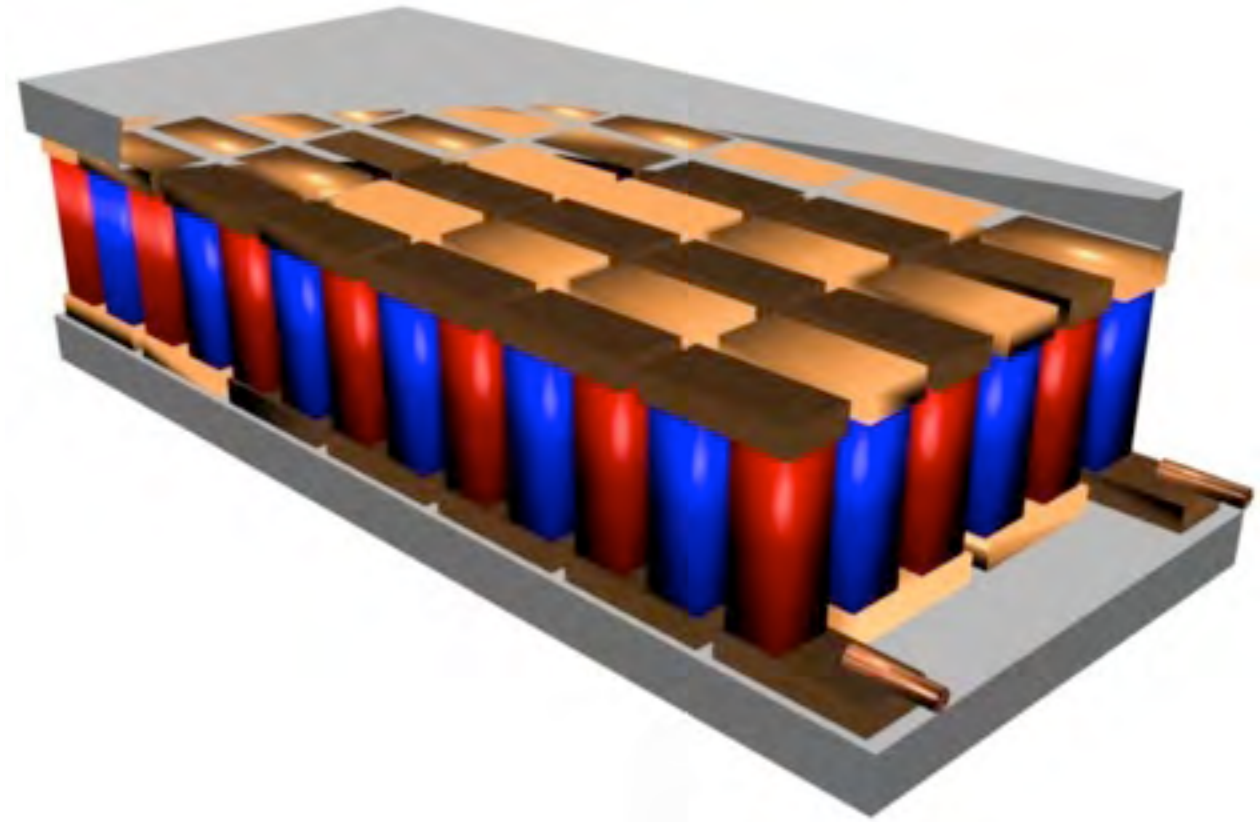
Thermoelectric Energy Harvesting



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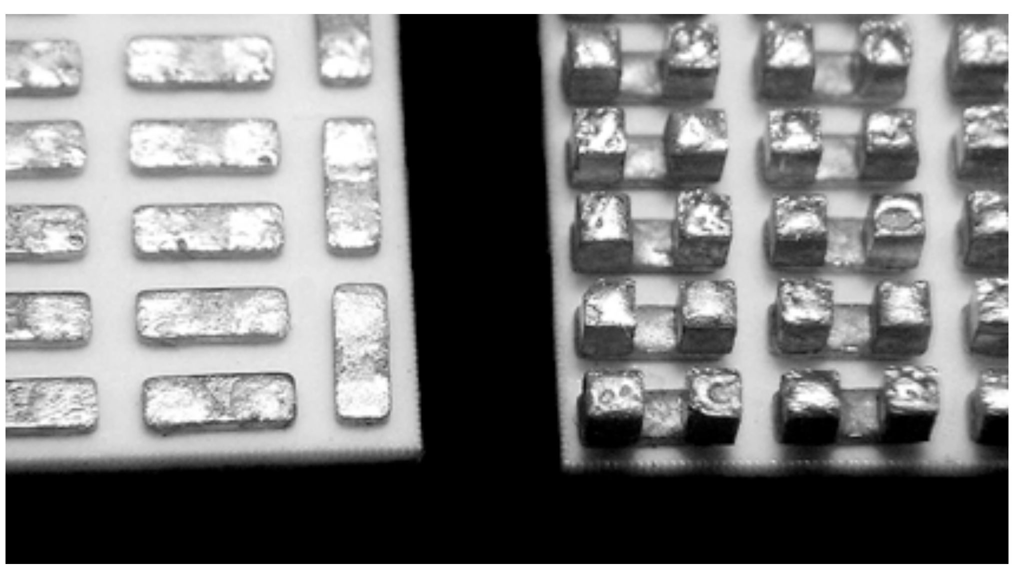


The University of Glasgow

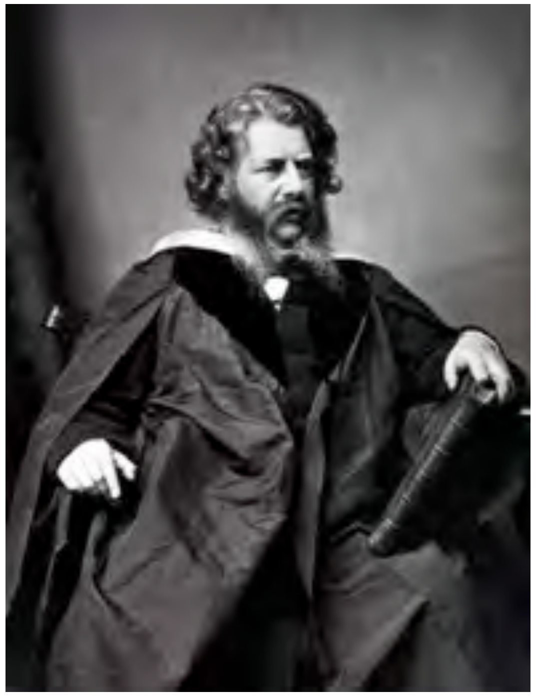
- Established in 1451
