

Nanostructured Thermoelectric Materials: From Superlattices to Nanocomposites

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Abstract

Energy transport in nanostructures differs significantly from macrostructures because of classical and quantum size effects on energy carriers. Experimental results show that the thermal conductivity values of nanostructures such as superlattices are significantly lower than that of their bulk constituent materials. The reduction in thermal conductivity led to a large increase in the thermoelectric figure of merit in several superlattice systems. Materials with a large thermoelectric figure of merit can be used to develop efficient solid-state devices that convert waste heat into electricity. Superlattices grown by thin-film deposition techniques, however, are not suitable for large scale applications. Nanocomposites represent one approach that can lead to high thermoelectric figure merit. This paper reviews the current understanding of thermal conductivity reduction mechanisms in superlattices and presents theoretical studies on the thermoelectric properties in semiconducting nanocomposites, aiming at developing high efficiency thermoelectric energy conversion materials.

1. Introduction

The central issue in thermoelectrics research is to increase thermoelectric figure of merit ZT . The best thermoelectric materials were succinctly summarized as “phonon-glass electron-crystal” (or PGEC in short), which means that the materials should have a low lattice thermal conductivity as in a glass, and a high electrical conductivity as in crystals [1]. The best thermoelectric materials are found in heavily doped semiconductors. Insulators have poor electrical conductivity and metals have low Seebeck coefficient. In semiconductors, the thermal conductivity has contributions from both electrons (k_e) and phonons (k_p), with the majority usually coming from phonons. The phonon thermal conductivity can be reduced without causing too much reduction in the electrical conductivity. A proven approach to reduce the phonon thermal conductivity is through alloying proposed in later 1950's [2]. The mass difference scattering in an alloy reduces the lattice thermal conductivity significantly without much degradation to the electrical conductivity. The commercial state-of-the-art thermoelectric cooling materials are based on alloys of Bi_2Te_3 with Sb_2Te_3 (such as $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$, p-type) and Bi_2Te_3 with Bi_2Se_3 (such as $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, n-type), each having a ZT at room temperature approximately equal to one [3].

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Low-dimensional materials, such as quantum wells, superlattices, quantum wires, and quantum dots offer new ways to manipulate the electron and phonon properties of a given material [4]. In the regime where quantum effects are dominant, the energy spectra of electrons and phonons can be controlled through altering the size of the structures, leading to new ways to increase ZT. In this regime, the low-dimensional structures can be considered to be new materials, despite the fact that they are made of the same atomic structures as their parent materials. Each set of size parameters provides a “new” material that can be examined, to a certain extent, both theoretically and experimentally, in terms of its thermoelectric properties. Thus searching for high ZT systems in low-dimensional structures can be regarded as the equivalent of synthesizing many different bulk materials and measuring their thermoelectric properties. Because the constituent parent materials of low-dimensional structures are typically simple materials with well-known properties, the low-dimensional structures are amenable to a certain degree of analysis, prediction and optimization. When quantum size effects are not dominant, it is still possible to utilize classical size effects to alter the transport processes, as for example the exploitation of interfaces and boundaries to scatter phonons more effectively than electrons. Investigations over the past decade on low-dimensional structures have exploited both quantum and classical size effects for electrons and phonons.

2. Superlattices – Engineering the Electron and Phonon Transport

In 1993, Dresselhaus and co-workers proposed the use of quantum wells to increase the power factor via quantum size effects of electrons [5]. The practical implementation of these quantum-well structures calls for superlattices or multiple quantum well structures. Meanwhile, there were also suggestions and experimental evidence that superlattices could be made into superior thermal insulators, promising a second route to improve the figure-of-merit [6]. Subsequent experimental studies have demonstrated significant thermal conductivity reduction in a wide variety of superlattices [7]. Most recently, significant enhancements of the thermoelectric figure-of-merit were reported in $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Se}_3$ superlattices along the cross-plane direction and $\text{PbTe}/\text{PbTeSe}$ quantum-dot superlattices along the film-plane direction [8, 9]. Table 1 compares the reported power factor of these structures with that of their corresponding bulk materials at room temperature. It is clear that thermal conductivity reduction plays a central role in the reported ZT enhancement.

