Nanostructured Materials For Thermoelectric Energy Conversion

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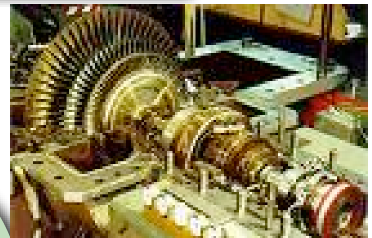
Outline

- Background and History
- State of the Art
- Thrusts
  - Molecules
  - Nanowires
  - Nanostructured Bulk Materials
- Summary

Power Generation

Hot (T_{hot})

$Heat_{in}$



Engine

Power

$Heat_{lost}$

$T_{out} > T_{ambient} + 100\ ^{o}C$

Cold ($T_{ambient}$)

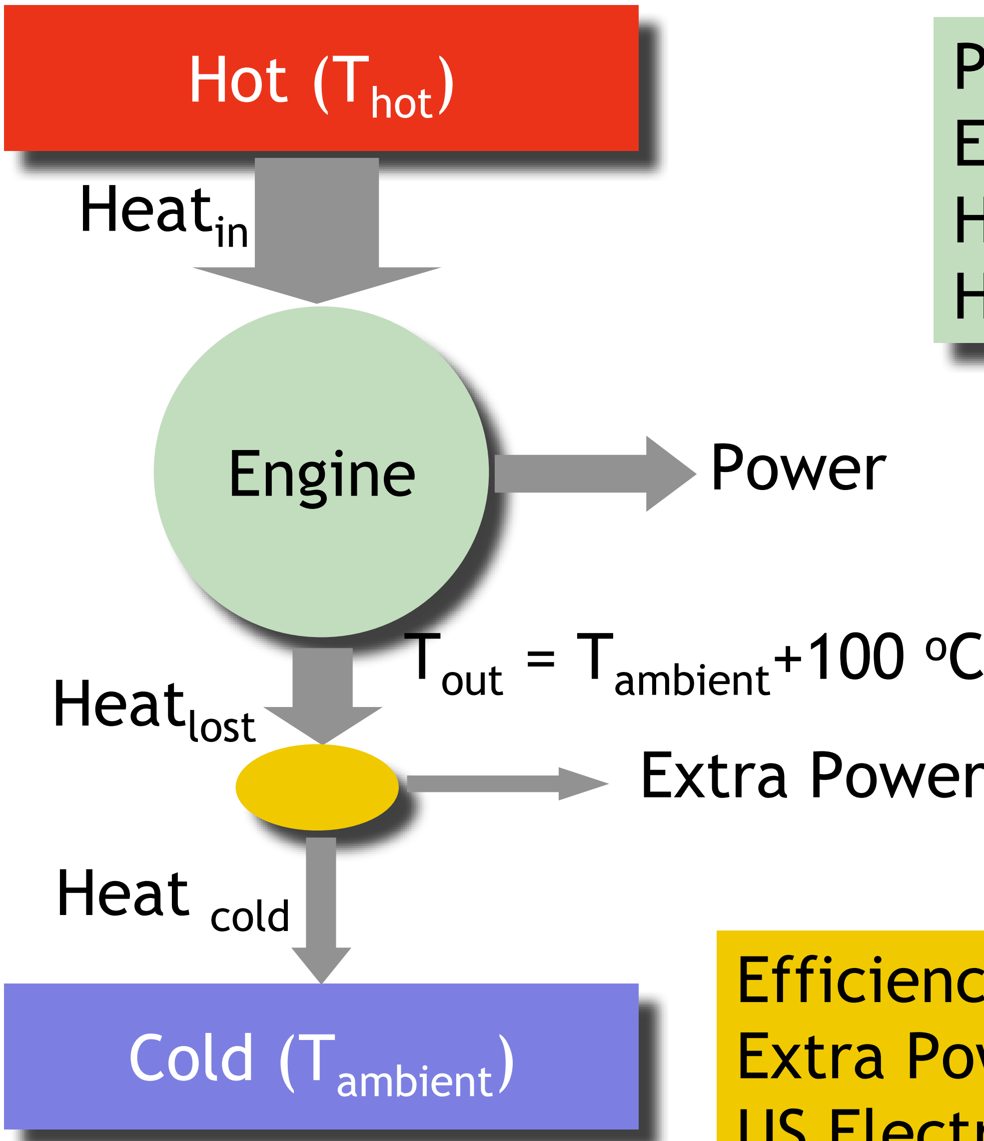
Power = 10 TrillionWatts

Efficiency = Power/$Heat_{in}$ ~ 40%

$Heat_{in}$ = 25 TW

$Heat_{lost}$ = 15 TW

Power Co-Generation

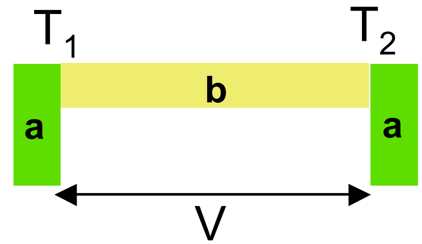


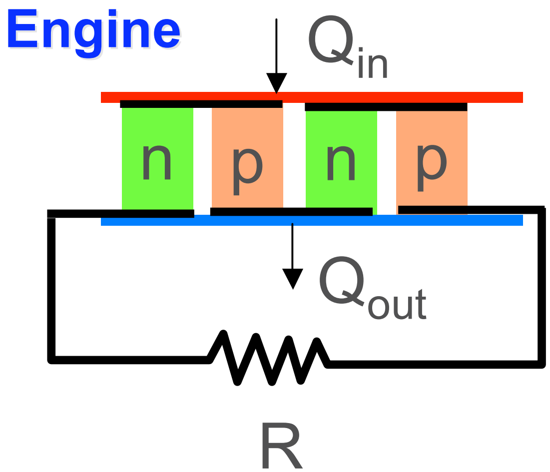
Power = 10 TrillionWatts
Efficiency = Power/$Heat_{in}$ ~ 40%
$Heat_{in}$ = 25 TW
$Heat_{lost}$ = 15 TW

Efficiency ~ 3 %
Extra Power = 0.45 TW
US Electrical Capacity = 1 TW (2005)

