



**Rohsenow Symposium on  
Future Trends of Heat Transfer  
May 16, 2003**

# **Nanostructures and Energy Conversion**

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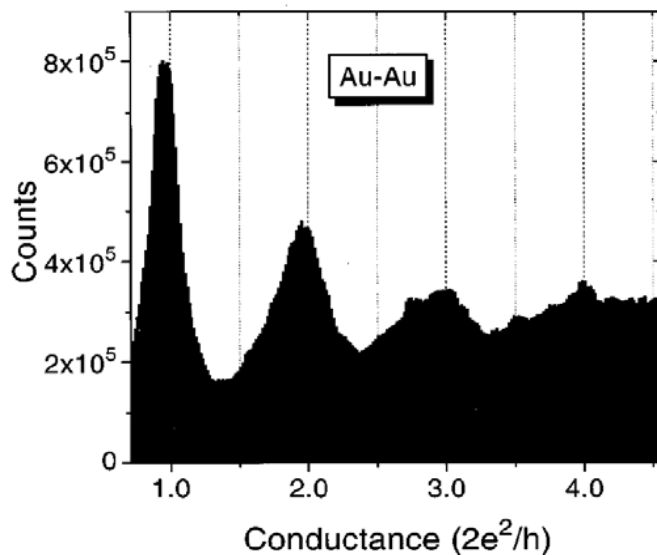
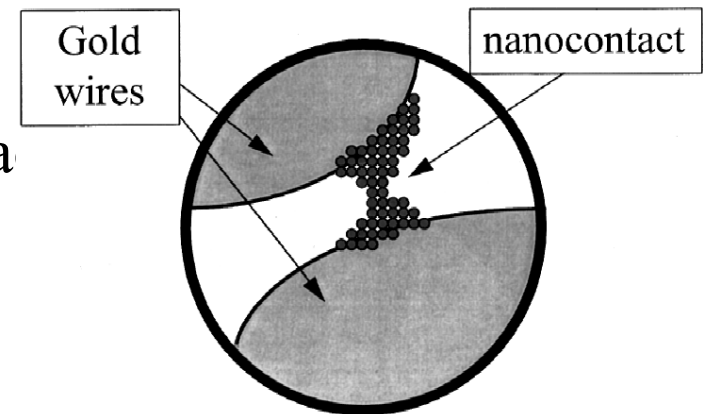
# Nanostructures will influence future trends in heat transfer because:

- Fundamental new laws of nature can be explored widening our understanding of important physical phenomena and opening up new research directions.
- New physical phenomena are introduced that can be exploited for practical applications.
- Interfaces play a more important role in nanostructures. Many more types of interesting interfaces are possible.
- Parameters that cannot be controlled independently in bulk systems, can however be controlled at the nanoscale.

# Fundamental New Laws

## Electrical Conductance Quantization in 1D

- Conductance  $G = I/V$
- Conductance quantization  $G = n \frac{2e^2}{h}$
- Ballistic transport in 1D systems
- Usually observed in very short contacts
- Pure quantum effect



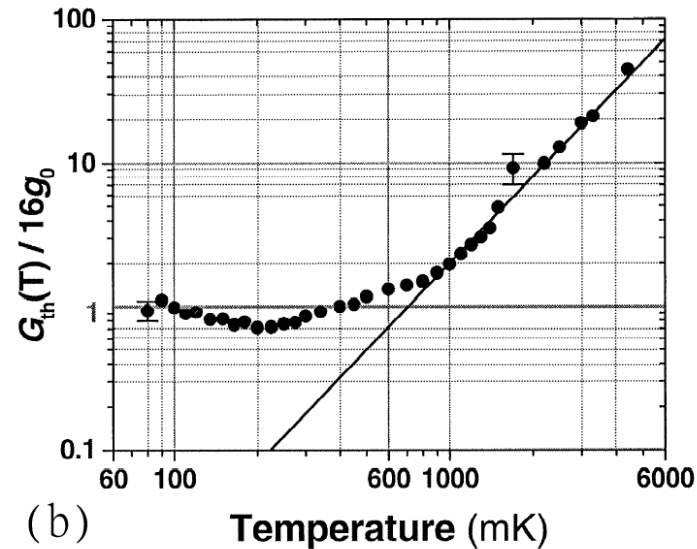
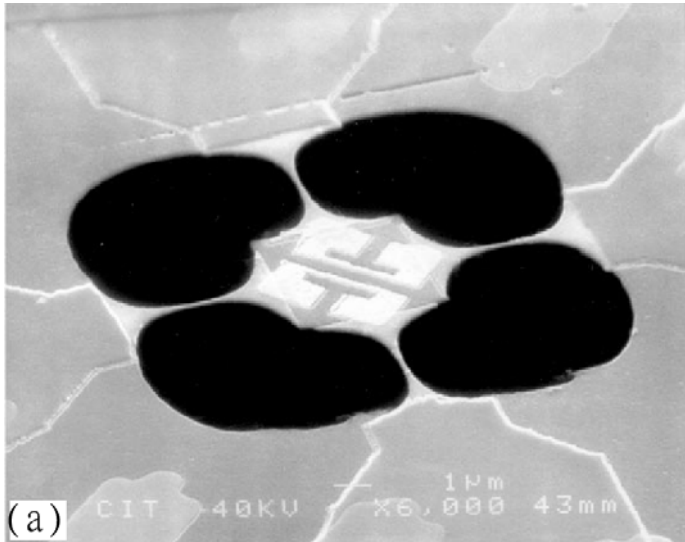
Last stages of the contact breakage process

