD is the difference between the density of the filler and the matrix materials, and D is the matrix density. As it is well known, the short wavelength limit scattering cross section is twice the geometrical cross section, and the long wavelength limit equals three times the Rayleigh expression (because there are three polarization branches; see eq 6.2.2 of ref 16.)

The nanoparticle phonon cross section contains a contribution related to the mass difference between the silicide and the matrix and also some contribution coming from the difference in elastic constants. Given the approximations involved in treating the system as an elastic medium, not much additional error is introduced by considering only the mass difference contribution. Doing so ensures that the reduced thermal conductivities computed constitute an upper bound, and the actual thermal conductivities may be even lower than those shown here.

Adding silicide nanoparticles into a $Si_{0.5}Ge_{0.5}$ matrix strongly reduces the composite's thermal conductivity. As shown in Figure 1, a 0.8% volume fraction may result in reductions between four and eight times below the alloy's thermal conductivity of 7.5 W/m-K. If the additional scattering effect of dopants is considered, the thermal conductivity will be even smaller. The higher the nanoparticle volume fraction, the lower the thermal conductivity. Low nanoparticle volume fractions, F , yield a contribution to the inverse phonon relaxation length proportional to F . The behavior will deviate from linearity for high volume fractions, however, due to multiple scattering effects. Additionally, a concentration of nanoparticles beyond a few percent might negatively affect electron mobility, as we discuss later.

A remarkable feature in Figure 1 is the appearance of a minimum thermal conductivity at an optimal nanoparticle size. This optimal size depends on the silicide employed, but it is always in the order of a few nanometers. Nevertheless, the minimum is very wide; even large deviations in particle size still yield thermal conductivities nearly as low

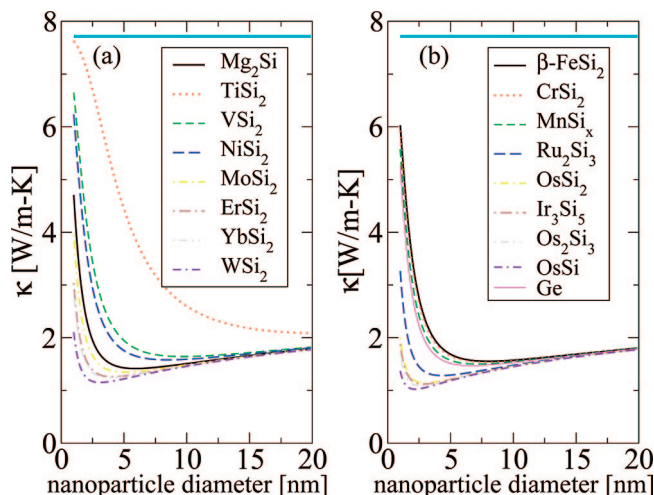


Figure 1. Calculated room temperature thermal conductivity of different nanocomposites with a fixed volume fraction of 0.8% silicide nanoparticles in $Si_{0.5}Ge_{0.5}$ matrix, as a function of nanoparticle size. (a) Metal silicides. (b) Semiconductor silicides. Upper horizontal line denotes the calculated SiGe thermal conductivity in the absence of nanoparticles.

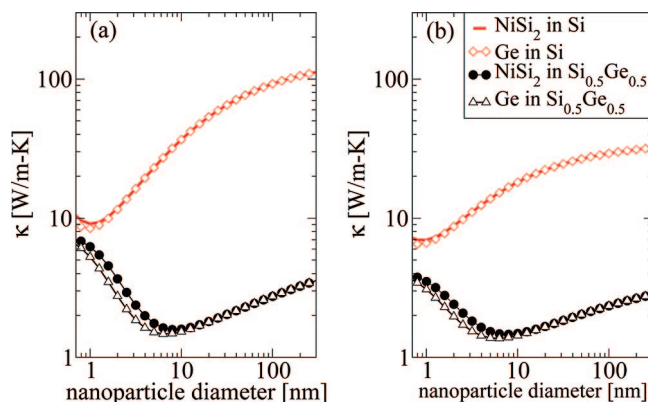


Figure 2. Thermal conductivity of nanocomposites with 0.8% volume fraction of NiSi₂ or Ge nanoparticles in a $Si_{0.5}Ge_{0.5}$ matrix (lower curves, in black), compared with the same nanoparticles in a pure Si matrix (upper curves, in red), as a function of nanoparticle size. (a) Results at 300 K. (b) Results at 900 K. The minimum is much lower and wider in the alloy matrix case.

