New Directions for Low Dimensional Thermoelectricity

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DOE /EPRI High Efficiency Thermoelectrics Workshop
FEBRUARY 17, 2004

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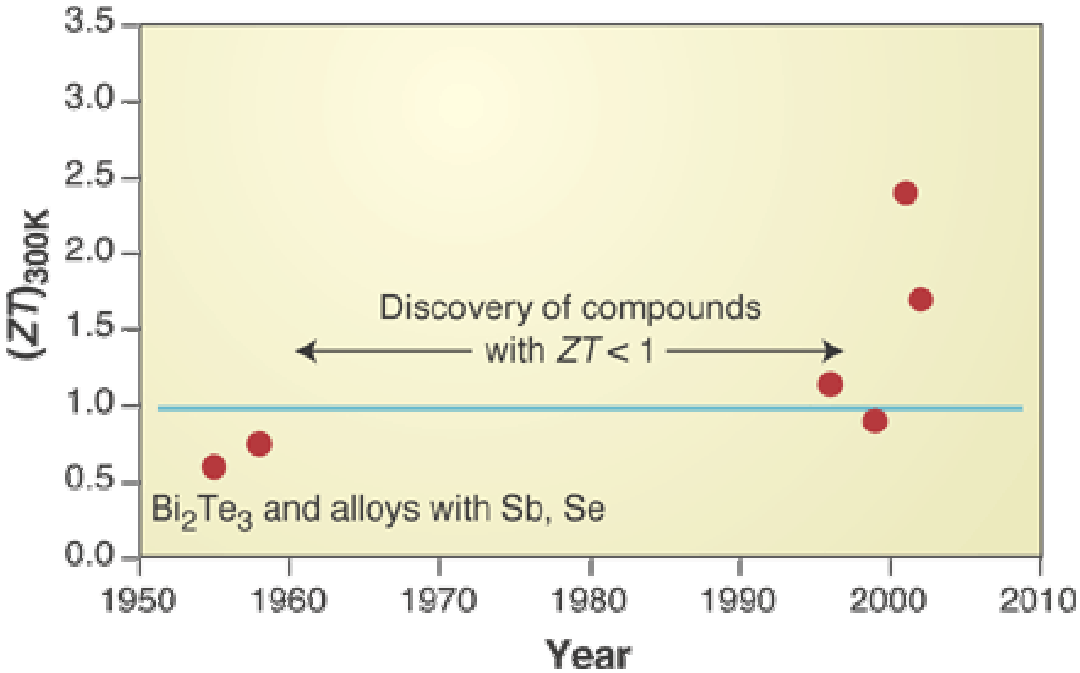
Steve Cronin, Harvard
Z. Ren, Boston College

Outline

- Overview of low dimensional thermoelectricity
- New physics to yield enhanced performance in 1D nanowire systems
- 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

Historical Perspective

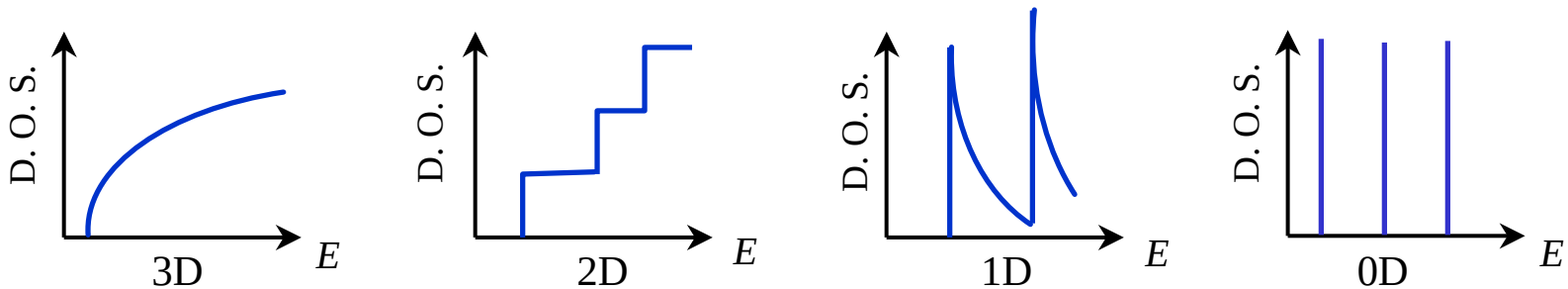


- Recent studies in nanostructured thermoelectric materials led to a sudden increase in $(ZT)_{300} > 1$
- Higher ZT reported experimentally at higher T.

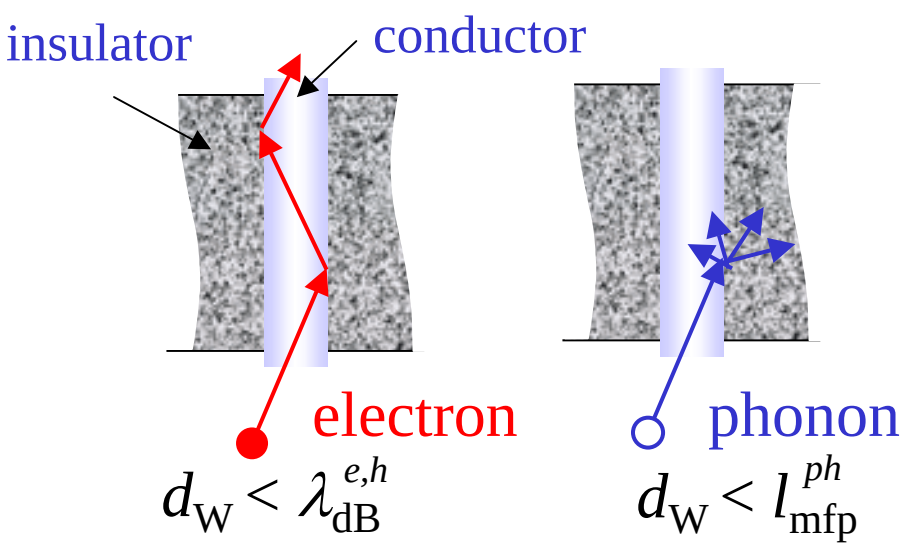
A. Majumdar, *Science* **303**, 777 (2004)

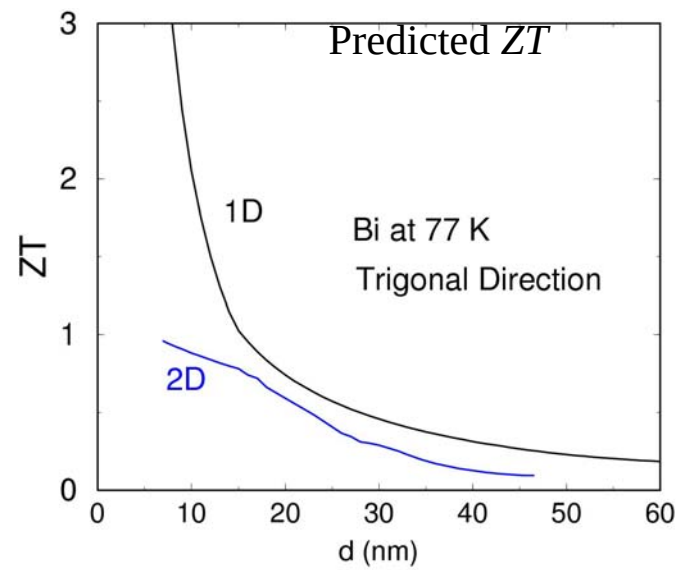
New Directions for Low Dimensional Thermoelectricity

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



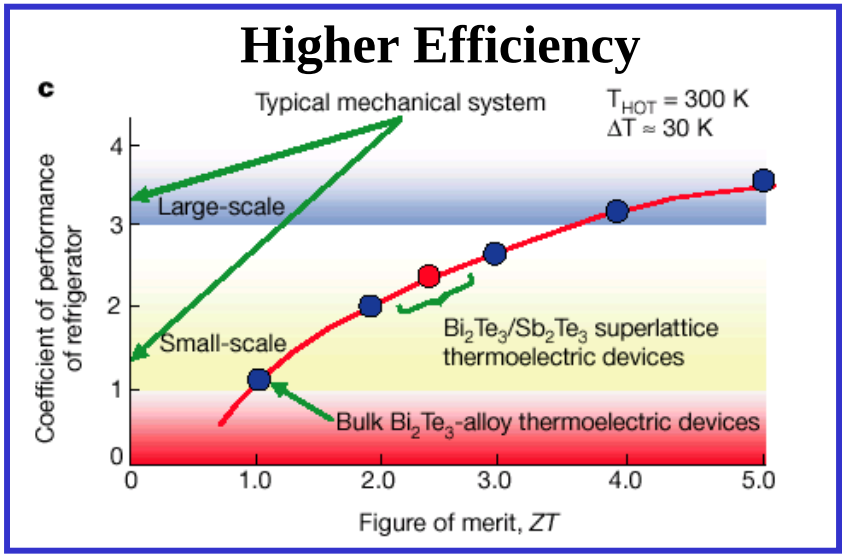
- Thermal conductivity can be significantly reduced by the scattering of unwanted heat flow at the interfaces

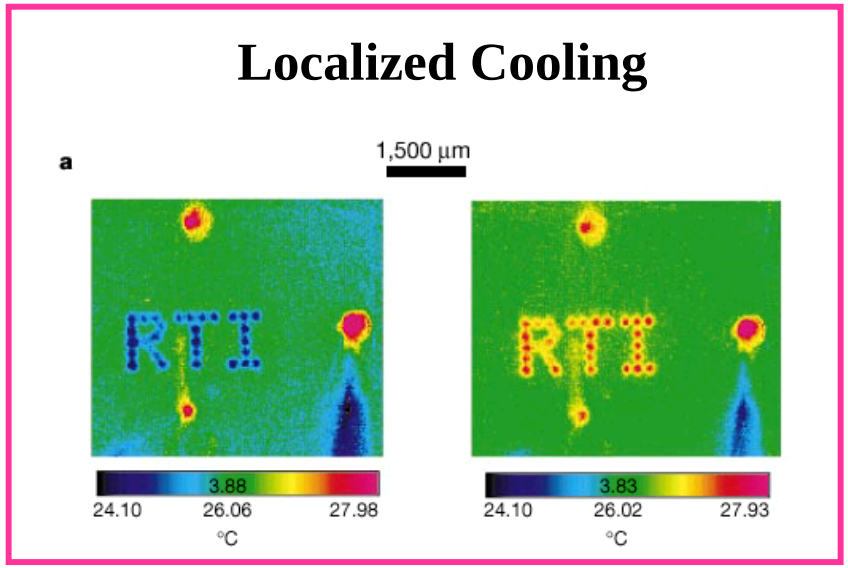




Thermoelectric Cooling Using Bi_2Te_3/Sb_2Te_3 Superlattice Structure

Bi_2Te_3
Sb_2Te_3

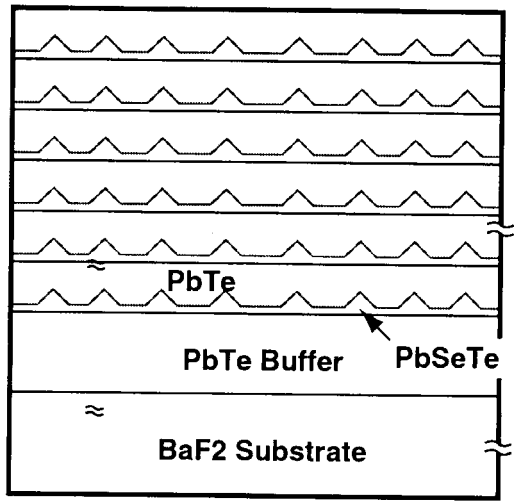




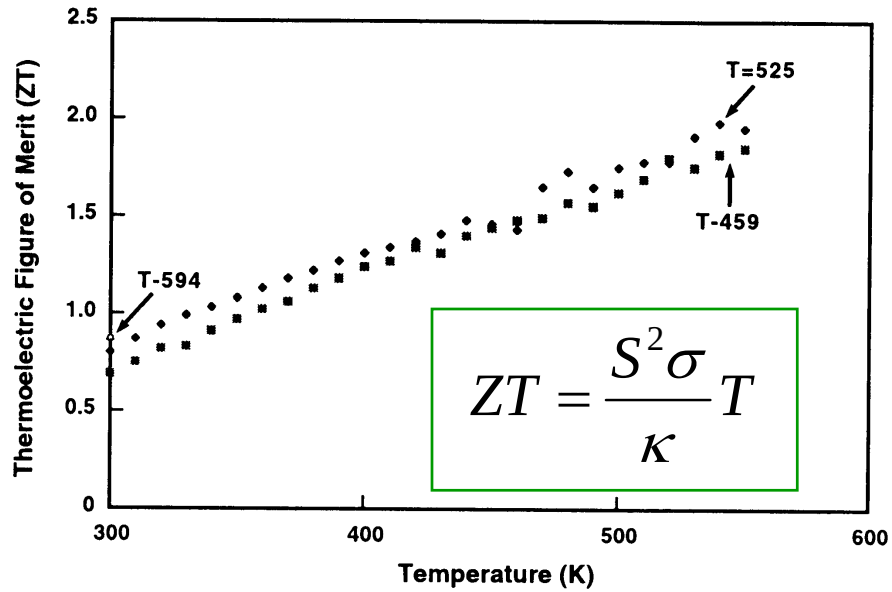
Enhanced cooling is accomplished by increased scattering of phonons at interfaces, thus lowering the lattice thermal conductivity.