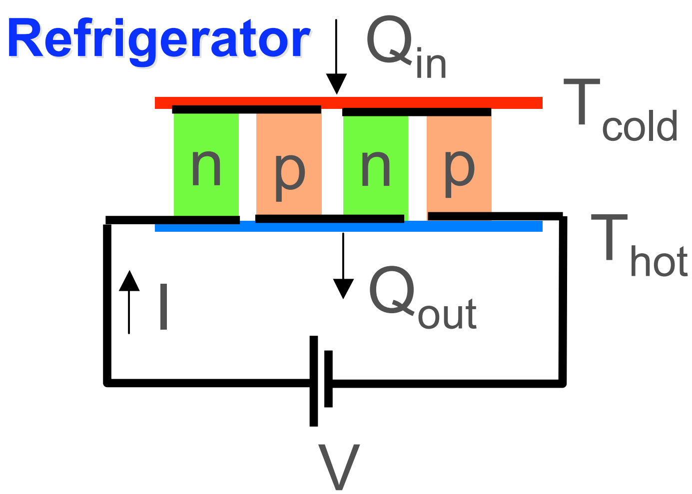
Thermoelectricity & Energy Conversion

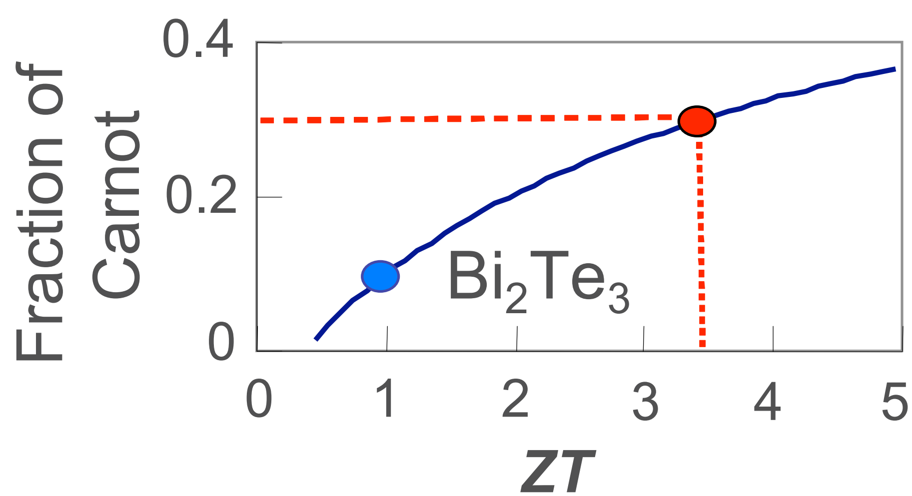
Seebeck Coefficient, $S = V/\Delta T$





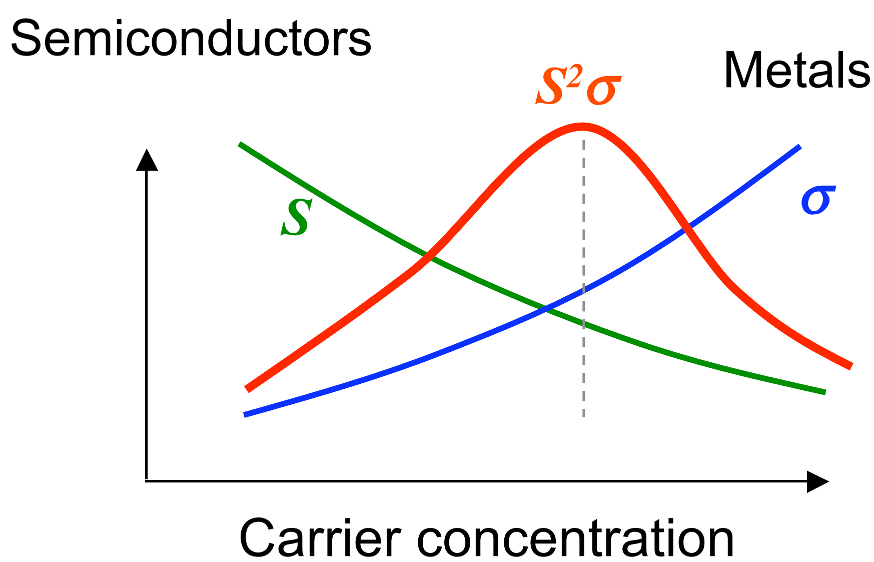
$$ZT = \frac{S^2 \sigma T}{k}$$

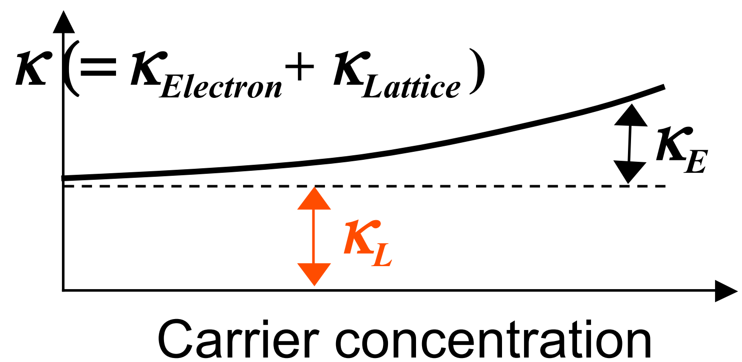




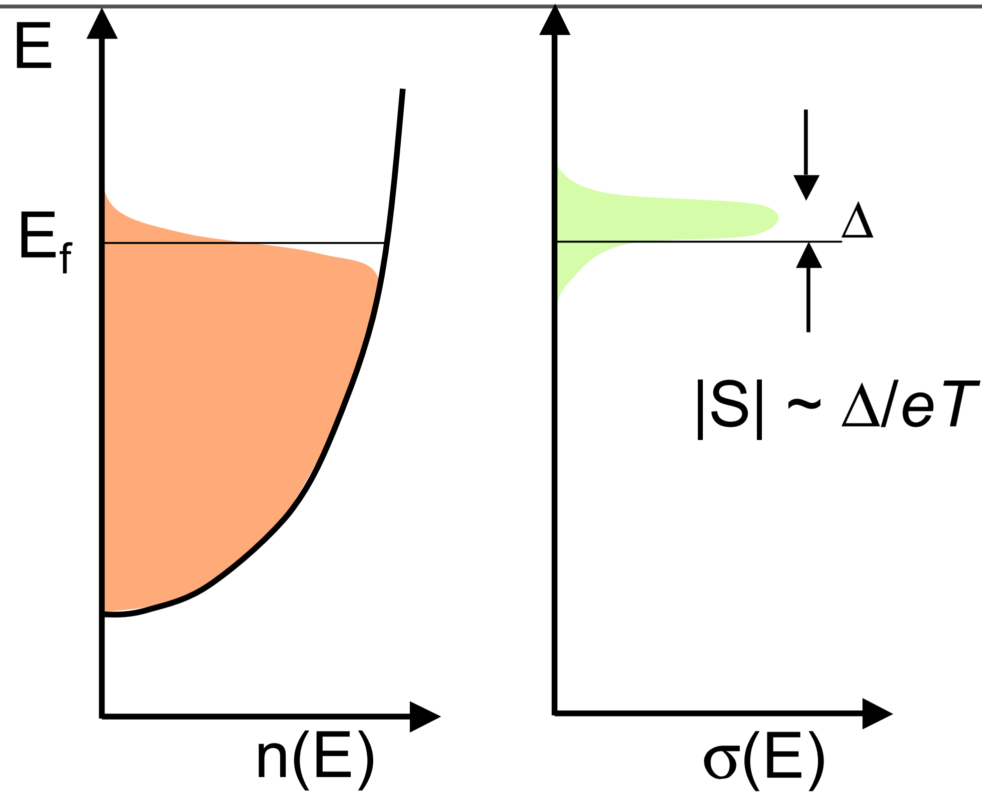
Some Trends

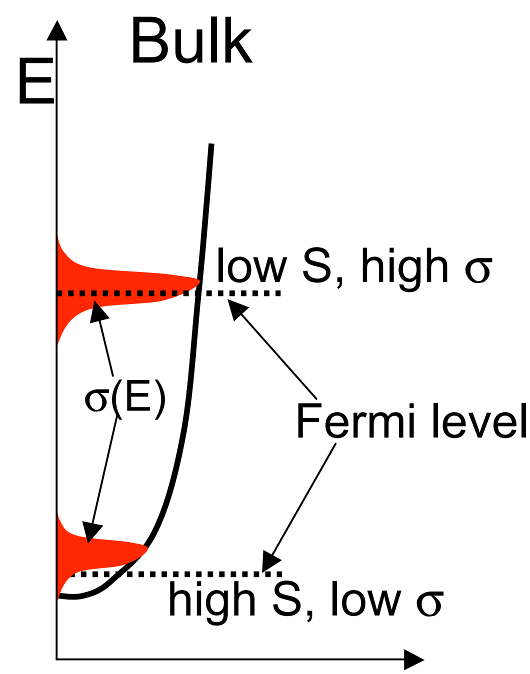
$$ZT = \frac{S^2 \sigma T}{k}$$





Origins of Thermoelectricity



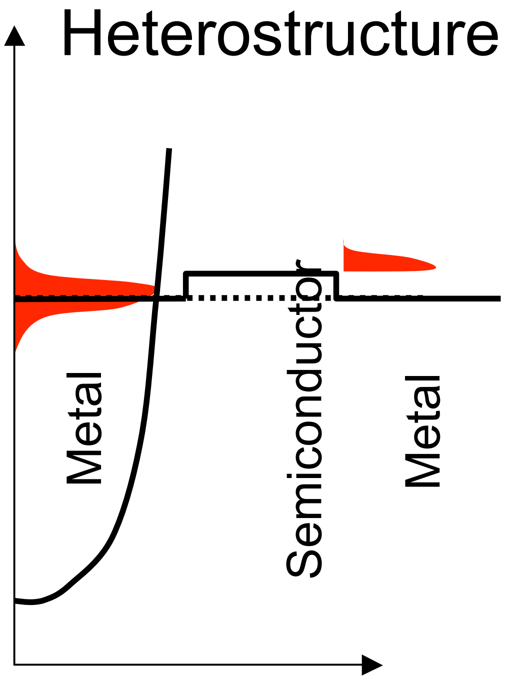


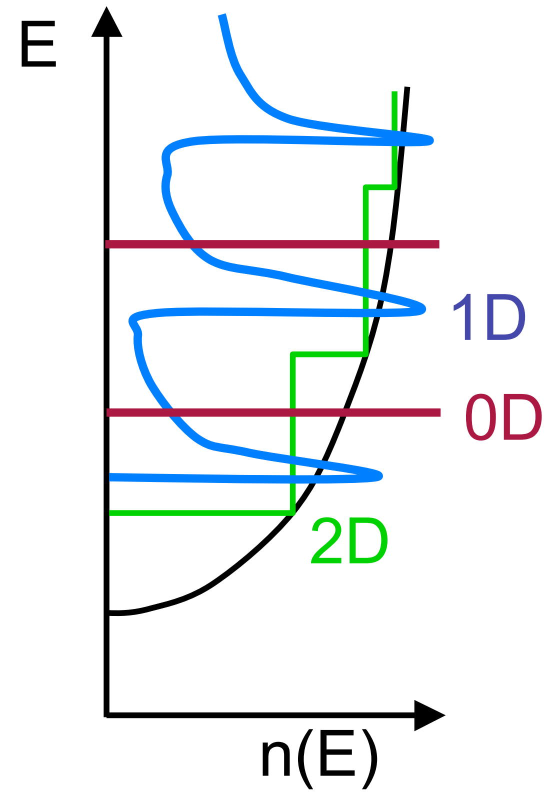
$$\sigma(E) = q^2 \tau(E) v^2(E) n(E) \left(-\frac{\partial f_{eq}}{\partial E} \right)$$

$$\sigma = \int \sigma(E) dE$$

$$S = \frac{1}{eT} \frac{\int \sigma(E)(E - E_f) dE}{\int \sigma(E) dE}$$

How do we increase $S^2\sigma$



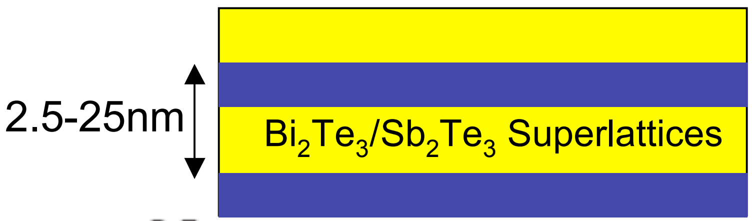


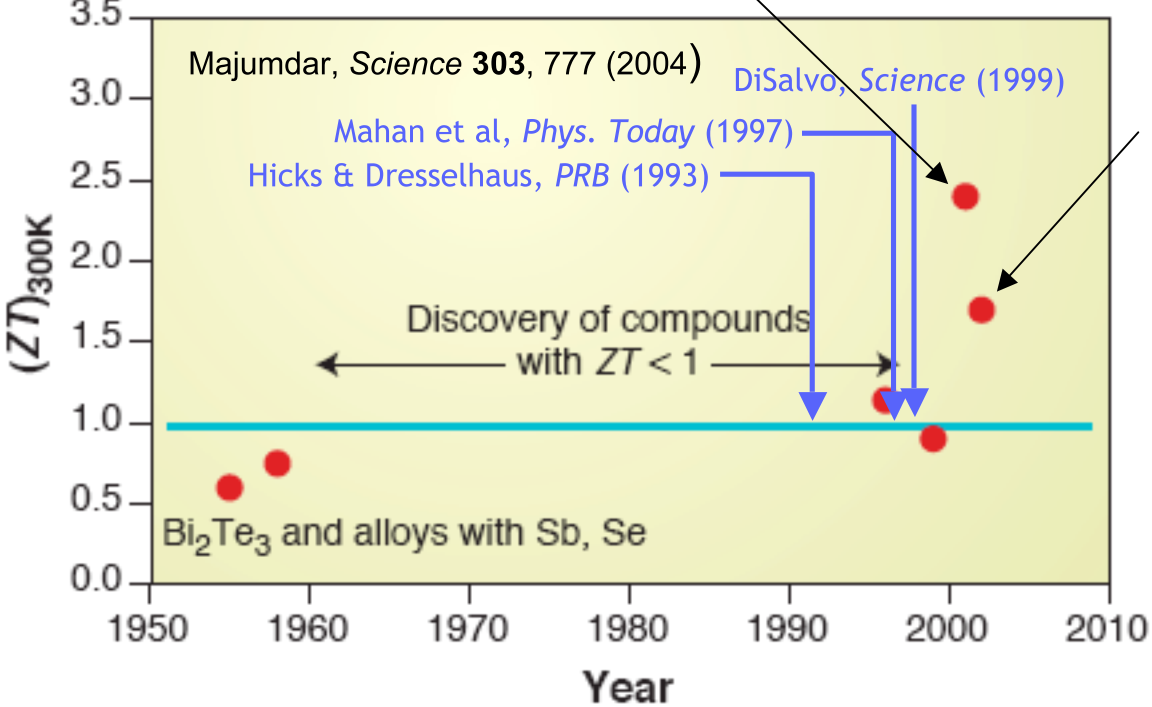
Quantum
Confinement

(Dresselhaus et al., 1993)

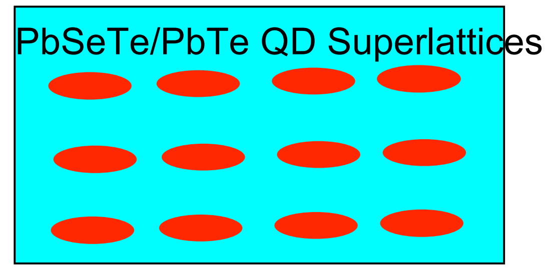
History

Venkatasubramanian et al. *Nature* **413**, 597 (2001)





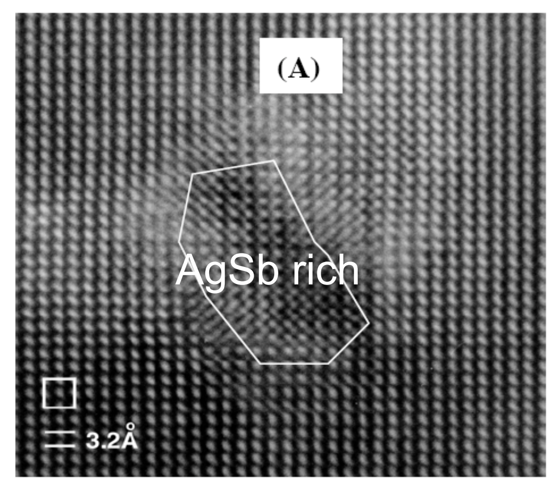
Harman et al., *Science* **297**, 2229 (2002)



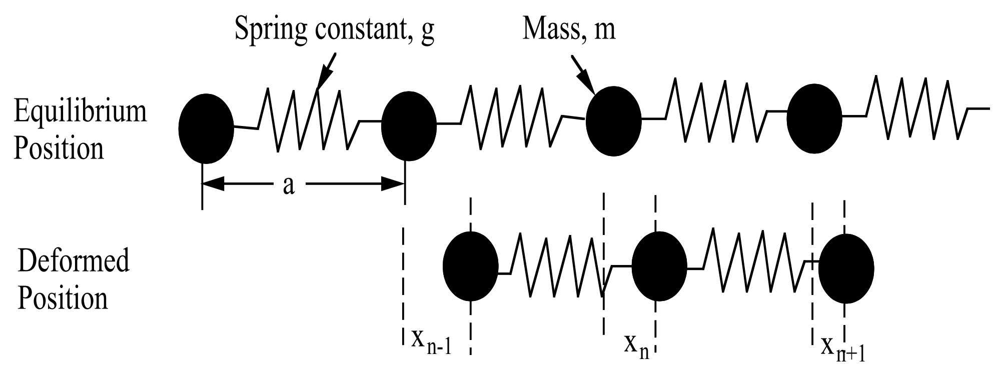
$$ZT = \frac{S^2 \sigma T}{k \downarrow}$$

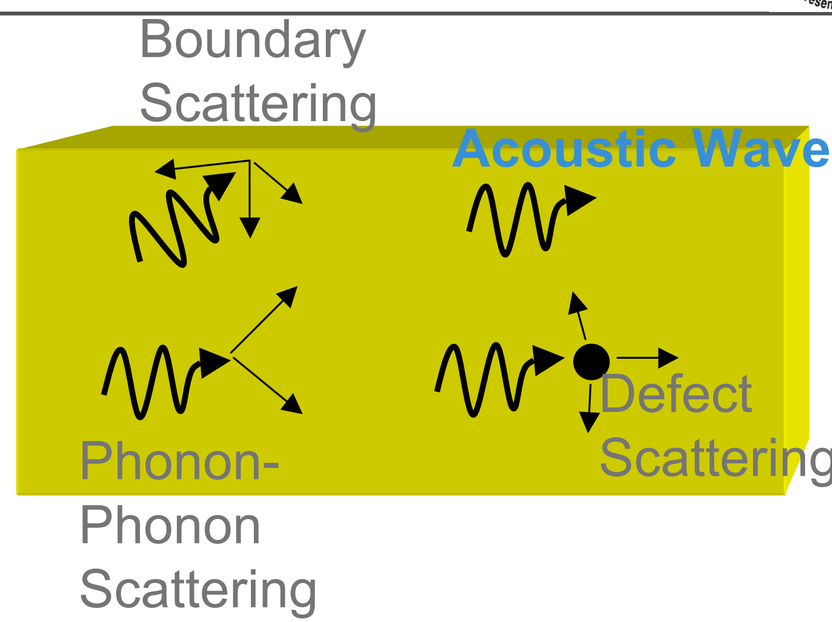
Hsu et al., *Science* **303**, 818 (2004)

$AgPb_{18}SbTe_{20}$
ZT = 2 @ 800K

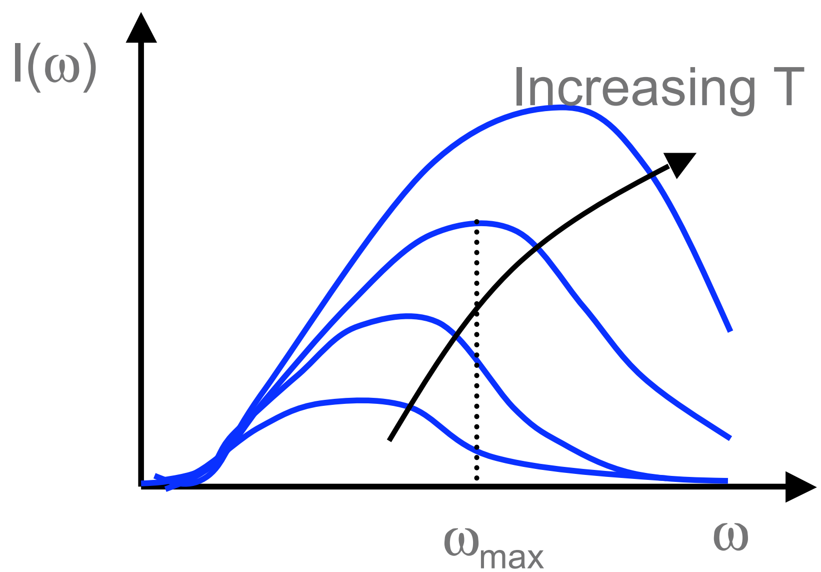


Heat Conduction in Non-Metals





Blackbody Phonon Radiation



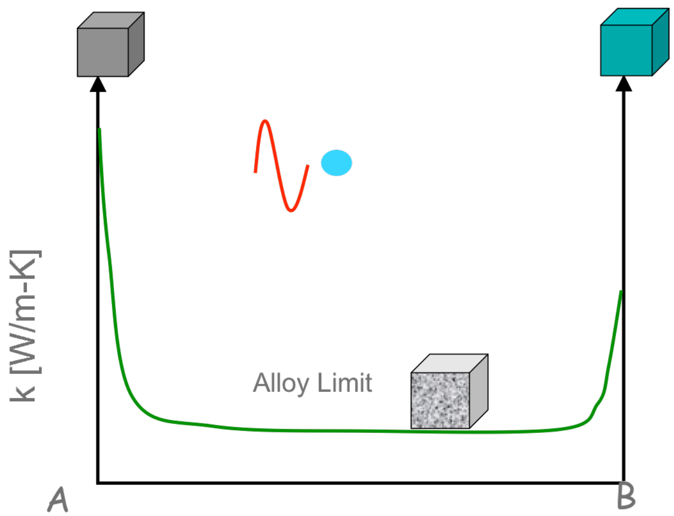
$$\omega_{max} \approx \frac{3k_B}{\hbar} T$$

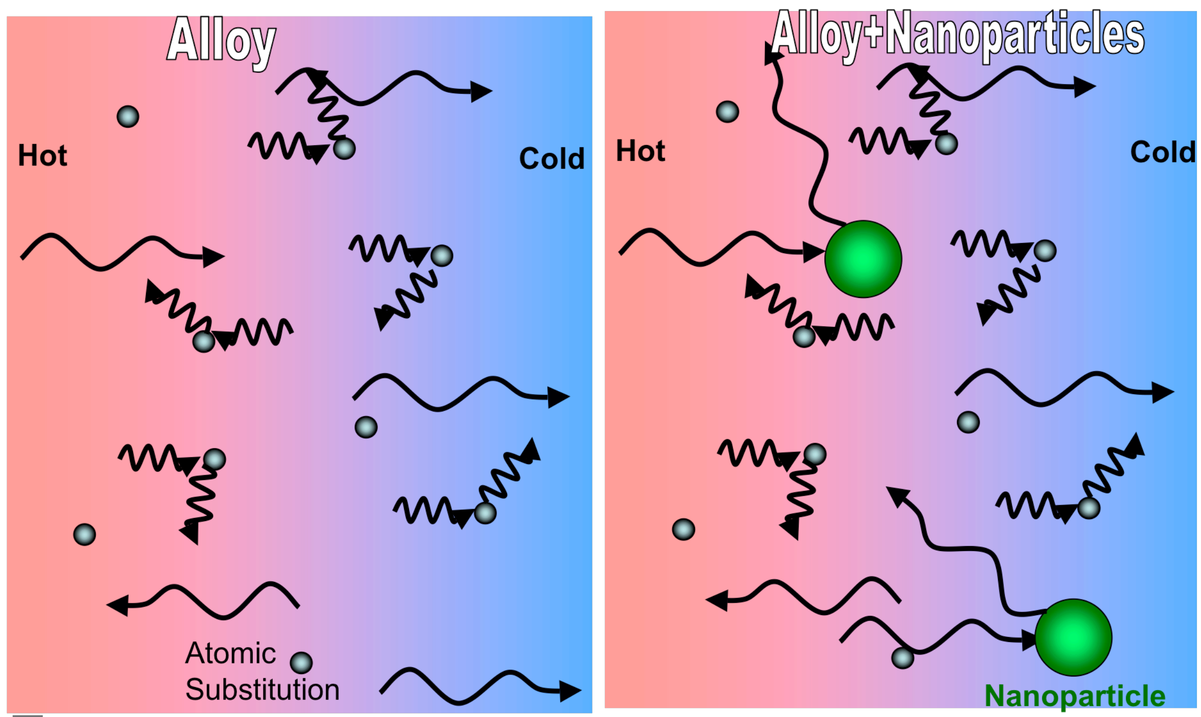
$$\lambda_{max} T \approx \frac{hc}{3k_B}$$