Histogram of conductance values built with 18,000 gold contact breakage experiments in air at room temperature, showing conductance peaks at integral values of  $G_0$ .

S. Datta, "Electronic Transport in Mesoscopic Systems"

# Fundamental New Laws

## Quantized Phonon Transport in 1D



(a) Suspended mesoscopic phonon device used to measure ballistic phonon transport. The device consists of an 4x4micron “phonon cavity” (center) connected to four  $\text{Si}_3\text{N}_4$  membranes, 60nm thick and less than 200nm wide. The two bright “C” shaped objects on the phonon cavity are thin film heating and sensing Cr/Au resistors, whereas the dark regions are empty space. (b) Log-log plot of the temperature dependence of the thermal conductance of the structure in (a) (Schwab et al., 2001).

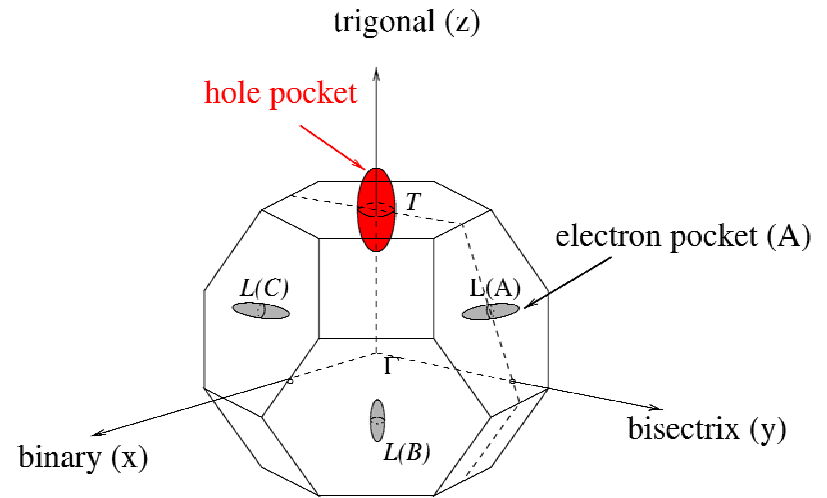
Universal quantum  
of thermal conductance