Theories have been developed to explain the thermal conductivity reduction in quantum wells and superlattices, first preceding the experiments and later concurrently with increasing experimental data. These models generally fall into two different camps. The first group treats phonons as incoherent particles, and considers interface scattering as the classical size effect that is analogous to the Casimir limit at low temperatures in bulk materials and Fuchs-Sonderheim treatment of electron transport [10, 11]. These classical size effect models assume that interface scattering is partially specular and partially diffuse, with the fraction of specular interface scattering as a fitting parameter. These models can explain experimental data for superlattices with periods thicker than ~ 5 mono-atomic layers. The other group of models is based on the modification of phonon modes in superlattices, considering the phonons as totally coherent. In superlattices, the

periodicity has three major effects on the phonon spectra: (1) phonon branches are folded due to the new periodicity in the growth direction, (2) mini band-gaps form, and (3) the acoustic phonons in the layer with a frequency higher than that in the other layer become flat, or confined due to the mismatch in the spectrum. The major impact of these changes is the phonon group velocity reduction in the cross-plane direction, which has been proposed as an explanation for the lowered thermal conductivity [12]. Comparison with experimental data (Fig.1), however, shows that the group velocity reduction alone is insufficient to explain the magnitude of the thermal conductivity reduction perpendicular to the film plane, and it fails completely to explain the thermal conductivity reduction along the film plane [13]. The reason is that the lattice dynamics model assumes phase coherence of the phonons over the entire superlattice structure and does not include the possibility of diffuse interface scattering, which destroys the perfect phase coherence picture. More recently, a partially coherent phonon transport model was established that can explain the thermal conductivity behavior in superlattices over the full range of period thicknesses, and in both the in-plane and the cross-plane directions [13]. Figure 2 shows an example of the model and experimental results [14] for GaAs/AlAs superlattices. These theoretical and experimental studies show that it is difficult to take advantage of wave effects in phonon transport processes, because the phonon thermal wavelength is small compared to the characteristic roughness and geometric variations of typical nanostructures. At room temperature, for example, the dominant phonon wavelength is ~10-20 Å in most materials [15]. It is well known that for an interface to be smooth, the wavelength must be much smaller than the interface roughness. Thus, slight interface imperfections, due to mixing of atoms or formation of steps, can easily destroy the phonon coherence. For thermoelectrics applications, this destroy of phonon coherence is actually beneficial. Figure 1 suggests that if phonons are coherent, the superlattice thermal conductivity reduction is not as large as experimentally observed, because phonons in the passing bands still carry heat and contribute to the heat conduction.

3. Thermoelectric Nanocomposites – A New Paradigm

The above discussion on the thermal conductivity reduction mechanism suggests that the periodicity of superlattices is not a necessary condition for thermal conductivity reduction. The reduced thermal conductivity in superlattices comes from the sequential interface scattering of phonons rather than the coherent superposition of phonon waves. This conclusion leads naturally to the idea of using nanocomposites as potentially a cheap alternative to superlattices in the quest for high ZT materials [16, 17]. Such nanocomposites can be in the form of nano-particles and nanowires embedded in a host matrix material, or mixtures of two different kinds of nanoparticles [17, 18]. A recent report on high ZT bulk thermoelectric materials indeed contains nanostructures [19]. With simple hot pressing procedure, Zhao et al. showed that the effective thermal conductivity of a Bi_2Te_3 nanocomposite with tubular Bi_2Te_3 nanowire inclusions is reduced, leading to a 25% increase in ZT compared to homogenous bulk materials [20].

We would like to point out that the addition of nanoscale inclusions has been attempted before [21]. For example, by the addition of BN and B_4C nanoparticles into a SiGe alloy, it was found that the thermal conductivity can be reduced appreciably.

