

NANOSTRUCTURES AND ENERGY CONVERSION

M. S. Dresselhaus

Department of Electrical Engineering and Computer Science
Massachusetts Institute of Technology
Cambridge, MA 02139
Email: millie@mgt.mit.edu

ABSTRACT

The unique properties of nanostructures associated with their low dimensionality give rise to new opportunities for research on nanoscale heat transfer and energy conversion. Inspired by Majumdar's analysis of the novel aspects of heat, mass, and charge flow across the interface between hard and soft materials, some perspectives about research frontiers in nanoscale heat transfer and energy conversion are provided.

INTRODUCTION

Starting from the visionary views of Majumdar about the nanoscale aspects of the interfaces between hard and soft matter [1], a wide range of challenging research problems are opened up by consideration of fundamental issues involving nanoscale thermal transport across such interfaces. His analysis further leads to a variety of interface issues in thermal transport and energy conversion phenomena that are unique to nanostructures and are not found in their bulk counterpart materials. It is the uniqueness of nanostructures regarding their nanoscale thermal properties that is here emphasized, by giving examples of thermal phenomena not present in typical bulk materials.

Uniqueness Properties of Interfaces

In his analysis of interfaces between soft and hard materials, Majumdar focuses on the dominance of different interactions at different length scales, showing several illustrative examples where interfaces give rise to increased phonon scattering and a reduction in thermal conductivity [1]. We here comment on two

unique and very different aspects of heat transport at interfaces in nanostructures that also depend on length scales, involve interesting fundamental science issues, and perhaps may give rise to useful applications some day.

In the first example we consider the case where interfaces between a nanostructure and vacuum can give rise to a heat pipe. An example of such a heat pipe is a defectless nanostructure in the form of a free cylinder one atom in thickness, such as a freely suspended single wall semiconducting carbon nanotube [2], approximately 1 nm in diameter. For such a structure the thermal conductivity in the direction of the nanotube axis can be very high, even higher than that of the best 3D thermal conductor [3]. This exceptionally high thermal conductivity arises largely because of the unique properties of nanostructures: (1) the carbon-carbon bond is the strongest chemical bond in nature, (2) the interfaces with the vacuum, along with a restricted number of final states to which scattering can occur, severely limits phonon-phonon scattering, (3) the sizable semiconductor bandgap virtually eliminates electron-phonon scattering, and (4) the high structural perfection that can be achieved severely limits the defect scattering mechanism. While graphite in-plane (along with diamond) has the highest thermal conductivity of known materials, the unique properties of the nanotube, enumerated above, further eliminates many of the possible scattering channels that occur in graphite, thereby allowing a single isolated carbon nanotube to behave like a wave guide for heat transfer [3]. Can such heat pipes be utilized in nanosystems, and can some of the unique properties of nano-heat pipes be used to design other structures at the nanoscale with enhanced thermal transport?

Interfaces can also give rise to thermal resistance, and Ma-

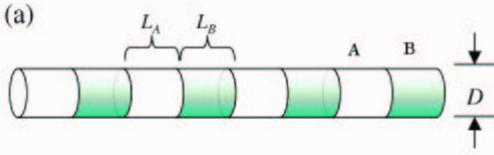


Figure 1. Schematic diagram of a superlattice nanowire consisting of interlaced quantum dots of materials A and B with lengths L_A and L_B and wire diameter D [5].

jumdar in his article [1] gives many examples of this situation which occurs most commonly for nanostructures. Our second example is based on the fact that thermal scattering lengths tend to be shorter than their electrical counterparts and this property can in appropriate situations be used in exploiting nanostructures for thermoelectric cooling and conversion between thermal and electrical energy. The reason why thermoelectricity is not more important today in power generation, cooling and energy conversion is that present thermoelectric materials are not commercially competitive because of their low thermoelectric figure of merit, normally written as $ZT = S^2\sigma T/\kappa$, where the various factors are, respectively, the Seebeck coefficient or thermopower (S), the electrical conductivity (σ), the temperature (T), and the thermal conductivity (κ). Commercially available thermoelectrics today have a ZT values of only about 1, while ZT values of greater than 3 would be required for commercially competitive energy conversion systems [4]. The laws of physics for materials cause S to decrease when σ increases, and for κ to increase when σ increases, and for this reason it has been extremely difficult to increase ZT significantly since the 1950s. However, the *physics of nanostructures* make it possible to vary S , σ and κ somewhat independently, allowing the demonstration of enhanced ZT under appropriately selected conditions. The greatest gains in ZT have been achieved by introducing interfaces such that phonons are preferentially scattered relative to electrons. One example of a system now under investigation in this context is the superlattice nanowire shown in Fig. 1 where the two constituents of the nanowire are selected to have small band offsets so that electrons can be easily transported down the nanowires while phonons are strongly scattered [5].