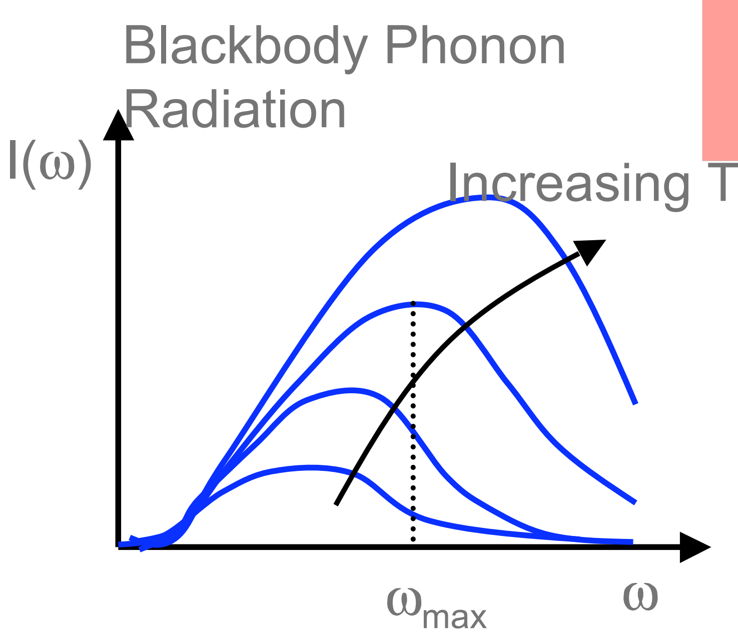
$$c_{light} = 3\times10^8\ m/s$$

$$c_{sound} \approx 3-10\times10^3\ m/s$$

Beating the Alloy Limit in Thermal Conductivity

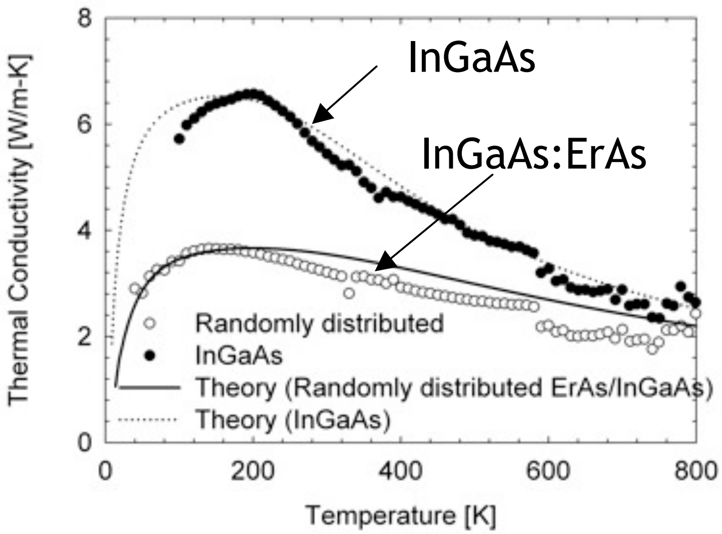


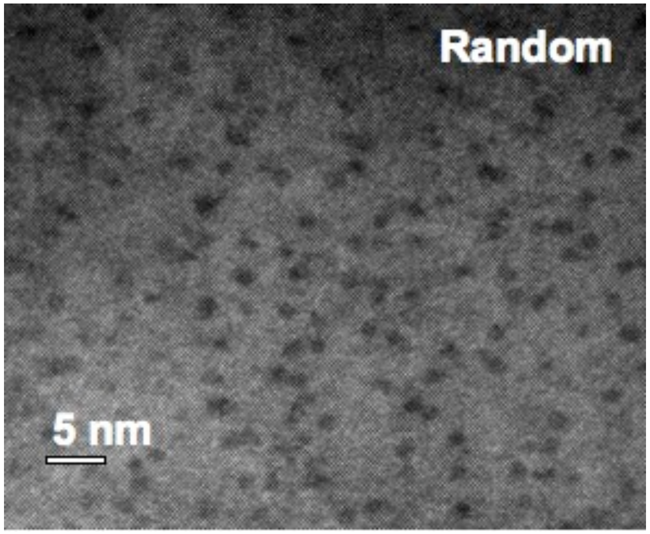


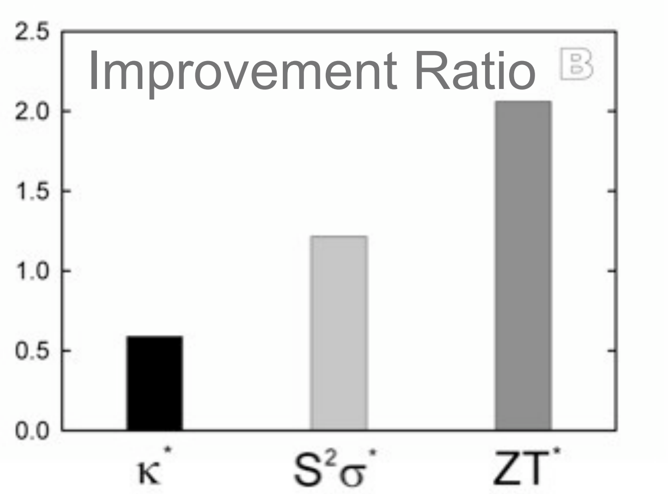


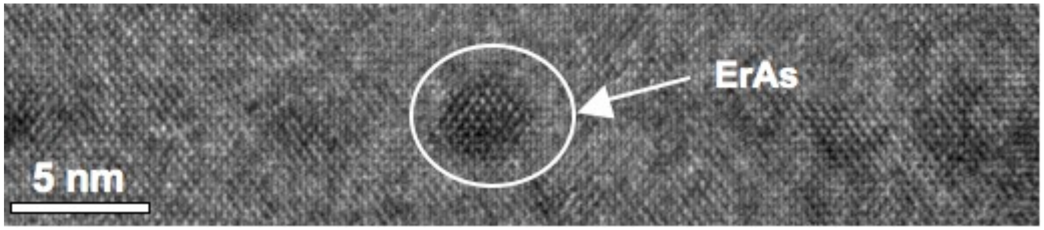
$$C_{sc} \propto \frac{d^6}{\lambda^4}$$

Thermal Conductivity of InGaAs:ErAs









Kim, Zide, Gossard, Klenov, Stemmer, Shakouri, Majumdar, *Phys. Rev. Lett.* (2006)

Criteria for Thermoelectric Materials

Electronic

1. Large density of states near Fermi level
2. Large gradient of density of states near the Fermi level: large effective mass semiconductors; heterostructures
3. High carrier mobility

Thermal

1. Low phonon group velocity: Heavy elements
2. Phonon scattering: Alloying, embedded nanoparticles,nanowires
3. Phonon filtering: heterostructures

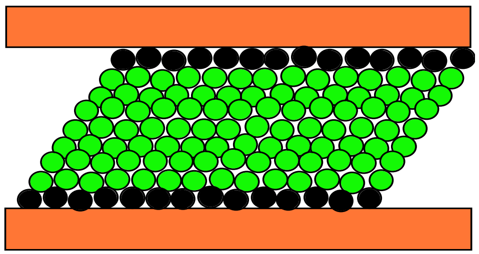
Outline

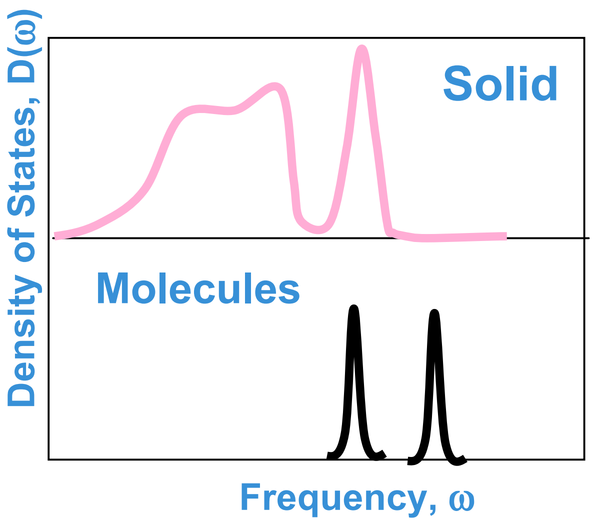
- Background and History
- State of the Art
- Program Thrusts
  - Molecules (collaboration with Rachel Segalman)
  - Nanowires
  - Nanostructured Bulk Materials
- Summary

Why Molecular Thermoelectrics?

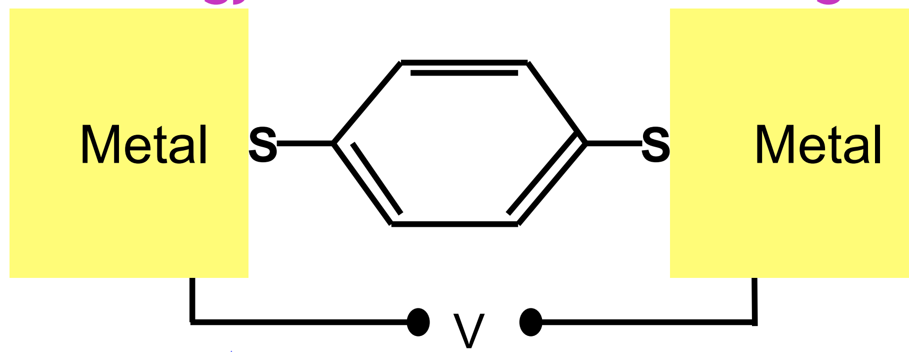
Large Thermal Impedance By Phonon Filtering

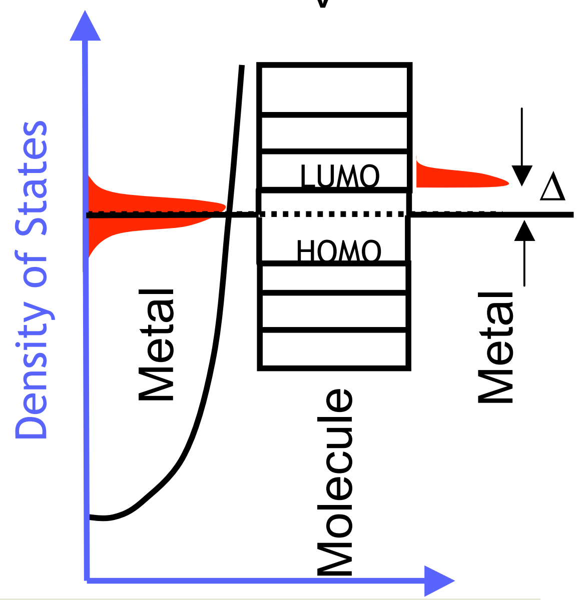
Molecular Heterostructures





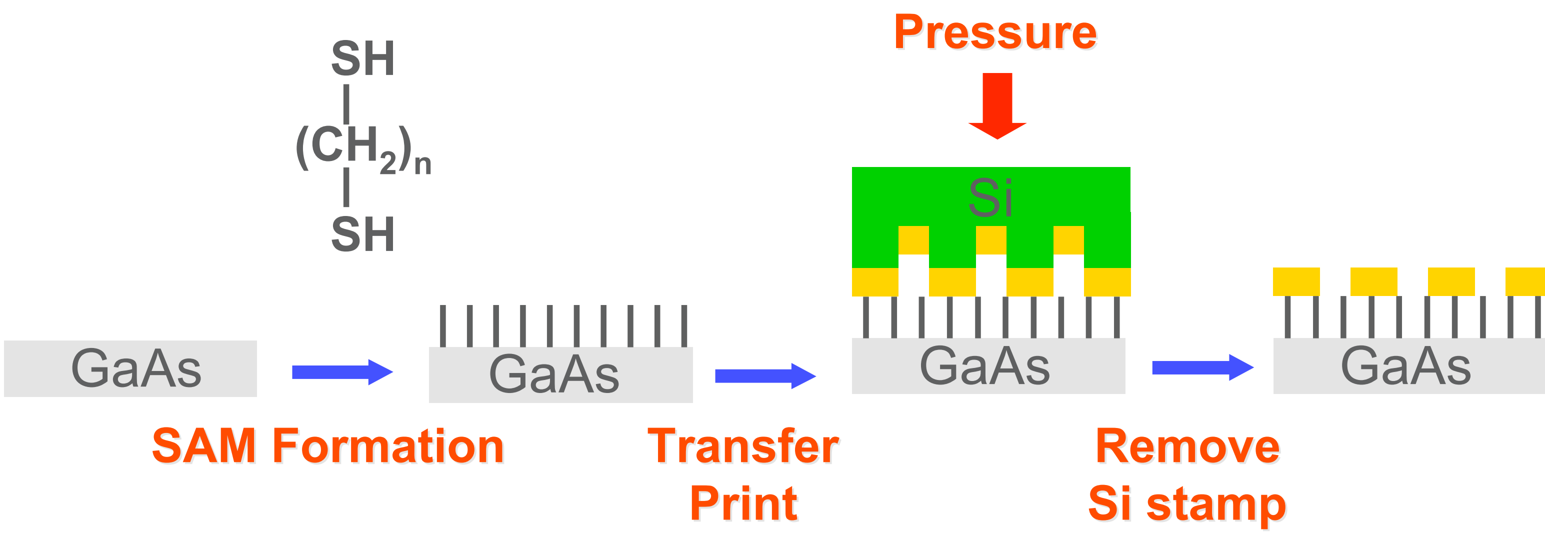
Potentially High Power Factor by Energy-Based Carrier Filtering