Unfortunately, the inclusions also reduce the electrical conductivity and thus the net gain in ZT was not large. This is because the added inert particles have a large bandgap and thus a high electric potential barrier that scatters electrons. To reduce the thermal conductivity without degrading the electron transport properties, one should work with constituent materials that have significant differences in lattice properties, but negligible differences in electronic properties. Recent experimental results on $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattices and $\text{PbTe}/\text{PbSeTe}$ quantum dots superlattices [8, 9] shows no significant reduction in the electrical conductivity was observed for current flow perpendicular to the interface of $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ superlattices and along the interface of $\text{PbTe}/\text{PbSeTe}$ quantum-dot superlattices. This demonstrates that by properly choosing the mismatch in electronic properties, the electron transport properties can be maintained at a level comparable to bulk materials or even enhanced using interfaces as energy filters or energy quantization barriers.

Although the nanocomposite approach seems promising, currently there are little theoretical or modeling works in the literature regarding thermoelectric properties of nanocomposites that one can rely on to achieve good design of nanocomposites. There exist a variety of challenges for simulation of both electron and phonon thermoelectric transport in nanocomposites. First of all, question often rises whether one needs to look into the wave effect in transport processes in nanostructures [15]. Another challenge to study the thermoelectric properties of nanocomposites is to simulate the electron and phonon transport in the whole composite structure with nanoparticles or nanowires embedded in a matrix material. The distribution of the size and location of nanoparticles can vary a lot. To accurately model the transport, the simulation box should be as large as possible, or even the same size as the sample made. The memory and computational time requirements for such a multiscale problem are very demanding. Instead of treating the whole structure, Yang and Chen [17,18] simplified the problem by dealing with periodic nanocomposites that can be constructed by a periodic stack of a unit cell.

Both the deterministic solution of phonon BTE and Monte Carlo simulation have been used to predict the thermal conductivity of nanocomposites with Si nanowires and nanoparticles embedded in Ge matrix [17,18]. The study shows that the prevailing approach to model thermal conductivity of nanocomposites, which includes the interface thermal resistance, or Kapitza resistance [22], with the Fourier heat conduction theory [23,24,25,²⁶], underpredicts the effect of interface for thermal conductivity reduction since the Fourier heat conduction theory is based on the diffusion picture and is not applicable when the phonon mean free path is longer than the characteristic length of the nanocomposites such as the particle diameter and/or interparticle separation distance. Figure 3 shows the size effect on the thermal conductivity of $\text{Si}_{1-x}\text{Ge}_x$ nanocomposites with Si nanoparticles embedded in Ge matrix. First of all, for fixed size of silicon nanoparticles, the less the atomic percentage of germanium, which has lower thermal conductivity than silicon, the lower is the effective thermal conductivity of the nanocomposites. This is very different from macroscale composites, in which the effective thermal conductivity increases with the decreasing volumetric fraction of the lower thermal conductivity component. This is caused by the ballistic transport of phonons in both the host material and the nanoparticles, and the interface resistance between the host material and the nanowires. The comparison of the thermal conductivity of the nanocomposites with 50nm silicon particles and 10nm silicon particles simply

aligned in germanium matrix shows that the thermal conductivity decreases as the size of the nanoparticles decreases. The comparison of thermal conductivity of nanocomposites with the corresponding alloy value also demonstrates that nanocomposite can be an effective approach to reduce the thermal conductivity and thus to develop high-efficiency thermoelectric material. Jeng et al also compared the thermal conductivity of periodic and random nanocomposites and found out that the randomness either in particle size or in particle location distribution causes only slight fluctuation but is not a dominant factor for thermal conductivity reduction [18]. Knowing that the phonon-interface scattering dominates the thermal conductivity reduction for nanocomposites, interfacial area per unit volume was proposed as a unified parameter to replace the nanoparticle size and the atomic composition to correlate the thermal conductivity of both periodic and random nanocomposites. Figure 4 shows that the thermal conductivity data of both periodic and random nanoparticle composites follows nicely into one curve as a function of interfacial area per unit volume. Figure 5 shows the temperature-dependent thermal conductivity of nanoparticle composites. Boundary scattering results in very different temperature dependence of the thermal conductivity of nanocomposites comparing to their bulk counterpart.

