NANOCOMPOSITES TO ENHANCE ZT IN THERMOELECTRICS

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ABSTRACT

The concept of using "self-assembled" and "force-engineered" nanostructures to enhance the thermoelectric figure of merit relative to bulk homogeneous and composite materials is presented in general terms. Specific application is made to the Si-Ge system for use in power generation at high temperature. The scientific advantages of the nanocomposite approach for the simultaneous increase in the power factor and decrease of the thermal conductivity are emphasized along with the practical advantages of having bulk samples for property measurements and a straightforward path to scale-up materials synthesis and integration of nanostructured materials into thermoelectric cooling and power generation devices.

1. OVERVIEW

During the fifteen years after the publication of the first papers on low dimensional or nanostructured thermoelectric materials [1, 2], the thermoelectrics field has greatly expanded in numbers of papers published and has increasingly attracted a multi-disciplinary science and

engineering community into fundamental and applied materials research. Many of these new entrants are working toward both accelerating the advances in the performance of thermoelectric materials and in speeding up their commercial exploitation. These are two goals for the research agenda discussed in this review. Concomitant with the large increase of interest by the research community that is reflected, for example, by the growth of the attendance and the number of papers presented at the 2007 MRS Fall Symposium on Thermoelectric Power Generation, there has also been a large expansion in the sales of commercial thermoelectric products, as documented by a strong and successful entry of thermoelectrics into the automotive market through thermoelectric cooling (or heating) devices. As reported by Lon Bell at the 2007 Industrial Physics Forum held in Seattle [3], over one million cooling (heating) thermoelectric-based car seat units were sold in 2007. In the case of hybrid vehicles (where the fuel consumption per kilometer traveled is monitored), studies showed that the use of thermoelectric car seats for cooling significantly reduced the use of air conditioning, resulting in a greater distance traveled per liter of gasoline and a payback within one year for the use of a car seat, with continued fuel economy benefits enjoyed after the first year of usage. The impact of such developments on enlarging the market for thermoelectric components could be dramatic, creating new opportunities for the use of advanced thermoelectric materials with superior performance. Nanostructured bulk materials and nanocomposites thus have an opportunity to compete for entry into such new applications areas. The thermoelectric materials industry seems ready for the introduction of a Moore's law type road-map for the future development of specific applications areas.

This review is written in the spirit that recent developments in the industrial sector are ushering in a transition to a new era, from a 15 year period when low dimensional thermoelectrics research was driven by implementing a variety of proof-of-principles demonstrations, and by establishing the basic concepts that would be used to further increase ZT. In this new era the focus will be on developing practical materials that can be readily integrated into devices and systems, and effectively compete in an expanded set of thermal management and power generation applications.

In this review the emphasis is on engineered nanostructured bulk materials for thermoelectric applications. Following the introductory overview, a few important general

considerations gained from the last 15 years of exploratory effort are summarized. Strategies for materials synthesis and characterization are then presented, followed by strategies for thermoelectric measurements that would yield the kind of information that could be used for improving the synthesis and characterization steps. This is followed by a brief discussion of modeling studies that would provide feedback to all steps in a process to enhance thermoelectric performance. These processes involve many trade-offs between the optimization of the Seebeck coefficients S, the electrical conductivity σ, and the thermal conductivity κ. The general framework for this discussion is summarized in the concluding remarks. Other contributions to this volume will address the issues that must be considered for specific materials, recognizing that the detailed considerations vary from one thermoelectric materials system to another.

2. SOME GENERAL CONSIDERATIONS

Low dimensional physics gives additional control to thermoelectric materials parameters (such as between S and σ or between σ and κ). These are materials parameters that are difficult to control independently in 3D materials. For low dimensional systems, size becomes a new control parameter. Designing interfaces to scatter phonons more effectively than electrons is now used in many cases to reduce the thermal conductivity of thermoelectric materials. Other approaches, such as energy filtering [4] or carrier pocket engineering [5] can be used additionally for enhancing ZT, the first introducing a barrier which allows high energy electrons to pass over the barrier but prevents low energy electrons from passing through, thereby augmenting the Seebeck coefficient. The second approach calls for designing the geometry of the nanostructure to allow as much as possible of the quantum well and barrier regions to contribute to enhancing ZT. Some examples of notable advances using these approaches have been in the quantum dot PbTe/PbSeTe superlattice, where the power factor ($S^2\sigma$) is increased at the same time as the thermal conductivity is reduced [6]. Also in the Bi_2Te_3/Sb_2Te_3 system, large decreases in κ are reported with only small decreases in $S^2\sigma$ [7]. These systems teach us that nanostructures can increase ZT over bulk values and that enhancements in ZT can come through both enhancing $S^2\sigma$ and reducing κ at the same time, which is a highly desirable strategy for going down the future thermoelectric materials road-map mentioned above. Nanostructures also appear in bulk materials, such as n-type and p-type PbTe-based complex chalcogenides [8, 9]. Self-assembling nanodomains (such as Ag_2Te nanoinclusions within the PbTe matrix) have been identified and proposed as the cause for significant increases in ZT, up to 1.7 in the intermediate 600 to 700K temperature range (see Fig. 1).