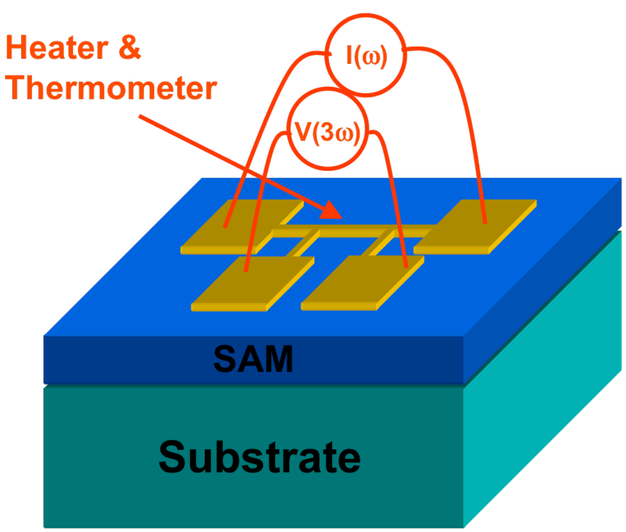


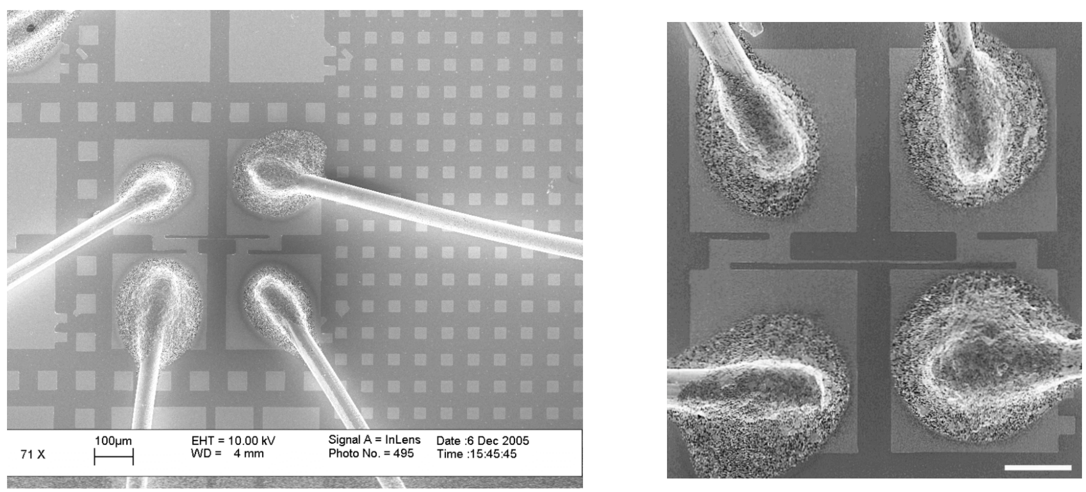
First measurement of thermal conductance of molecules
First measurement of thermopower of molecules

Preparation of Molecular Interfaces



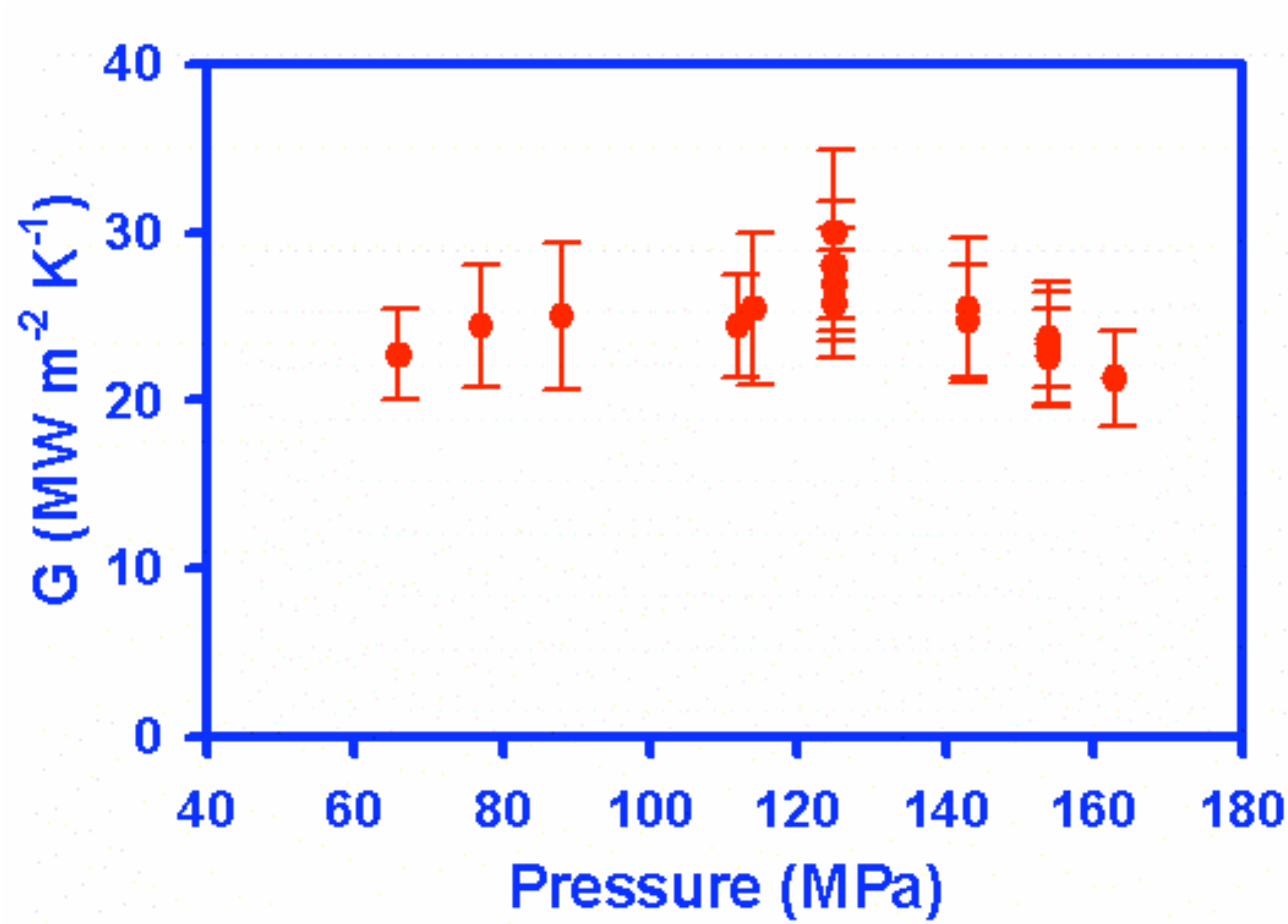
Loo et al., *J.Vac. Sci. Technol. B* **20**, 2853 (2002)

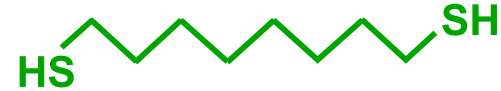




100 microns

Effect of Fabrication Pressure

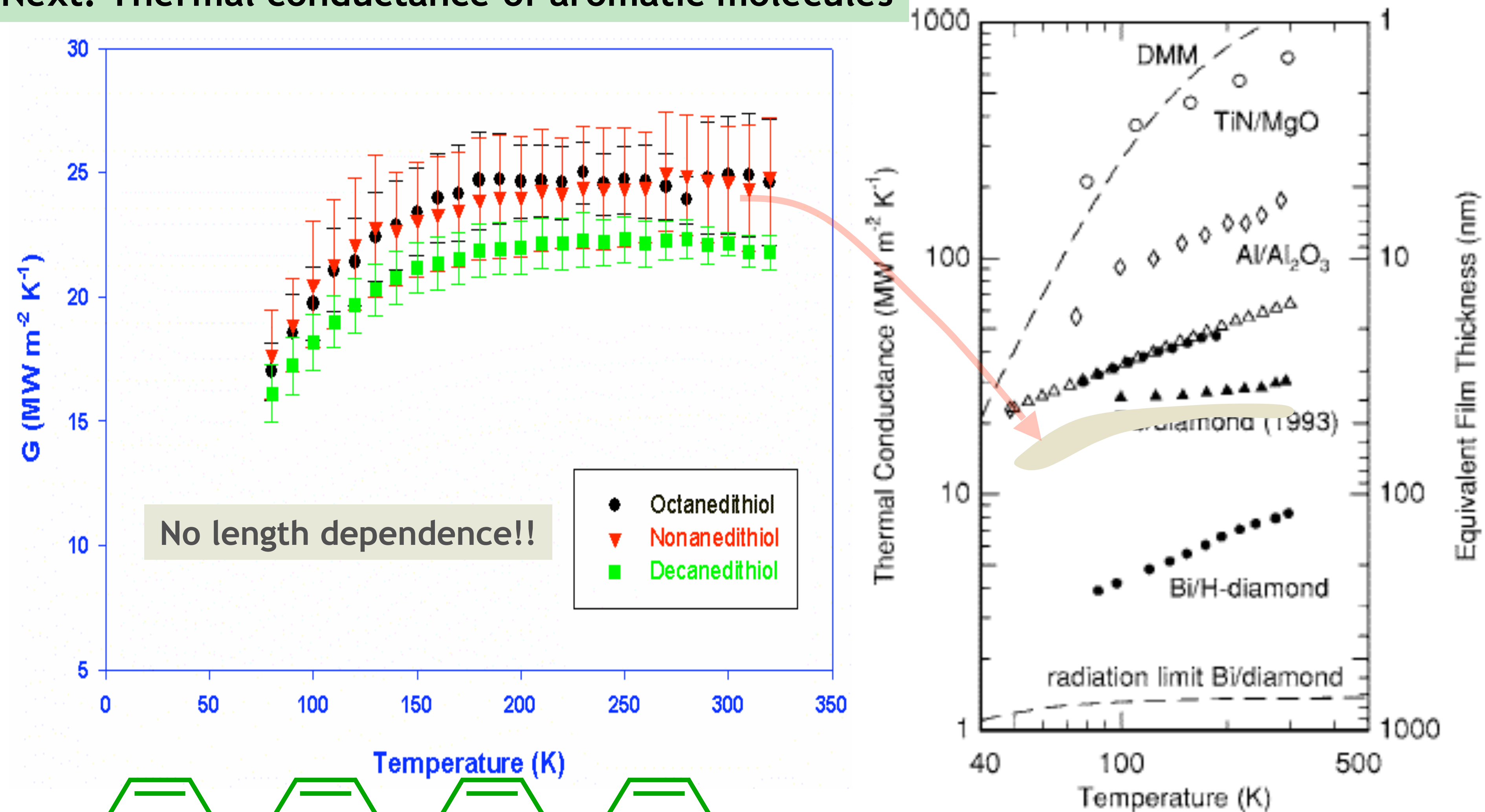


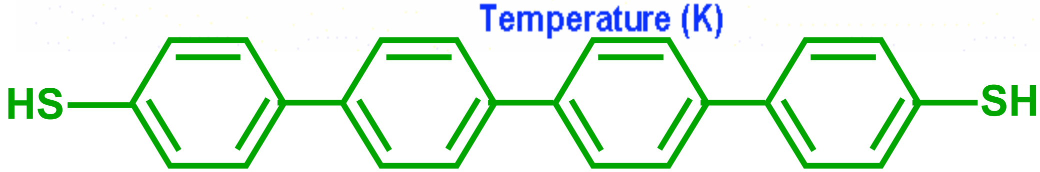


Wang, Segalman, Majumdar, *Appl. Phys. Lett.* (2006)

Thermal Conductance of Molecular Interfaces

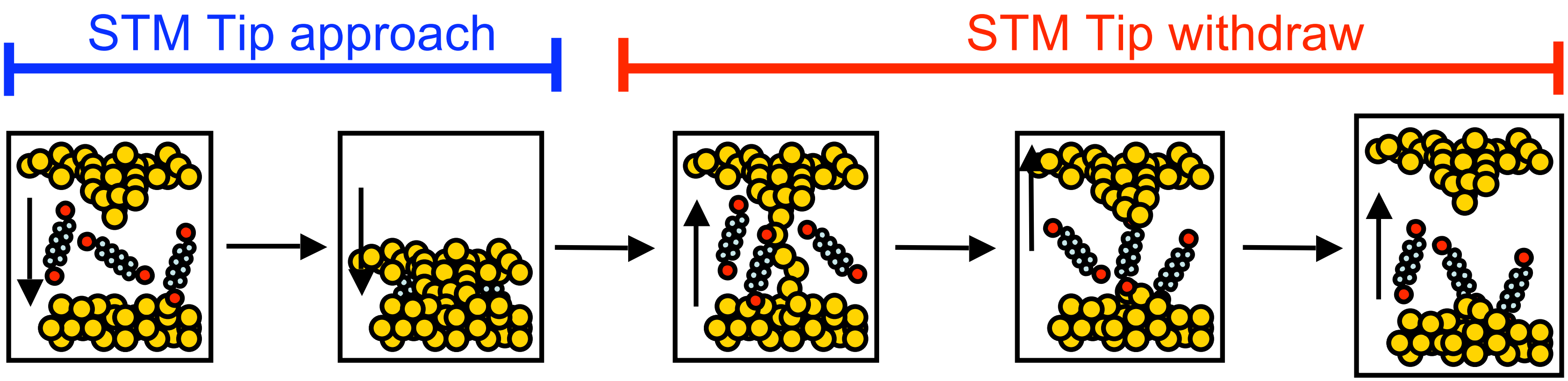
Next: Thermal conductance of aromatic molecules





Lyeo, Cahill, Phys. Rev. B. **74**, 144301 (2006)

Electrical Transport in Single Molecules

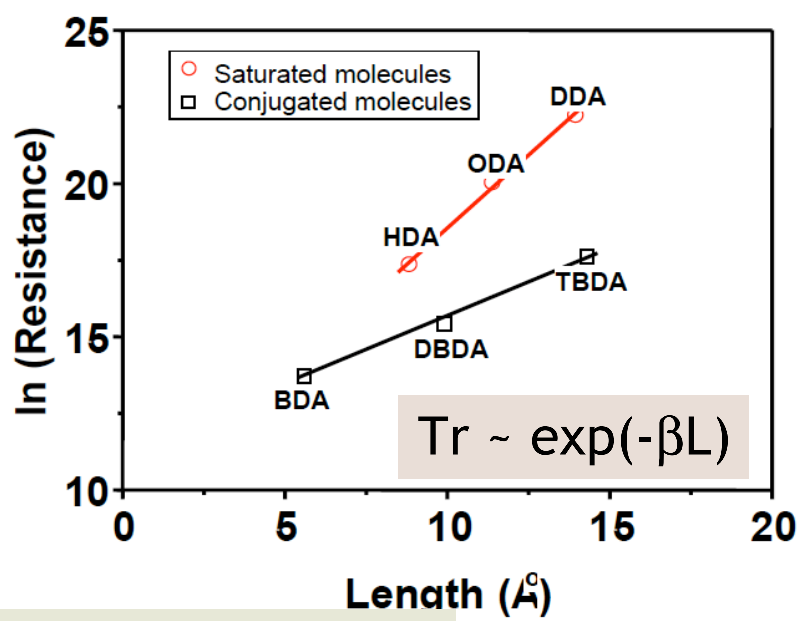


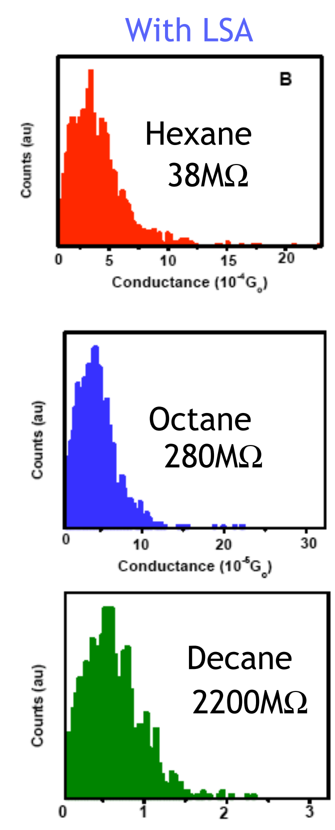
Tip speed: 2 – 40 nm/s

$$I = \frac{2e^2}{h}\left[\int \tau(E)\left(\frac{\partial F}{\partial E}\right) dE\right] V$$