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

Enhanced *ZT* in $PbSe_xTe_{1-x}$/PbTe Quantum Dot Superlattices



$PbSe_xTe_{1-x}$ quantum dots in PbTe layers



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

- Enhancement of *ZT* at 300 K in quantum dot superlattice is more than a factor of two relative to best available bulk PbTe
  - More favorable carrier scattering mechanism due to adsorbed or precipitated Te
  - Partial carrier confinement in quantum dots of $PbSe_{0.98}Te_{0.02}$
  - Lower lattice thermal conductivity in alloy
- *ZT* = 2 is obtained in quantum dot superlattice

Harman et al. Science **297***, 2229 (2002)*

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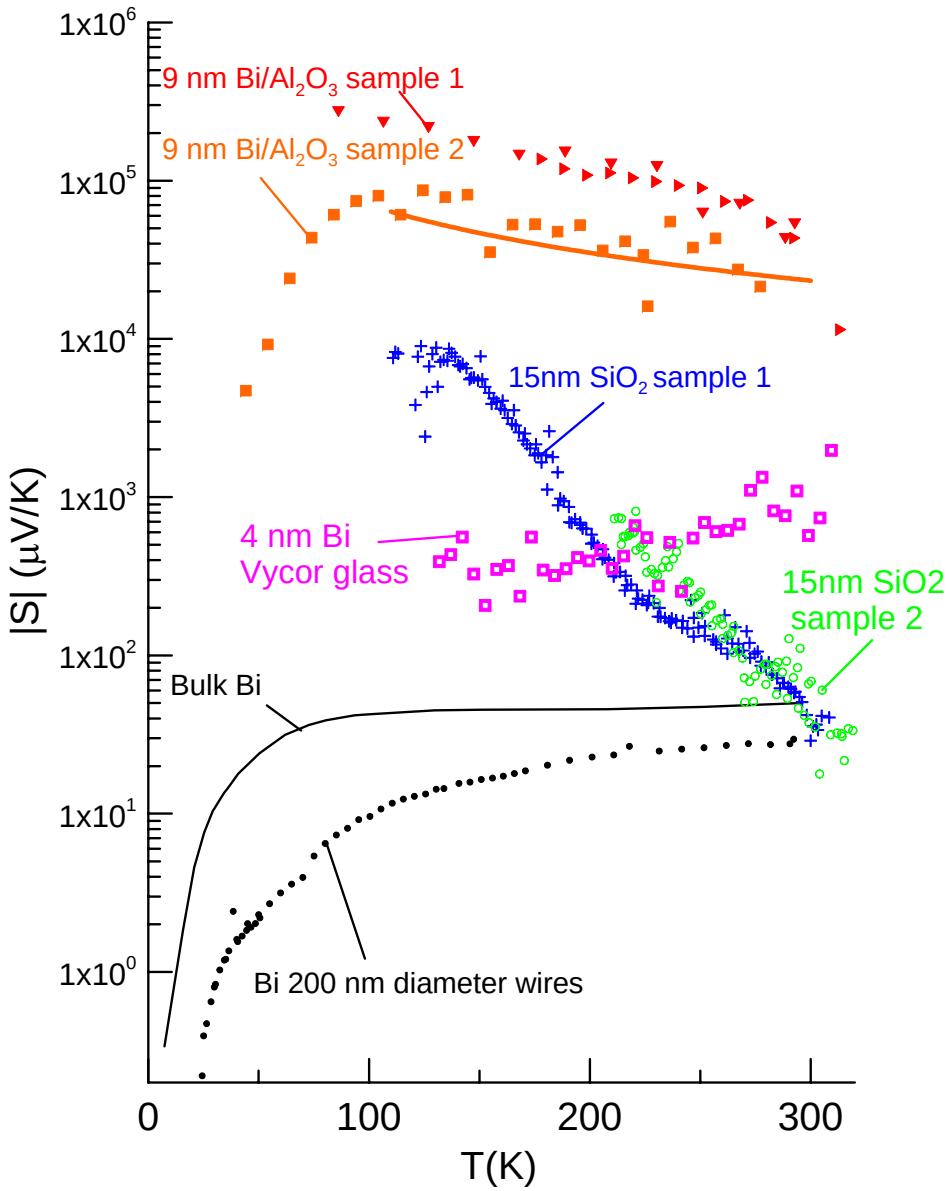
THERMOPOWER 4-15 nm Bi-NANOWIRES



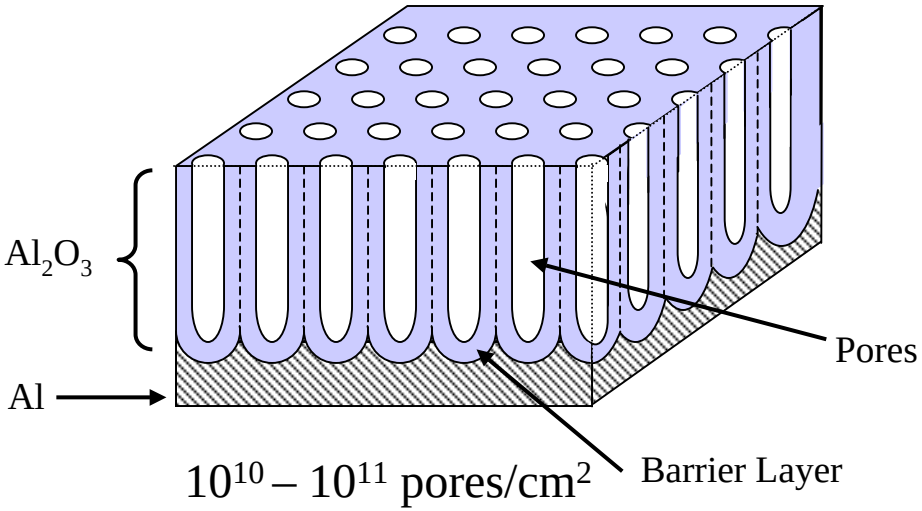
- Data on bulk nanowire composites

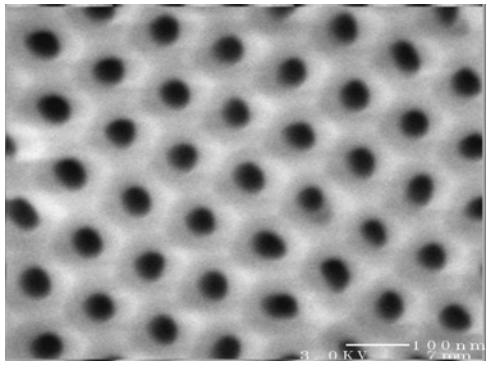
$$\frac{\text{Thermopower 9 nm wires}}{\text{Thermopower bulk Bi}} = 1000$$

- $S(9\ \text{nm}) \propto T^{-1}$ for $T>100$ K
- Localization effects occur below d_w = 4 nm wire diameter
- Model calculations describe S(T) observations well

J. Heremans & al..

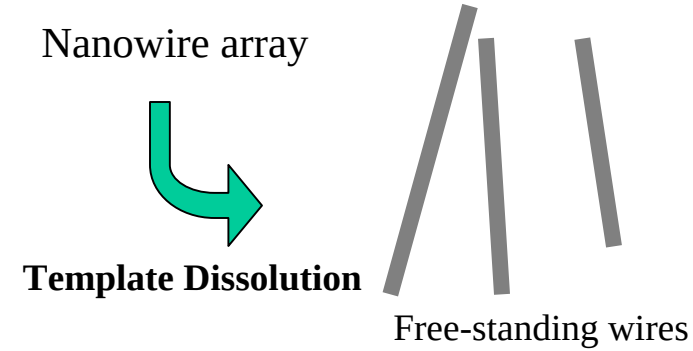
Self-assembled Alumina for growing bismuth nanowires



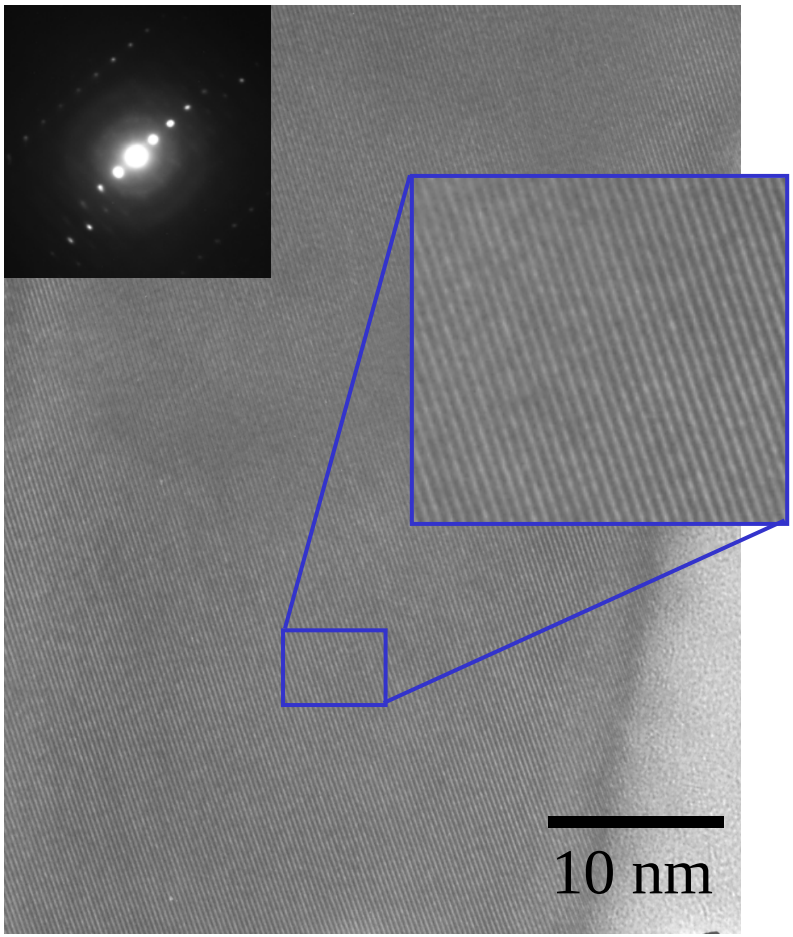


SEM image of the surface of an anodic alumina template with self-assembled nanopore structure

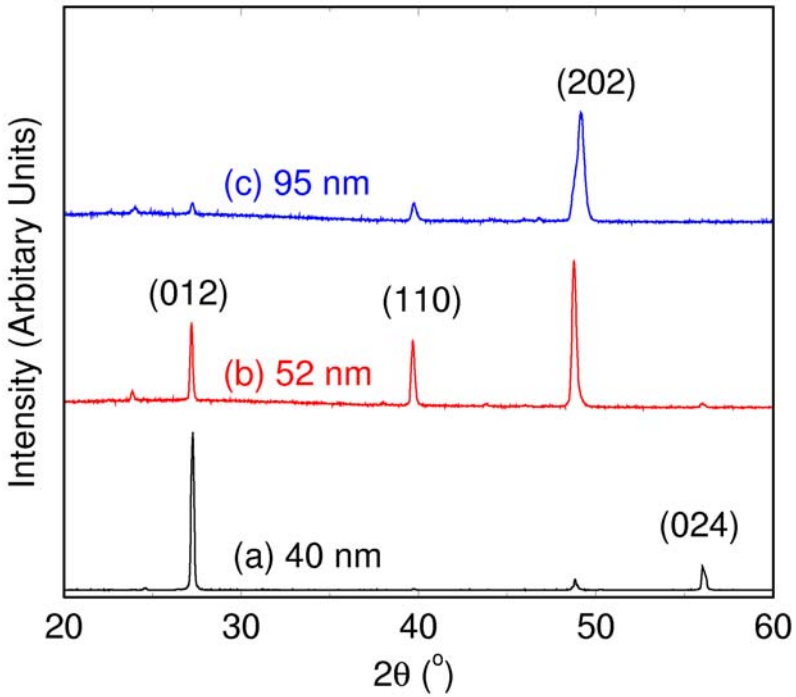
- Applications
  - Templates for growing ordered arrays of bismuth nanowires and nanotubes
  - Bismuth introduced by pressure injection, vapor phase growth or electro-chemically



Single Crystal Nanowires

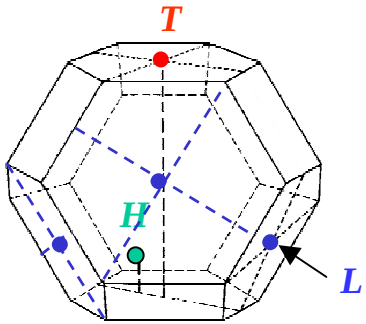


TEM and electron diffraction of a 40-nm nanowire ($Bi_{0.85}Sb_{0.15}$)



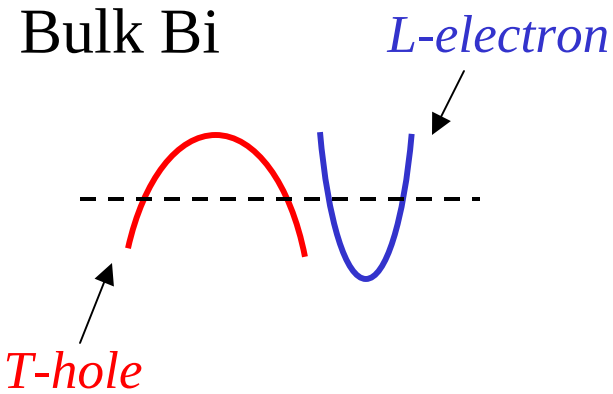
X-ray diffraction of Bi nanowire arrays with different diameters.

Semimetal-Semiconductor Transition in Bi (SM-SC)



- Bi
  - Group V element
  - Semimetal in bulk form
  - The conduction band (*L*-electron) overlaps with the valence band (*T*-hole) by ~ 38 meV (77 K)

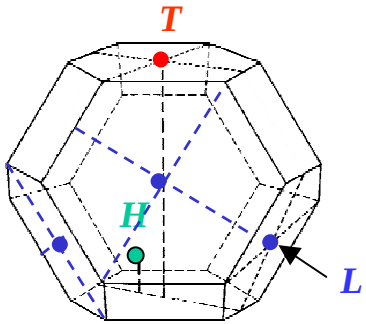
Bulk Bi



Semimetal

New physical phenomenon associated with quantum confinement used to increase *ZT*

Semimetal-Semiconductor Transition in Bi (SM-SC)



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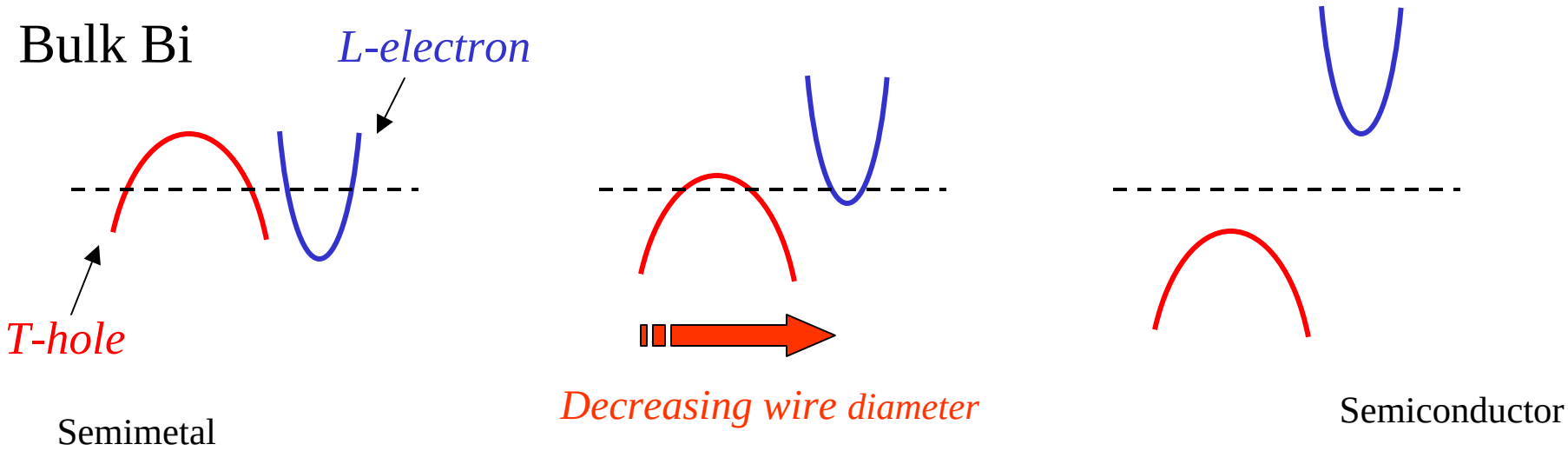
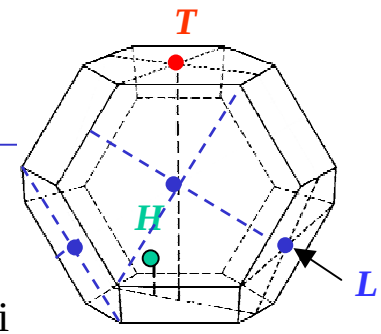