$$g_0 = \pi^2 k_B^2 T/3h$$

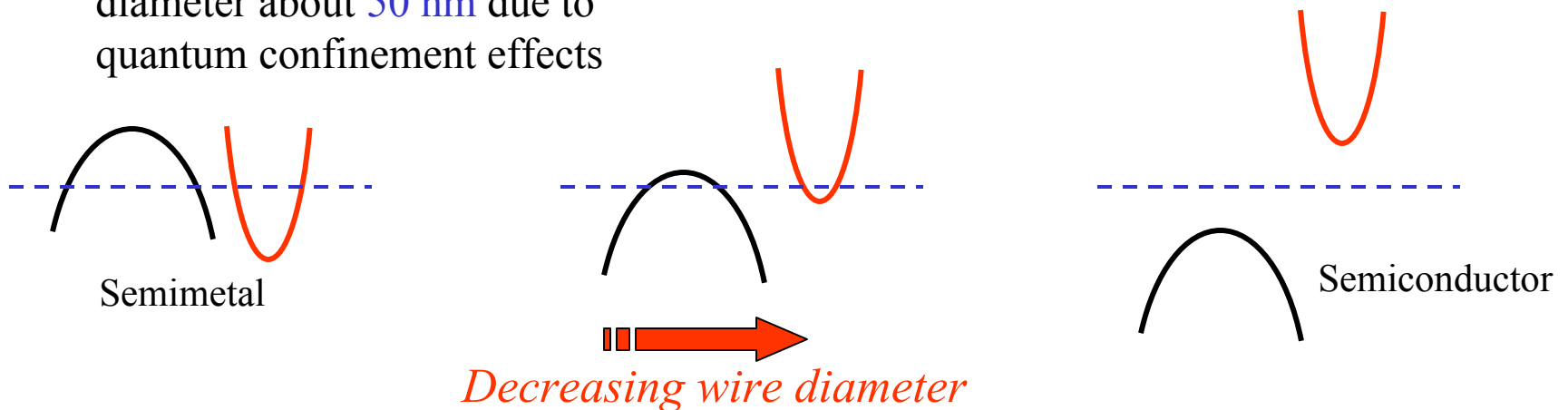
Ballistic phonon transport

# New Physical Phenomena in Nanostructures: Semimetal-Semiconductor Transition in Bi

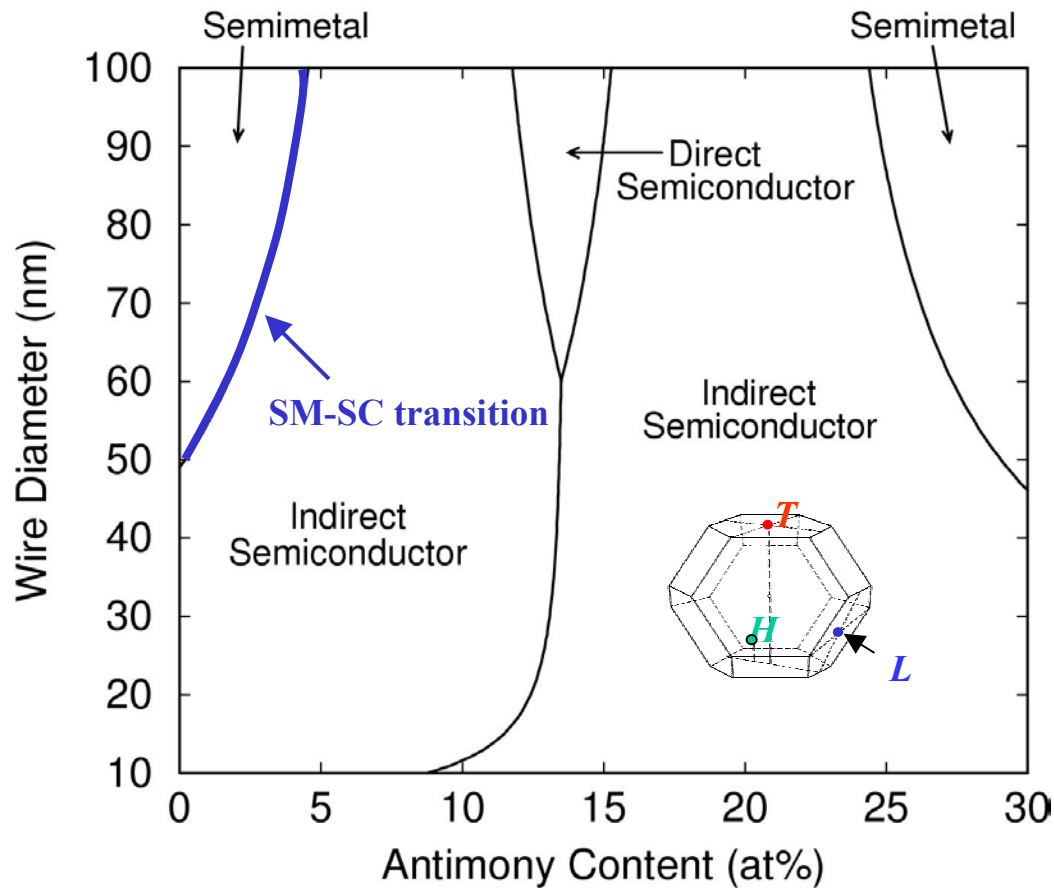
- Bi
  - Group V element
  - Semimetal in bulk form
  - The conduction band ( $L$ -electron) overlaps with the valence band ( $T$ -hole) by 38 meV
- Bi nanowire
  - **Semimetal-semiconductor** transition occurs at a wire diameter about 50 nm due to quantum confinement effects



Brillouin zone of Bi



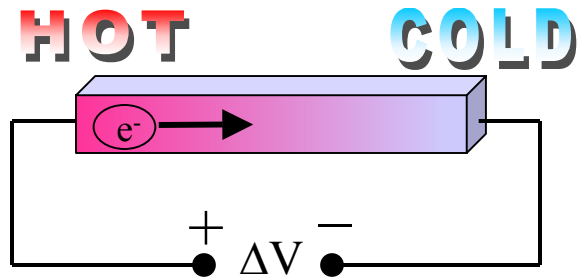
# New Electronic Phases not Present in Bulk: Predicted Phases of $\text{Bi}_{1-x}\text{Sb}_x$ Nanowires