- 7 Nobel Laureates
- 16,500 undergraduates, 5,000 graduates and 5,000 adult students
- £130M research income pa

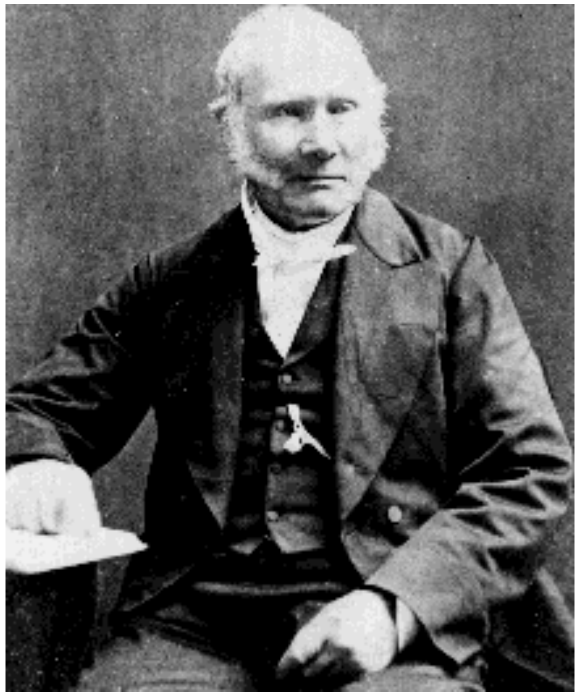
- 400 years in High Street
- Moved to Gilmorehill in 1870
- Neo-gothic buildings by Gilbert Scott