as the minimum. This is very advantageous for manufacturing nanoparticle-in-alloy thermoelectrics. It implies that a very accurate control of the nanoparticle size is not essential in order to produce the desired lowering of thermal conductivity. Nanoparticles as large as 30 nm thick still reduce the composite's thermal conductivity considerably. This is also clearly seen in the logarithmic plot of Figure 2, both at room and high temperature.

On the other hand, if one inserts silicide nanoparticles into a pure Si or Ge matrix, the effect is very different (Figure 2). Although there is still a minimum at a given optimal size, its value is considerably higher than in the alloy matrix case, when the same volume fractions are compared. No less importantly, the minimum is much narrower in this case. Whereas 100 nm particles already reduce the thermal conductivity of the alloy matrix, their effect is almost negligible in the single crystal matrix. This trend is suddenly reversed when the particle size is below a certain threshold

(around 20 nm); then the rate of thermal conductivity reduction upon particle size decrease is faster for the single crystal matrix.

The reason why nanoinclusions in the alloy are more effective than in the single crystal may seem counterintuitive. In principle, an alloy has shorter phonon mean free paths (MFPs) than a perfect crystal, and it might be argued that the effect of added scattering mechanisms would be negligible. The explanation is that, although the phonon MFP in the alloy is on average shorter than the nanoinclusion separation, it varies enormously with frequency. Phonons at the higher end of the spectrum have MFPs of the order of the lattice spacing, whereas for long wavelength phonons the MFP is orders of magnitude longer with a typical frequency dependence inversely proportional to its fourth power. These low frequency phonons carry most of the heat in the alloy. Because of the rapid frequency dependence of the alloy scattering rate, the heat carrying phonons in the alloy have MFPs longer than the nanoinclusion spacing and are thus effectively scattered by the nanoparticles in the alloy matrix.

In the pure crystal matrix, the high frequency phonons, which are only weakly affected by spaced enough nanoparticles, still contribute appreciably to the heat flow. Therefore the thermal conductivity is not strongly modified by large, far apart nanoparticles, in strong contrast with the alloy case. Upon further reduction of the nanoparticle distance, the slope of the thermal conductivity reduction becomes steeper for the pure crystal matrix, since the nanoparticle scattering rate becomes comparable to the intrinsic anharmonic rate. But even then, the alloy matrix case always yields a smaller thermal conductivity.

Introducing nanoinclusions may lead to undesirable additional scattering of electrons in the material, thus undermining the power factor. In what follows, we estimate the order of magnitude of this effect, assuming that the silicide is well lattice-matched with the SiGe matrix. This is a reasonable assumption for various silicides, for example NiSi₂ or CoSi₂, whose lattice structure integrates seamlessly into the zinc-blende host.

The thermoelectric power factor of a material can be evaluated from microscopic theory as a function of the band structure and electron scattering rate. For a SiGe alloy, the scattering rate of electrons is given as a combination of various mechanisms, one of them being the “alloy scattering term”. This term yields an energy independent contribution to the electron mean free path of the form $\Lambda^{-1} \sim \Lambda_a^{-1}x(1 - x)$, where Λ_a is a constant and x is the Si volume fraction (see eq 6.8.4 of ref 16). The corresponding relaxation rate depends on energy as $E^{0.5}$, yielding a contribution to the mobility that has a temperature dependence $T^{-0.5}$.¹⁵

Nanoparticles introduce an additional scattering rate. This rate can be expressed in terms of the electron scattering cross section, $\sigma_c: \tau_c^{-1} = \sigma_c v_e / V$, where V is the volume containing one nanoparticle and v is the electron velocity. To estimate the cross section, we approximate the nanoparticle’s potential by a square well of height u with spherical shape and radius a . We are interested in the long wavelength limit of the

scattering rate, since the band edge properties largely determine the Seebeck coefficient and power factor. In addition, for a square well the cross section diminishes at shorter wavelengths.