Conductance

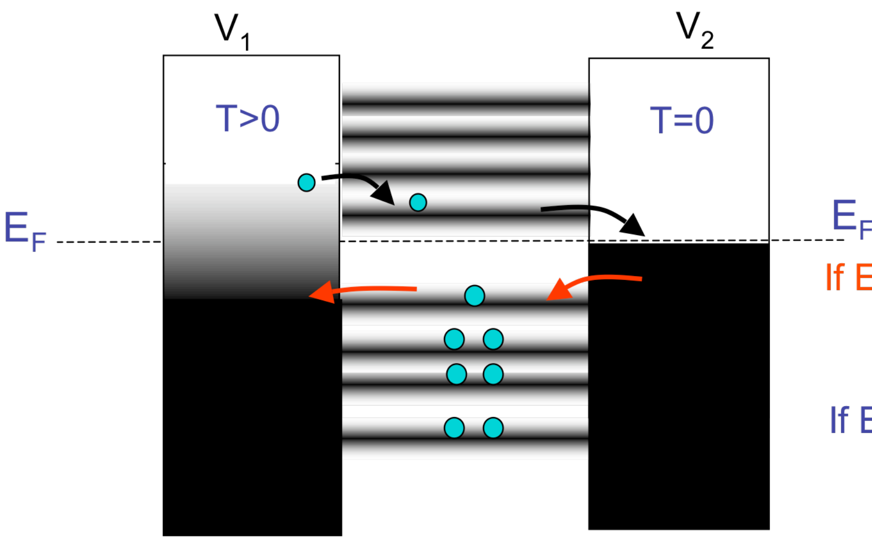
$G_{mol} = Tr.G_o$





Jang, Reddy, Majumdar, Segalman, *Nano Letters* (2006)

Thermopower of Molecular Junctions

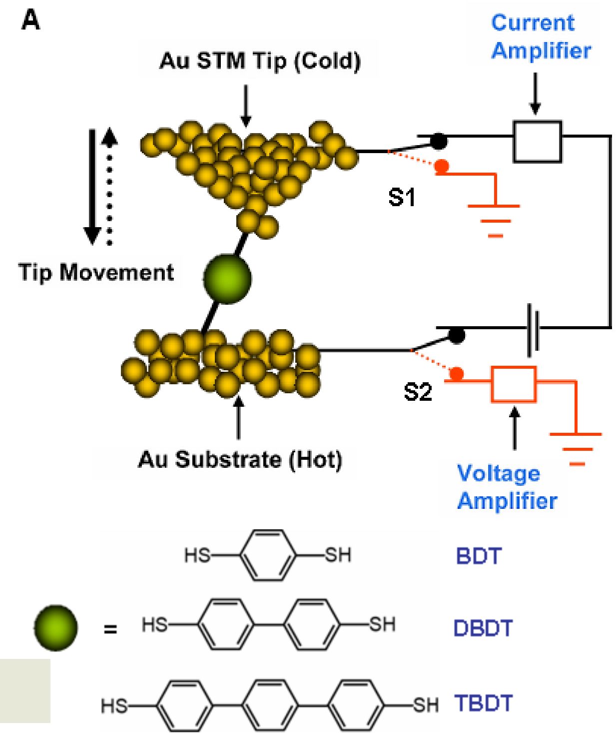


If E_F close to LUMO

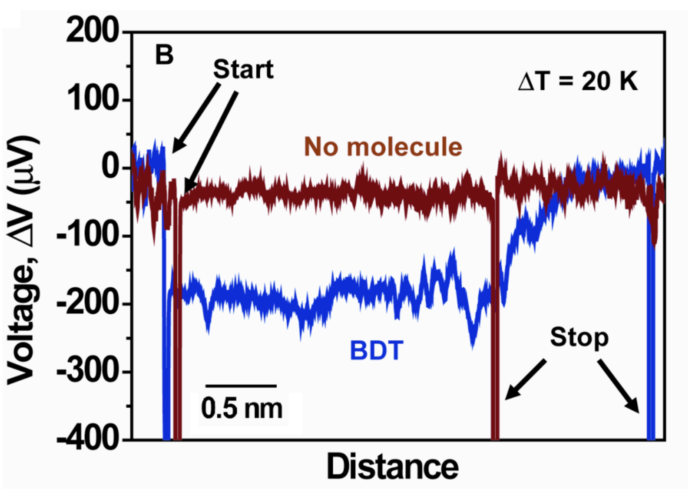
$V_1 > V_2$

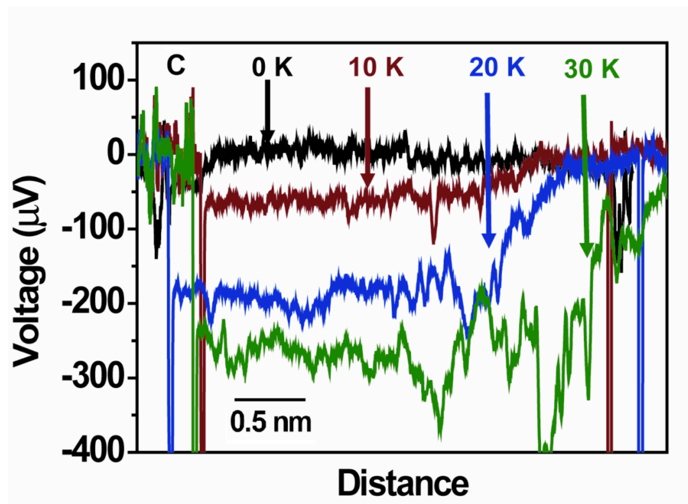
If E_F close to HOMO

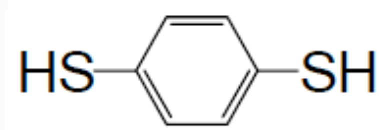
$V_1 < V_2$



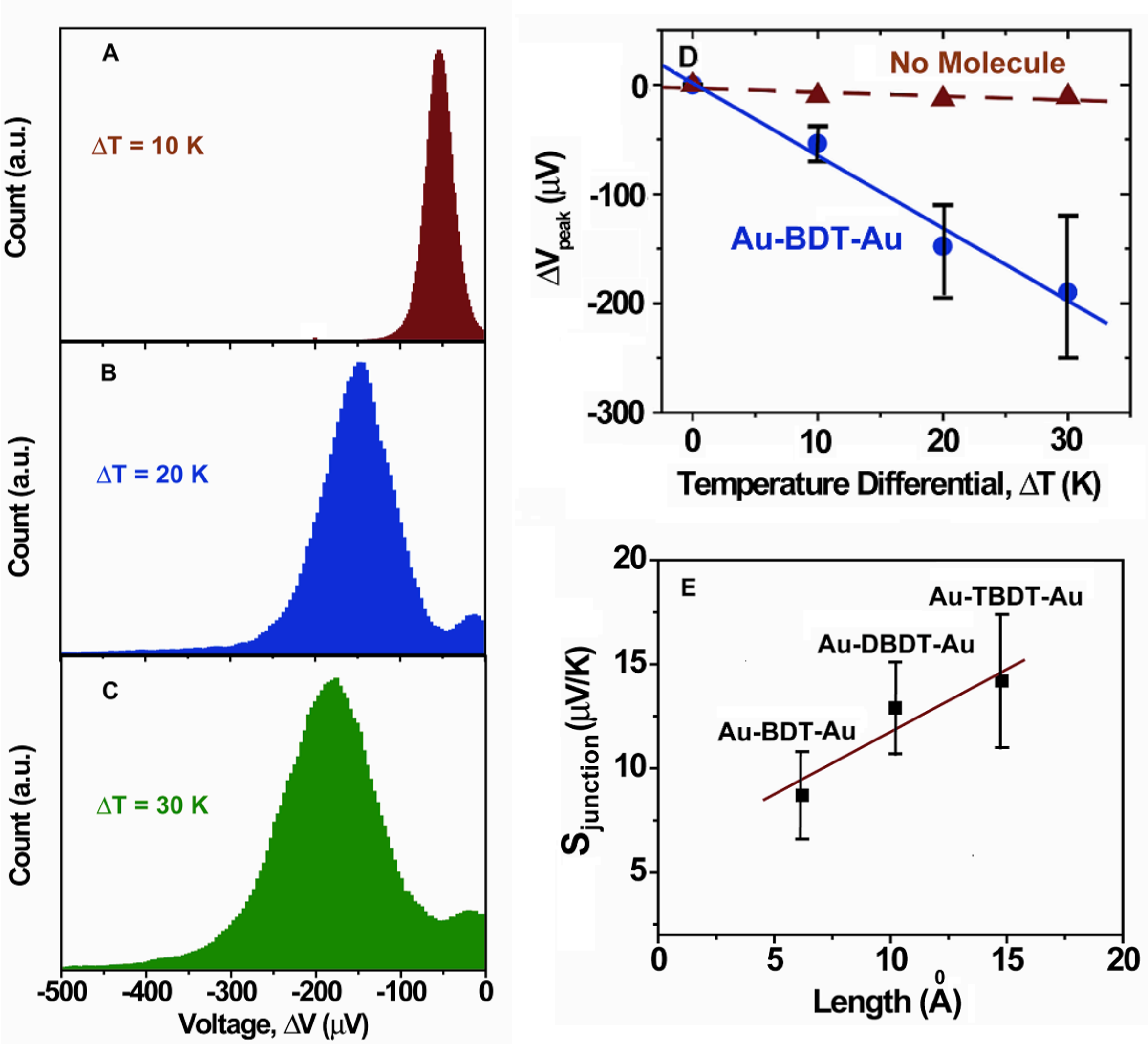
Reddy, Jang, Segalman, Majumdar, *Science* (2007)





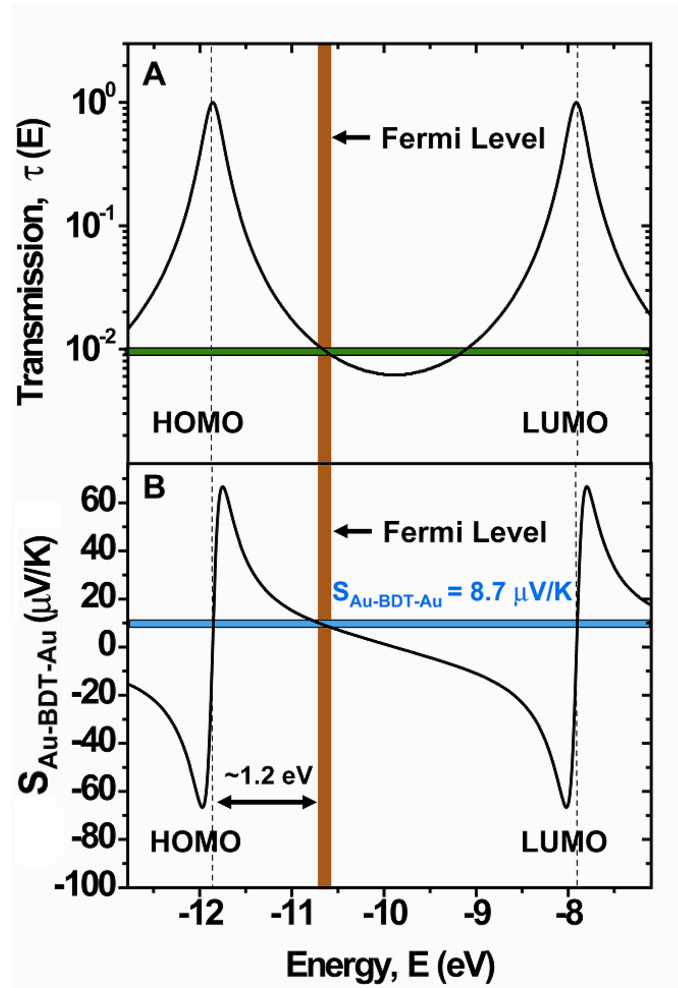


Thermopower of Molecular Junctions



From >2000 consecutive measurements

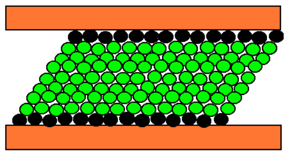
$$S = \frac{V}{\Delta T} = -\frac{\pi^2 \kappa_B^2 T}{3e}\left(\frac{1}{\tau(E)}\frac{\partial \tau(E)}{\partial E}\right)_{E=E_f}$$

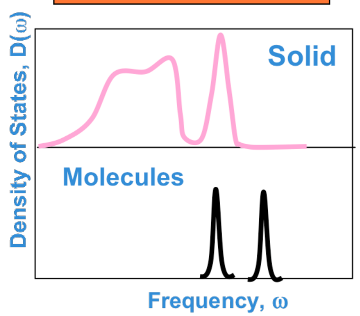


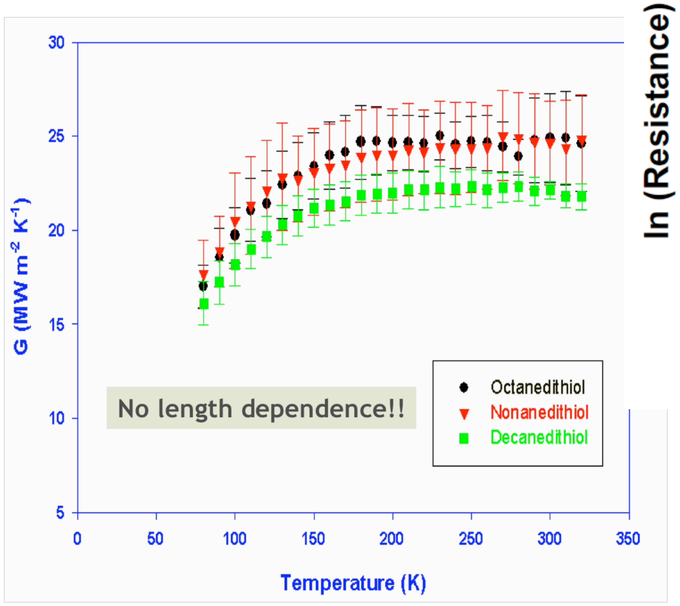
Paulsson & Datta, *PRB* (2003)