- New phase is at largest wire diameter to have direct gap semiconductor when 10 carrier pockets are degenerate in energy

# Thermoelectric Effect and Applications

- **Seebeck effect**



$$S = -\frac{\Delta V}{\Delta T}$$

$S > 0$  for p-type

$S < 0$  for n-type

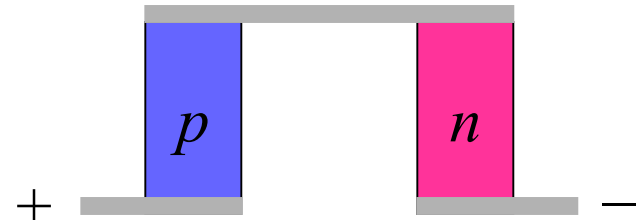
- **Thermoelectric cooling**

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

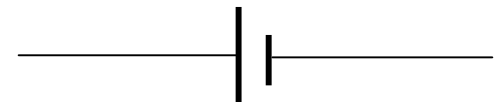
- **Power Generation**

- Use waste heat to generate electricity

Heat Source



*Thermoelectric Generator*



# Application of Low Dimensionality for enhancing thermoelectric Performance

Seebeck Coefficient      Conductivity      Temperature

$$ZT = \frac{S^2 \sigma T}{\kappa}$$

Thermal Conductivity

$ZT \sim 3$  for desired goal

Difficulties in increasing  $ZT$  in bulk materials:

$$S \uparrow \iff \sigma \downarrow$$

$$\sigma \uparrow \iff S \downarrow \text{ and } \kappa \uparrow$$

$\Rightarrow$  A limit to  $Z$  is rapidly obtained in conventional materials

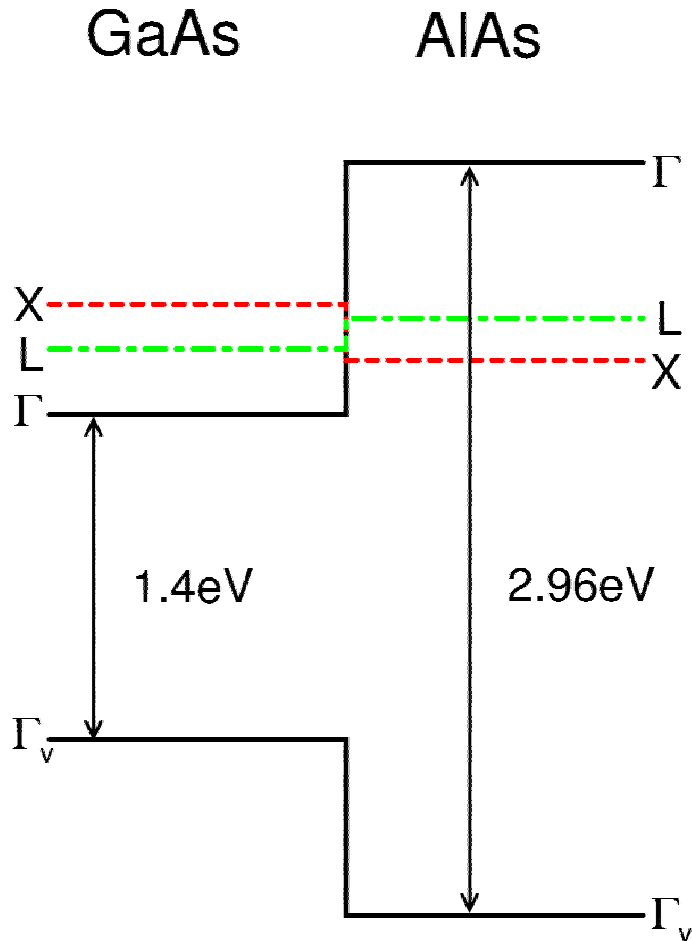
$\Rightarrow$  So far, best bulk material ( $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ ) has  $ZT \sim 1$  at 300 K

## *Low dimensions give additional control:*

- Enhanced density of states due to quantum confinement effects  
 $\Rightarrow$  Increase  $S$  without reducing  $\sigma$
- Boundary scattering at interfaces reduces  $\kappa$  more than  $\sigma$
- Possibility of carrier pocket engineering to get thermoelectric contribution in both quantum well and barrier regions