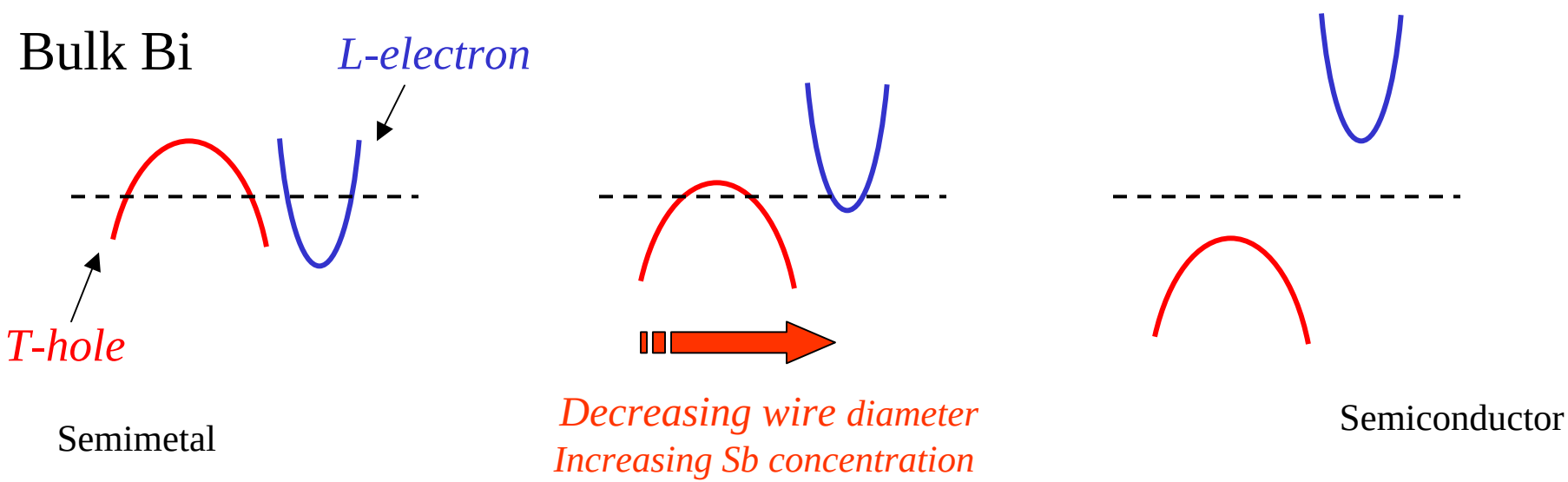
Lin *et al.*, Phys. Rev. B **62**, 4610 (2001)

Semimetal-Semiconductor Transition in Bi (SM-SC)



- Bi
  - Group V element
  - Semimetal in bulk form
  - The conduction band (*L*-electron) overlaps with the valence band (*T*-hole) by ~ 38 meV (77 K)

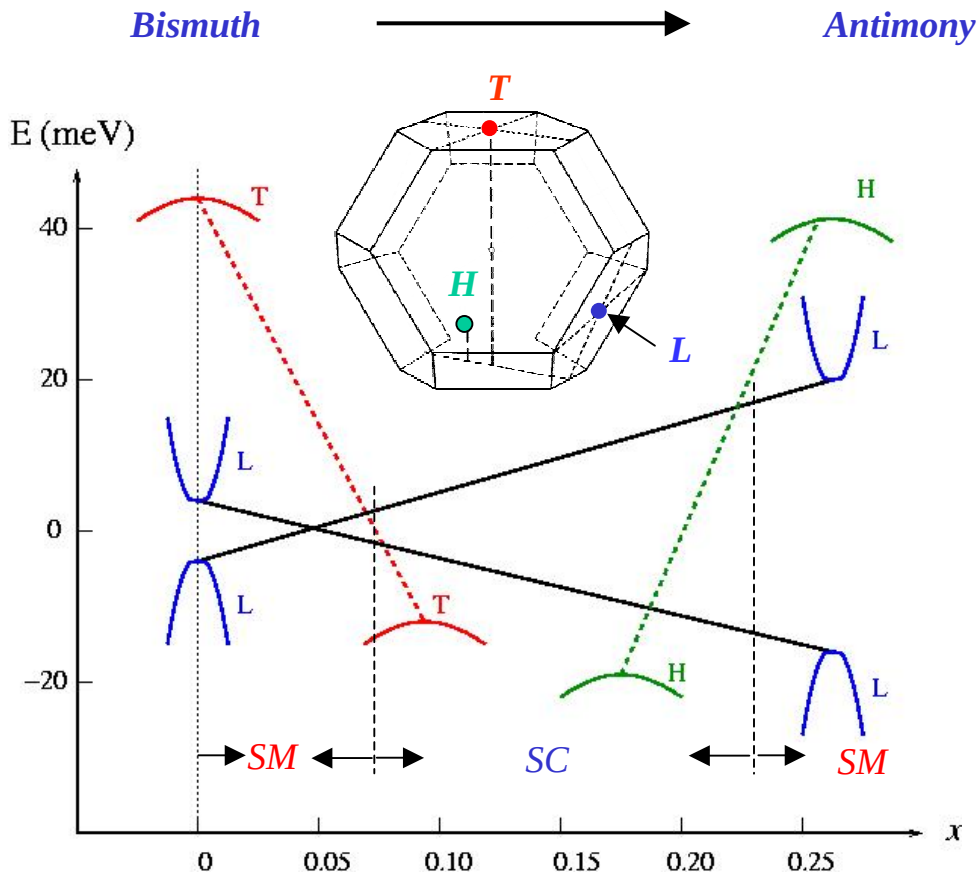
- Sb alloying
  - Group V element
  - Complete solubility with Bi
  - Moves down the *T*-point valence band edge in energy relative to the *L*-point carriers



Lin *et al.*, Phys. Rev. B **62**, 4610 (2001)
Rabin *et al.*, Appl. Phys. Lett. 79, 81 (2001)

Band Structure of $Bi_{1-x}Sb_x$ Alloy

- Alloy system provides additional control on *ZT*
- Bi and Sb
  - Group V elements
  - Semimetals in bulk form
  - Completely miscible with each other
  - Introduction of Sb in Bi moves down the *T*-point valence band edge in energy relative to the *L*-point carriers
  - Provides a promising approach to achieve desirable band structure (i.e., semiconducting) in Bi

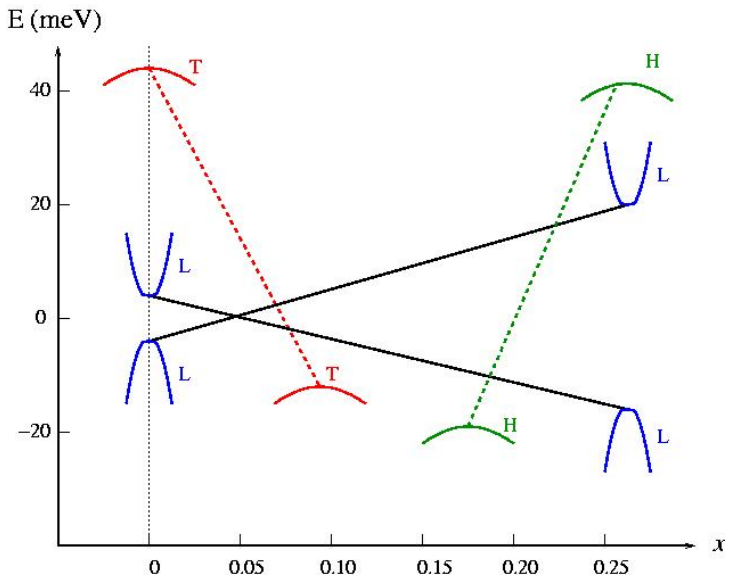


Band structure of $Bi_{1-x}Sb_x$ alloy as a function of Sb concentration *x*.

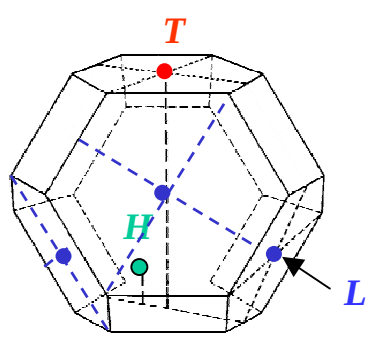
SM: Semimetal
SC: Semiconductor

Predicted Properties of $Bi_{1-x}Sb_x$ Nanowires

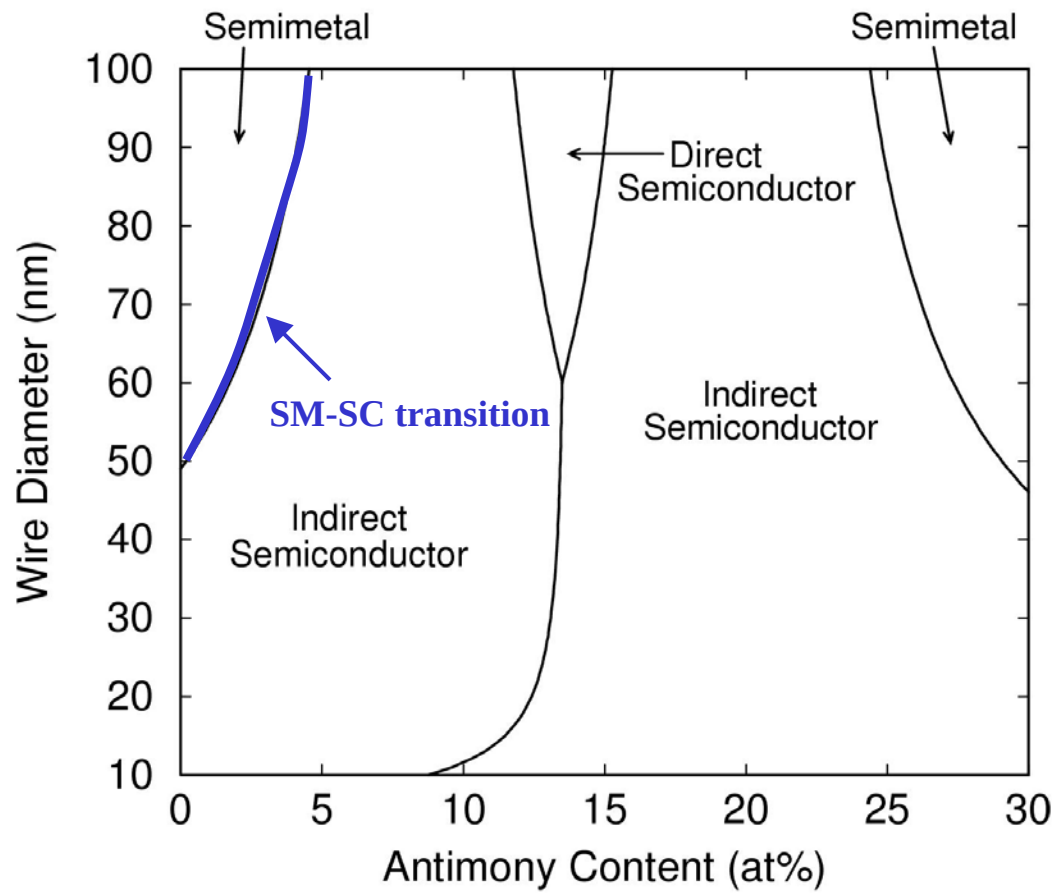
Band structure of bulk $Bi_{1-x}Sb_x$ alloy



Sb Content



Phase diagram of $Bi_{1-x}Sb_x$ nanowires

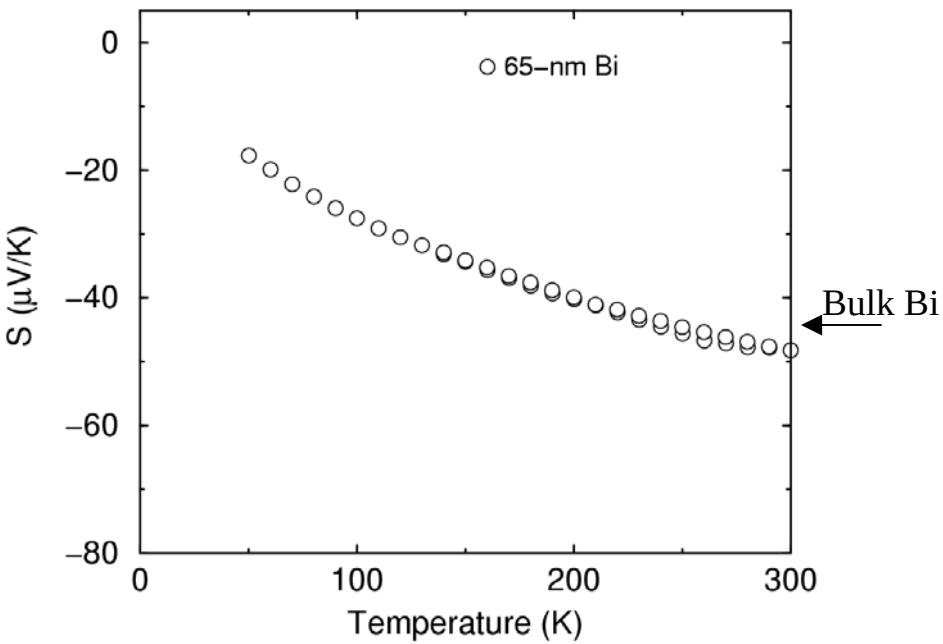


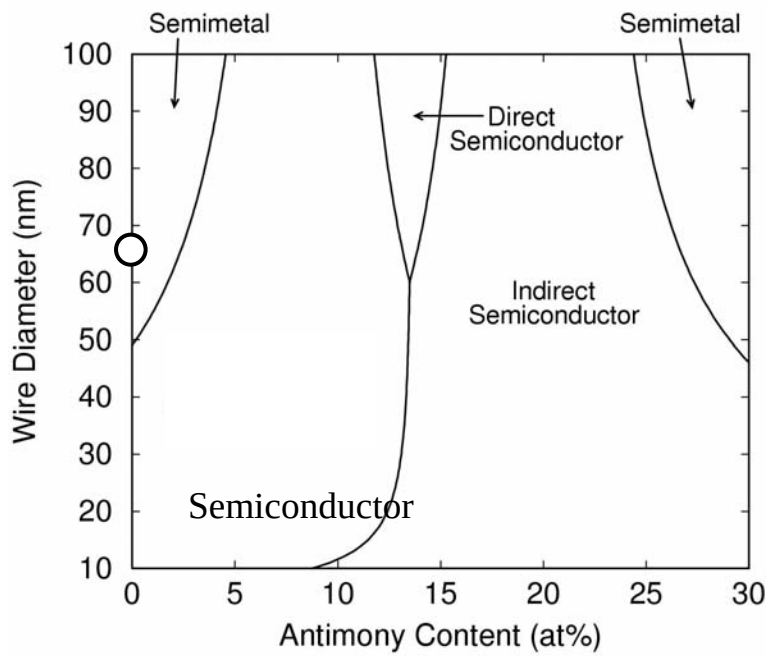
Rabin *et al*., Appl. Phys. Lett. 79, 81 (2001)

Enhanced Thermoelectric Performance

Lin *et al.*, Appl. Phys. Lett. **81**, 2403 (2002)

