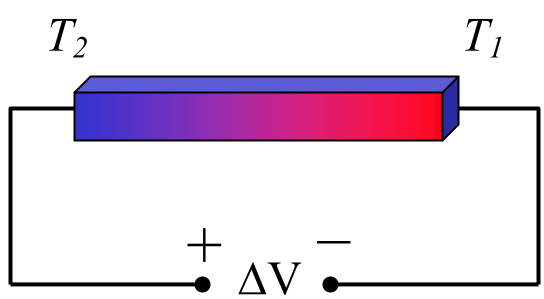
2.57 Nano-to-Macro Transport Processes
Fall 2004
Lecture 20

Guest lecture by Prof. Mildred S. Dresselhaus

1. Outline
-Overview of low dimensional thermoelectricity
-New physics to yield enhanced performance in 1D nanowires
-Quantum dot superlattice nanowires – model calculations
-Newly emerging research directions
-New methods for synthesis and assembly of nanowires

- Self assembled composite nanostructures
- New 3D crystalline materials with quantum dots
- New thermoelectric tools

2. Introduction to Thermoelectricity

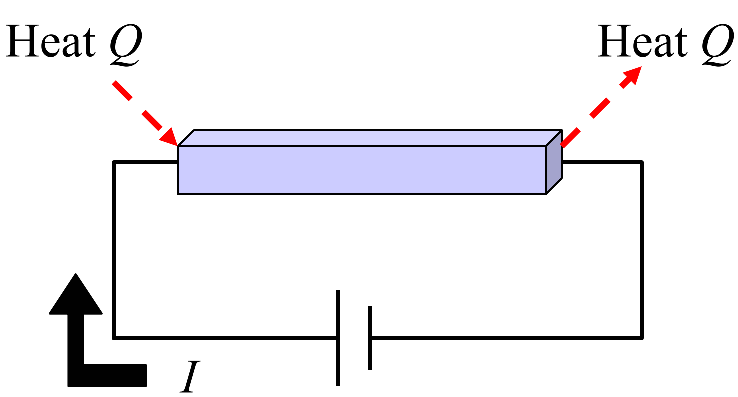


Physically, when one side of the conductor (or semiconductor) is hot, electrons have higher thermal energy and will diffuse to the cold side. The higher charge concentration in the cold side builds an internal electric field that resists the diffusion. The Seebeck voltage is the steady-state voltage accumulated under the open circuit condition. We can express this as

$$S = -\frac{\Delta V}{T_2 - T_1} \text{ (V/K)},$$

where S > 0 for p-type semiconductors, and S < 0 for n-type materials.

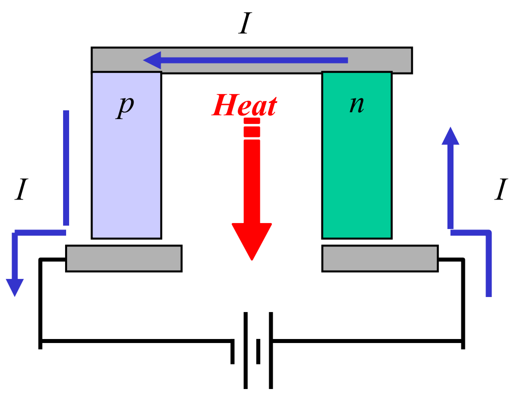
In the following figure, we demonstrate the idea of Peltier Effects.



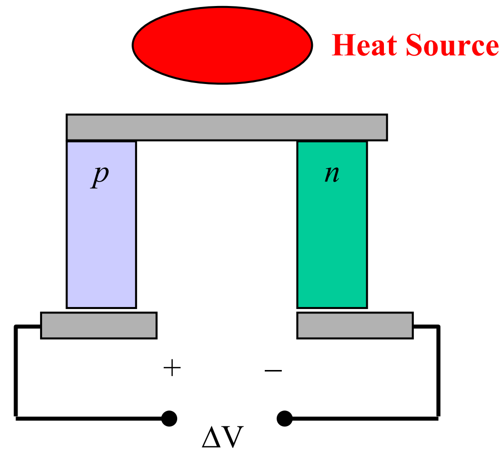
$$\pi = \frac{Q}{I}$$

In this case, heat is carried by carriers (absorbed at the left and rejected at the right end). The Peltier coefficient is defined as $\Pi = Q / I$.