Famous Glasgow Scholars


William Thomson (Lord Kelvin)


James Watt


William John Macquorn Rankine


Rev Robert Stirling


Rev John Kerr


Joseph Black


John Logie Baird


Adam Smith

James Watt Nanofabrication Centre @Glasgow

Vistec VB6 & EBPG5

E-beam lithography

Süss MA6 optical lith

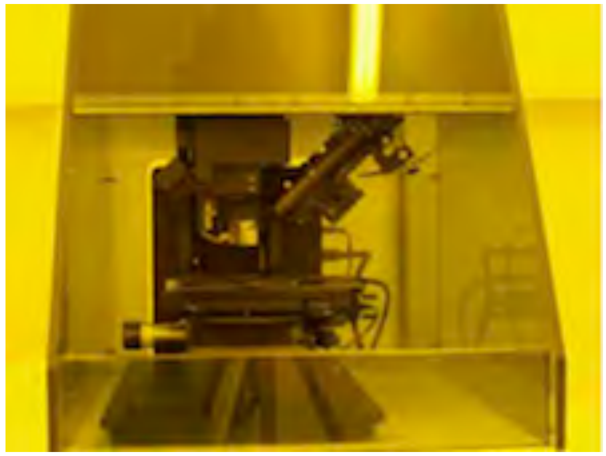
- 750 m^2 cleanroom - pseudo-industrial operation
- 18 technicians + 4 PhD technologists
- EPSRC III-V National Facility
- Processes include: MMICs, III-V, Si/SiGe/Ge, integrated photonics, metamaterials, MEMS (microfluidics)
- Commercial access through Kelvin NanoTechnology
- http://www.jwnc.gla.ac.uk