To conclude, thermal conductivity of nanocomposites can be effectively reduced which renders nanocomposite approach as potentially a cheap alternative to superlattices for high ZT material development. The challenge is to properly choose the mismatch in electronic properties between the constituent materials so that the electron transport properties can be maintained or even enhanced. The modeling tool for electron transport in nanocomposites is also relatively rare [27] but the methodology developed for studying thermal conductivity of nanocomposites can be extended to study the electron performance of nanocomposites and thus facilitate the material optimization.

4. Summary

Low-dimensional materials such as superlattices offer new ways to manipulate the electron and phonon properties of a given material. The reduction in thermal conductivity is the dominant reason leading to a large increase in the thermoelectric figure of merit in several superlattice systems, which can be used to develop efficient solid-state devices that convert waste heat into electricity. Superlattices grown by thin-film deposition techniques, however, are not suitable for large scale applications. Nanocomposites can realize similar thermal conductivity reduction and thus represent a cheap approach that can lead to high thermoelectric figure merit. Properly choosing the mismatch in electronic properties between the constituent materials is still a challenge. Modeling the electron transport in nanocomposites can facilitate finding a solution.

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References

- [1] G. Slack, in CRC Handbook of Thermoelectrics (Ed: D.M. Rowe), CRC Press (1995) pp.407-440.
- [2] A.F. Ioffe, Semiconductor Thermoelements and Thermoelectric Cooling, Infosearch Ltd. (1957).
- [3] H.J. Goldsmid, Thermoelectronic Refrigeration, Plenum Press (1964).
- [4] T.M. Tritt, Ed., Semiconductor and Semimetals **71** (2001).
- [5] L.D. Hicks and M.S. Dresselhaus, Phys. Rev. **B 47**, 16631 (1993).
- [6] G. Chen, Phys. Rev. **B 57**, 14958 (1998).
- [7] B. Yang, and G. Chen, Thermal Conductivity: Theory, Properties and Applications (Ed: T.M. Tritt), Kluwar Press (2005), pp. 167-186
- [8] T.C. Harman, P.J. Taylor, M.P. Walsh, and B. E. LaForge, Science **297**, 2229 (2002).
- [9] R. Venkatasubramanian, E. Silvana, T. Colpitts, and B. O'Quinn, Nature **413**, 597 (2001).
- [10] C.R. Tellier and A.J. Tossier, Size Effects in Thin Films, Elsevier (1982).
- [11] G. Chen, J. of Heat Trans, **119**, p. 220, (1997).
- [12] S. Tamura, Y. Tanaka, and H. J. Maris, Phys. Rev. **B 60**, p. 2627 (1999).
- [13] B. Yang and G. Chen, Phys. Rev. **B 67**, 195311 (1-4), (2003).
- [14] W. S. Capinski, H. J. Maris, T. Ruf, M. Cardona, K. Ploog, and D. S. Katzer, Phys. Rev. **B 59**, p. 8105 (1999).
- [15] G. Chen, D. Borca-Tasciuc, and R.G. Yang, "Nanoscale Heat Transfer" in "Encyclopedia of Nanoscience and Nanotechnology", eds. H.S. Nalwa, American Scientific Publishers (2004), Vol. 7, pp. 429-459.
- [16] G. Chen, Semiconductors and Semimetals **71**, 2003 (2001)
- [17] R.G. Yang and G. Chen, Phys. Rev. **B 69**, 195316 (2004).
- [18] M.S. Jeng, R.G. Yang and G. Chen, Phys. Rev. **B.**, submitted (2005)
- [19] K.F. Hsu, S. Loo, F. Guo, W. Chen, J.S. Dyck, C. Uher, T. Hogan, E.K. Polychroniadis, and M.G. Kanatzidis, Science, **303**, 819, 2004.
- [20] X.B. Zhao, X.H. Ji, Y.H. Zhang, et al, Appl. Phys. Lett. **86**, 062111 (2005)
- [21] N. Scoville, C. Bajgar, J. Rolfe, J.P. Fleurial, and J. Vandersande, Nanostructured Materials, **5**, pp. 207-223, 1995.
- [22] P.L. Kapitza, J. Phys. **4**, 181 (1941); E.T. Swartz and R.O. Pohl, Rev. Mod. Phys. **61**, 605 (1989).
- [23] Y. Benvensite and T. Miloh, J. Appl. Phys. **69**, 1337 (1991).
- [24] C.-W. Nan, R. Birringer, D.R. Clarke, and H. Gleiter, J. Appl. Phys. **81**, 6692 (1997);
- [25] S. Torquato and M.D. Rintoul, Phys. Rev. Lett. **75**, 4067 (1995).
- [26] R. Lipton and B. Vernescu, J. Appl. Phys. **79**, 8964 (1996).
- [27] D.J. Bergman and L.G. Fel, J. Appl. Phys. **85**, pp. 8205-8216 (1999)