3. Applications



Refrigerator
(Cooling of
electronics)



Power generator
(Waste heat recovery)

In the above figure, we show two major applications of thermoelectricity: refrigerator and power generator. The efficiency of the refrigerator can be evaluated by $ZT = \frac{S^2\sigma}{k}T$, in which S is seebeck coefficient, σ is electrical conductivity, and k denotes thermal conductivity. Compared with mechanical refrigeration, thermoelectric cooling offers the following advantages:

-No moving parts
-Environmentally friendly
-No loss of efficiency with size reduction
-Can be integrated with electronic circuits (e.g. CPU)
-Localized cooling with rapid response

However, the current ZT value (~1) for TE cooling still lags behind that of mechanical refrigeration (ZT~3).

4. Thermoelectric Properties of Conventional Materials

In the following figure, we present the variations of three parameters against the carrier concentration. The ZT value reaches the maximum in the middle of the figure. However, we should not use semimetals because they have both holes and electrons as carriers, which have different signs of S and the effects will cancel out in the cooling process. Therefore, we should focus on the edge of semiconductors.

To increase ZT, we want $S\uparrow, \sigma\uparrow, k\downarrow$. There is confliction in satisfying all these requirements. In the figure, we can find $S\uparrow, \sigma\downarrow$ and $\sigma\uparrow, k\uparrow$. Basically we need to balance these factors. The best alloy $Bi_{0.5}Sb_{1.5}Te_3$ has ZT ~ 1 at 300 K.

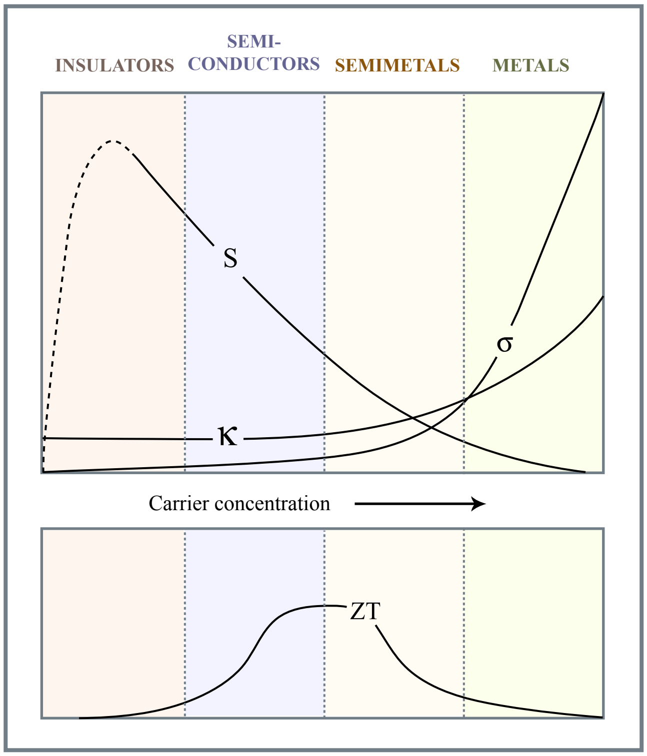


Figure by OCW.

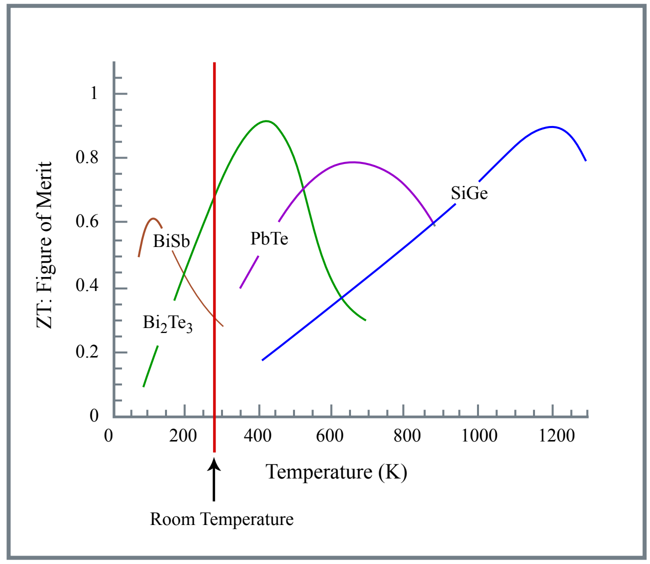


Figure by OCW.