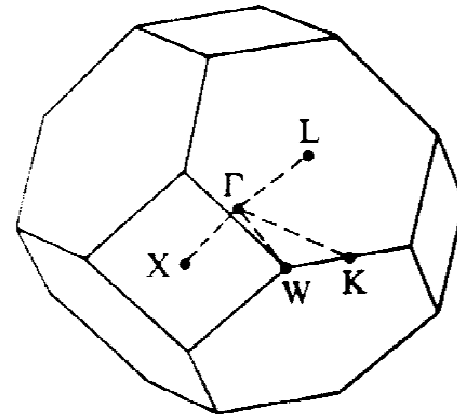


# Carrier Pocket Engineering Approach to Enhance $Z_{3D}T$



Application of Carrier Pocket Engineering Concept in GaAs/AlAs quantum well superlattice systems

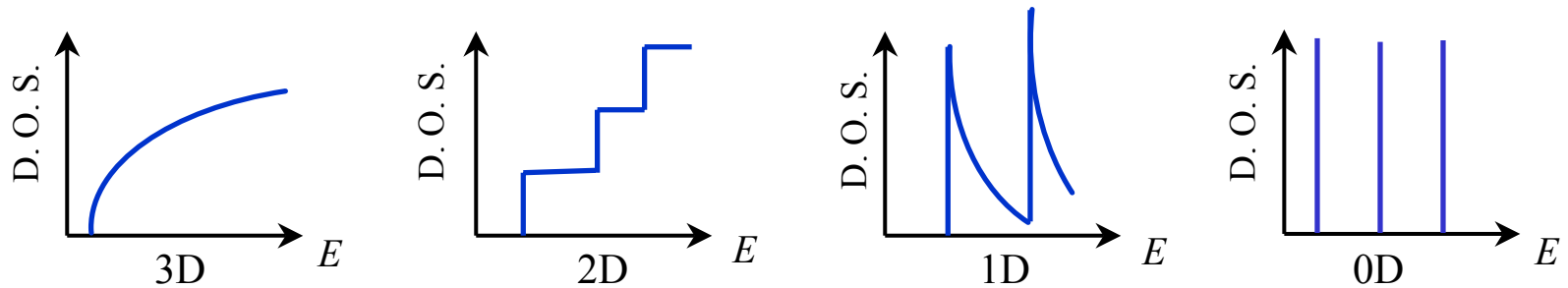
- Optimization of well and barrier widths
- Determination of lattice growth orientation
- Enhancement in  $ZT$  from various carrier pockets other than  $\Gamma$  point pockets



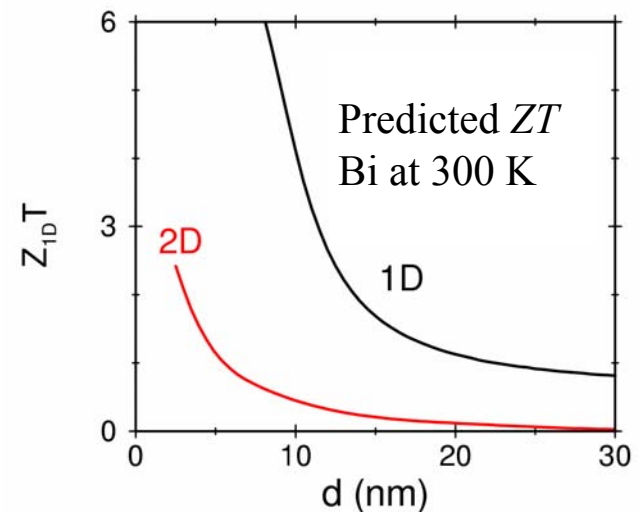
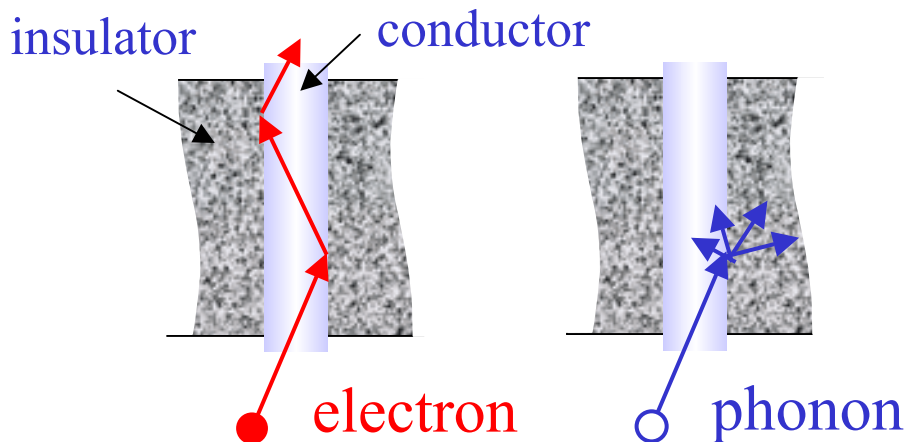
- Concept successfully applied to GaAs/AlAs and Si/Si<sub>1-x</sub>Ge<sub>x</sub> superlattices.