Quick Summary

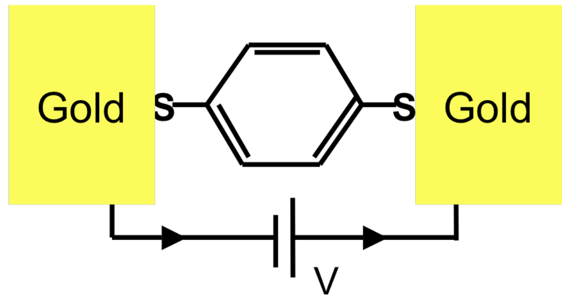
Thermal Conductance

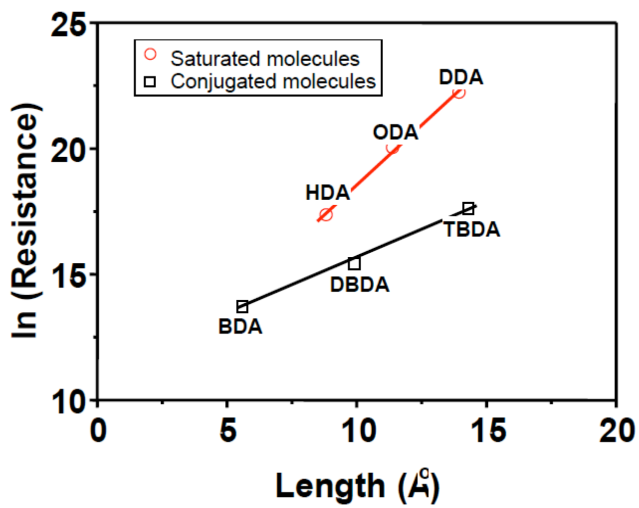




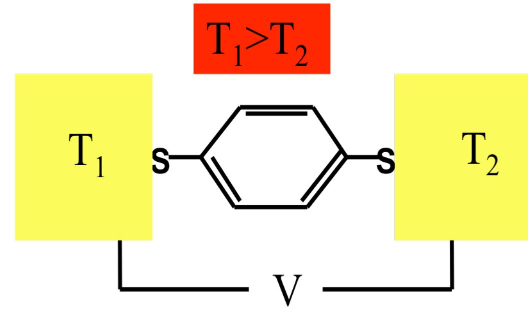


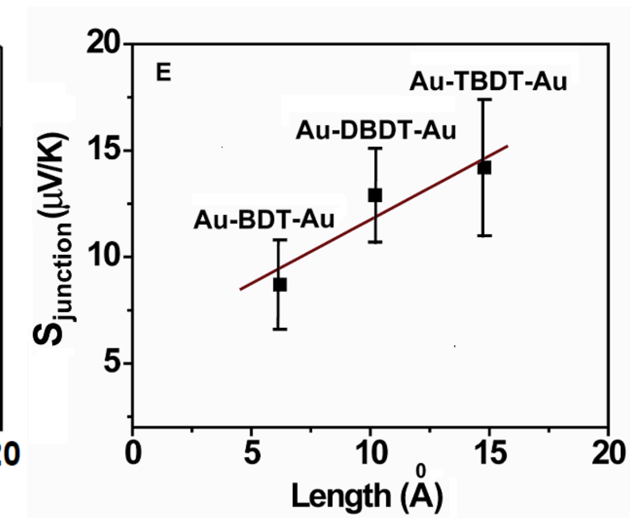
Electrical Conductance





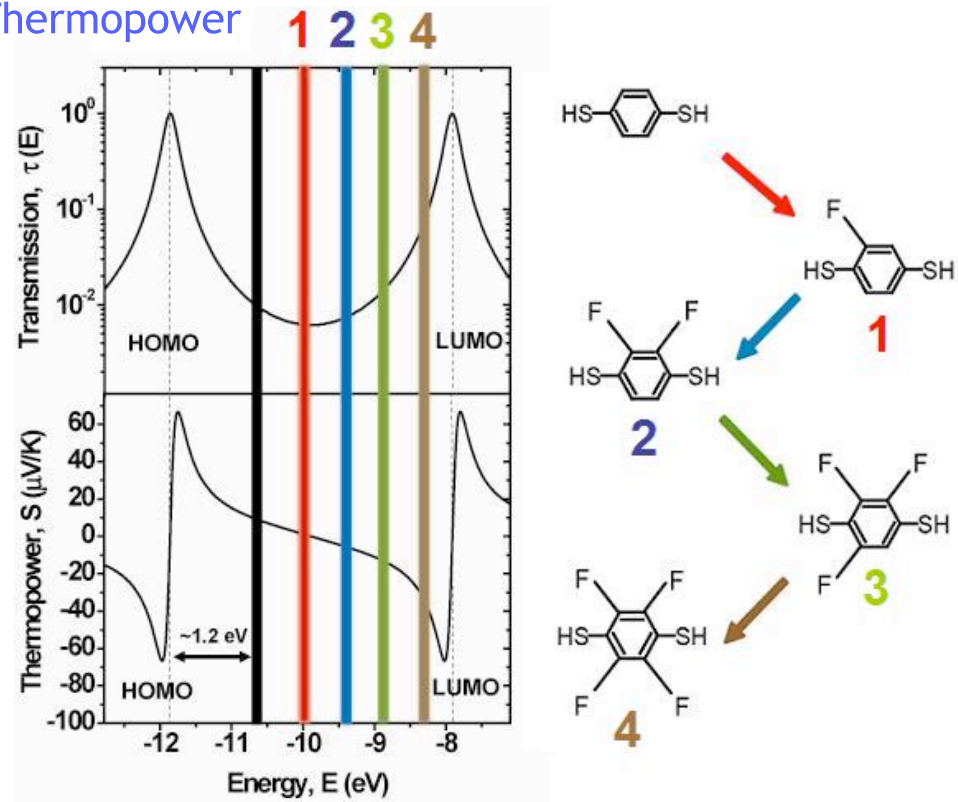
Thermopower





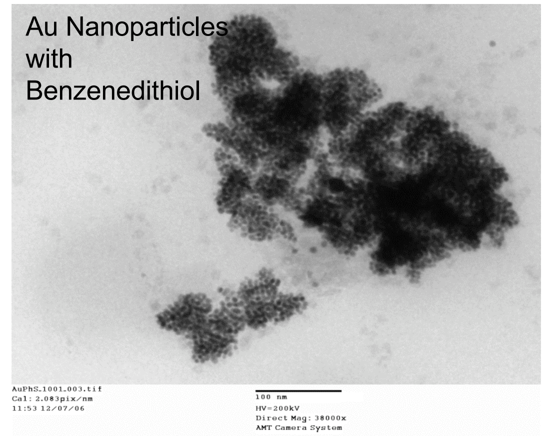
Future Work

Controlling Conductance & Thermopower



Collaboration: Don Tilley (CSD, LBNL)

Synthesizing Metal-Molecule Heterostructure Assemblies



Collaboration: Elena Shevchenko (Molecular Foundry, LBNL)

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- Background and History
- State of the Art
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  - Molecules
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  - Nanostructured Bulk Materials
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Criteria for Thermoelectric Materials

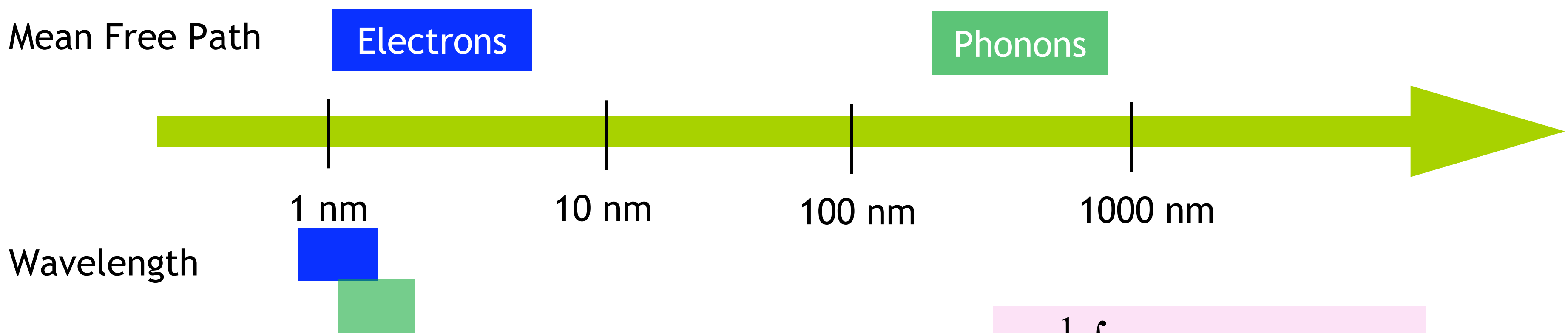
Electronic

1. Large density of states near Fermi level
2. Large gradient of density of states near the Fermi level: large effective mass semiconductors; metal-molecule heterostructures
3. High carrier mobility

Thermal

1. Low phonon group velocity: Heavy elements
2. Phonon scattering: Nanowires, alloying, embedded nanoparticles
3. Phonon filtering: Frequency-dependent scattering

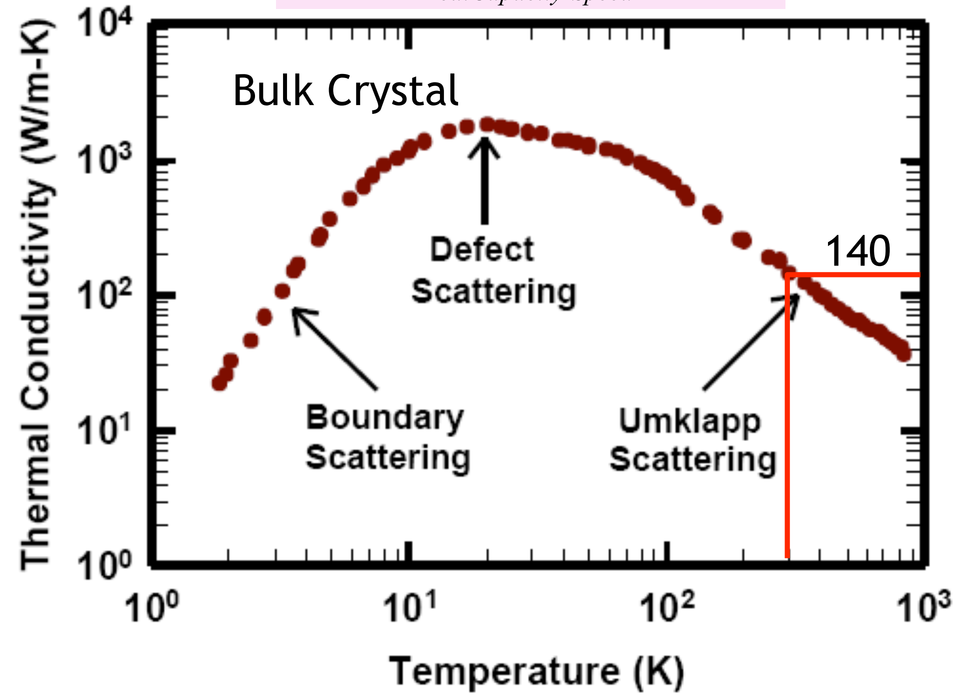
Transport Length Scales for Si @ 300 K



Temperature (K)	$(S^2\sigma T)_{max}$ (W/m-K)	Dopant density (cm^{-3})
500	0.65	1.02×10^{19}
400	0.46	5.72×10^{18}
300	0.28	2.85×10^{18}
200	0.14	8.11×10^{17}
100	0.0339	6.58×10^{16}

$$ZT_{bulk} = \frac{S^2\sigma T}{k} = \frac{0.28}{140} \approx 0.002$$

$$k = \frac{1}{3}\int \underbrace{C(\omega)}_{HeatCapacity}\ \underbrace{v(\omega)}_{Speed}\underbrace{\ell(\omega)}_{MFP}d\omega$$

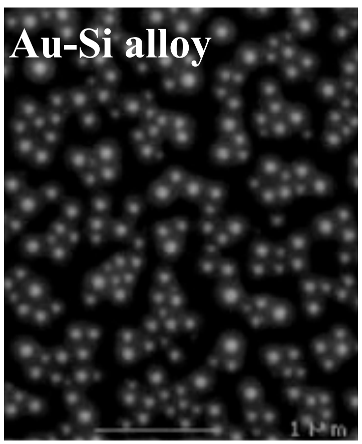


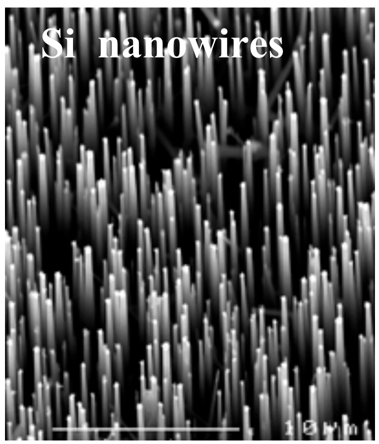
Nanowire Synthesis

Vapor-Liquid-Solid (VLS) Technique

Si/Au alloy **Phase Separation**

Elongation to nanowires



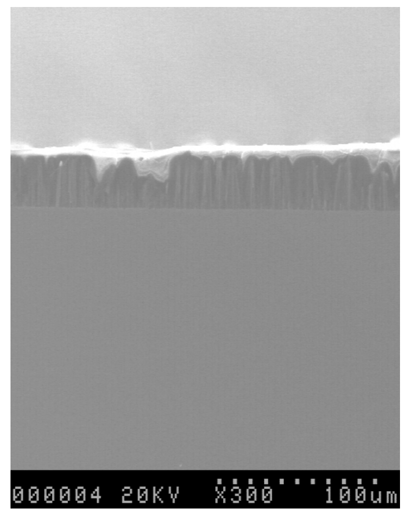


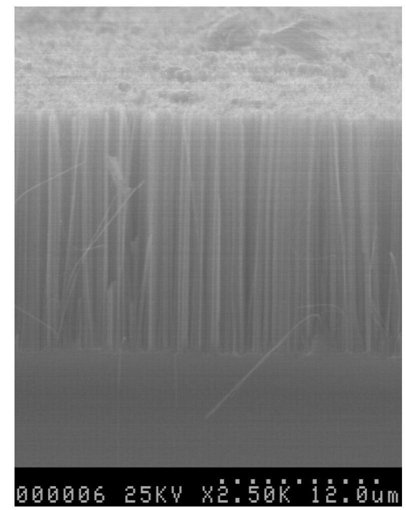
Wafer-Scale Wet Etching Process

Reduction: $Ag^+ + e^-$ -----> Ag $E^0_{red} = 0.7996$ V

Oxidation: $Si + 6F^-$ -----> $SiF_6^{2-} + 4e^-$ $E^0_{ox} = 1.24$ V

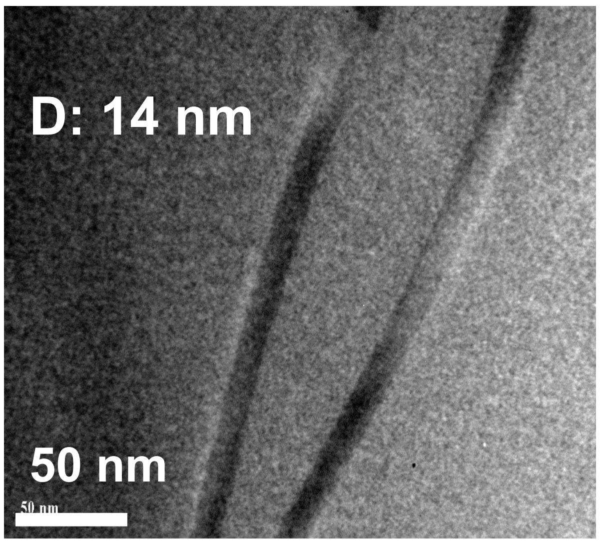
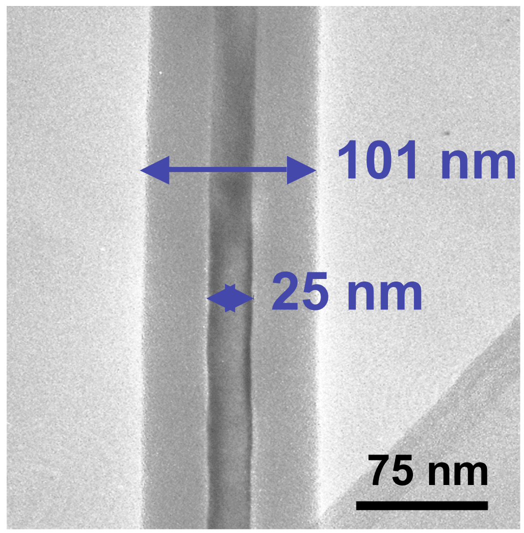
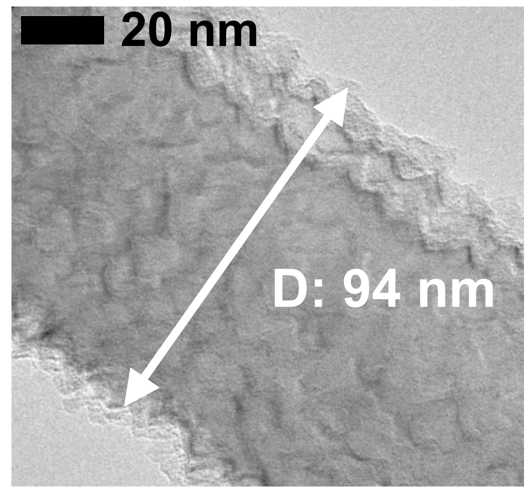
Etching of Si at 50 ^{0}C in 5M HF, 0.02M $AgNO_3$ for 1h