10 RIE / PECVD

5 Metal dep tools

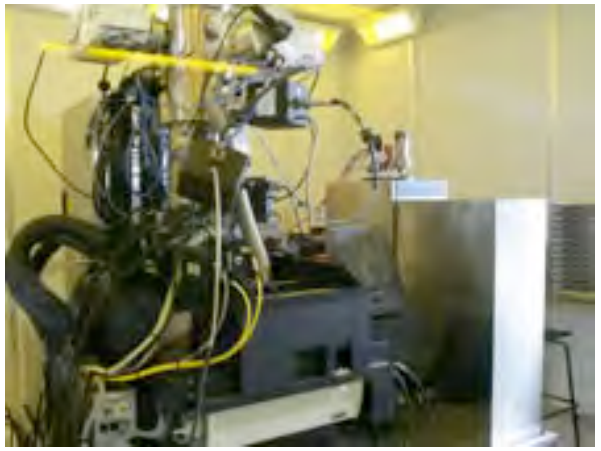
4 SEMs: Hitachi S4700

Veeco: AFMs



Electron Beam Lithography Capability

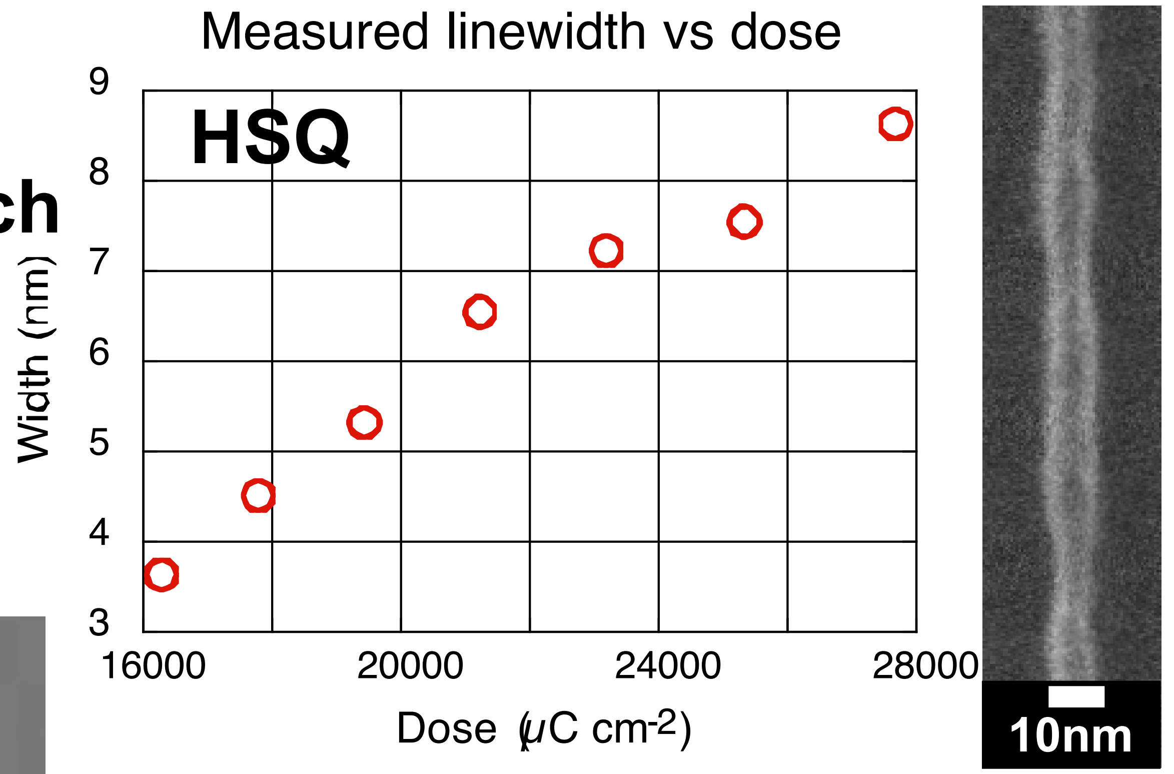
30 years experience of e-beam lithography