Table I Thermoelectric Properties of Superlattices with high ZT [8,9]

| Thermoelectric Properties at 300 K | PbTe-PbSeTe Quantum Dot SLs | PbTe-PbSe Bulk Alloy | Bi ₂ Te ₃ -Sb ₂ Te ₃ SLs | Bi ₂ Te ₃ -Sb ₂ Te ₃ Bulk Alloy |
|--|-----------------------------|----------------------|--|---|
| S^2s ($\mu\text{Wcm}^{-1}\text{K}^{-2}$) | 32 | 28 | 40 | 50 |
| k ($\text{Wm}^{-1}\text{K}^{-1}$) | 0.6 | 2.5 | 0.5 | 1.45 |
| ZT | 1.6 | 0.34 | 2.4 | 1.0 |

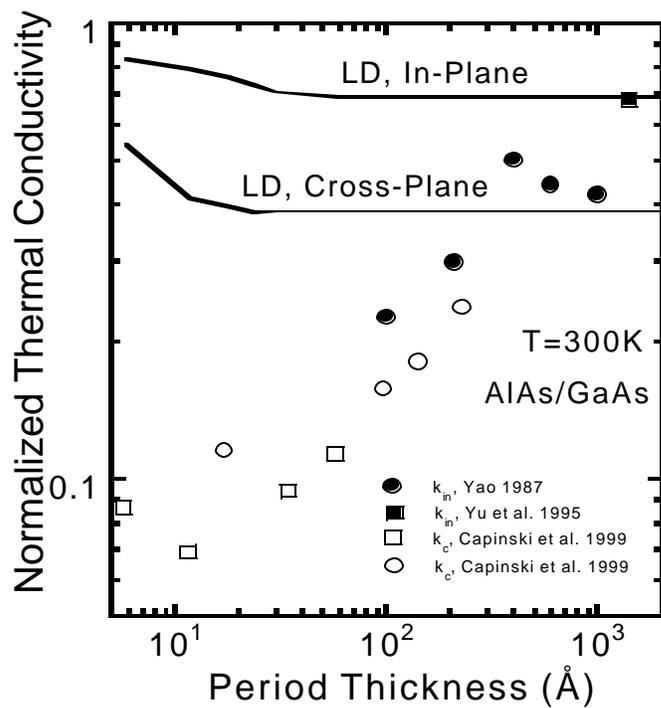


Figure 1 Comparison of lattice dynamics model results (lines) and experimental data on GaAs/AlAs SLs (dots) thermal conductivity for both in-plane (solid dots) and cross-plane (empty dots).