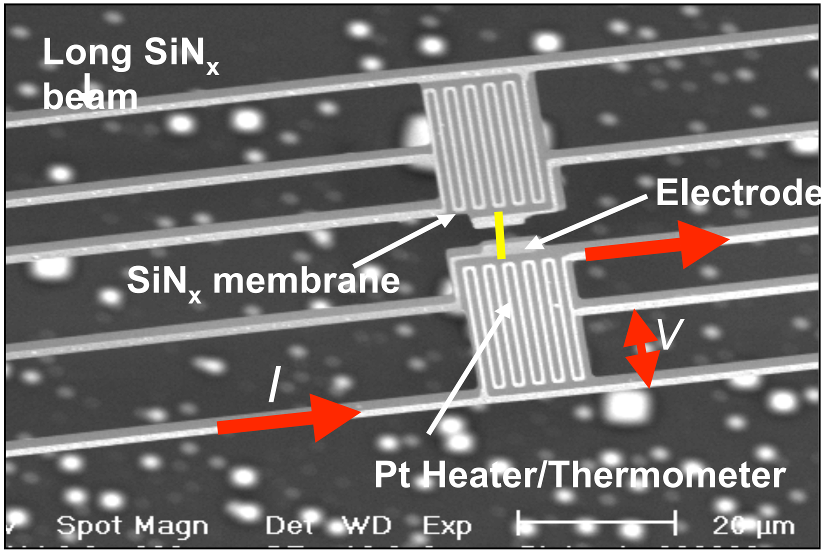


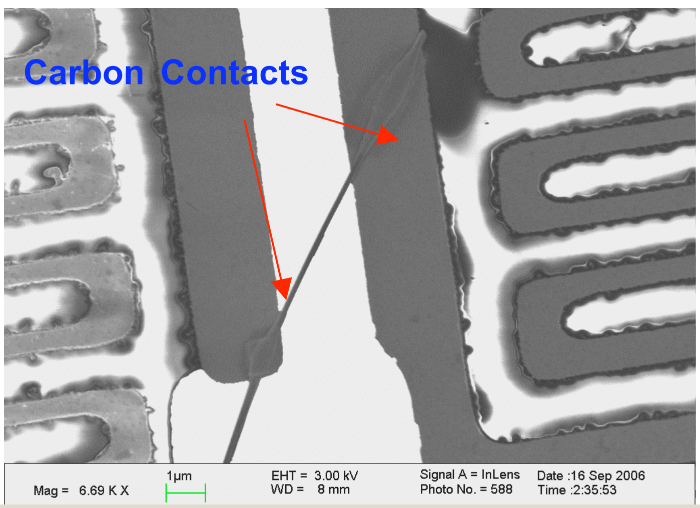
P-Si (100) (10^{15} cm^3) , 0.04M $AgNO_3$ 1h at 50 ^oC.

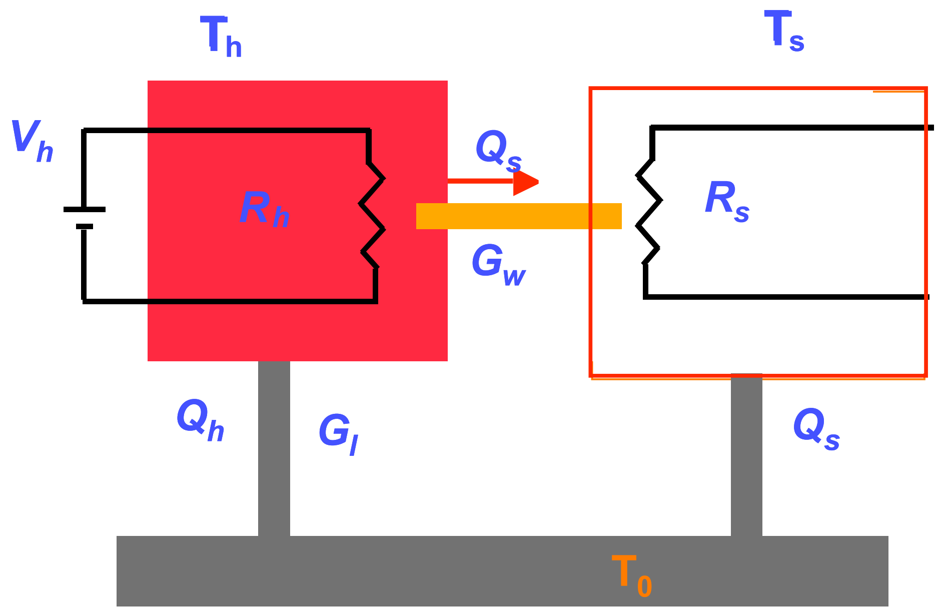
Si Nanowires

Thin SiNW		Rough SiNW
Bottom up: Vapor Liquid Solid (VLS) SiNW		Top down: Electrolessly Etched (EE) SiNW
As-grown	Size reduced by oxidation & etching	
		
10 - 20 nm, Uniform	20 - 40 nm, Tapered	30 - 100 nm, Rough surface

Measurement Technique





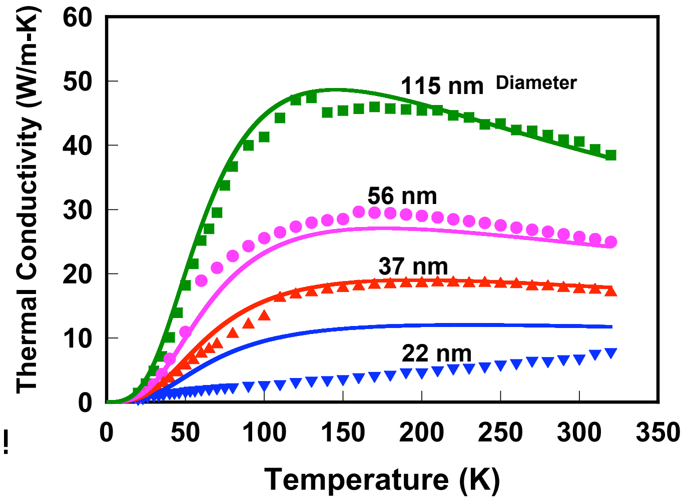


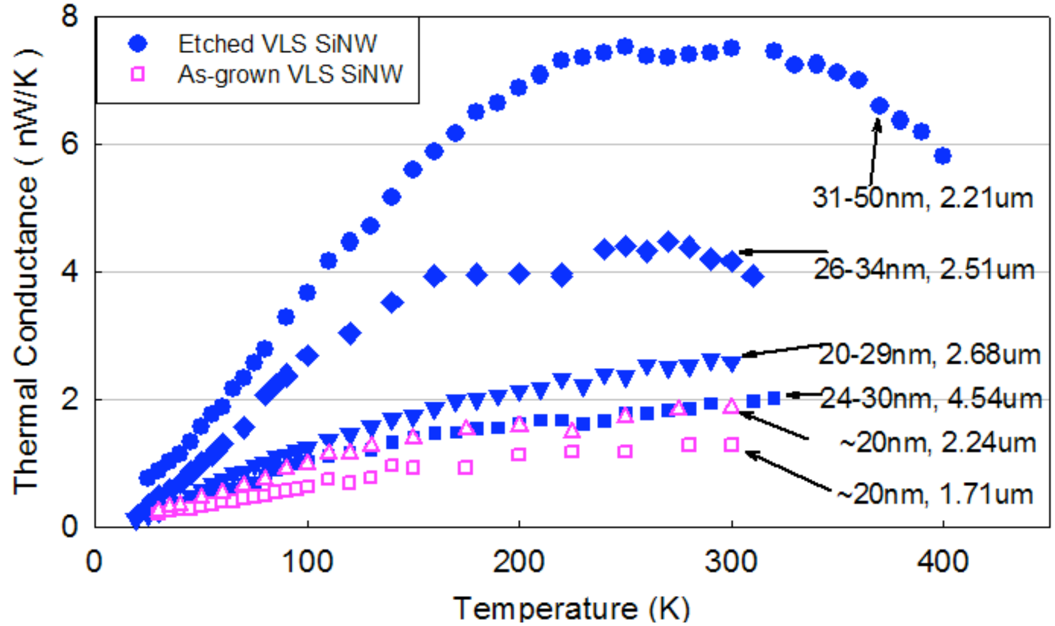
$$G_W = \frac{Q_s}{T_h - T_s}$$

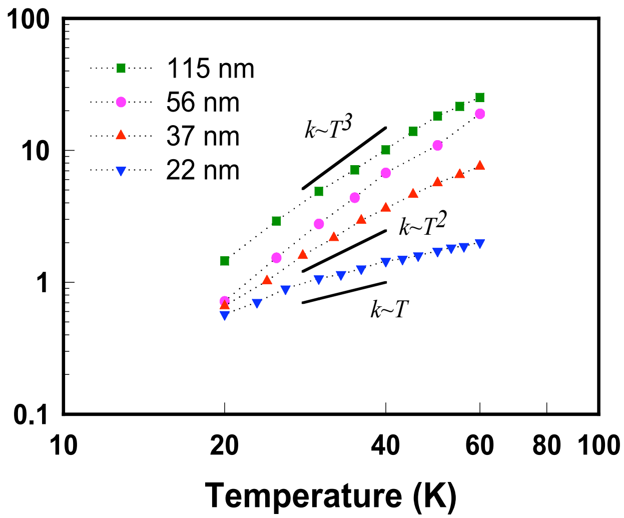
$$k_W = G_W \frac{l}{A}$$

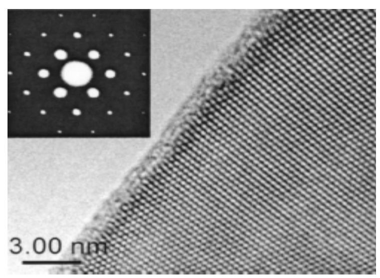
Kim, Shi, Majumdar, McEuen, *PRL* **87**, 215502 (2001);
Shi, Li, Yu, Jang, Kim, Yao, Kim, Majumdar, *JHT* **125**, 881 (2003)

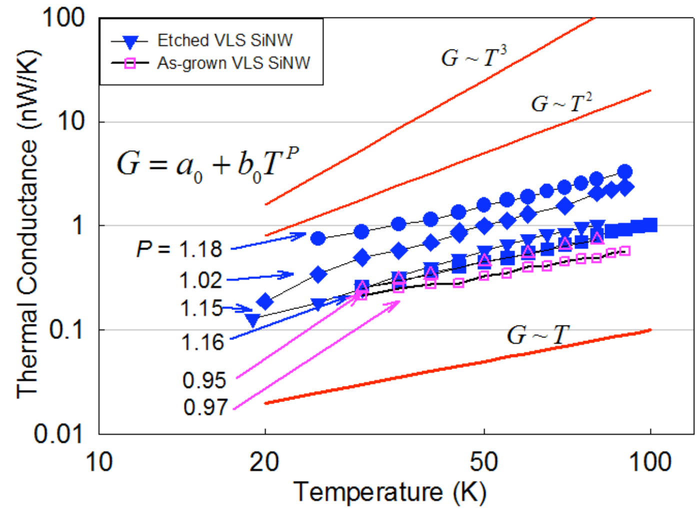
Thermal Transport in VLS SiNWs









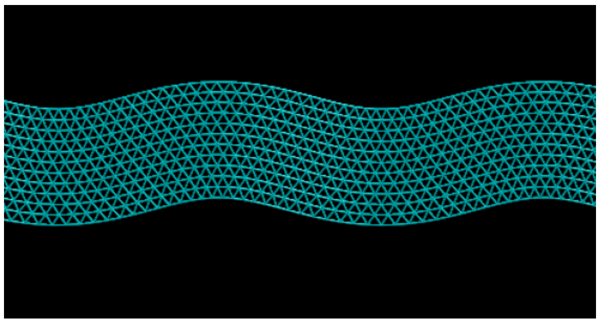


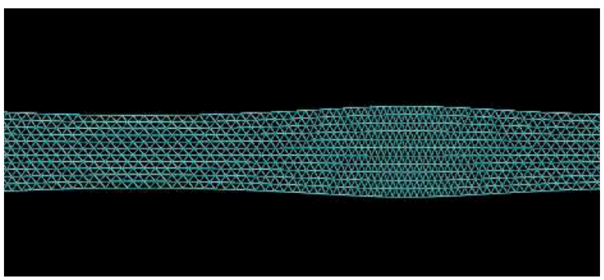
Li, …, Yang, Majumdar, APL (2003)

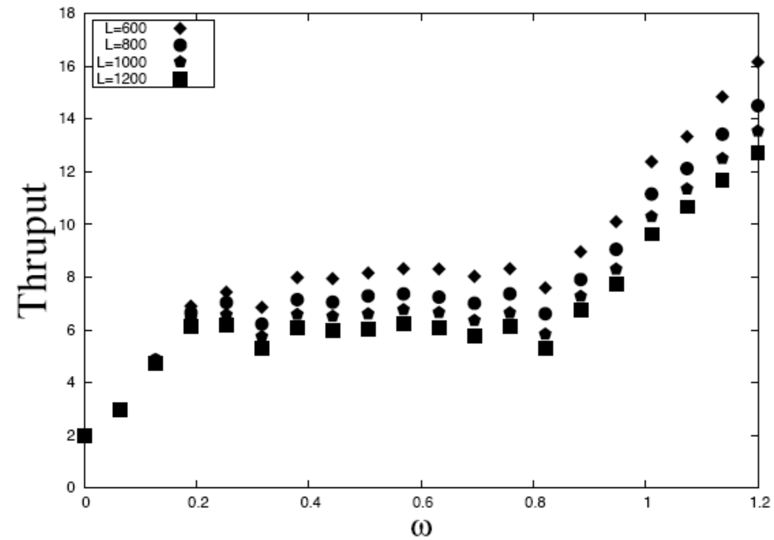
Theory

Landauer formula for the conductance:

$$G = \frac{1}{2\pi\hbar}\int_0^\infty \mathcal{T}(\omega)\frac{\hbar^3\omega^2}{k_B T^2}\frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T}-1)^2}\,d\omega$$







Atomistic simulation of entire wire with defects, to treat coherent multiple scattering

Observed linear behavior does not come from quantum of thermal conductance, but from quantum confinement and the location of scattering (at the boundary).