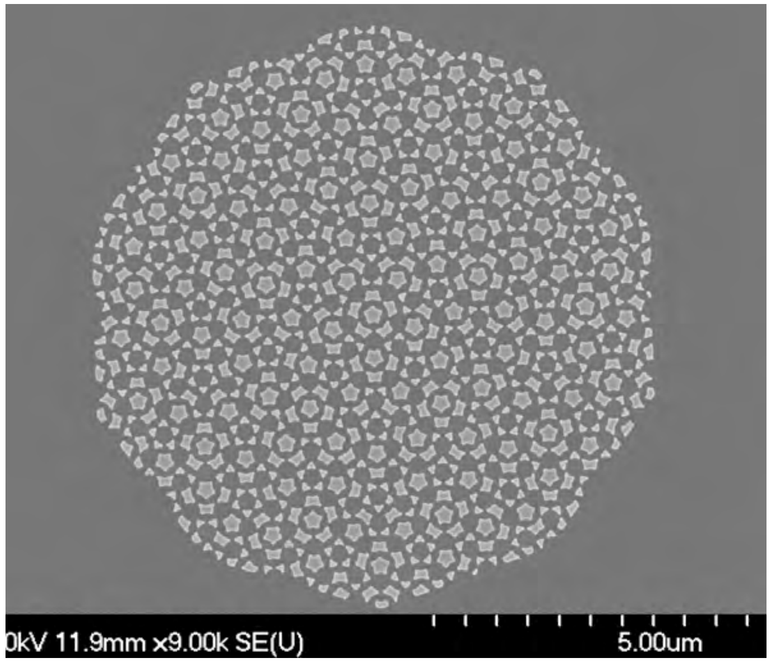


Vistec VB6

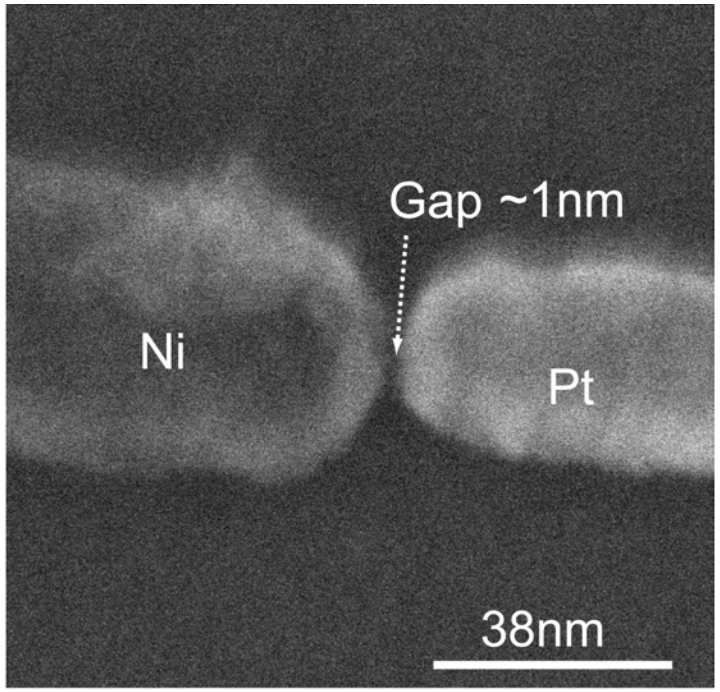
Vistec EBPG5

Sub-5 nm single-line lithography for research