Nanocomposite thermoelectrics (Fig. 2) provide a route for producing bulk quantities of materials containing nanostructured constituents that can be engineered to enhance ZT, using modeling for guidance in optimizing performance for a particular class of materials by a feedback process (Fig. 3), involving synthesis, materials characterization, thermoelectric properties measurement and modeling. Nanoparticle composites were initially conceptualized in two formats: (1) the compaction of two types of nanoparticles into a bulk heterogeneous material and (2) the introduction of nanoparticles as inclusions into a bulk host material with a lower melting point than the nanoparticles [10]. The advantages of the nanocomposite approach include: (1) the numerous interfaces that are introduced to scatter phonons more effectively than electrons can be optimized by control of the parameters for the initial nanoparticle constituents and by control of the processing parameters of their compaction into bulk nanocomposites, (2) a potential for cutting costs in the various processes involved in the scale-up and self-assembly of
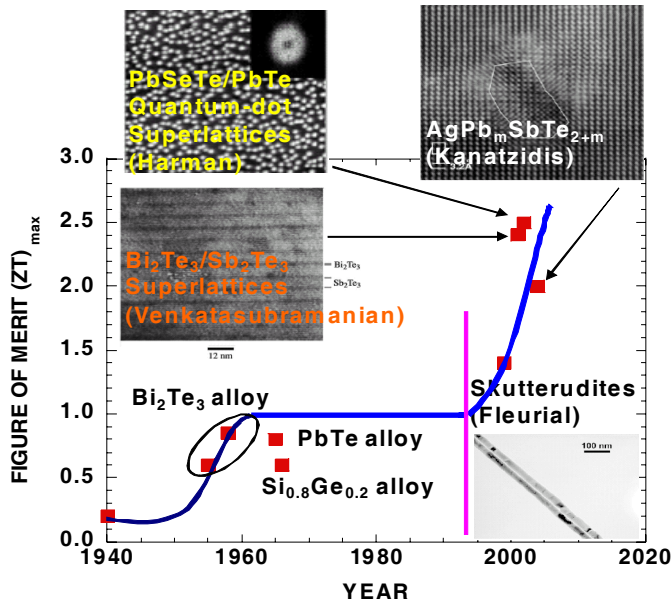
Figure 1. A summary of recent history of increasing the thermoelectric figure of merit ZT. After a 30 year plateau of slow improvement, introduction of new concepts, many related to nanostructuring, have now dramatically increased the figure of merit.
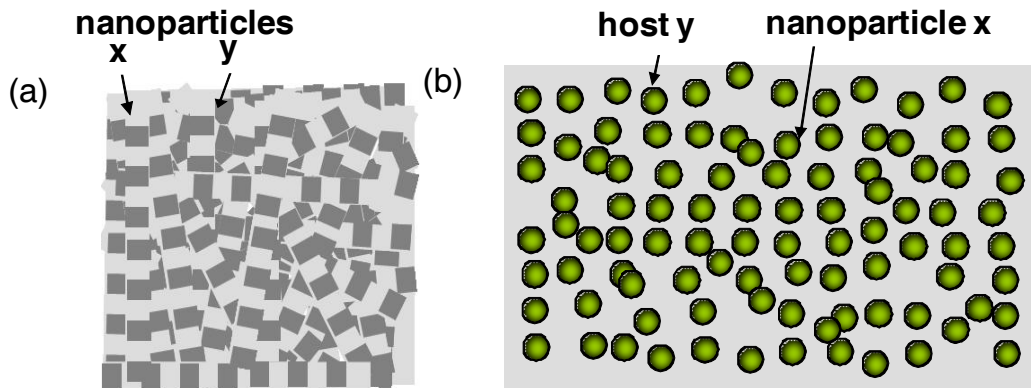

Figure 2. Cartoons of (a) a nanocomposite made up with nanoparticles x and y and (b) a nanoparticle composite made up with nanoparticles x in host material y.
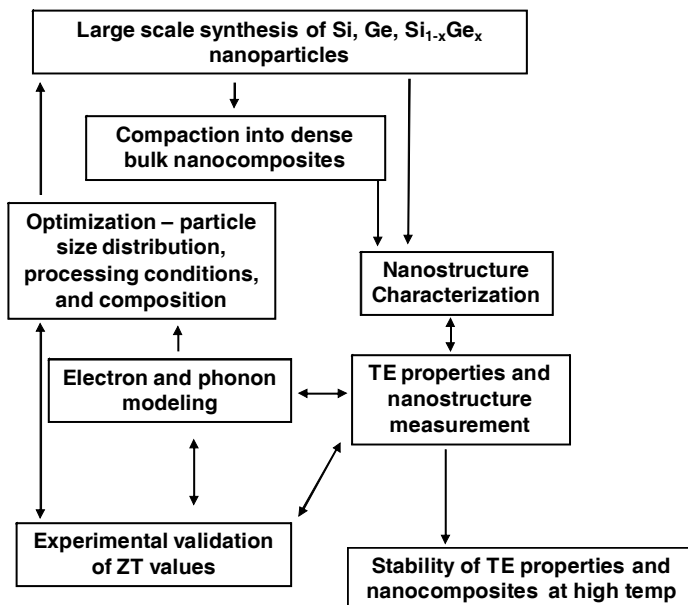

Figure 3. A block diagram of the nanocomposite study feedback process. The block diagram shows the important relationship between synthesis, characterization, thermoelectric measurements, and modeling.

the composites, and (3) the applicability of the approach to many materials systems with promising thermoelectric properties for operation in interesting temperature regimes, such as for automotive and industrial waste heat recovery or space vehicle power systems. In principle, the nanocomposite approach is expected to produce a thermoelectric material with properties superior to the bulk constituents contained in the composite. Descriptions of early efforts in this direction have already appeared in the literature [10].