The superlattice nanowire introduces new variables into the system which allow independent variation of S , σ and κ , such as the wire diameter, and the length of each of the nanowire segments [5]. An experimental demonstration of enhanced thermoelectric performance with ZT exceeding 2 through preferential interface scattering by phonons relative to electrons has been reported for the two-dimensional (2D) superlattice of $\text{BiTe}_3/\text{Sb}_2\text{Te}_3$ [6]. In principle, the nanowire quantum dot superlattice in Fig. 1 offers more degrees of freedom for achieving independent control of the various observables occurring in ZT

than the simple 2D superlattice, which focuses more directly on controlling the thermal conductivity [6, 7].

Nanostructure design can be used to vary the relative importance of the various scattering mechanisms involved in thermal conductivity. For example, when considering thermal conduction in a nanowire, the effect of phonon-interface scattering with the wire boundary becomes increasingly important relative to phonon-phonon scattering as the nanowire diameter decreases.

Single Nanowire Studies

Thermal transport measurements on mats of nanowires do not generally give reliable information about the individual nanowires because the contact thermal resistance between adjacent nanowires tends to dominate the measurements. For this reason, the use of materials with high thermal conductivity for cooling purposes requires great care in reducing thermal contact resistance.

Thus single nanowire measurements are necessary for quantitative thermal transport measurements. Here the Majumdar group has pioneered the field by developing the instrumentation to make such measurements [8] and the group has gone on to make extensive temperature-dependent thermal conductivity $\kappa(T)$ measurements on Si nanowires [9] in the diameter range $22 \leq d_w \leq 115$ nm. The results show a large decrease in the peak of $\kappa(T)$ associated with umklapp processes as the wire diameter decreases, indicating a growing importance of boundary scattering and a corresponding decreasing importance of phonon-phonon scattering with decreasing wire diameter. At their smallest wire diameter of 22 nm, a linear $\kappa(T)$ dependence was reported experimentally, consistent with a linear T dependence that might be observed in the specific heat for a 1D system, and a T -independent mean free path and velocity of sound.

Model calculations for $\kappa(T)$ based on a radiative heat transfer model have also been carried out for Si nanowires [10]. These results show that the predicted $\kappa(T)$ behavior for Si nanowires is similar to that observed experimentally in the range of $37 \leq d_w \leq 115$ nm regarding the functional form of $\kappa(T)$ and the magnitude of the relative decrease in the maximum thermal conductivity κ_{max} as a function of d_w . However, the model calculations predict a substantially larger magnitude for $\kappa(T)$ (by 50% or more) than is observed experimentally. Furthermore, the model calculations (see Fig. 2) do not reproduce the experimentally observed linear T dependence for the 22 nm nanowires, but rather predict a 3D behavior for the density of states and for the specific heat in nanowires with 22 nm diameter [10], indicating that yet smaller diameter nanowires are needed to observe 1D behavior in $\kappa(T)$, consistent with Raman and STM studies on smaller diameter nanowires.

Measurements on individual nanowires allow exploration of the unique properties of nanowires for nanoscale heat transfer and energy conversion, including the dependence of these phe-

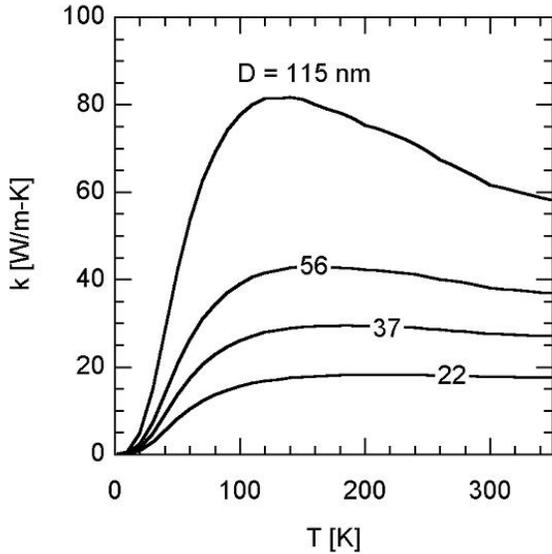


Figure 2. Predicted temperature-dependent thermal conductivity of Si nanowires of various diameters [10].