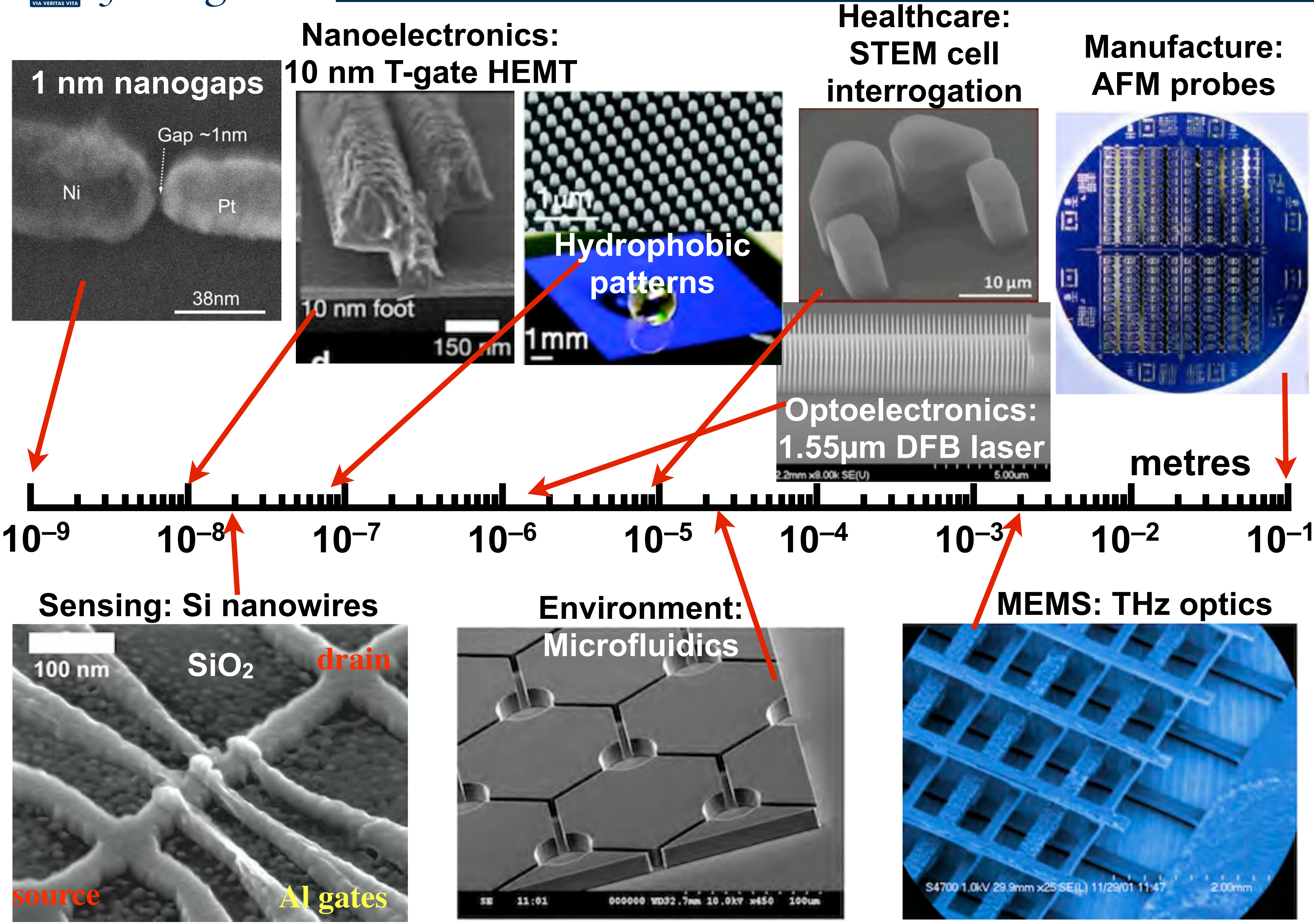


Penrose tile: layer-to-layer alignment 0.46 nm rms



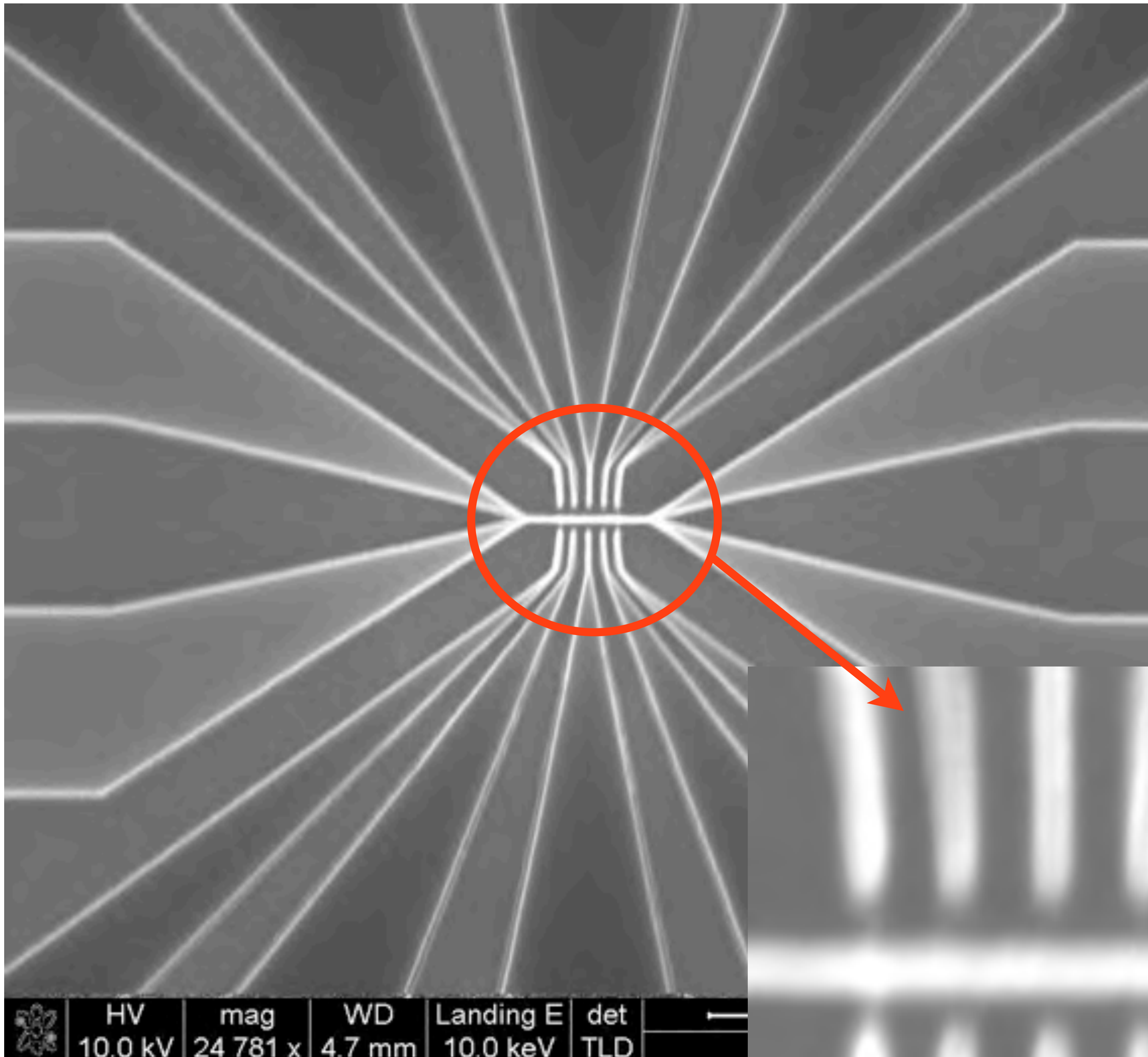
Alignment allows 1 nm gaps between different layers