Some general principles that have helped to conceptualize strategies to be used in preparing nanocomposite thermoelectric materials are now presented. First, we briefly summarize what some key publications teach us about possibilities regarding the reduction of the thermal conductivity and the enhancement of the power factor. The studies on silicon nanowires by the Majumdar group [11, 12] (Fig. 4) teach us that boundary scattering arising from decreasing the diameter of the nanowires is effective in decreasing the thermal conductivity especially at low temperatures, while forming superlattices with Ge along the nanowire length are more effective in reducing the thermal conductivity at higher temperatures [11, 12]. These experimental findings are supported overall by the modeling of these systems by Dames and Chen [13, 14], which also teaches us that modeling studies on wires allow a natural way for introducing periodic boundary conditions in the context of a temperature gradient, as is needed for the description of thermoelectric transport. This advance is also used in model calculations of the thermal conductivity for various kinds of nanocomposite systems (such as ordered and aligned, staggered, or random nanoparticles) [15]. These studies teach us that the reduction in the thermal conductivity depends predominantly on the surface area/volume ratio, which is here denoted by the term "interface density" (Fig. 5). This work teaches us that we should use systems with certain types of disorder as desirable for thermoelectric applications [16, 17]. The results of Fig. 5 raise another issue regarding the possibility of having a physical system with a thermal conductivity below that for the minimum thermal conductivity for the 3D alloy [18] with the same composition as that of the constituents of the composite, as suggested by the modeling results in Fig. 5.

A third concept for considering the reduction in the thermal conductivity is to consider the relative contribution of phonons to the lattice thermal conductivity according to their mean free path (mfp) or to their wavelength Λ_{ph} (see Fig. 6). This figure shows that the contributions of phonons to the thermal conductivity in silicon according to their phonon mean free path covers many orders of magnitude of their mfp [19]. Thus at 300K about 80% of the heat is carried by phonons with a mfp $< 10\mu$m, and 40% is carried by those with a mfp < 100nm. This study teaches us that we need to have phonon scatterers that are effective over a broad range of Λ_{ph} and down to less than 10nm to optimize thermoelectric performance. Such an idea was intensively studied for $Si_{1-x}Ge_x$ alloys around 1990 [20], the experimental approach relying on introducing a fine, randomly distributed dispersion of inert nanoinclusions into an otherwise undisturbed large grain host material. Significant reductions in the lattice thermal conductivity values were observed but difficulties in the bulk nanocomposite synthesis process hampered reproducibility of the results.

Regarding the power factor, theory suggests that since the Seebeck coefficient is proportional to the factor $(E-E_F)$, energy barriers introduced by interfaces or boundaries could act as energy filters, removing low energy electrons from the transport stream and thereby increasing the Seebeck coefficient. Such effects were reported experimentally at an early time for the $PbTe/Pb_{1-x}Eu_xTe$ system in quantum well superlattice [21–23]. Also some years ago, Mahan and Sofo [24] suggested that localized impurity resonant states should be present for rare earth
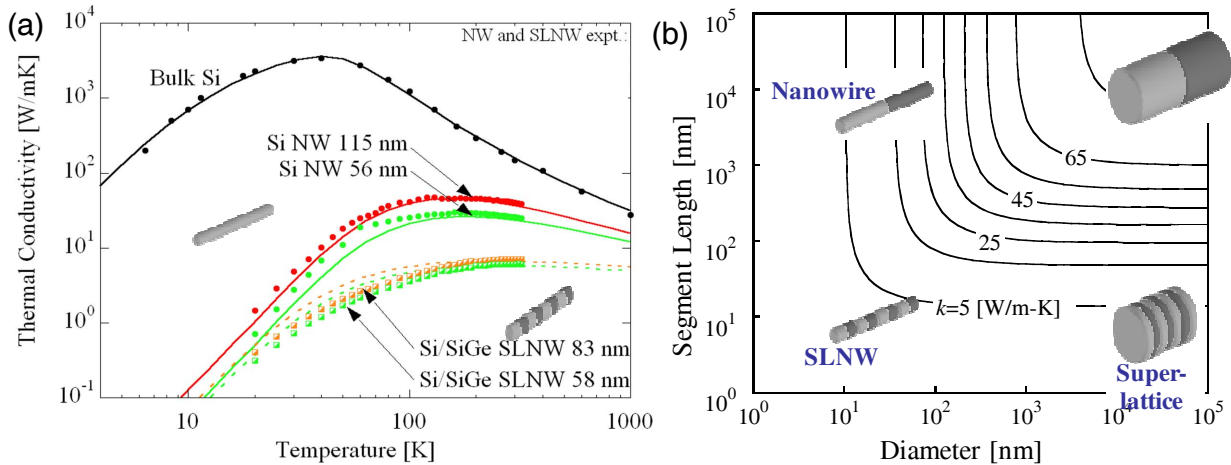
Figure 4. (a) Measured temperature dependence of the thermal conductivity of bulk Si, different diameter Si nanowires, and different diameter Si/SiGe superlattice nanowires. (b) Contours of constant thermal conductivity for Si/Ge superlattice nanowires as a function of wire diameter and segment length L=L_{Si}=L_{Ge}, at 300K. The conductivity plateau approaches the bulk series average of 78.1W/(m K).
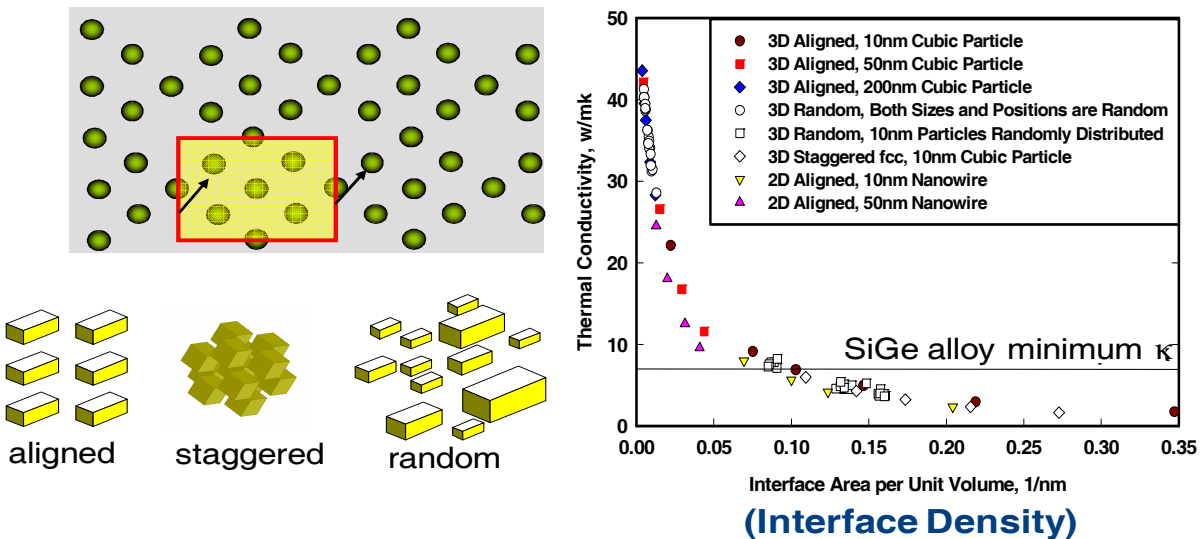