# 1D Nanostructures and Thermoelectricity

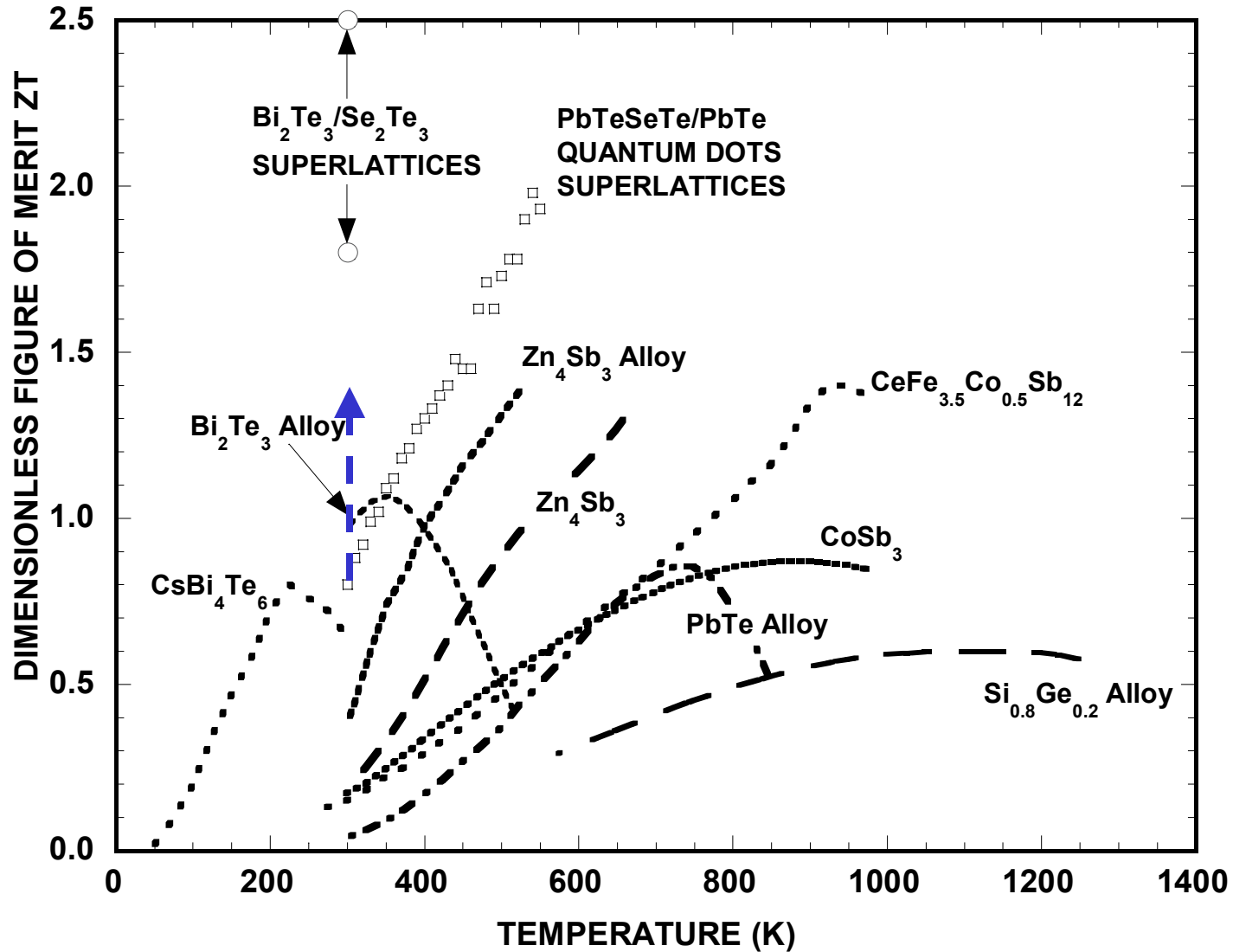
- Electronic properties may be dramatically modified due to the **electron confinement in nanostructures** which exhibit low-dimensional behaviors