nomena on wire diameter and nanowire crystalline orientation. Such a knowledge base is needed to gain a detailed understanding of nanoscale heat transfer and to control the unique properties of nanowires for specific thermal device applications.

Quantized Thermal Conductance

It was first predicted theoretically by Landauer and later shown experimentally in 1988 that the electrical conductance of a ballistic conductor is quantized in units of $g_e = e^2/h$ in accordance with the number of conducting channels n_{cc} that support ballistic electron transport [11]. The corresponding quantization of thermal transport in units of $g_0 = \pi^2 k_B^2 T / 3h$ has recently been demonstrated experimentally [12, 13].

To show quantized thermal conductance phenomena a mesoscopic phonon resonator and wave guide device were constructed that included four ~ 200 nm wide and 85 nm thick Si_3N_4 nanowire-like nano-constrictions. This system was used to establish the quantized thermal conductance limit of the measured temperature dependence of the thermal conductance of this nanowire-like structure [12, 13]. For temperatures above 0.8 K, the thermal conductance follows a T^3 law, but as T is further reduced, a transition to a linear T dependence is observed, consistent with a phonon mean free path of $\sim 1 \mu\text{m}$, and a thermal conductance value approaching $16g_0$, corresponding to four massless phonon modes per channel and to the 4 channels in their phonon waveguide structure. Ballistic phonon transport occurs when the thermal phonon wavelength (380 nm for the experimental structure of Ref. [13]) is somewhat greater than the width of

the phonon waveguide at the waveguide constriction. This work demonstrates the conditions for ballistic thermal transport, and opens the possibility of detailed studies of ballistic thermal transport phenomena in nanostructures.

ACKNOWLEDGMENT

The author wishes to thank Professors Gang Chen, Arun Majumdar and Ken Goodson, Dr. Gene Dresselhaus and members of her research group for stimulating conversations and ONR contract N00014-03-1-0865 for support of this research.

REFERENCES

- [1] A. Majumdar, in the Proceedings of this Symposium (May 2003).
- [2] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College Press, London, 1998).
- [3] P. Kim, L. Shi, A. Majumdar, and P. L. McEuen, *Phys. Rev. Lett.* **87**, 215502 (2001).
- [4] Gang Chen, M. S. Dresselhaus, G. Dresselhaus, J.-P. Fleurial, and T. Caillat. In *International Materials Review, Vol. 48*, edited by M. J. Bevis, pages 45–66, Institute of Materials Journals, 1 Carlton House Terrace, London SW1Y 5DB, 2003.
- [5] Yu-Ming Lin and M. S. Dresselhaus, *Phys. Rev. B* (2003). submitted 03/01/03.
- [6] Rama Venkatasubramanian, E. Siivola, Thomas Colpitts, and Brooks O’Quinn, *Nature (London)* **413**, 597–602 (2001).
- [7] T. C. Harman, P. J. Taylor, M. P. Walsh, and B. E. LaForge, *Science Magazine* **297**, 2229–2232 (2002).
- [8] A. Majumdar, *Annual Review Mater. Sci.* **29**, 505–585 (1999).
- [9] D. Li, Y. Wu, P. Kim, L. Shi, N. Mingo, Y. Liu, P. Yang, and A. Majumdar, unpublished (2002).
- [10] Chris Dames and Gang Chen. In *The 21st International Conference on Thermoelectrics: ICT Symposium Proceedings, Long Beach, CA, 2002*.
- [11] S. Datta, *Transport in mesoscopic systems* (Cambridge University Press, Cambridge, UK, 1995).
- [12] K. Schwab, E. A. Henriksen, J.M. Worlock, and M. L. Roukes, *Nature* **404**, 947–977 (2000).
- [13] K. Schwab, J.L. Arlett, J.M. Worlock, and M. L. Roukes, *Physica E* **9**, 60–68 (2001).