Figure 5. Monte Carlo simulation of the thermal conductivity and phonon transport in different types of SiGe nanocomposites. Results indicate that the thermal conductivity of the SiGe nanocomposite could be below that of the SiGe alloy above an interface density of 0.10 /nm.

impurities at the Fermi energy, again showing a mechanism for substantially increasing the Seebeck coefficient [24]. This work was further developed more recently by the Mahanti group [25], providing more theoretical guidance about how such resonant states can be achieved. Demonstration that the power factor of a nanostructured sample can be increased at the same time that the thermal conductivity is reduced was already demonstrated experimentally in the $Si_{1-x}Ge_x$ system (see Fig. 11 in Ref. [10]). To obtain high ZT values, research effort should be given in future work to identify favorable conditions promoting a simultaneous increase in power factor and a reduction in thermal conductivity.

Even though many people are now working toward optimizing nanocomposite materials for their thermoelectric performance, there are still many gaps in fundamental knowledge about the thermoelectric properties and physical mechanisms involved in controlling the thermoelectric properties of nanocomposite materials. There are potentially a host of promising materials systems awaiting discovery and exploration for their thermoelectric behavior. Thus fundamental studies must be well supported during this critical period so that applications development is not slowed down in advancing this important energy technology. It is believed that the performance of most good bulk thermoelectric materials can be improved by nanostructuring.
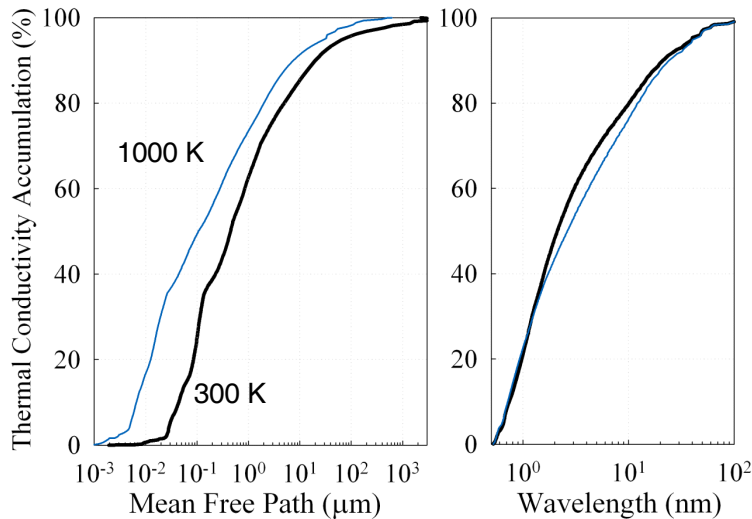

Figure 6. Calculation of the Si thermal conductivity accumulation as a function of the phonon mean free path (left) and phonon wavelength (right). The figures show that the majority of the heat conduction is carried by phonons with a mean free path greater than 10nm.