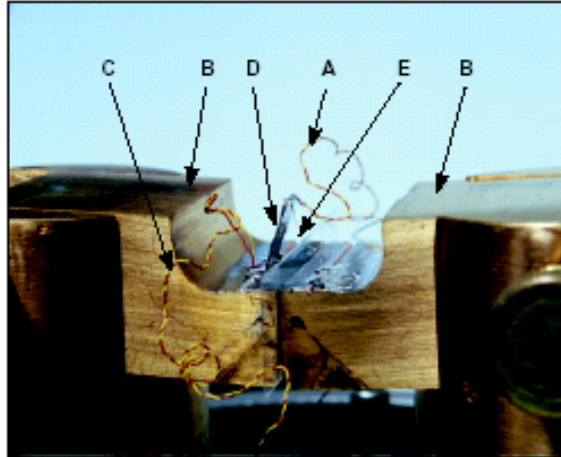
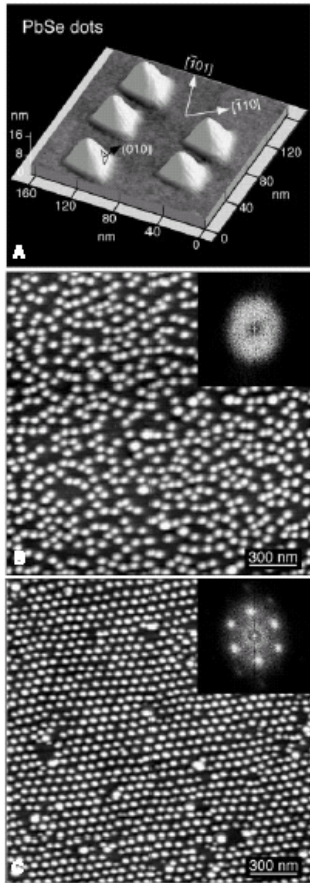
- Thermal conductivity can be significantly reduced by the **scattering of unwanted heat flow** at the interfaces



# STATE-OF-THE-ART

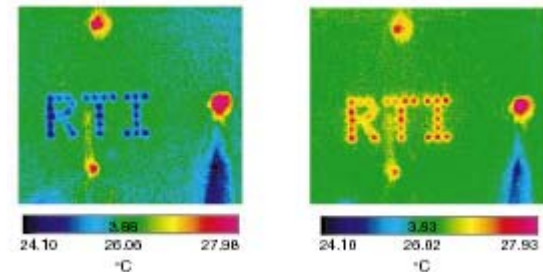
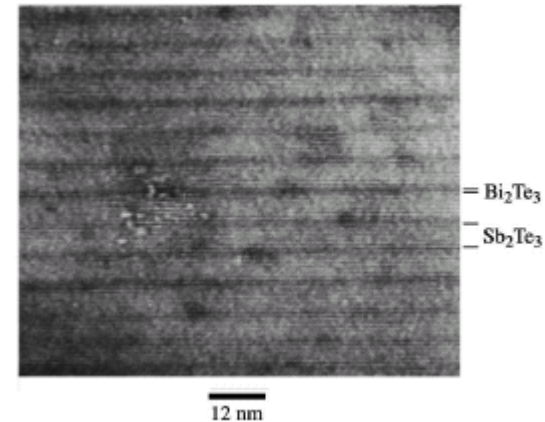


# WINNING STRUCTURES



**PbTe/PbTeSe Quantum Dot Superlattices**

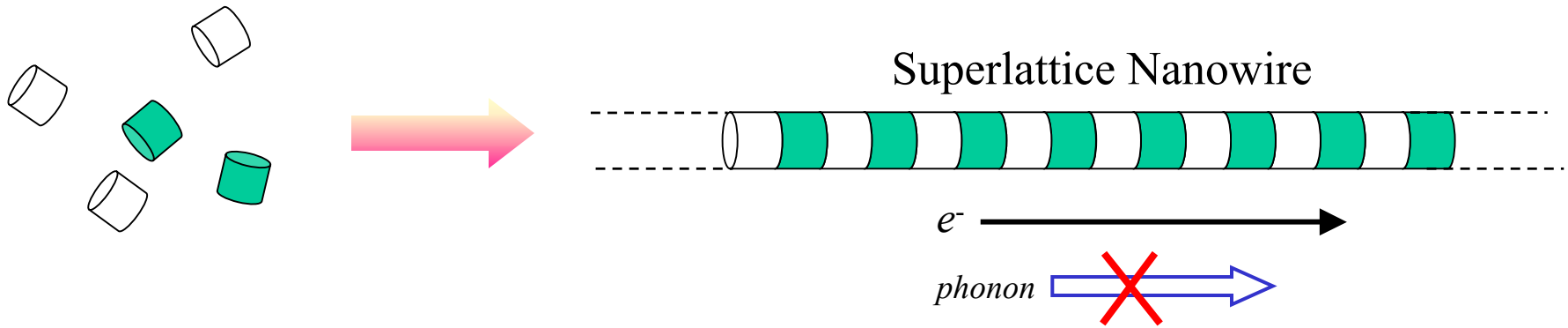
Ternary:  $ZT=1.3-1.6$   
 Quaternary:  $ZT=2$   
 $\Delta T=43.7$  K, Bulk  $\Delta T=30.8$  K  
 T.C. Harman, Science, 2002