If the potential is positive so that there are no bound states in the nanoparticle, the cross section is energy independent in a first approximation, and smaller than $4\pi a^2$.²⁰ The corresponding contribution to the mean free path due to this scattering process is thus $\Lambda_{np} > L^3 / (4\pi a^2) \sim a / (3F)$, where $F = 4/3\pi(a/L)^3$ is the nanoparticle volume fraction. We should now compare this term with the other frequency independent scattering term: the alloy scattering contribution. The magnitude of the latter is found from the known mobility measurements of SiGe alloys. The alloy scattering mobility term in SiGe is about $\mu_{\text{alloy}} \approx \mu_0 / [(4x(1 - x))(T/300)^{0.5}]$ cm²/Vs, with $\mu_0 \sim 140$ for P type and ~ 190 for N type material.¹⁵ Using the relation between mobility and relaxation time, $\mu(T) \sim e\tau(k_B T) / m^*$, yields an alloy-limited mean free path $\Lambda_{\text{alloy}} < 10$ nm for SiGe at room temperature. This implies that the electron mean free path will not be strongly affected by the nanoparticles if they are sufficiently spaced. In the absence of resonances close to the band edge, we should use volume fractions smaller than $F < a/30$ nm. In other words, for the 0.8% volume fraction considered earlier, the effect of nanoparticles larger than 2 nm on the electronic mean free path would be negligible. Since the nanoparticle contribution to the electron scattering rate does not depend on temperature, the argument remains valid at high temperature.

Several experimental and theoretical works suggest that nanoparticles may actually enhance the power factor with respect to that of the matrix. In the case of ErAs in InGaAs, this has been partly ascribed to the fact that the nanoparticles donate carriers, reducing the needed amount of dopant impurities in the matrix and thus enhancing electron mobility.⁴ Additionally, long-range potential screening tails can sharpen the energy dependence of the electron scattering rate and result in an increased Seebeck coefficient.³ We speculate that the same effects may take place in silicide/germanide: SiGe nanocomposites with an additional improvement of the thermoelectric figure of merit.

The calculations presented indicate that a SiGe matrix nanocomposite with around 1% volume fraction of silicide nanoinclusions may have a room temperature $ZT > 0.5$, five times larger than the best alloy room temperature value. At 900 K, a thermal conductivity reduction of 2.5 times is expected, leading to ZT above 1.7. This would enable the application of SiGe in room and intermediate temperature thermoelectric energy conversion applications, such as micro coolers and power generators, monolithically integrated in Si microchips. The technological advantages of this enabled integration might have important consequences in the future development of microelectronics energy management.

In conclusion, we have found a promising class of nanocomposites based on silicide/germanide nanoparticles embedded in a SiGe alloy matrix with a thermoelectric figure of merit potentially above 0.5 at room temperature and close to 2 at high temperature. Such nanocomposite opens the way

to monolithic integration of thermoelectric devices into Si-based technology. The nanocomposite thermal conductivity has been calculated, showing the existence of a minimum at an optimal nanoparticle size. For 0.8% silicide volume fraction with 2–10 nm particles, the minimum thermal conductivity is between 4 and 5 times smaller than the SiGe alloy room temperature value in the 17 silicide cases investigated. We find strikingly different behaviors between the alloy and single crystal matrix cases; the thermal conductivity minimum is much lower and wider in the alloy case. This emphasizes the importance of using an “alloy” matrix. We also showed that the nanoparticles are not expected to reduce the power factor. Finally, we remark that the nanoparticle-in-alloy approach is not restricted to the concrete cases addressed here, but can be applied to a very wide range of thermoelectric alloys, provided that the appropriate nanoparticle compatible material can be found such that well lattice matched particles may be synthesized inside the matrix.

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