In the current investigations, people have tried different compositions to improve ZT. At different temperature ranges, in the right figure we have different best materials. The ZT values are still less than 1.0 after 40 years.

5. Motivation for Nanotech Thermoelectricity

To further improve the efficiency, low dimensional materials give additional control in

-Enhanced density of states due to quantum confinement effects (we can increase S without reducing σ) □

-Boundary scattering at interfaces reduces k more than σ □

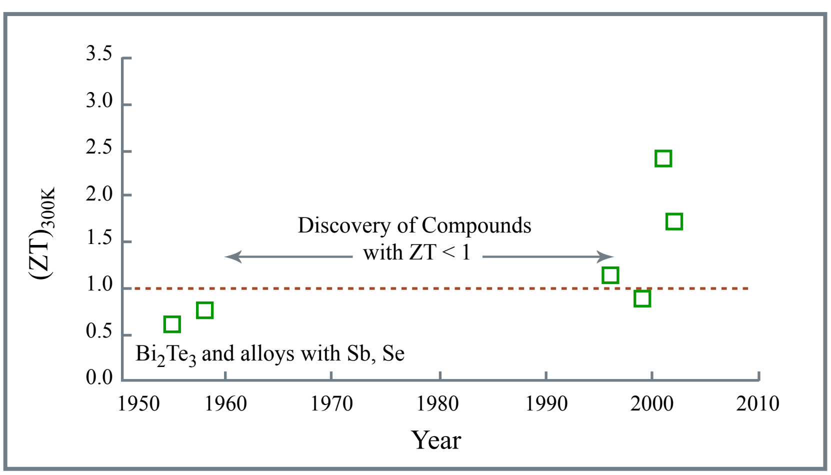
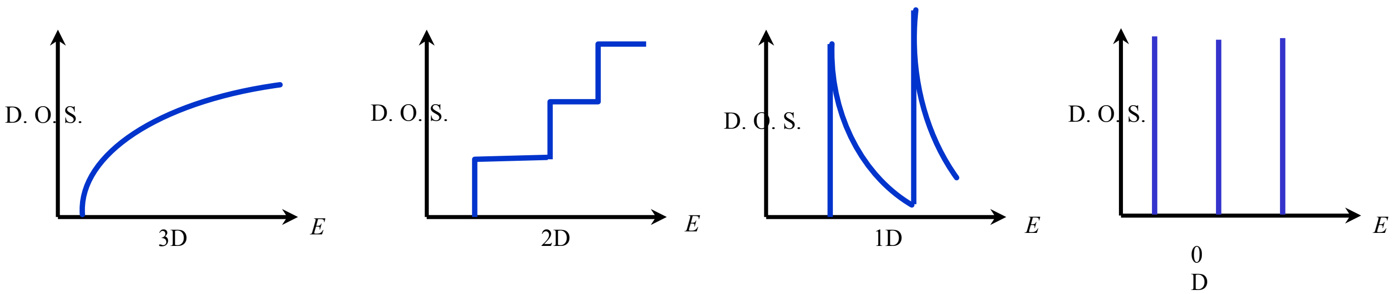


Figure by OCW. After Majumdar. *Science* 303, no. 777 (2004).

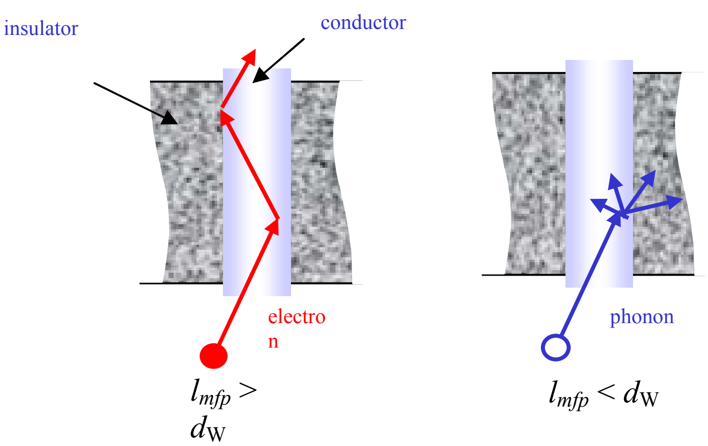
The above figure summarizes the recent advances in nanostructured thermoelectric materials, which led to a sudden increase in $(ZT)_{300K} > 1$. Higher ZT reported experimentally at higher T.