3. STRATEGY FOR MATERIALS SYNTHESIS

Referring to the right side of Fig. 3, we see a pathway in going from nanoparticle synthesis to practical devices. In this short section, we present a strategy for handling the top 4 boxes in Fig. 3. Depending on the desired temperature range and the ancillary materials requirements dictated by the specific applications, such as hardness, toughness, elasticity etc., a materials system is selected and a method for the preparation of the pertinent nanoparticles is developed. The nanoparticles are then characterized to verify that they do indeed have the desired properties at the nanoparticle level. One method for making nanoparticles from a good bulk sample could be ball milling, which is the approach our group used to make $Si_{1-x}Ge_x$ nanoparticles, but there are many other chemical or mechanical approaches to making nanoparticles of Si, Ge, and their alloys. The characterization of the nanoparticles and their structure is handled by a collection of characterization tools to measure their average size and size distributions, their structural properties and defects, etc. The appropriate doping to achieve the desired n-type and p-type carrier concentration and the chemical composition of the constituents is usually established in the preparation of the nanoparticles.

These nanoparticles are then compacted by some adequate technique so that the nanostructure of the resulting nanocomposite has a size distribution similar to the starting nanoparticles, showing minimal growth in the mean particle size. Other critical requirements are that the mass density of the nanocomposite be within 1% to 5% of the theoretical density, based on the constituents present in the starting powder. Characterization of the nanostructure, grain boundaries, defects, and chemical composition is established by TEM, SEM, and x-ray

diffraction. These are used to evaluate the average particle and crystallite size, and to evaluate crystal phases, sample purity, and the presence of lattice strain. Dynamic light scattering is used at the nanoparticle level to evaluate the particle size and agglomeration of nanoparticles. BET (Brunauer-Emmett-Teller) analysis is done to determine the surface area, pore sizes, and the particle agglomerate size and distribution. Mechanical property measurements are necessary at this stage for verification that the ancillary properties of the nanocomposite meet the necessary requirements for the intended application. Thermal testing at the temperature of use is also necessary to insure that the desired nanostructure is maintained under thermal operating conditions for the desired service time.

Feedback between the thermoelectric measurements, discussed in Section 4, and the synthesis/characterization steps is used to optimize the synthesis and compaction processing conditions. Guidance from the modeling (see Section 5) is provided for modifications to the growth and processing conditions (as indicated in Fig. 3). Since nanocomposite systems have very complex nanostructures, the modeling calculations make many simplifying assumptions, and while they do not have predictive capabilities at the present time, a combination of the feedback from the modeling and the thermoelectric and physical properties measurements offer constructive guidance for the optimization of the synthesis and compaction parameters.

4. STRATEGY FOR THERMOELECTRIC MATERIALS MEASUREMENTS

To check the measurement accuracy and reproducibility, round robin measurements of thermoelectric properties, such as for S, σ, and κ as a function of temperature, are carried out using different experimental systems. This has become a common practice among experimental groups in the thermoelectrics field. A second strategic approach is the use of model systems where more control of experimental parameters are possible in order to increase our understanding of the mechanisms which control the thermoelectric parameters for nanostructured systems. Thus, for the development of the SiGe nanocomposite materials system for thermoelectric applications, bulk Si samples with nanoscale grains ("nano bulk" Si) are investigated without the complications of the germanium alloying. This approach was adopted to increase our understanding of the doping process to produce n-type and p-type samples, to gain insights into the ball milling process parameters for preparing nanoparticles, and into the compaction process parameters for preparing the nanocomposite materials.

With the guidance gained from studies of n-type and p-type nano bulk Si, we have found that we can more quickly identify a first order approximation to the range of desirable processing conditions that are useful for the preparation of the $Si_{1-x}Ge_x$ nanocomposite materials, allowing us to focus more on the optimization of the Ge concentration and on the tuning of the processing conditions for the ball milling and compaction processing steps. For example, Fig. 7(a) shows results for the temperature-dependent thermal conductivity and ZT for n-type nano bulk Si material produced by preparing Si nanoparticles by ball milling, and then compacting them into bulk pellets to within 1% of theoretical mass density. A large decrease in thermal conductivity is found for all the nanocomposite samples across the entire temperature range from room temperature to 1300K. For example, as much as a 20-fold decrease in κ is seen at room temperature arising from the nanostructuring, reaching a value only ~20% higher than that of the state-of-practice bulk $Si_{0.8}Ge_{0.2}$ alloy material currently used by NASA for powering several deep space science exploration probes. Studies like this help us determine the trade-off between adding carriers to increase the phonon-electron scattering which reduces the thermal conductivity

but at the same time increases the heat carried by the electrons directly. These studies also provide guidance to optimizing the processing parameters for preparation of the nanoparticles and nanocomposites. Translating the measurements of the thermal conductivity and other thermoelectric parameters to the determination of ZT itself shows an increase in ZT from between 150 to 350% over the single crystal value, depending on the processing conditions, and a ZT_{max} that is more than 2/3 of the state-of-practice n-type $Si_{0.8}Ge_{0.2}$ material now in use. The large decrease in thermal conductivity offsets the much smaller decrease in charge carrier mobility and electrical conductivity for these materials.