$\Delta T=32.2$  K,  $ZT \sim 2-2.4$   
 R. Venkatasubramanian, Nature, 2001

	PbTe/PbSeTe	Nanostructure	Bulk	Bi <sub>2</sub> Te <sub>3</sub> /Sb <sub>2</sub> Te <sub>3</sub>	Superlattice	Bulk
Power Factor ( $\mu\text{W}/\text{cmK}^2$ )		32	28		40	50.9
Conductivity (W/mK)		0.6	2.5		0.5	1.26

# Superlattice Nanowire for Thermoelectrics



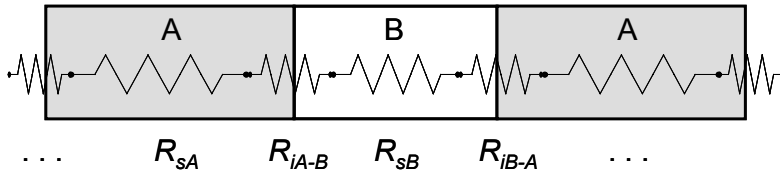
- Advantages
  - Benefit from both the superlattice and the nanowire structures
  - Enhanced thermopower due to **sharper density of states** than ordinary 1D nanowires (**enhance  $S$** )
  - **Reduction of the lattice thermal conductivity** by increasing the phonon scattering at the segment interfaces (**decrease  $\kappa$** )

$$ZT = \frac{S^2 \sigma}{\kappa} T$$

# Size Effect in 1D Thermal Conductivity

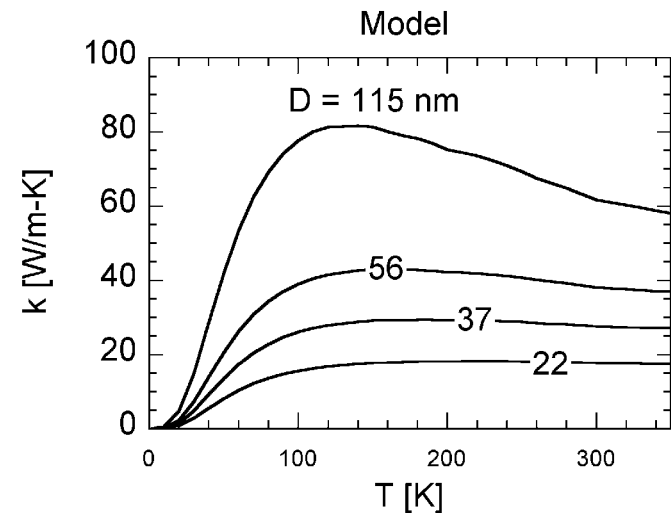
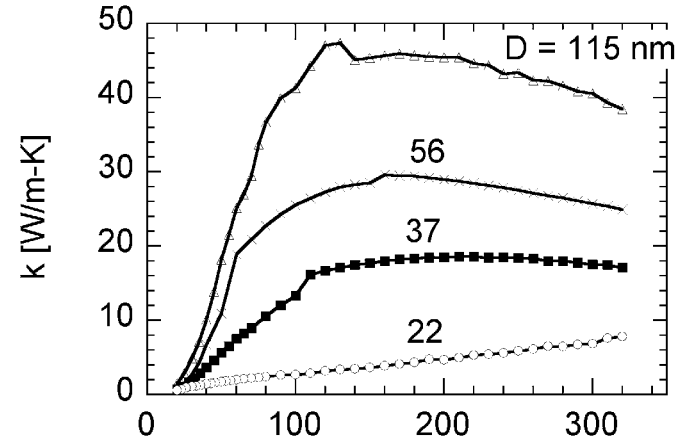
## PHONON RADIATION + DEBYE MODEL

- **Gray Radiation Approximation:** Neglects confinement, tunneling, coherence, spectral nature.
- **Debye:** Retain only acoustic modes. A single group velocity characterizes each material.
- **Bulk Scattering:** Incorporated at end of calculation via Matthiessen's Rule.



- Compare  $k(T)$  with pure Si nanowires [5]
  - No known data for segmented wires
- Qualitative agreement is good for all but smallest wire.
  - Model  $k$  is higher by ~50-150%
- Possible sources of error:
  - Finer grains than bulk - segmented Si?
  - Gray assumption.
  - Choice of  $\omega_D$ :

Experiment, courtesy of D. Li [Huxtable et al 2002]



Dames and Chen (2002)

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