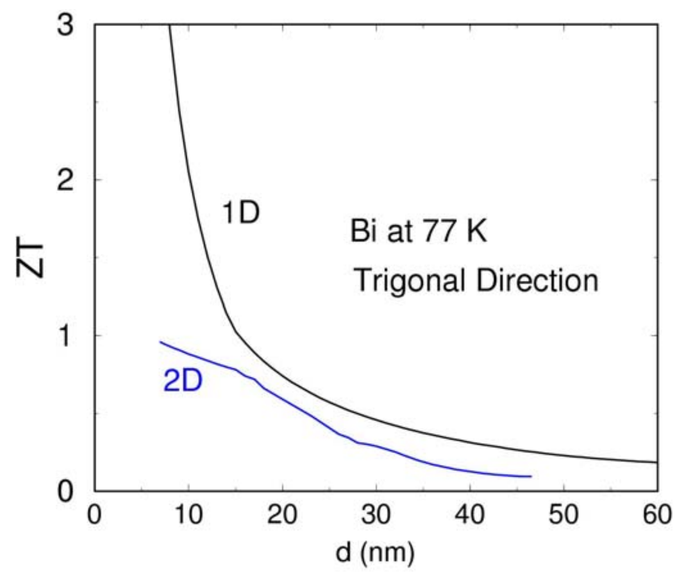
6. New Directions for Low Dimensional or Nanotech Thermoelectricity

1) Electronic properties may be dramatically modified due to the electron confinement in nanostructures, which exhibit low-dimensional behaviors. Recall the following cases given in homework.



2) Thermal conductivity can be significantly reduced by the scattering of phonons at the interfaces. In the following case, the electrical conductivity is not strongly affected.





In the above right figure, the 1D structure shows promise of increasing ZT to 3 at a 10 nm diameter. In the next two figures, thermoelectric cooling using a Bi_2Te_3/Sb_2Te_3 superlattice structure is reported. Enhanced cooling is accomplished by increased scattering of phonons at interfaces, thus lowering the lattice thermal conductivity.

Figure removed for copyright reasons.

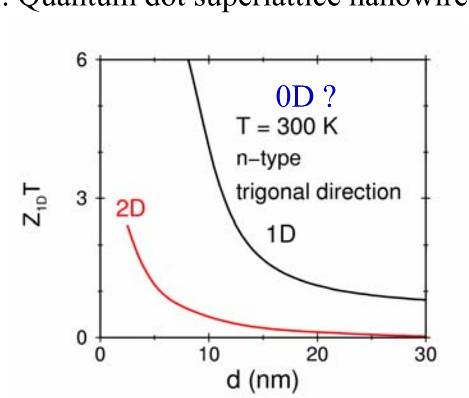
Venkatasubramanian et al., Nature **413**, 589 (2001)

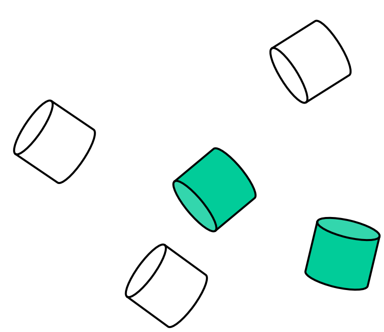
Figure removed for copyright reasons.

Harman et al. J. Electron. mater. Lett. ***29****, L1 (2000)*

In the above work, enhancement of ZT at 300 K in a quantum dot superlattice is more than a factor of two relative to best available bulk PbTe because
-Favorable carrier scattering mechanism due to PbSeTe quantum dots
-Lower lattice thermal conductivity in alloy
And ZT = 3 at 600 K reported at MRS Boston in 2003.