Future Direction

- Understanding phonon transport in sub-20 nm NWs and explore possibility of coherent scattering (e.g. localization)

- Reducing thermal conductivity of doped SiNW < 1 W/m-K

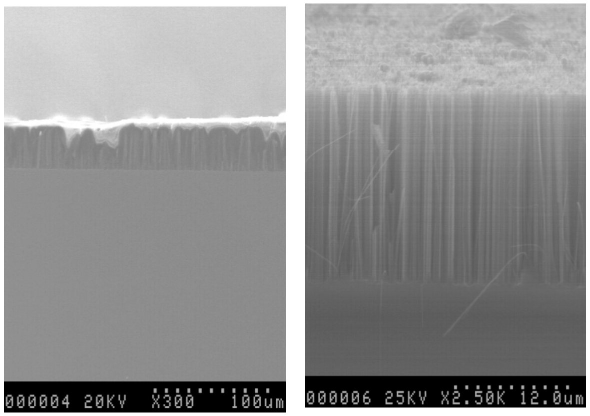
- Measuring S and σ of Si NW

Outline

- Background and History
- State of the Art
- Program Thrusts
  - Molecules
  - Nanowires
  - Nanostructured Bulk Materials
- Summary

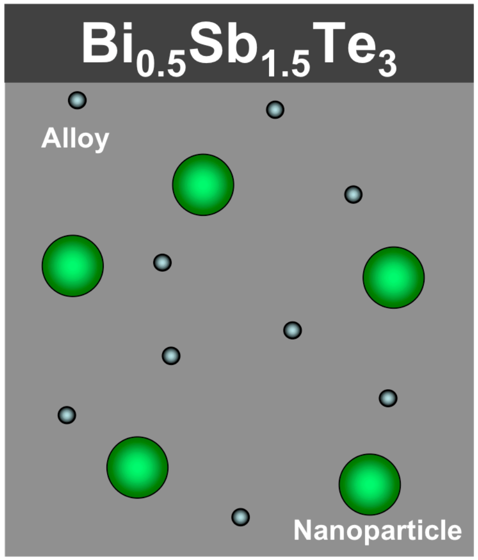
Bulk Nanostructures

Wafer-scale Nanowire Arrays

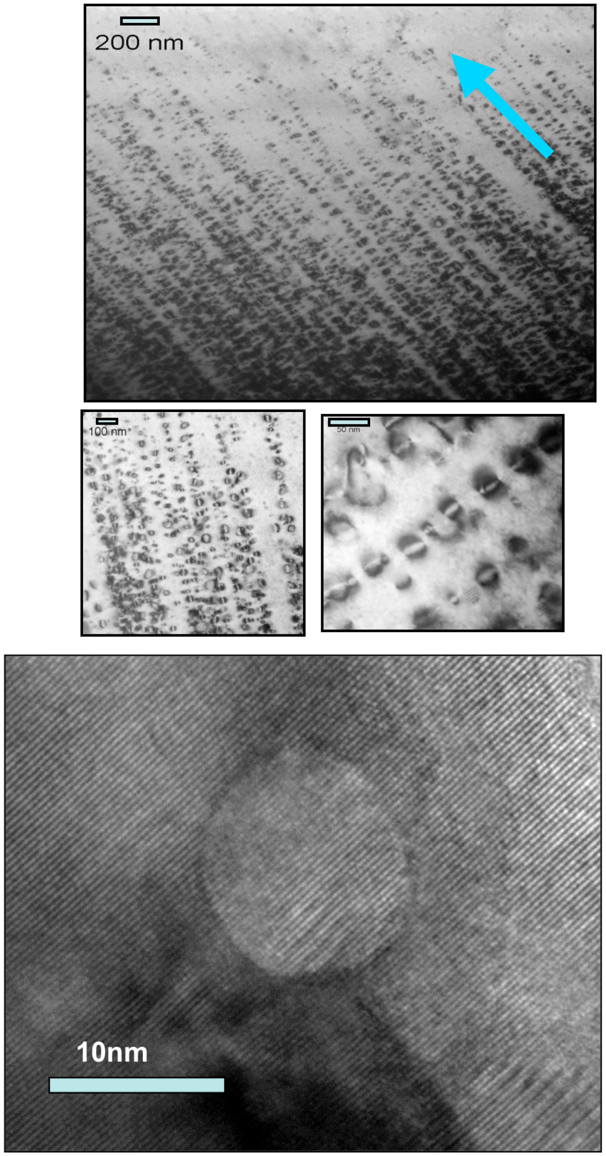


P-Si (100) (10^{15} cm^3) , 0.04M $AgNO_3$
1h at 50 ºC.

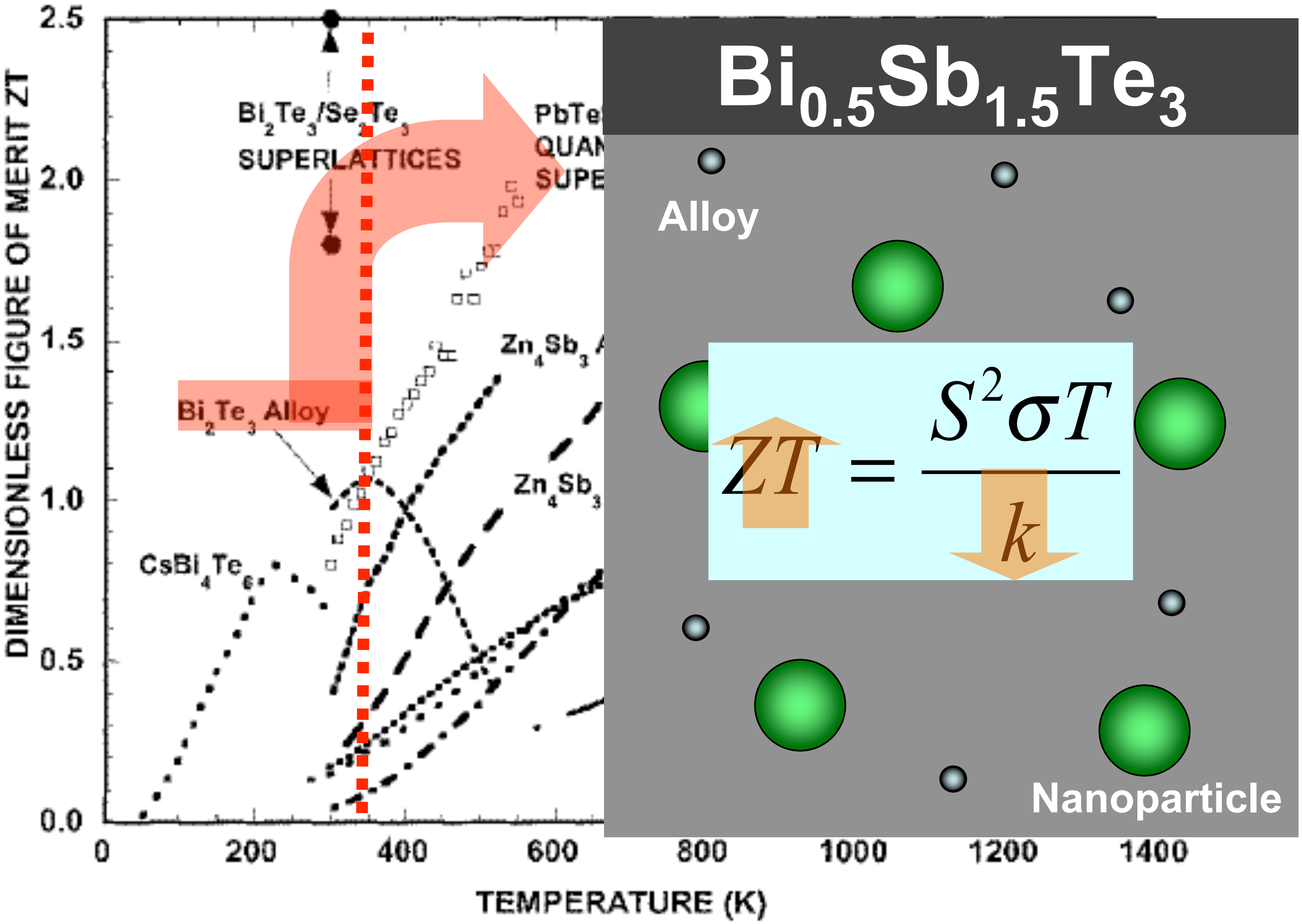
Sintered Nanoparticle Composite



Radiation Induced Nanostructure



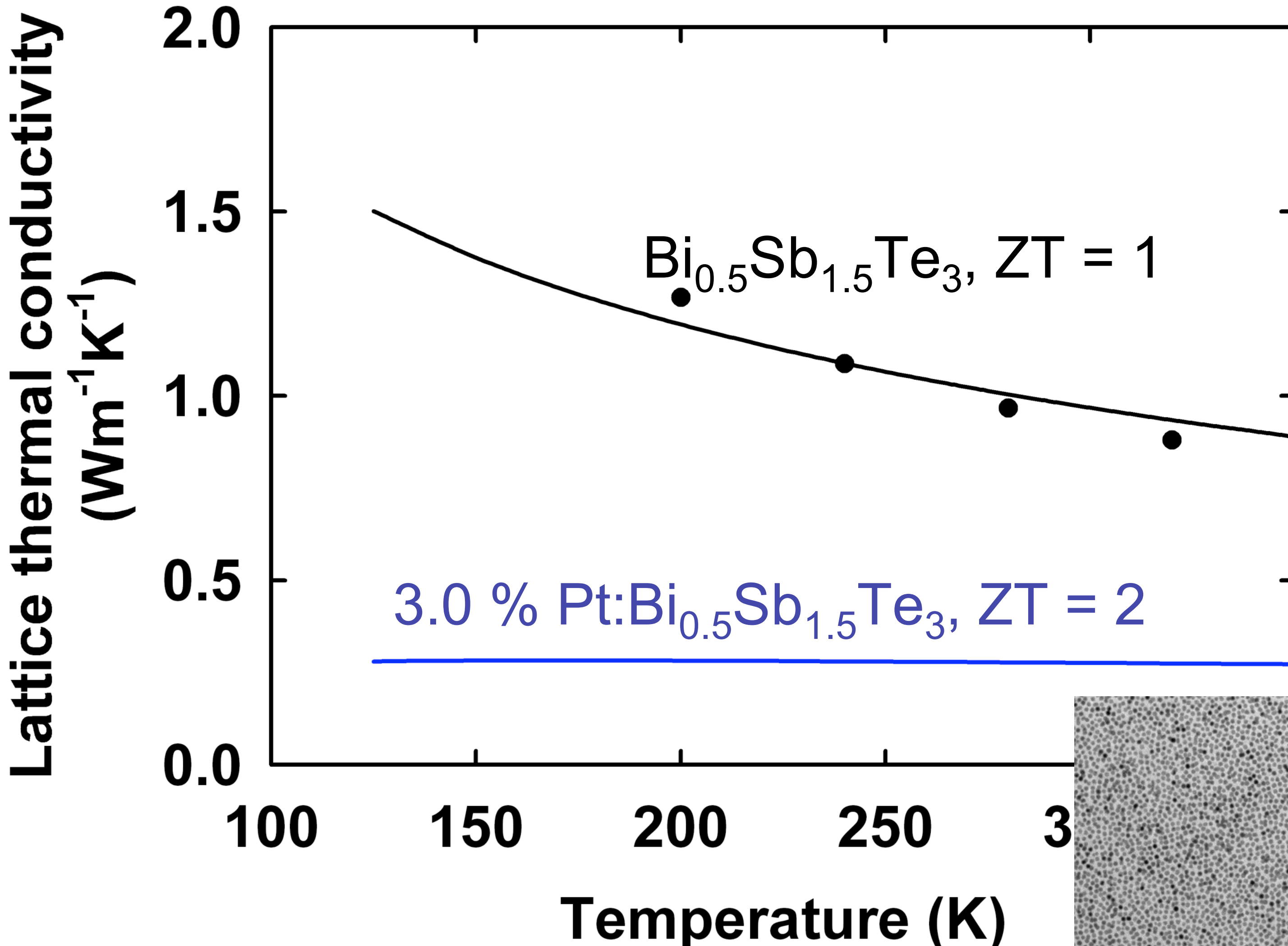
Bulk Nanoparticle-BiSbTe

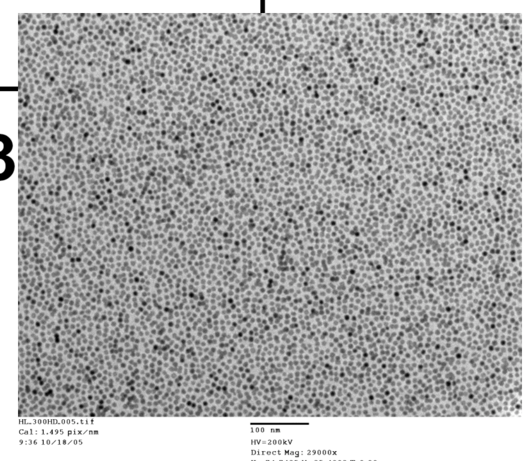


$$ZT = \frac{S^2 \sigma T}{k}$$

Chen et al., International Materials Reviews 48, 45 (2003)

Lattice TC of Pt:$Bi_{0.5}Sb_{1.5}Te_3$





Summary

- Molecular Thermoelectrics
  - First measurement of molecular monolayer thermal conductance
  - Last-step analysis of single molecule electrical conductance
  - First measurement of thermopower of molecular junctions
- Nanowires
  - Thermal conductance of sub-20 nm nanowires shows reduction beyond conventional theoretical predictions
  - It may be possible to reduce nanowire thermal conductivity below 1 W/m-K using surface nanostructuring
- Bulk Nanostructures
  - 3 different methods of synthesizing nanostructured bulk thermoelectric materials

Future Directions

- Molecular Thermoelectrics
  - Aromatics
  - Organometallics
  - Novel Metal-Molecule Heterostructures
  - Predictive modeling of molecular thermoelectrics
- Nanowire
  - Phonon transport in sub-20nm semiconductor wires
  - Thermal conductivity < 1 W/m-K by roughening & doping
  - Thermopower and electrical conductivity measurements
- Bulk Nanostructures
  - Impact of type of nanostructuring on ZT

Overall Concept