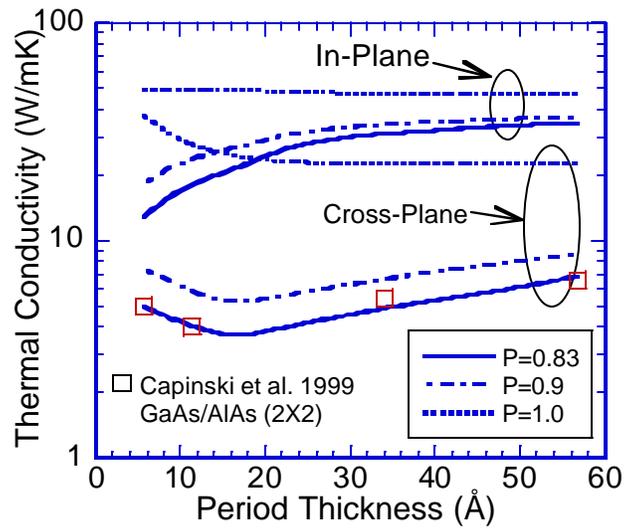


Figure 2 Thermal conductivity of GaAs/AlAs SLs predicted by assuming that the complex wavevector is related to the interface diffuse scattering, p representing the fraction of specularly scattered phonons.

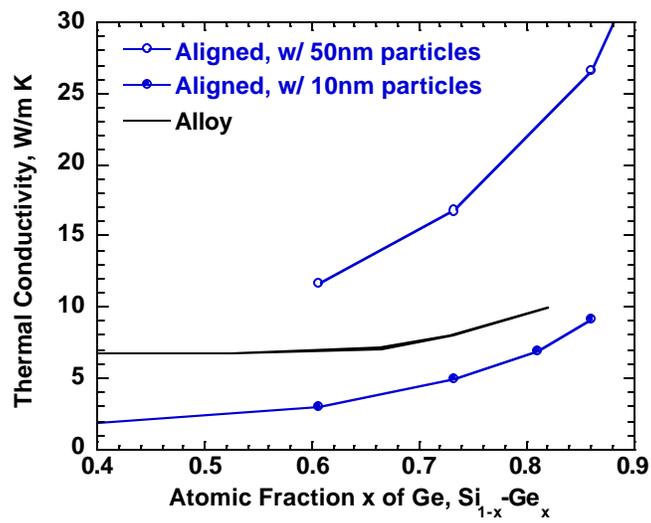


Figure 3 Size effects on the thermal conductivity of nanoparticle composites. Also shown is the thermal conductivity of Si-Ge alloy.

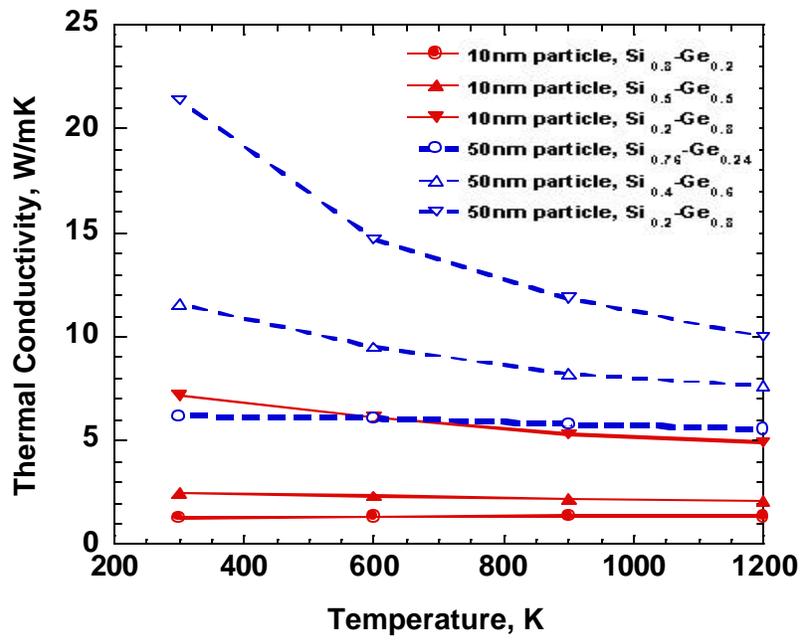


Figure 5 Temperature-dependent thermal conductivity of nanoparticle composites.