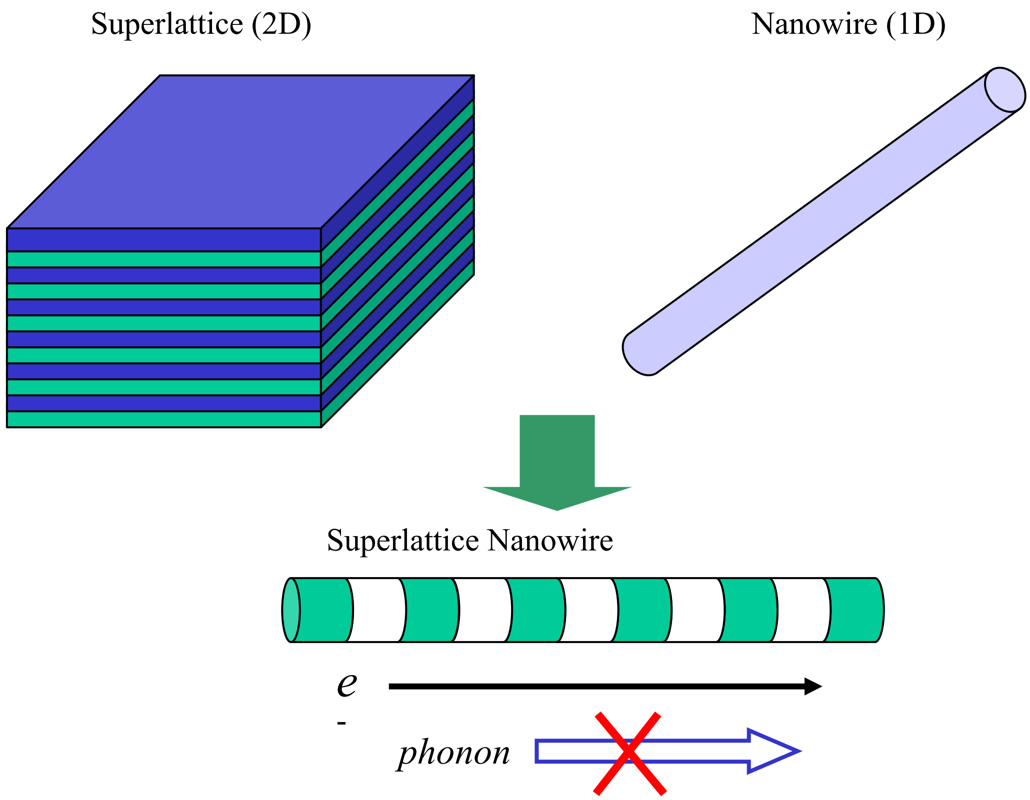
7. Quantum dot superlattice nanowires – model calculations





Quantum Dots

We have discussed the seebeck coefficient enhancement in 2D and 1D structure. Reducing the dimension to 0D may further increase S. However, difficulty exists in making connections to different quantum dots. This problem is solved by combining the idea of superlattice and nanowires. The new structure (superlattice nanowire) will restrict heat conduction but allow electrons to pass.



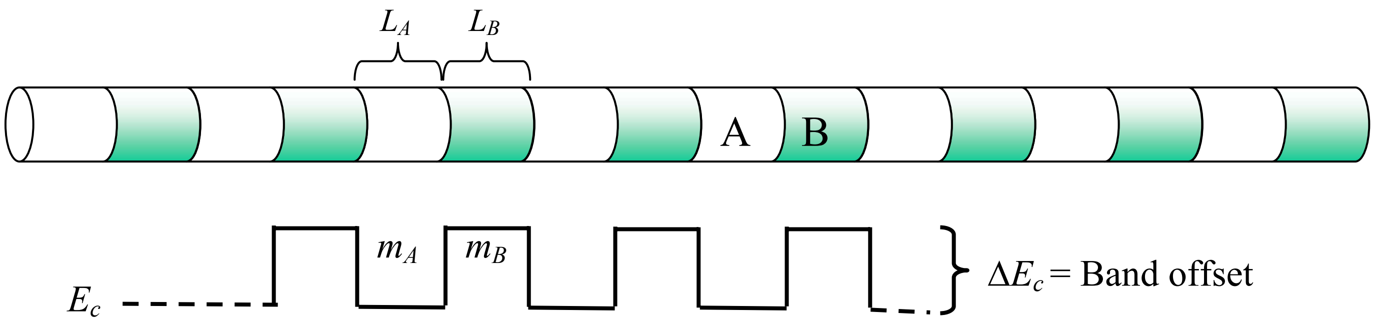
In the following figures, three superlattice nanowires are presented.

Photo removed for copyright reasons. See Figure 3 in Piraux et al. "Giant magnetoresistance in magnetic multilayered nanowires." *Appl. Phys. Lett.* 65, no. 2484 (1994).

Photo removed for copyright reasons. See Fig. 2b in Wu, Fan, and Yang. "Block-by-block growth of single-crystalline Si/SiGe superlattice nanowires." *Nano Lett.*, 2 (2002): 83.