Measured Seebeck coefficient





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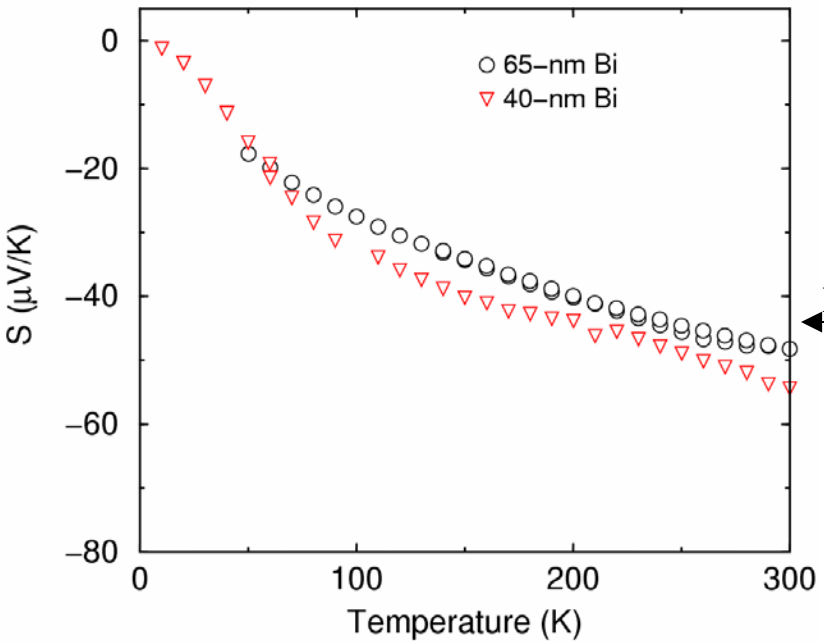
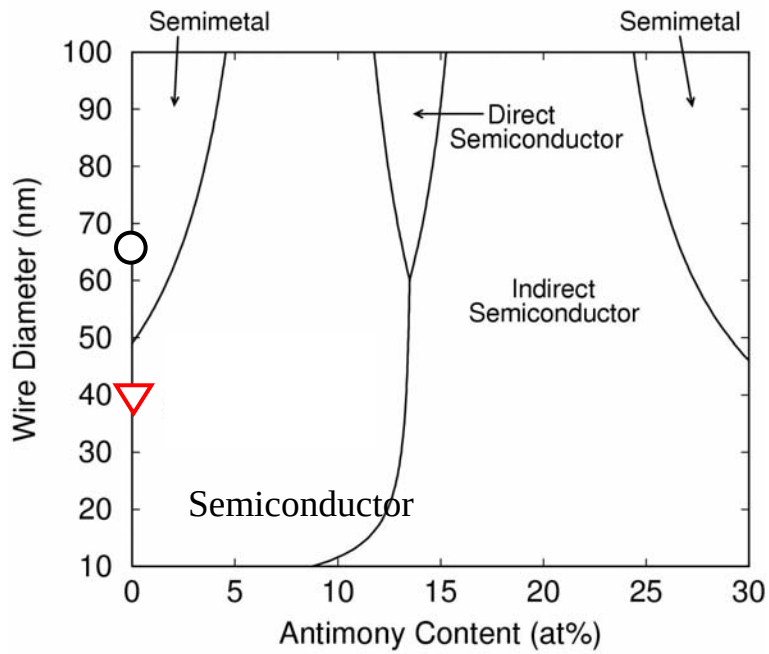


Increasing thermopower

Bulk Bi



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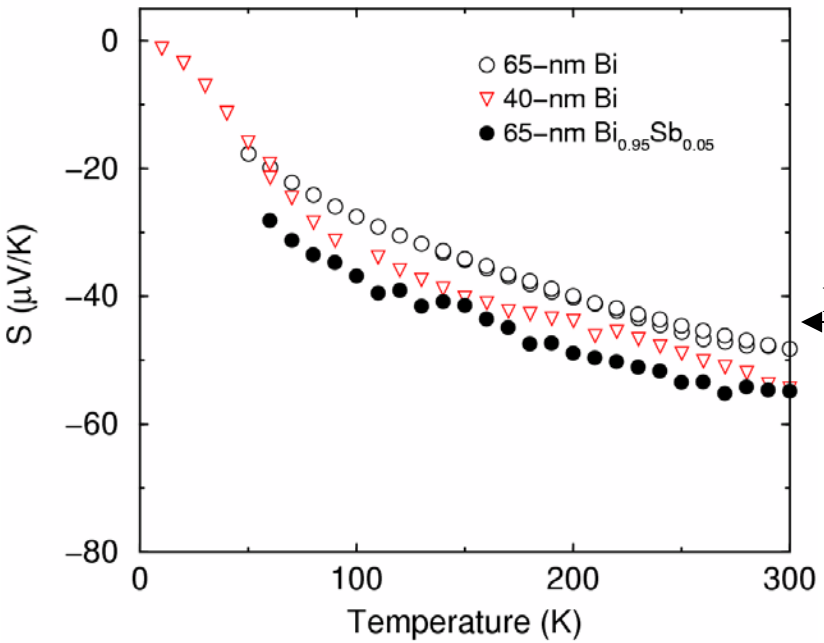

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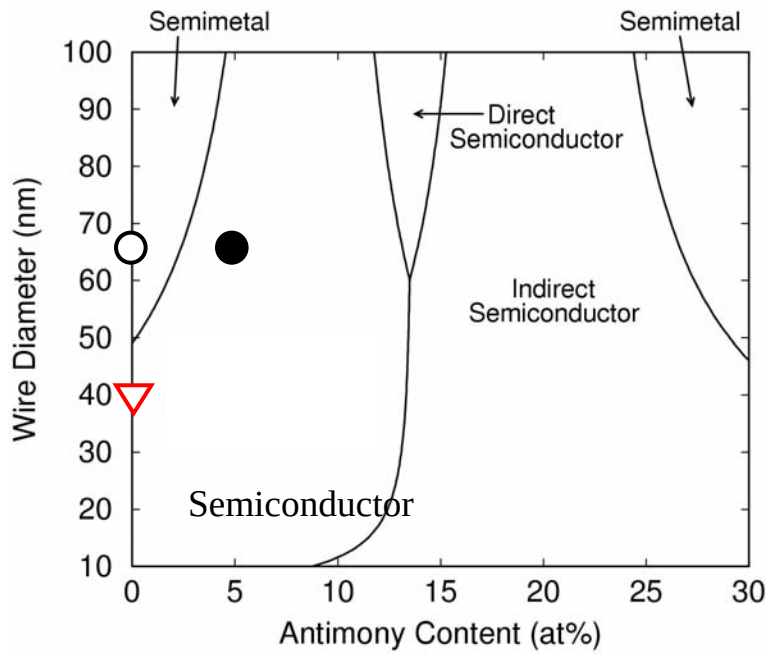

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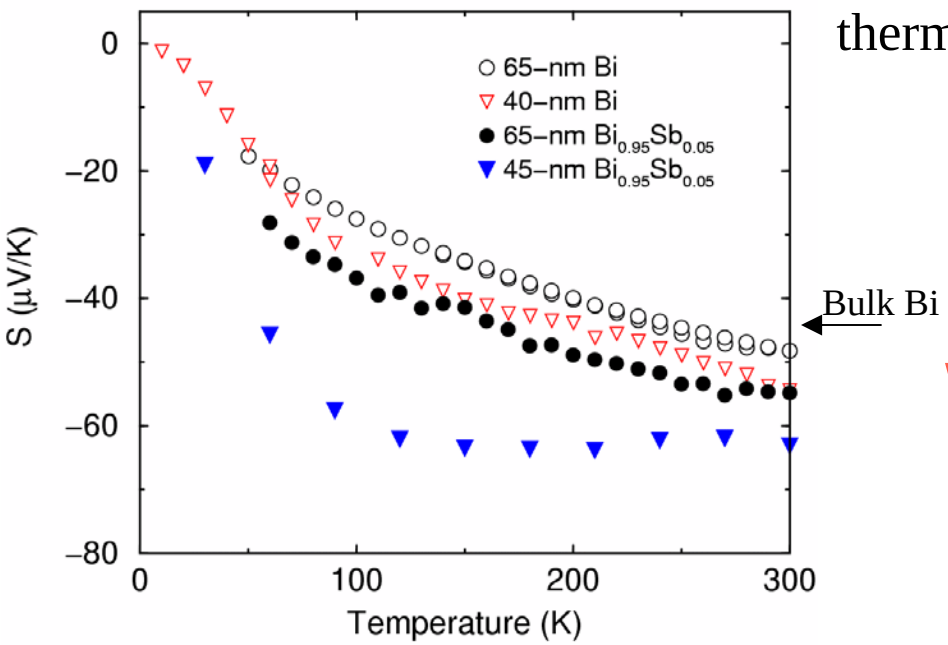

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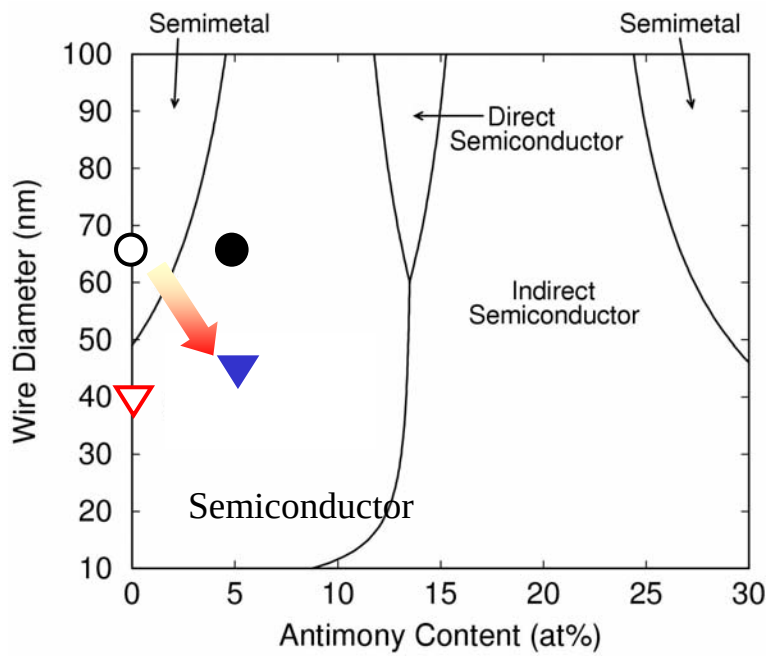
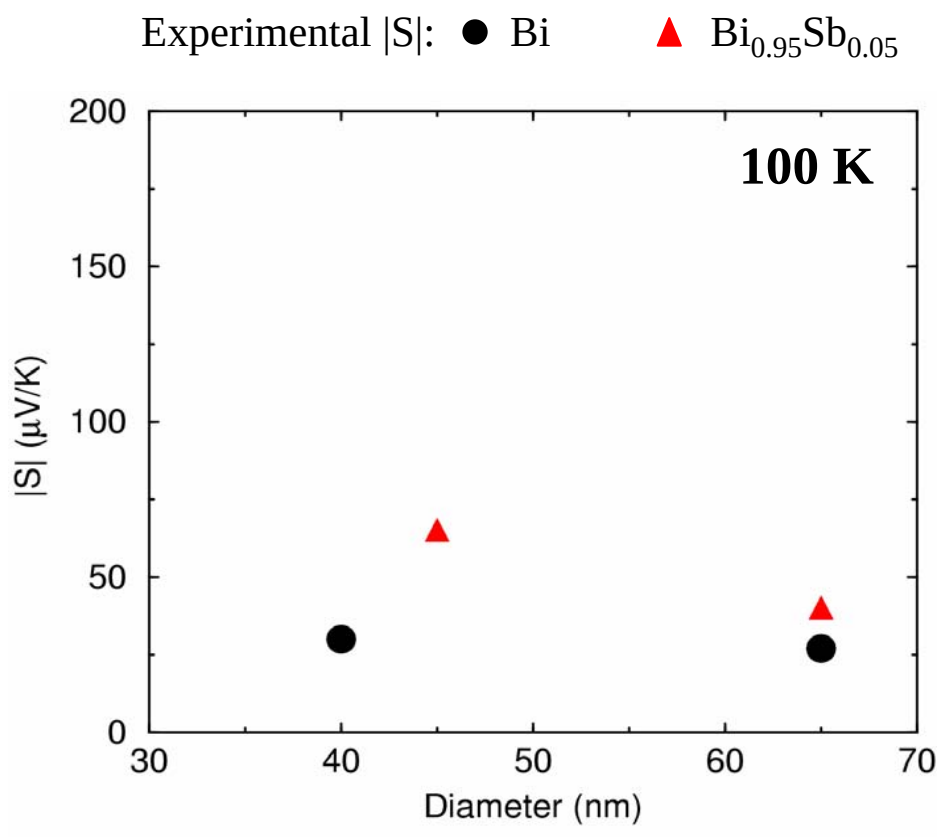


Thermopower is enhanced in semiconducting Bi nanowires due to both the size effect and the Sb alloying effect.

Comparison with Theoretical Calculations

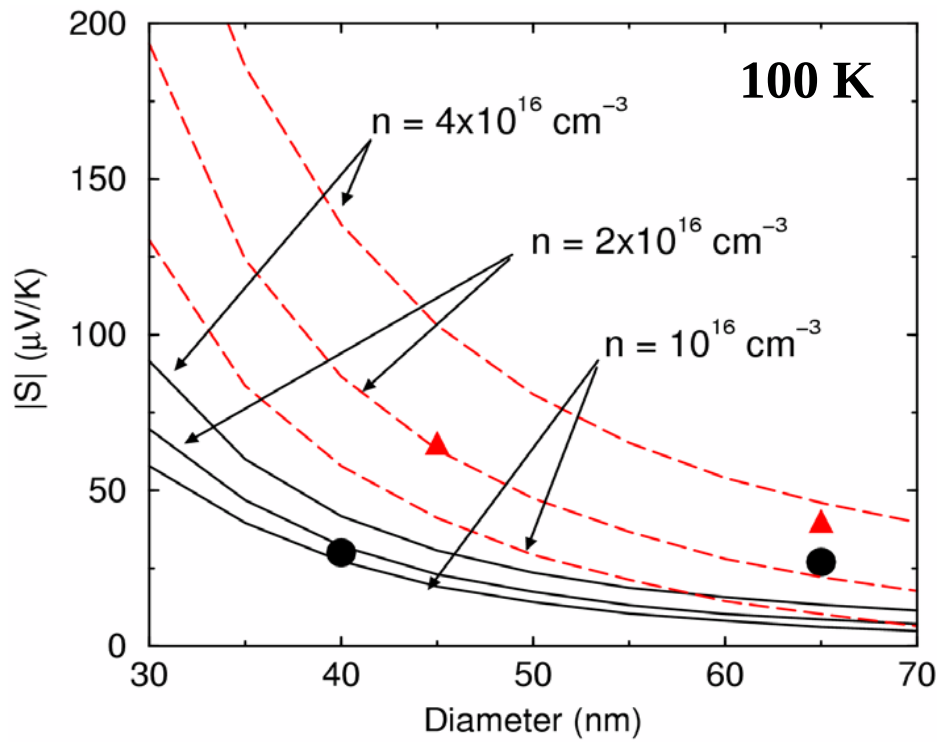


4 experimental points shown above

Lin *et al.*, Appl. Phys. Lett. **81**, 2403 (2002)

Comparison with Theoretical Calculations

Experimental |S|: ● Bi ▲ $Bi_{0.95}Sb_{0.05}$



Theoretically predicted |S| at 100 K

Bi ——— $Bi_{0.95}Sb_{0.05}$ - - - - - -

Lin *et al*., Appl. Phys. Lett. **81**, 2403 (2002)