Adding just small amounts of Ge has a dramatic effect on decreasing the thermal conductivity and increasing the ZT values in p-type nano bulk Si (Fig. 7(b)). For example at 1100K, the thermal conductivity is reduced from the best p-type nano bulk Si sample at 90 to 80mW/(cm K) for the 2.5% nanobulk dilute alloy which translates to a large increase in ZT_{max} from ~0.20 to ~0.35. These model systems studies are then used in our work to achieve significant enhancements in ZT for n-type and p-type $Si_{1-x}Ge_x$ systems over state-of-practice materials, to be reported elsewhere. Another strategic concern is the thermal stability of the nanocomposites at the service temperature for actual operations of nanocomposite-based materials in service. Thermal stability issues have been examined by structural and thermoelectric properties measurements of the nanocomposite materials after continuous operation at service temperature. Specific results have been obtained after continued operations at 1275K, showing encouraging results that nanostructures can survive these operating conditions, and that the ZT does not significantly change. This research direction needs to be pursued further in the future.

5. GUIDANCE FROM MODELING STUDIES

The modeling of nanocomposite thermoelectric materials is difficult because of the complexity and heterogeneity of the physical system. Since there is little possibility for predictive models for the near future, the focus is on interpreting experimental observations and looking to modeling for guidance in experimental strategies to control processing parameters to manage the trade-offs occurring in S, σ, and κ when processing parameters are varied. Experimental observations are used to establish the relative importance of various scattering mechanisms for electrons and phonons which modeling uses to guide more convergent strategies for managing the trade-offs in selecting processing parameters, such as the dopant species and concentration. In managing such trade-offs, materials science issues must also be considered, since, for example dopants do more than just vary the carrier concentration. They also affect the compaction process and either promote or retard particle aggregation.

In the modeling, phonon and electron scattering processes and transport are explicitly considered, with special consideration given to the effect of nanostructuring on these processes. From the kinetic expression $\kappa = Cv\Lambda/3$ for κ, only the mean free path Λ can be varied effectively. For bulk systems, the dominant phonon scattering mechanisms are phonon-phonon scattering, phonon-electron scattering, and phonon-alloy (point defect) scattering. The phonon-phonon scattering is most important overall for reducing the thermal conductivity in the $Si_{1-x}Ge_x$ system, with electron-phonon scattering being especially important for reducing κ for long wavelength phonons and point defect scattering being more important for the short wavelength phonons (see Fig. 8(a)). Nanostructures introduce a variety of extended point defects, interfaces, and grain
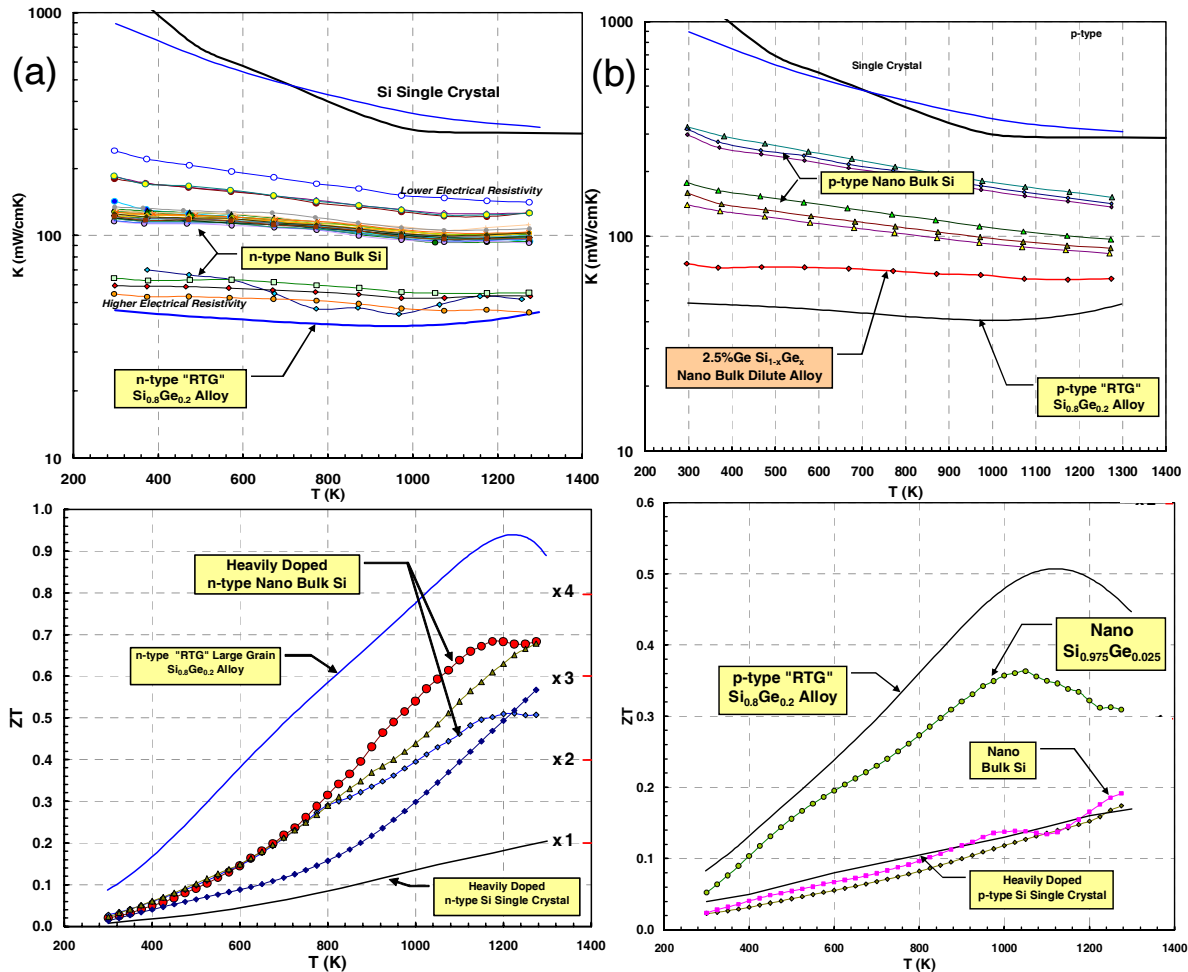
Figure 7. Thermal conductivity and ZT measurements of (a) n-type and (b) p-type nano bulk Si, which provides a model system for studying $Si_{1-x}Ge_x$ nanocomposites. The figure shows that nanostructuring and a small amount of Ge (x=2.5%) increase the ZT of nano bulk Si to about 2/3 of the bulk $Si_{0.8}Ge_{0.2}$ alloy level in the present state-of-practice material.