Photo removed for copyright reasons. See Figure 1d in Bjork, M.T., et al. "One-dimensional Steeplechase for Electrons Realized." *Nano Lett. 2*: 2 (2002): 87-89.

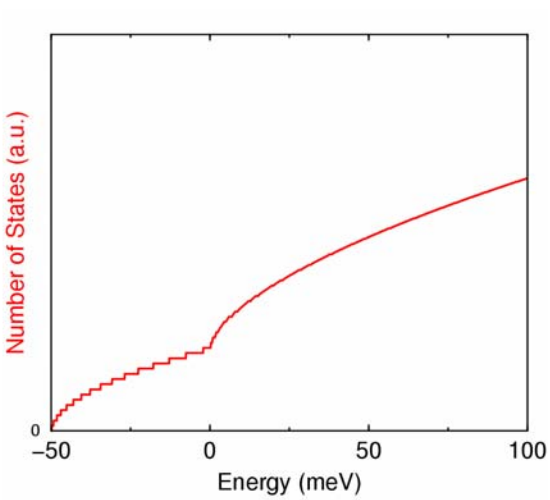
The theoretical modeling of this structure includes the following key parameters
–Wire diameter: d_W
–Segment lengths: L_A and L_B (assumed to be equal)
–Subband potential barrier: ΔEc
–Effective masses: m_A and m_B
–Phonon mean free path: L



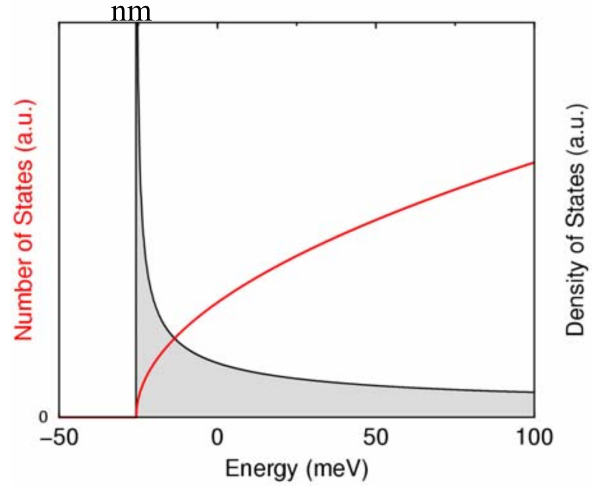
Y-M. Lin and M.S. Dresselhaus., Phys. Rev. B **68**, 0753045 (2003)

The utilized approaches are
–Determination of the (sub)band structure
–Derivation of the dispersion relation E(k) along the wire axis
–Calculation of thermoelectric properties based on Boltzmann transport equations

$L_A = L_B = 60$ nm

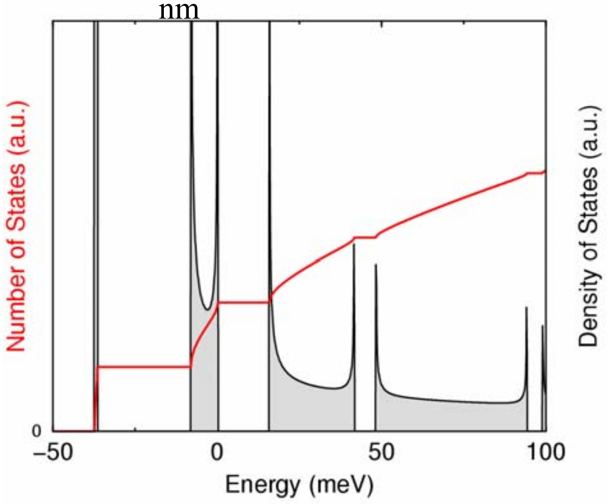


$L_A = L_B = 1$ nm

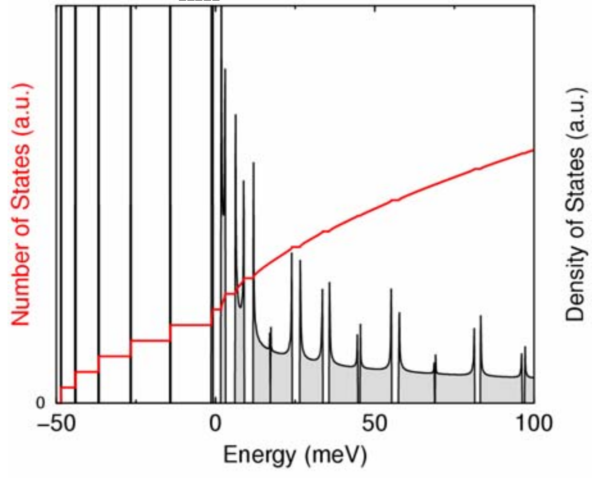


In the above figures, the DOS for classical limit and alloy limit are shown. In real applications, we want more sharp pulses (~10) but not too many. In the following figures, the left one is suitable, while the right one already shows the trend to be a 3D structure.