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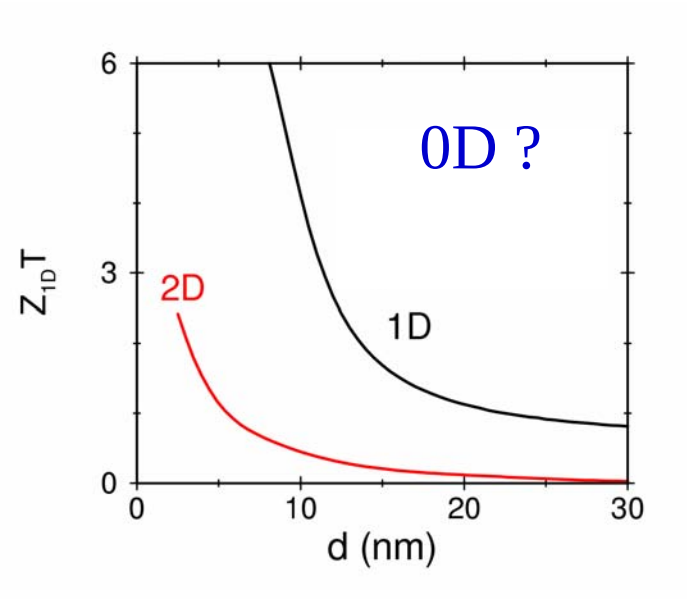
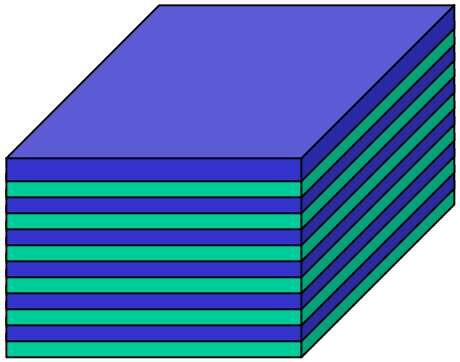
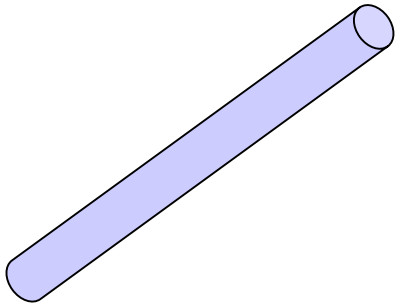
New Possibilities: Beyond 1D Nanowires

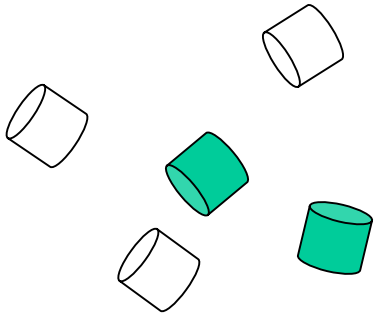


Superlattice (2D)



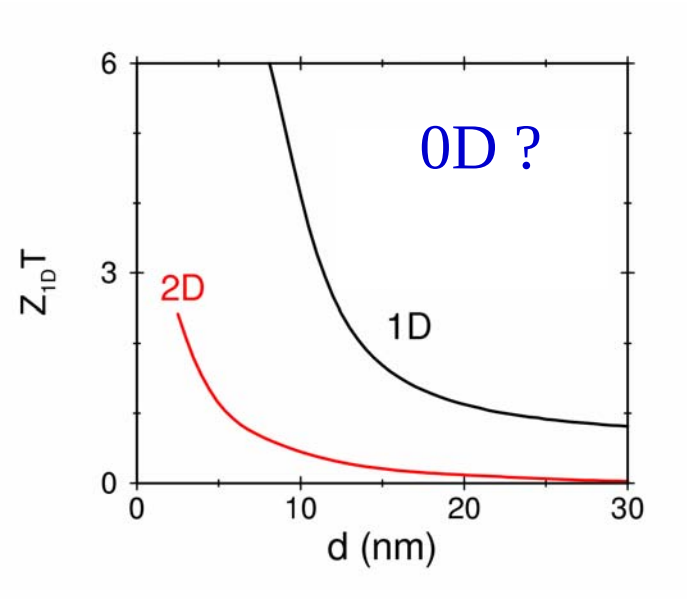
Nanowire (1D)



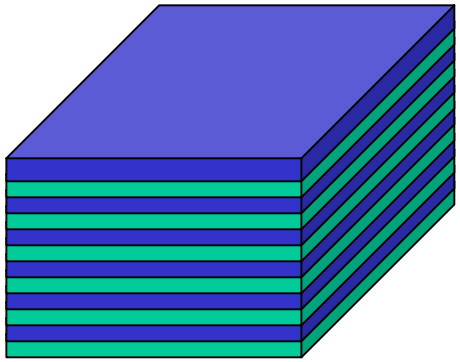


Quantum Dots

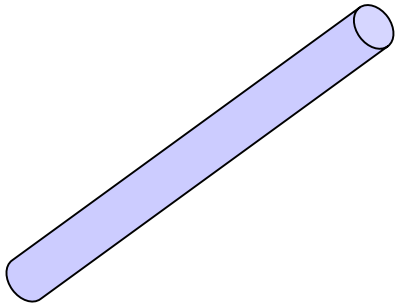
New Possibilities: Superlattice Nanowires

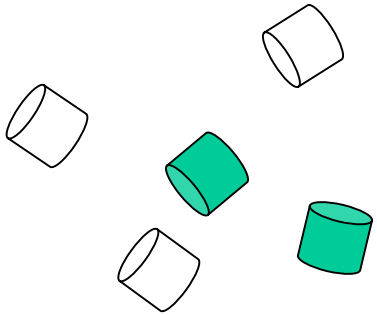


Superlattice (2D)



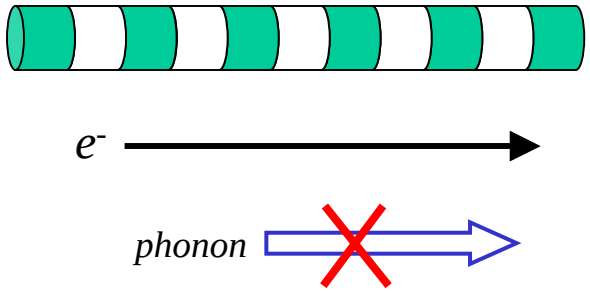
Nanowire (1D)





Quantum Dots

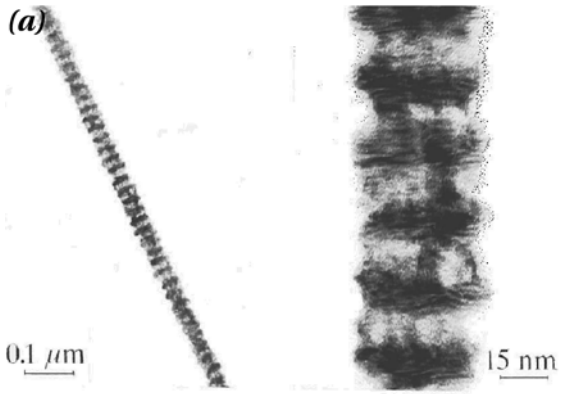
Superlattice Nanowire



Fabrication of Superlattice Nanowires

- Electrochemical Growth in Porous Films
  - Co/Cu superlattice nanowires

Co/Cu SL nanowire

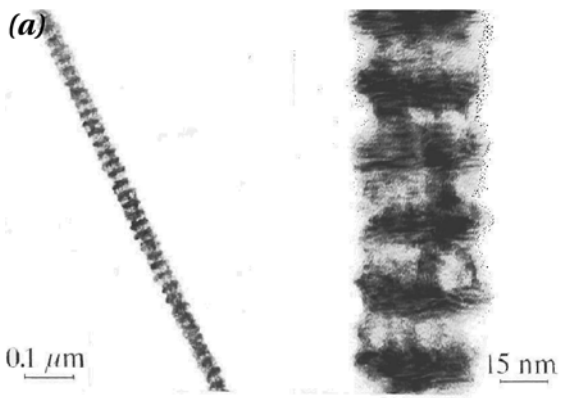


Piraux *et al.* (1994)

Fabrication of Superlattice Nanowires

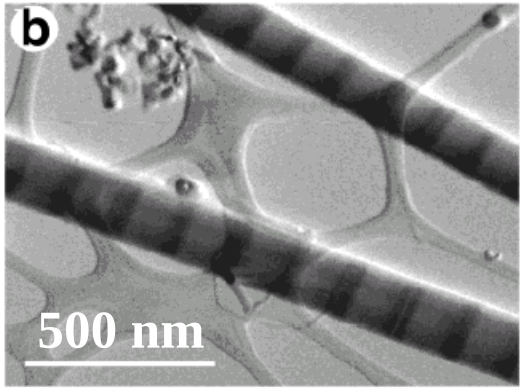
- Electrochemical Growth in Porous Films
  - Co/Cu superlattice nanowires
- Vapor-Liquid-Solid Growth
  - Laser-assisted growth, e.g. Si/SiGe SL nanowires

Co/Cu SL nanowire



Piraux *et al.* (1994)

Si/SiGe SL nanowire

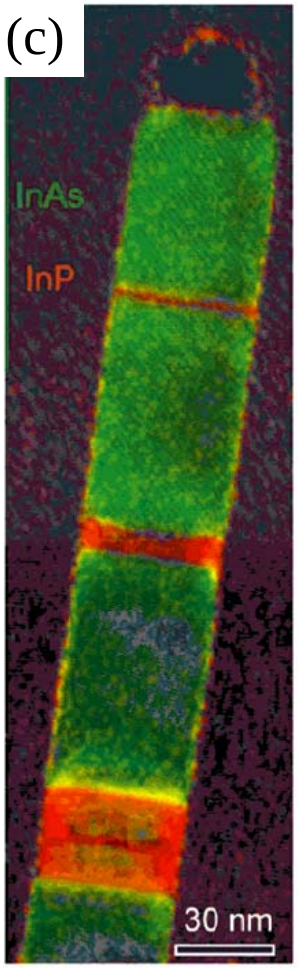


Yang *et al.* (2002)

Fabrication of Superlattice Nanowires

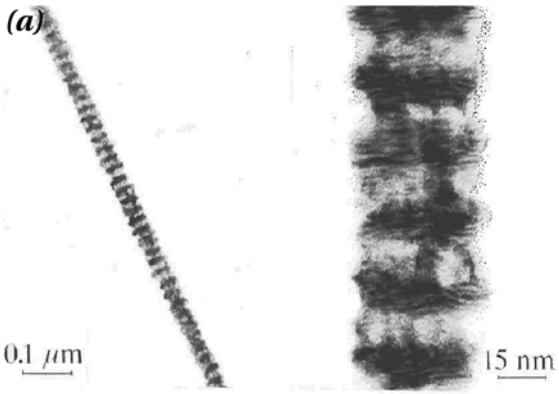
- Electrochemical Growth in Porous Films
  - Co/Cu superlattice nanowires
- Vapor-Liquid-Solid Growth
  - Laser-assisted growth, e.g. Si/SiGe SL nanowires
  - Chemical beam epitaxy, e.g. InP/InAs SL nanowires

InAs/InP SL nanowire



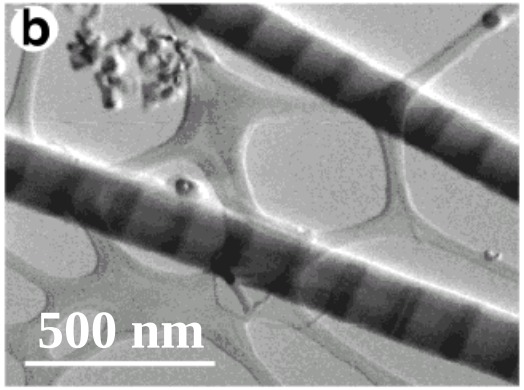
Samuelson *et al*. (2002)

Co/Cu SL nanowire



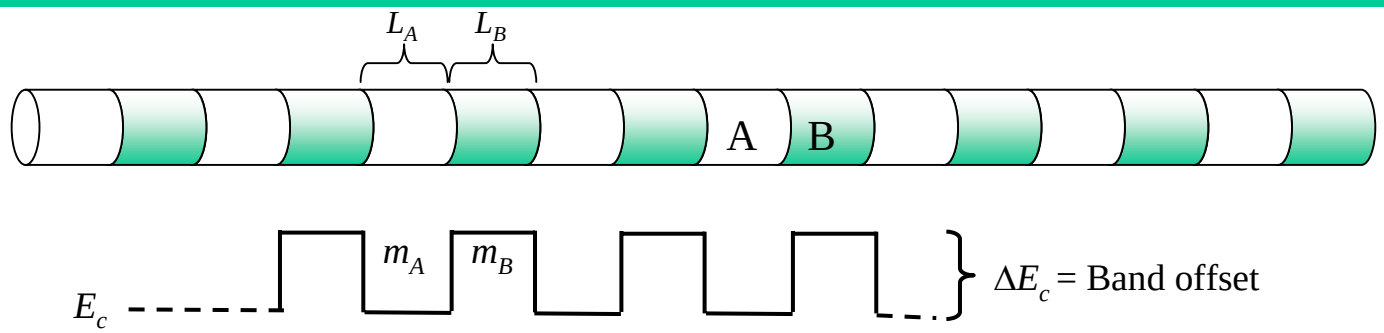
Piraux *et al*. (1994)

Si/SiGe SL nanowire



Yang *et al*. (2002)

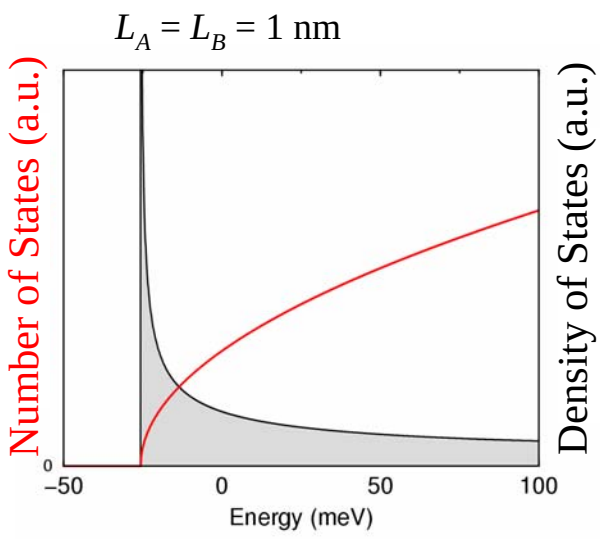
Theoretical Modeling



- Key parameters
  - Wire diameter: d_W
  - Segment lengths: L_A and L_B (assumed to be equal)
  - Subband potential barrier: ΔE_c
  - Effective masses: m_A and m_B
  - Phonon mean free path: Λ
- Approaches
  - 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

Density of States in SL Nanowire

$m_A = m_B = 0.5\ m_0$
$V = 50$ meV

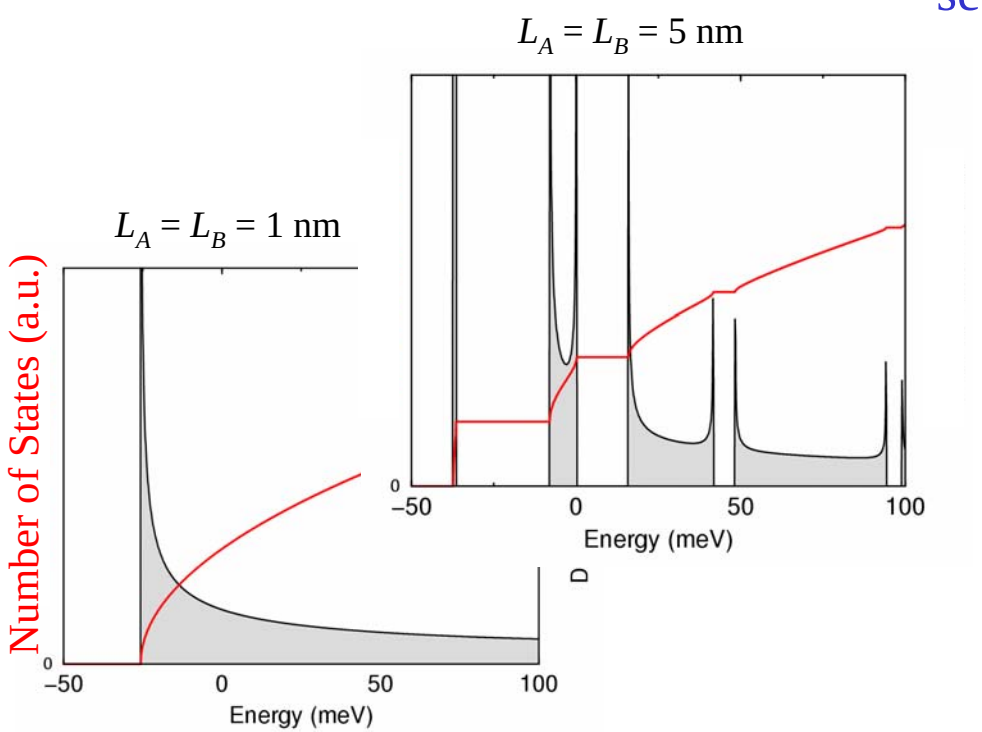


- The density of states approaches that of an alloy system for very short segment lengths.