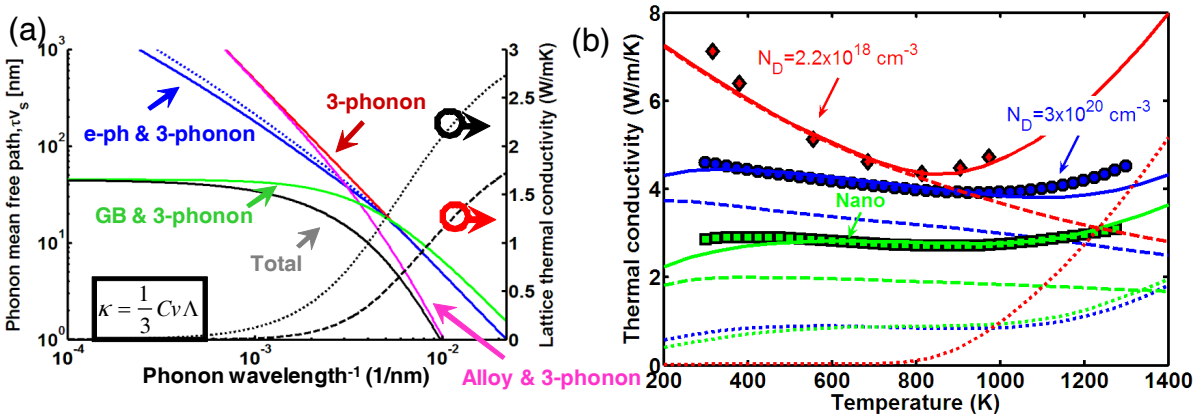**Figure 8.** Effect of nanostructuring on the thermal conductivity of $Si_{0.8}Ge_{0.2}$. (a) shows how small grains could effectively scatter long wavelength phonons, and (b) shows how the measurement results of a nano sample compare with a bulk sample, along with a breakdown of the electron and phonon contributions to the thermal conductivity.

boundaries associated with the nanoparticles and with the compaction processes that cover a wide range of phonon scattering wavelengths, which is a main reason why nanostructuring is so effective in reducing κ (see Fig. 8(b)). The nano-scattering effect is especially effective at long wavelengths, but also at shorter wavelengths through the presence of nanoparticles with a wide distribution of sizes. However, the carrier concentration must be optimized, as is shown in Fig. 8(b), where a large decrease in the lattice thermal conductivity due to nanostructuring is seen for a concentration of 3×10^{20}cm^{-3} carriers. While nanostructuring does not much change κ_e (the electrical contribution to κ - dotted curves), the carrier concentration needs to be limited so that κ_e does not increase κ too much; that is, carriers are desirable for increasing electron-phonon scattering, but undesirable for their contribution to κ_e. In considering this trade-off, the contribution of carriers to the power factor must be simultaneously optimized for the temperature range where the nanocomposite material will be used.

Here modeling also provides guidance. The validity of modeling S, σ, κ, and ZT vs temperature for pure silicon was documented years ago [26, 27] and also for $Si_{1-x}Ge_x$ bulk alloys for a variety of carrier concentrations [28, 29]. The extended point defects and grain boundaries introduce energy filtering effects for electrons (Fig. 9) which suppress transport by low energy electrons. Thus carriers with energies above the barrier associated with the grain boundary (E-E$_B$) preferentially determine and enhance S and therefore are expected to enhance ZT. Intravalley scattering to the same carrier pocket or to an equivalent carrier pocket in the Brillouin zone (such as the Δ carriers for Si) experience only a small decrease in σ, unlike inter-valley scattering to a different type of valley (e.g., Δ to L) which is expected to cause large changes in the power factor. Even though most nanocomposite samples produced to date result in some reduction in σ, the large decrease in κ is dominant over the much smaller decrease in σ, yielding an overall increase in ZT, as confirmed by the modeling results shown for Si in Fig. 10.

Although preliminary experimental results to date show enhancement of ZT for n-type and p-type nanocomposite $Si_{0.8}Ge_{0.2}$ relative to bulk materials of the same composition, the experimental optimization of the processing parameters and the modeling results are at the work-in-progress stage, with significant increases in performance expected in the future as the process optimization improves, guided by modeling, which also is still in the development stage.