$L_A = L_B = 5$ nm

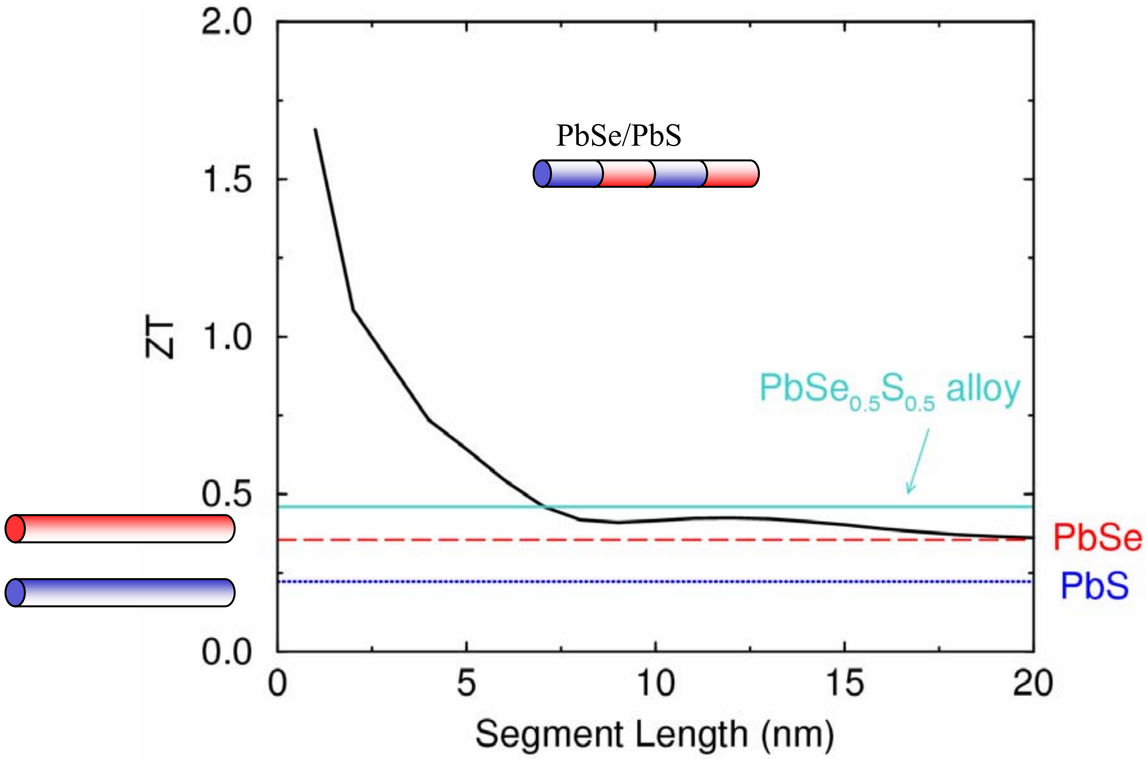


$L_A = L_B = 20$ nm



The following presents ZT for [001] n-type PbSe/PbS SL nanowires as a function of segment length at 77 K. Greater enhancement is predicted for SL nanowires with diameters of 5nm.