Density of States in SL Nanowire

$m_A = m_B = 0.5\ m_0$
$V = 50$ meV

- Mini-bands are formed as the segment length increases.



Density of States in SL Nanowire

$m_A = m_B = 0.5\ m_0$
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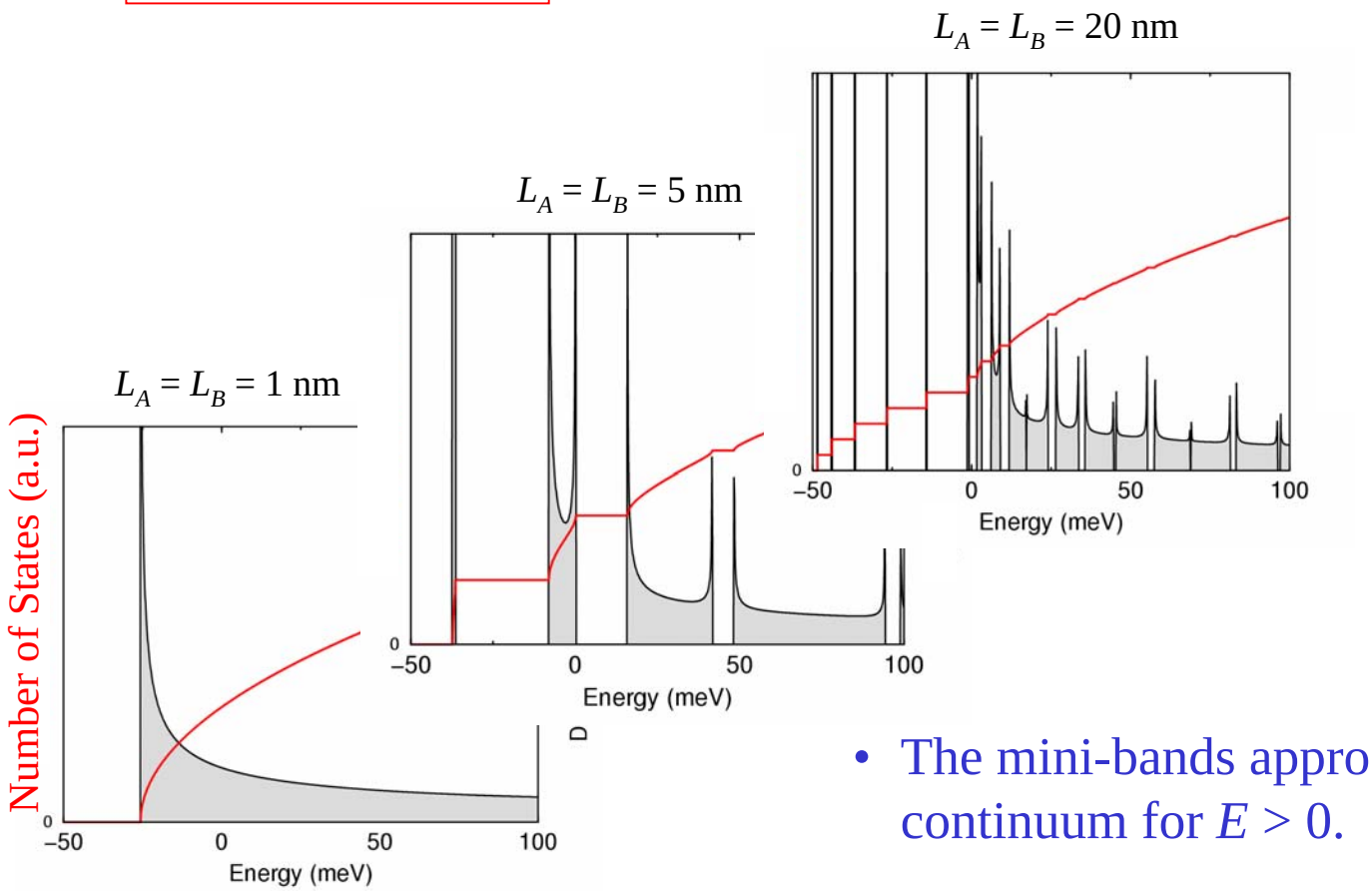
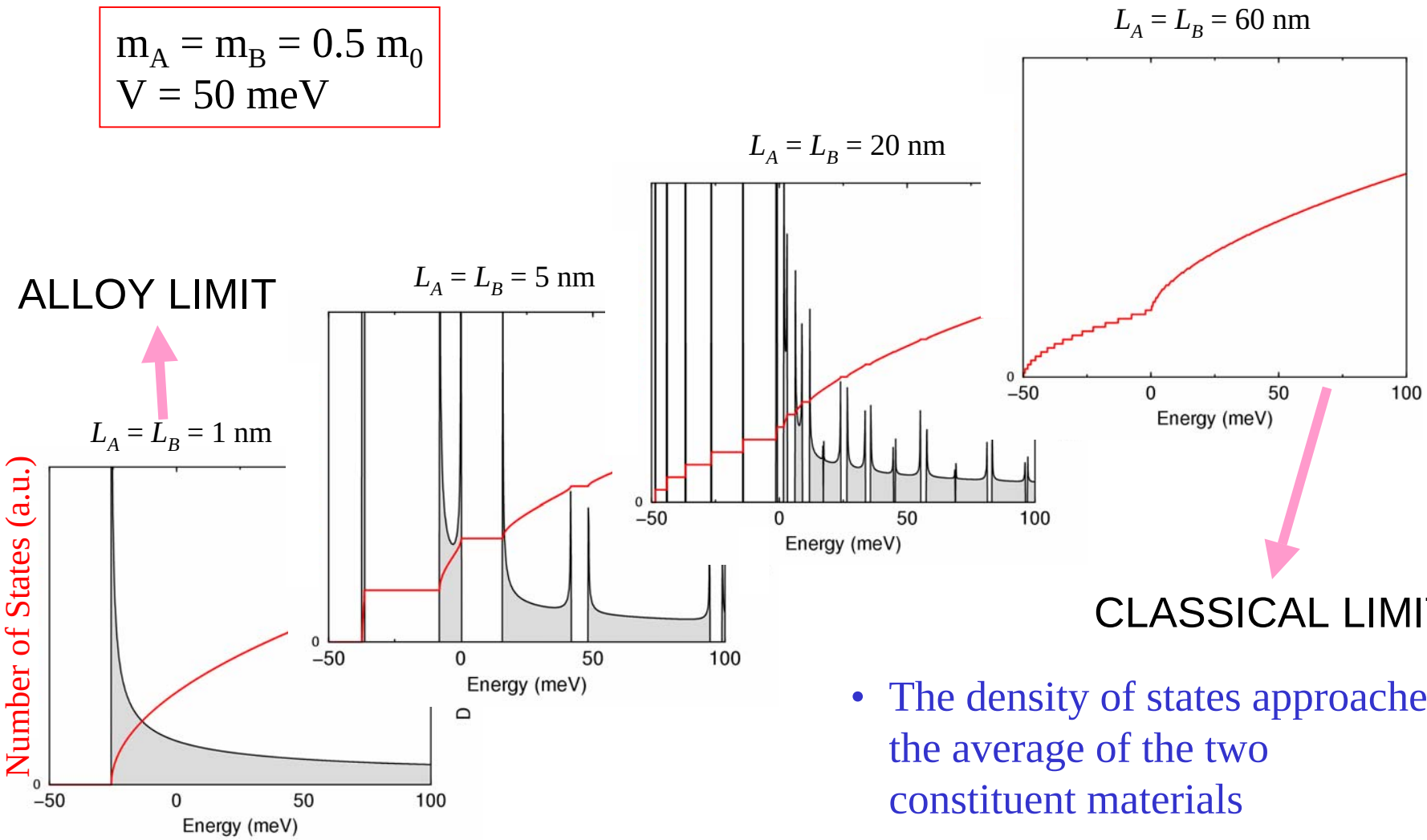


- The mini-bands approach a continuum for $E > 0$.

Density of States in SL Nanowire

$m_A = m_B = 0.5\ m_0$
$V = 50$ meV

ALLOY LIMIT



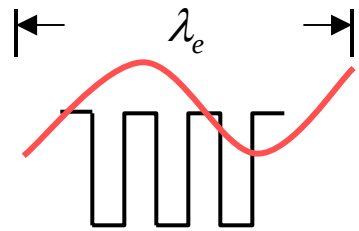
CLASSICAL LIMIT

- The density of states approaches the average of the two constituent materials

Density of States Profile

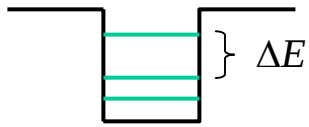
- Criteria for Alloy Limit

$$L << \lambda_e \qquad \varepsilon \equiv \frac{L\sqrt{2mV}}{2\pi\hbar} << 1$$



- Criteria for Classical Limit

$$\Delta E << kT \qquad \delta \equiv \frac{\hbar}{kTL}\sqrt{\frac{V}{2m}} << 1$$



Segment Length	1 nm	5 nm	20 nm	60 nm
ε	0.13	0.64	2.57	7.73
δ	6.17	1.23	0.30	0.1

Lattice Thermal Conductivity

Phonon transport in SL nanowires: (C. Dames & G. Chen; S1.2):

$$\frac{2L}{\kappa} = \underbrace{4\left(\frac{1}{C_A v_A t_{AB}} + \frac{1}{C_B v_B t_{BA}}\right)\left[1 - \frac{t_{AB} + t_{BA}}{2}\right]}_{\text{Interface scattering}} + \underbrace{\frac{L}{\kappa_A} + \frac{L}{\kappa_B}}_{\text{Bulk}} + \underbrace{\frac{3}{d_W \alpha}\left(\frac{1}{C_A v_A} + \frac{1}{C_B v_B}\right)}_{\text{Wire boundary scattering}}$$

Effective scattering lengths:

Bulk – $\Lambda_B = \frac{3\kappa}{Cv}$

Interface – $\Lambda_I = \frac{3}{4}L$

Boundary – $\Lambda_b = \frac{\alpha}{3} d_W$

C : heat capacity

v : sound velocity

t_{AB} : phonon transmissivity from A to B

κ : thermal conductivity

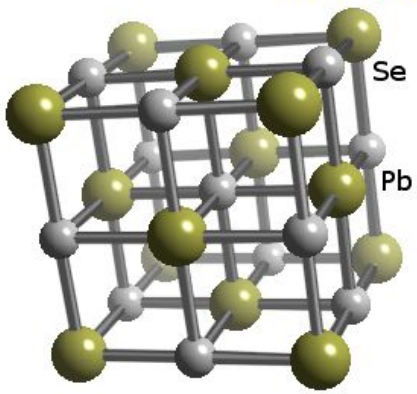
L : segment length

α : geometric factor, 0.75 - 1.0 for cylindrical wires

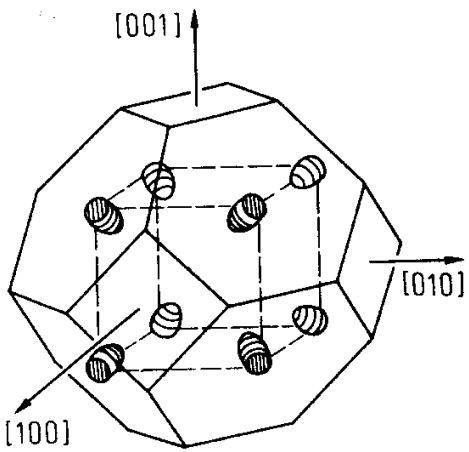
SL nanowires – $\Lambda_{SL}^{-1} = \Lambda_B^{-1} + \Lambda_I^{-1} + \Lambda_b^{-1}$

Lead Salts SL Nanowires

Lead Salts – PbS, PbSe, PbTe



- NaCl-like FCC lattice structure
- Low thermal conductivity
- Direct-gap semiconductor at the *L*-point of the Brillouin zone
- Bandgap between conduction and valence bands:
  PbS > PbTe > PbSe
- Lattice Constant:
  PbS < PbSe < PbTe

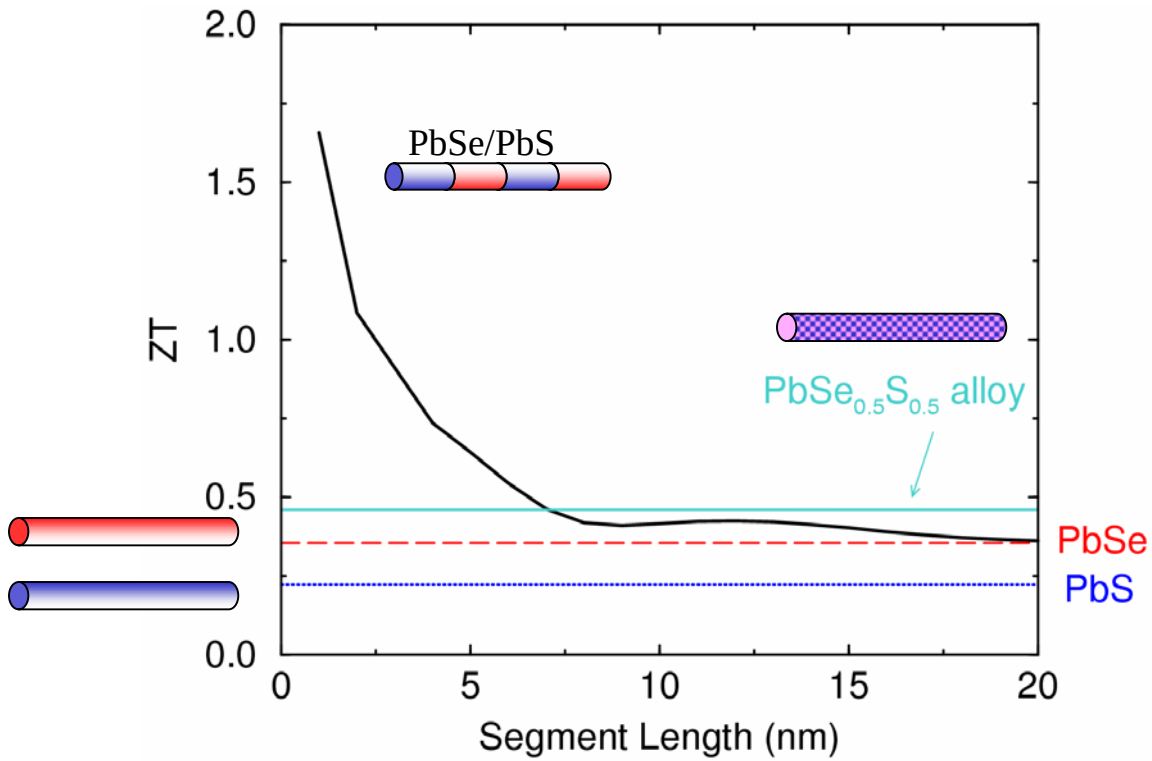


Bulk Property	PbS	PbSe	PbTe
Lattice Constant (Å)	5.94	6.12	6.46
E_g at 77 K (meV)	307	168	215