6. CONCLUDING REMARKS

This review presents a rationale and strategy for using nanostructuring and the preparation of nanocomposite materials as a means to enhance thermoelectric performance in bulk size samples with significant heat capacity for power generation and cooling applications by using interfaces covering a wide range of length scales to scatter phonons more effectively than electrons. The approach is applicable to both n and p type samples for a wide variety of materials, though the details for each materials system are different. Although enhancement in ZT has already been demonstrated in n-type and p-type nanocomposite $Si_{1-x}Ge_x$ systems, further enhancement in ZT is expected with better understanding of theoretical issues, better control of materials processing parameters, and of doping levels. A strong interplay and feedback between modeling, synthesis, materials characterization, and measurements are essential for progress with the design and preparation of high ZT nanocomposite materials for thermoelectric applications.

$$\frac{1}{\tau_m} \approx \frac{2\pi}{\hbar} \sum_{k'} \left| \left\langle \psi_k \left| U(r) \right| \psi_{k'} \right\rangle \right|^2 (1 - \cos \theta)$$
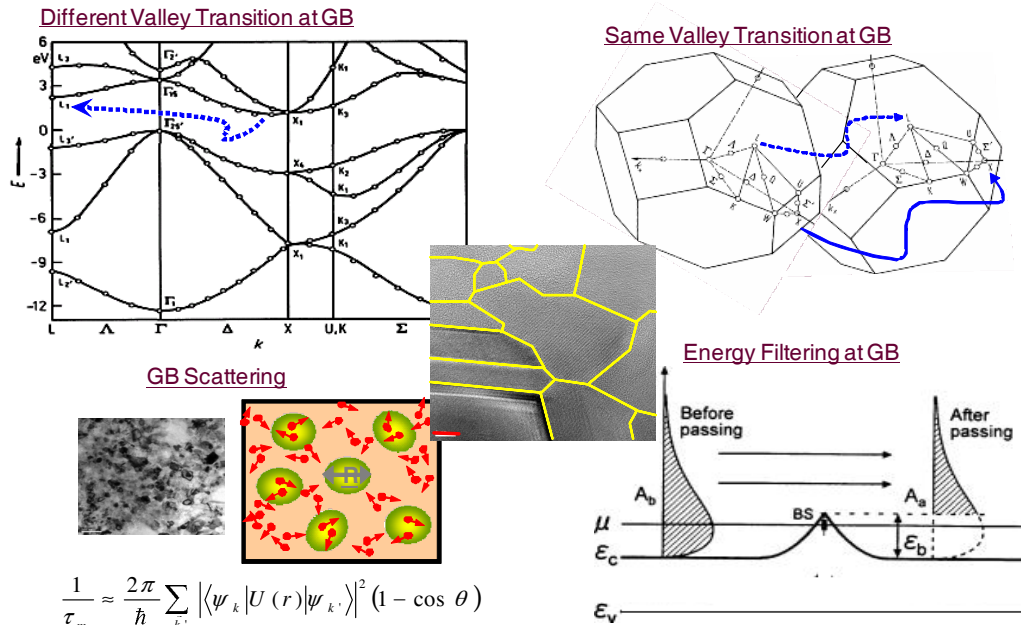
Figure 9. Schematic of different types of electron scattering mechanisms at grain boundaries (GB), including intervalley scattering, intravalley scattering, grain boundary filtering, and an equation used to describe the scattering rate.
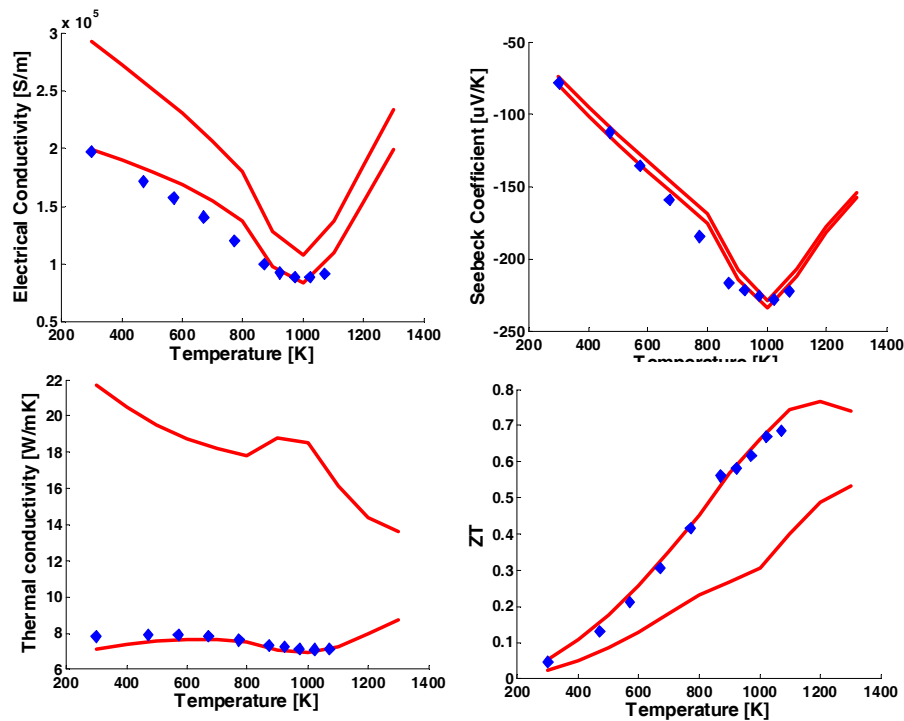

Figure 10. Comparison of nano Si measurement results with model calculations on bulk Si and on nano Si. Solid curve: Bulk Si model, Dotted curve: Nano Si model, Points: Measurement results.

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