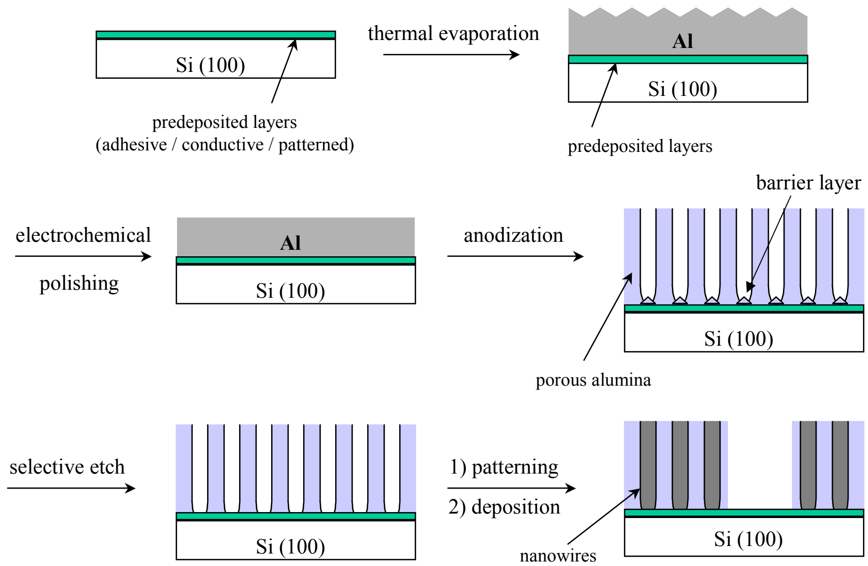
Wire diameter: 10 nm



8. Newly emerging research directions

1) New methods for synthesis and assembly of nanowires

The following figure demonstrate the idea of making standing nanowires.

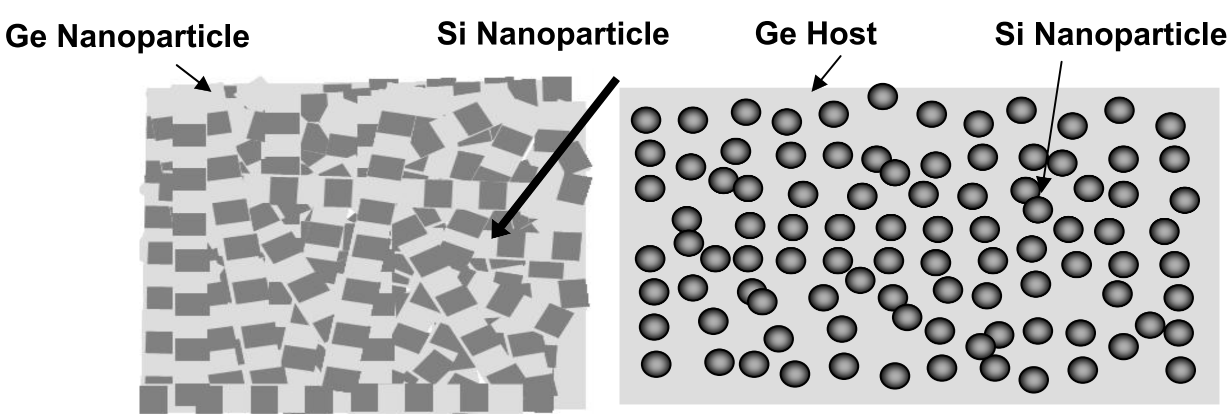


Two pictures of nanowires are shown below.

Photo removed for copyright reasons.

Rabin *et al*., Adv. Funct. Mater. (2003)

2) Nanoparticle Composite Synthesis



Gang Chen, MIT

In the above figures, the idea of using nanoparticle composites is demonstrated. Expectations include:
-Reduced thermal conductivity.
-Electrical conductivity comparable to or better than bulk.
-Increased thermoelectric figure of merit.
-Cheap, self-assembly method

3) New Nanoscale Tools for Thermoelectric Measurements
Scanning thermoelectric microscopy (SThEM) allows measurements of the spatial profiles of the thermoelectric voltage, carrier concentration and electron energy band of a p-n junction to 2 nm resolution. The following work has general implications on electronics and opto-electronics of nano-systems.

Diagram and graphs removed for copyright reasons.

SThEM measurement set-up

Thermoelectric voltage profile across p-n junction with 2nm resolution

Carrier profiles and electronic band energies across p-n junction

H.-K. Lyeo et al. , Science **303***, 816 (2004)*

9. Conclusions
1) Model systems show that:
ZT for 0D nanowire superlattice
> ZT for 1D quantum wires
> ZT for 2D quantum wells
> ZT for bulk for same material
2) New research directions now being pursued:
-Self assembled bulk composites of nanostructures
-New 3D crystalline materials with quantum dots
-New thermoelectric tools at the nanoscale
3) Objective
–To have compact technology for cooling, especially for electronics and opto-electronics
–To have efficient method for converting thermal to electrical energy, including waste heat recovery