ZT Enhancement in SL Nanowires

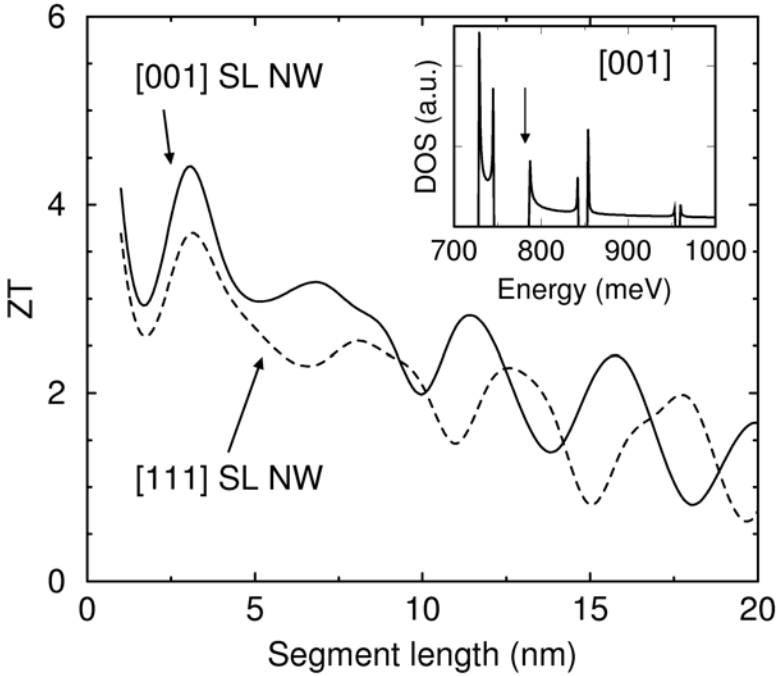
Segment Length Dependence

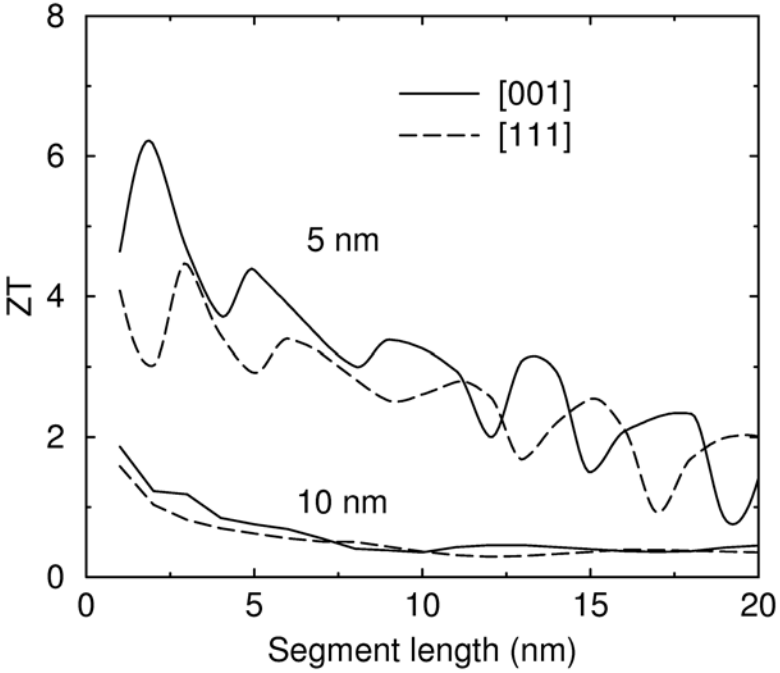
Wire diameter: 10 nm



ZT for [001] *n*-type PbSe/PbS SL nanowires as a function of segment length at 77 K.

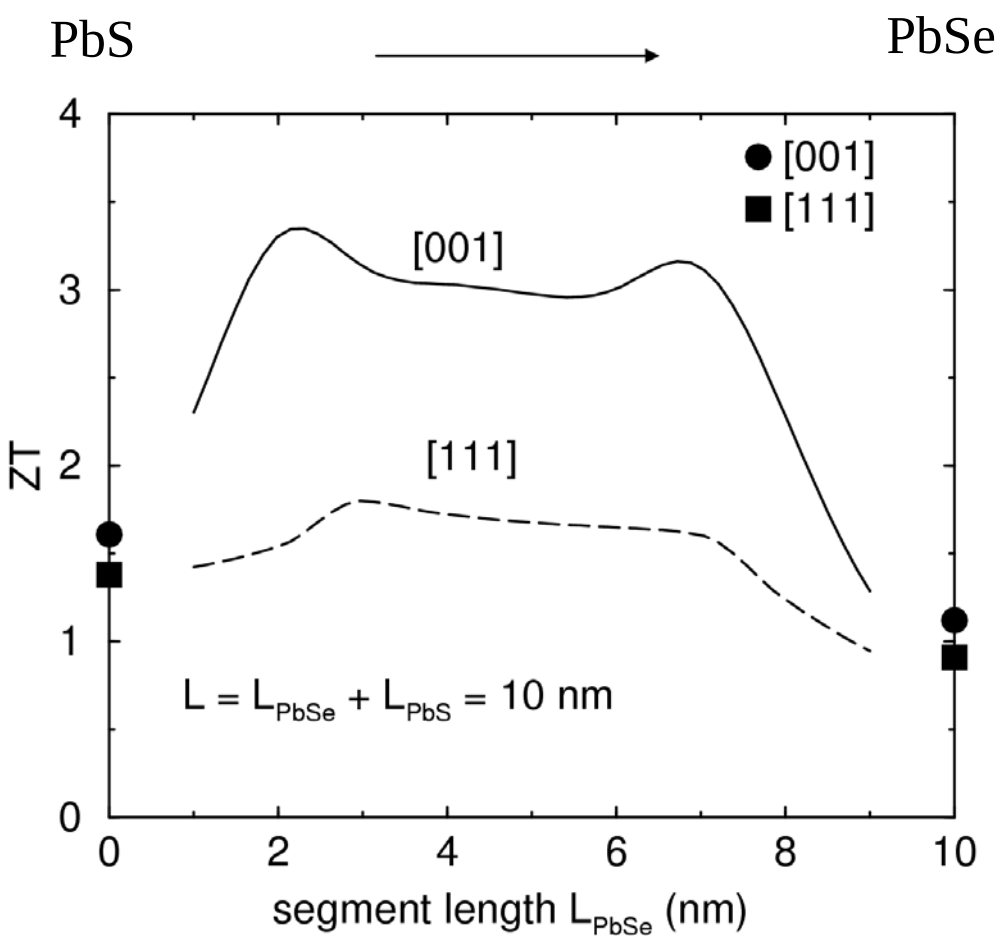
ZT Dependence on Structural Parameters





- Position of Fermi level is critical
- As wire diameter decreases oscillatory behavior develops due to greater prominence of van Hove singularities.

Asymmetric Segment Lengths



ZT for PbSe/PbS SL NWs

Wire diameter: 5 nm

ZT can be further optimized by adopting asymmetric segment lengths for the two constituent materials.

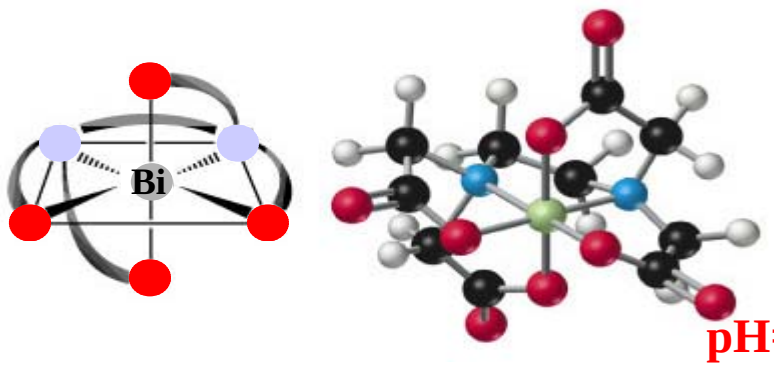
Outline

- Overview of low dimensional thermoelectricity
- New physics to yield enhanced performance in 1D nanowire systems
- 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

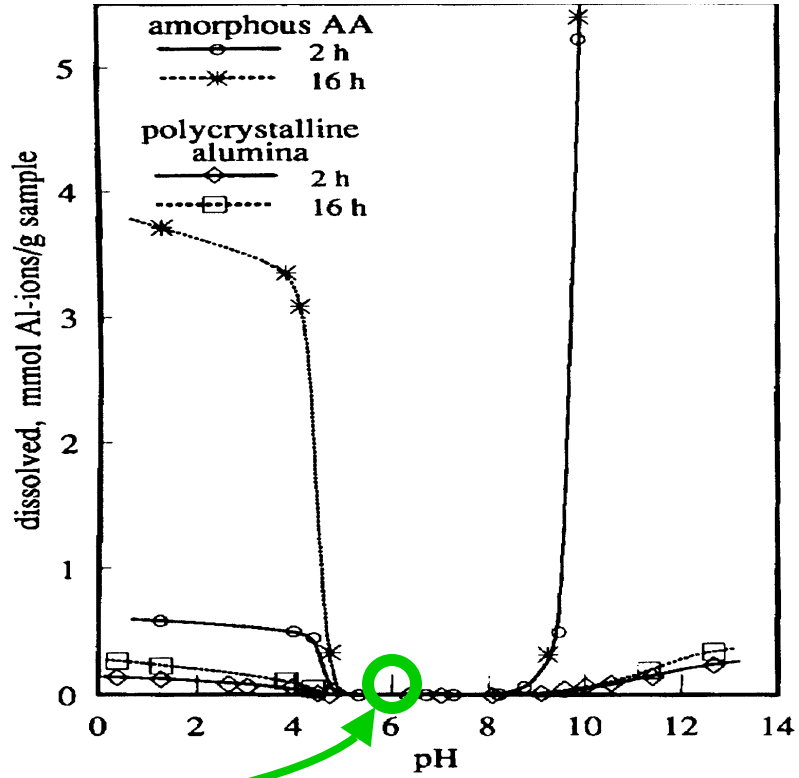
An Electrolyte for Bismuth Deposition

Acidic electrolytes, needed for the stability of the Bi ion, cause damage to the template. Instead, a chelating ligand is used to stabilize the solvated form of the bismuth ion.

$Bi(NO_3)_3 \cdot 5H_2O$ + EDTA
(ethylenediaminetetraacetic acid)



Dissolution Rate of Anodic Alumina

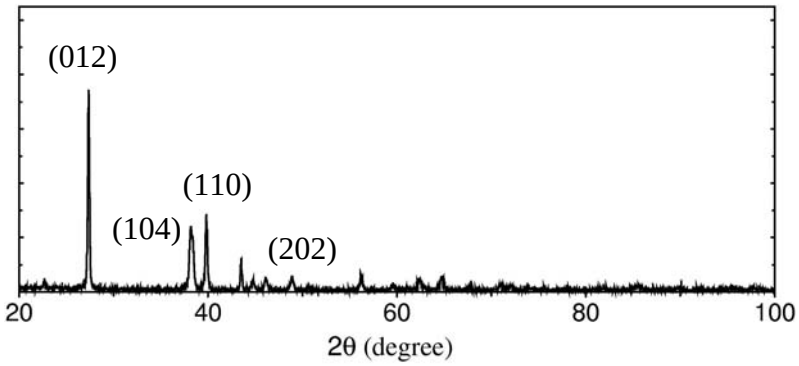


pH=6

No noticeable degradation of the template for days.

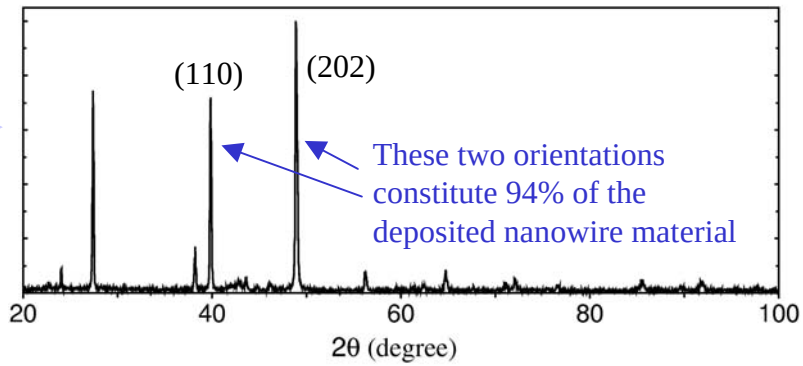
DRAWBACK: The reduction potential of bismuth is shifted to lower potentials.
➔ Selective deposition becomes more difficult.

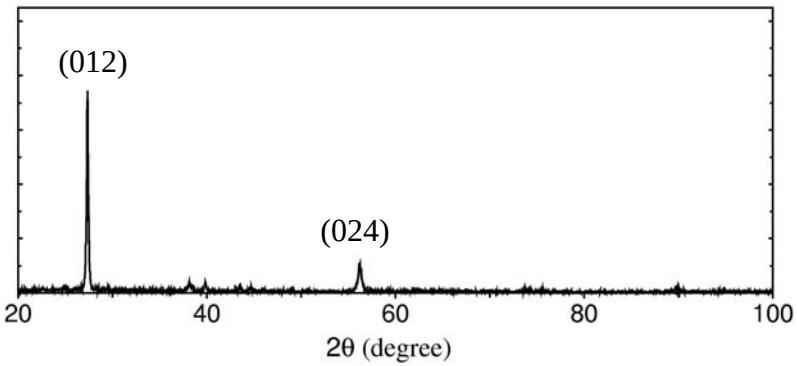
Improving the Quality of Electrodeposited Bismuth Nanowire Arrays



"regular" electrodeposition :
most conditions result in polycrystalline nanowire arrays
(powder pattern)

melting and recrystallization in H_2/N_2 atmosphere

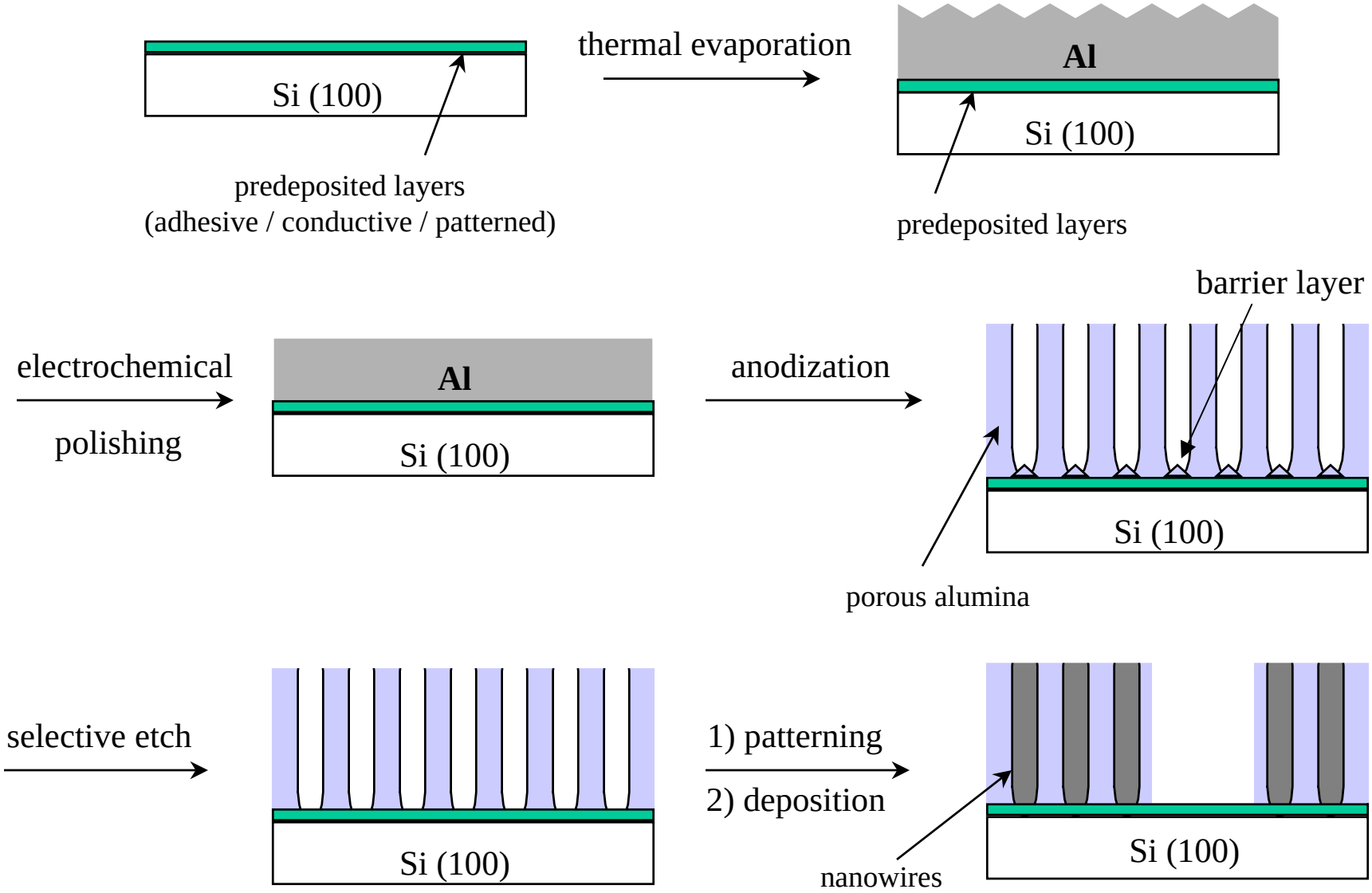




"improved" electrodeposition :
modifications that improved the deposition potential control led to oriented bismuth nanowire arrays

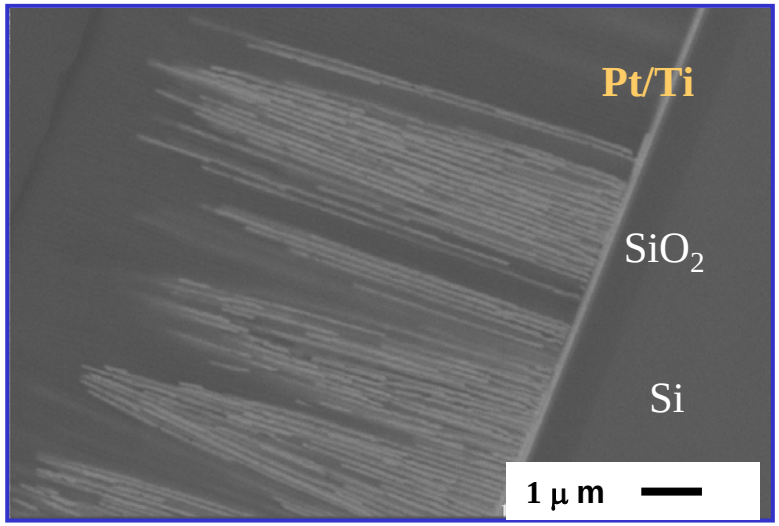
Alumina Templates on Silicon Wafers

Our Concept

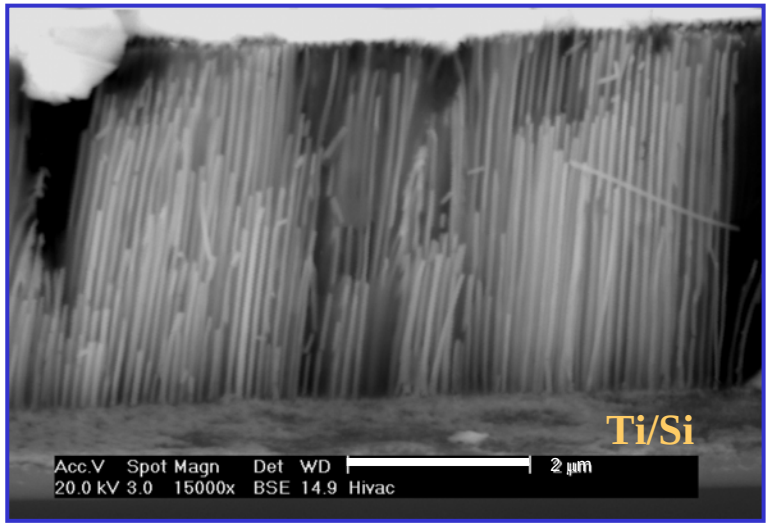


Nanowire Growth on the Silicon Support

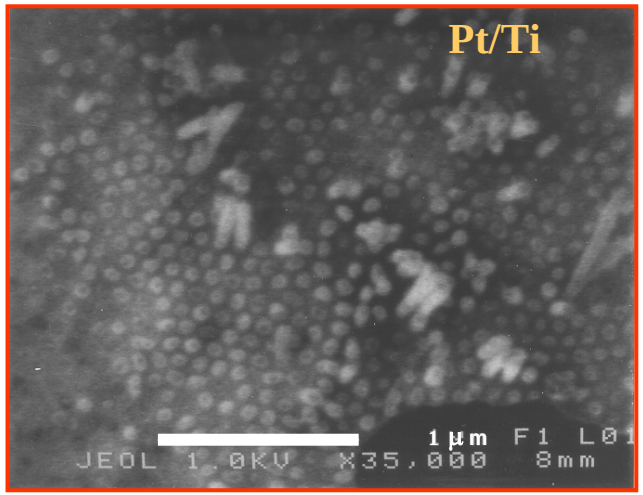
Bismuth nanowires



Bismuth Telluride nanowires (JPL)

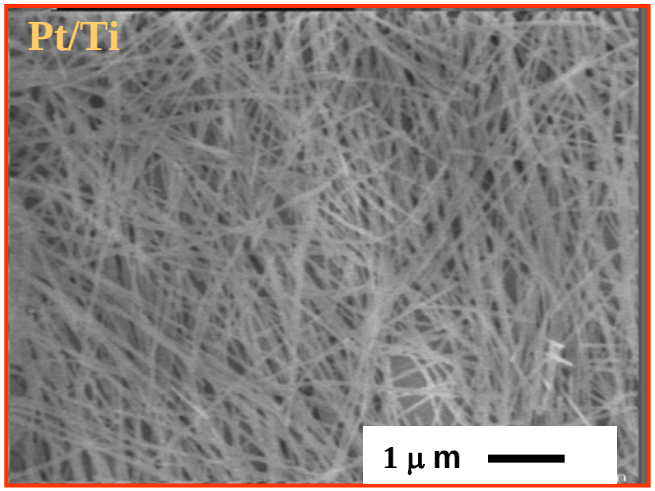


Gold nanorods



Substrate-supported nanowires after the etching of the anodic alumina template

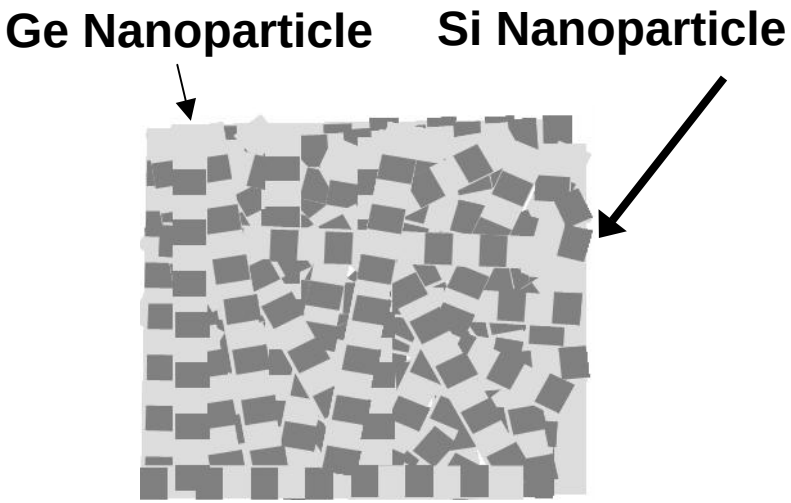
Bismuth nanowires

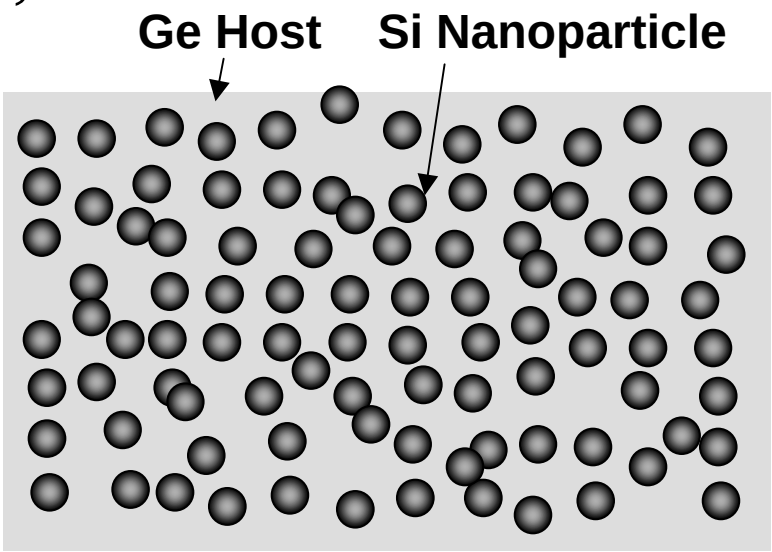


Rabin *et al*., Adv. Funct. Mater. (2003)

Nanoparticle Composite Synthesis

Gang Chen, MIT





- **Nanocomposites**

(1) Cold / Hot Pressing
(2) Induction Heating

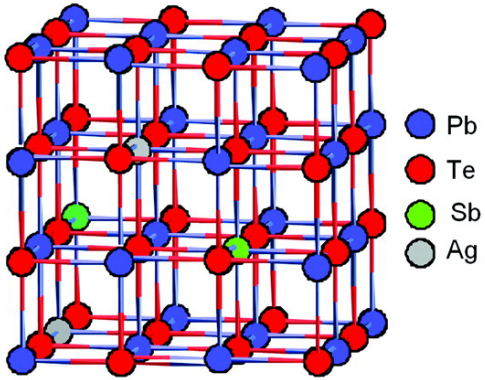
- **Nanoparticles**

(1) Commercial
(2) From Nanowires
(3) Study core-shell structures

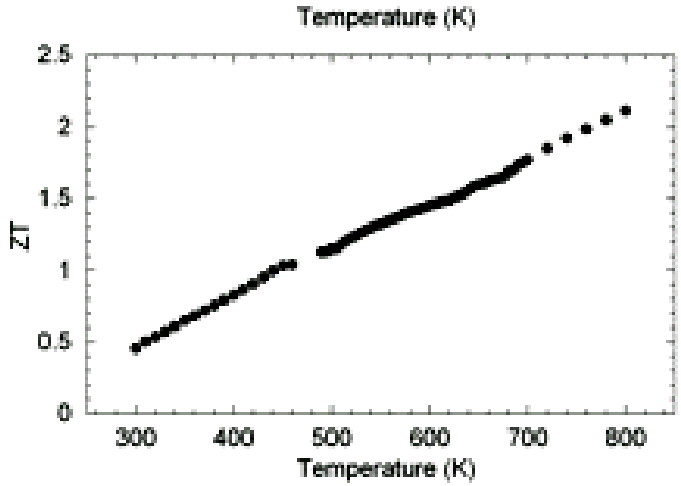
<u>Expectations:</u>

- Reduced thermal conductivity.
- Electrical conductivity comparable to or better than bulk.
- Increased thermoelectric figure of merit.
- Cheap, self-assembly method

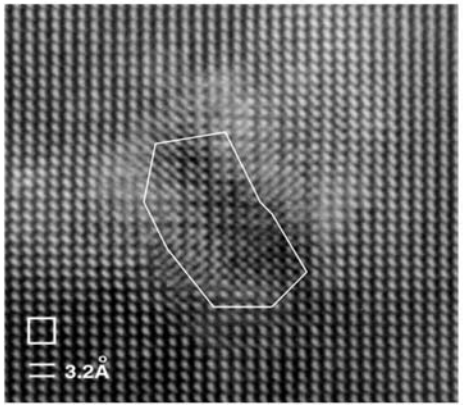
New 3D Crystalline Thermoelectric Materials with Quantum Dots



$AgPb_mMTe_{2+m}$
M = Bi, Sb



ZT vs T for $AgPb_{18}SbTe_{20}$



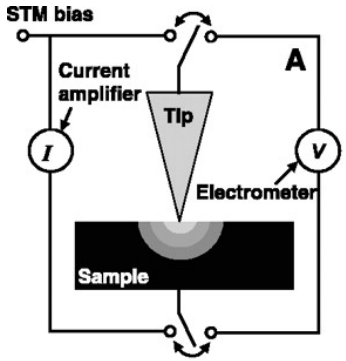
Quantum dot is rich in AgSb and is surrounded by a PbTe rich region

- High power factor of 28 μW/cmK^2 and high ZT = 2.1 at 800 K in $Ag_{1-x}Pb_{18}SbTe_{20}$ may be due to self-assembled quantum dots.
- The $AgPb_mMTe_{2+m}$ system is not yet optimized for highest ZT.

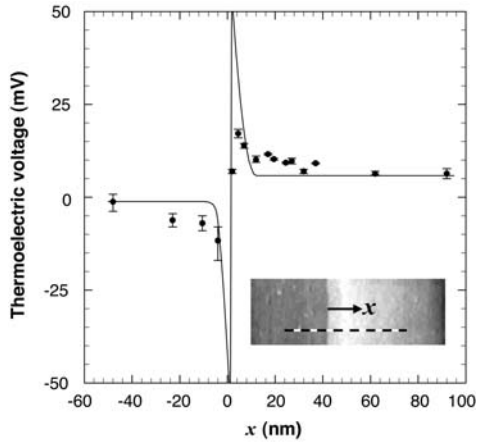
K.F. Hsu et al. (Kanatzidis), Science **303**, *818 (2004)*

New Nanoscale Tools for Thermoelectric Measurements

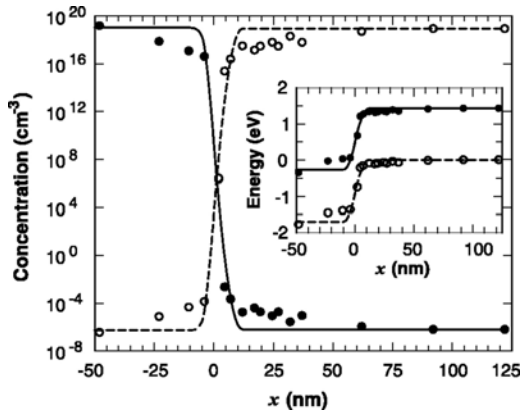
Scanning thermoelectric microscopy (SThEM) allows measurements of the spatial profiles of the thermoelectric voltage, carrier concentration and electron energy band of a p-n junction to 2 nm resolution.



SThEM measurement set-up



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



Carrier profiles and electronic band energies across p-n junction

•This work has general implications on electronics and opto-electronics of nano-systems.

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

Conclusions

- Model systems show that:
  ZT for 0D nanowire superlattice is greater than
  ZT for 1D quantum wires which is greater than
  ZT for 2D quantum wells which is greater than
  ZT for bulk for same material, because of greater opportunity for the control of individual parameters
- 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