James Watt Nanofabrication Centre Technology



SET Process Development @ Glasgow

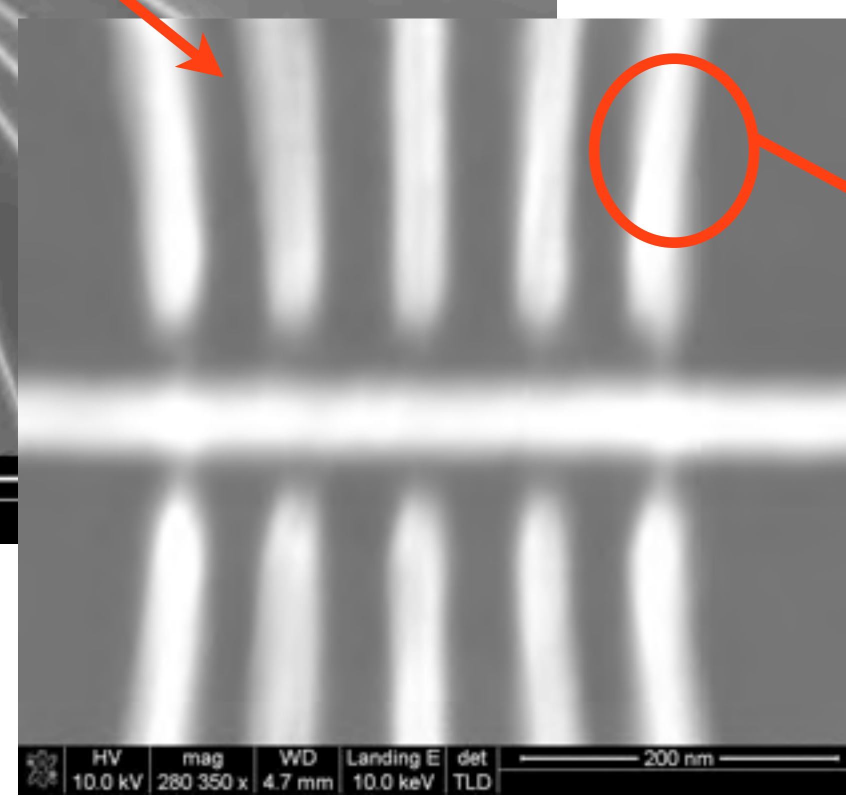
University of Glasgow

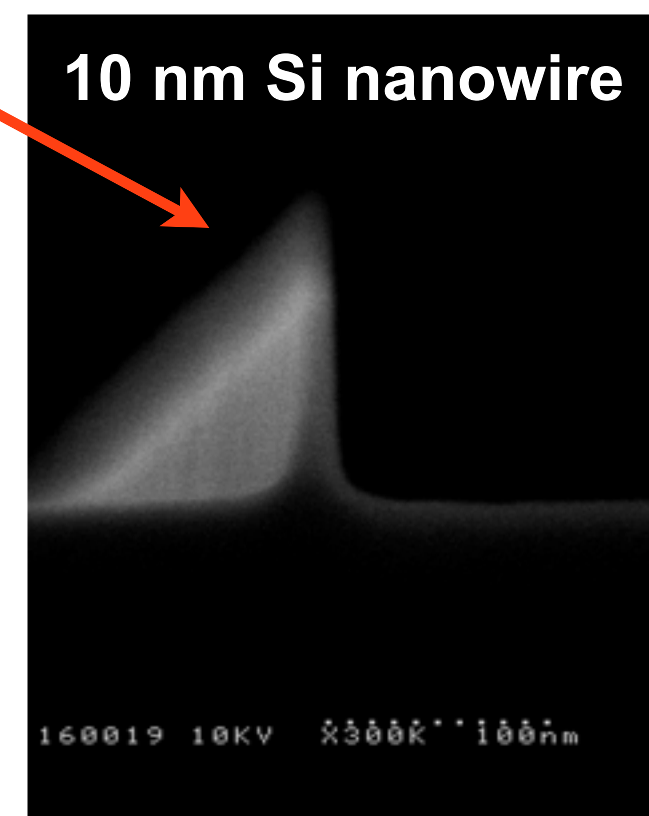


10 nm features achieved for SET devices

Electrical properties now being optimised

Example of low damage process integration





10 nm wires with 10 nm spacing

Thermoelectrics History

- History: Seebeck effect 1822

heat –> electric current

- Peltier (1834): current –> cooling

- Thomson effect: Thomson (Lord Kelvin) 1850s

Thermoelectric History and Early Applications

- Ioffe: physics (1950s), first devices 1950s - 1960s, commercial modules 1960s

Early applications:

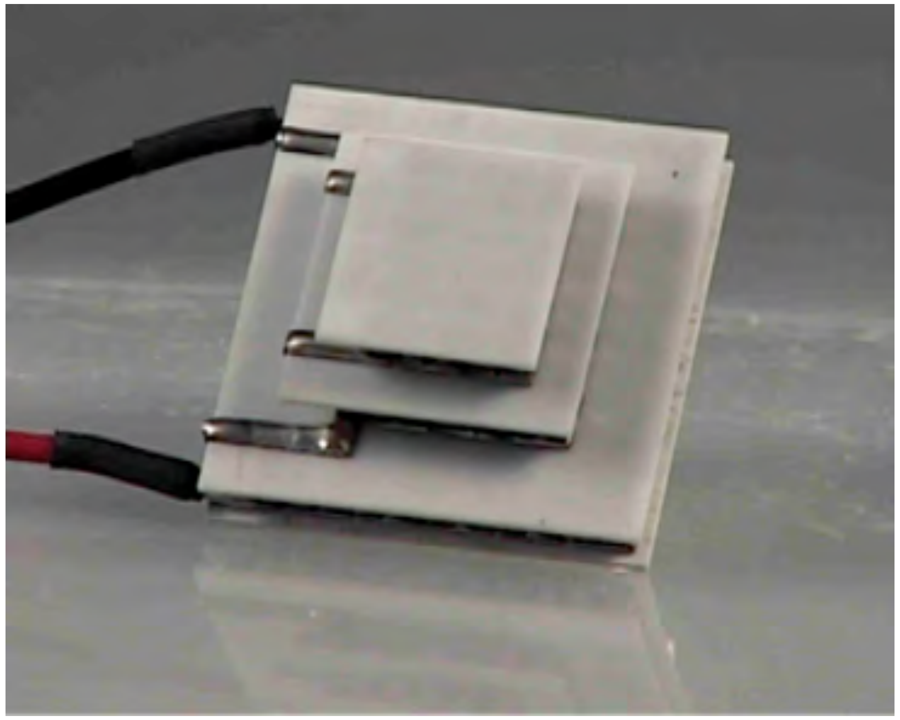
- Peltier coolers for military applications - rf / mm-wave electronics
- Peltier coolers for civilian applications (telecoms lasers, beer! etc...)
- Thermoelectric generators for deep space missions (NASA)
- Thermoelectric generators – industrial energy harvesting (oil drilling)

As renewable energy interest increases, renewed interest in thermoelectrics

Why Use Thermoelectrics?

- No moving parts –> no maintenance
- Peltier Coolers: fast feedback control mechanisms –> $\Delta T < 0.1$ ˚C
- Scalable to the nanoscale –> physics still works (some enhancements) but power ∝ area / volume
- Most losses result in heat
- Most heat sources are "static"
- Waste heat from many systems could be harvested

home, industry, background



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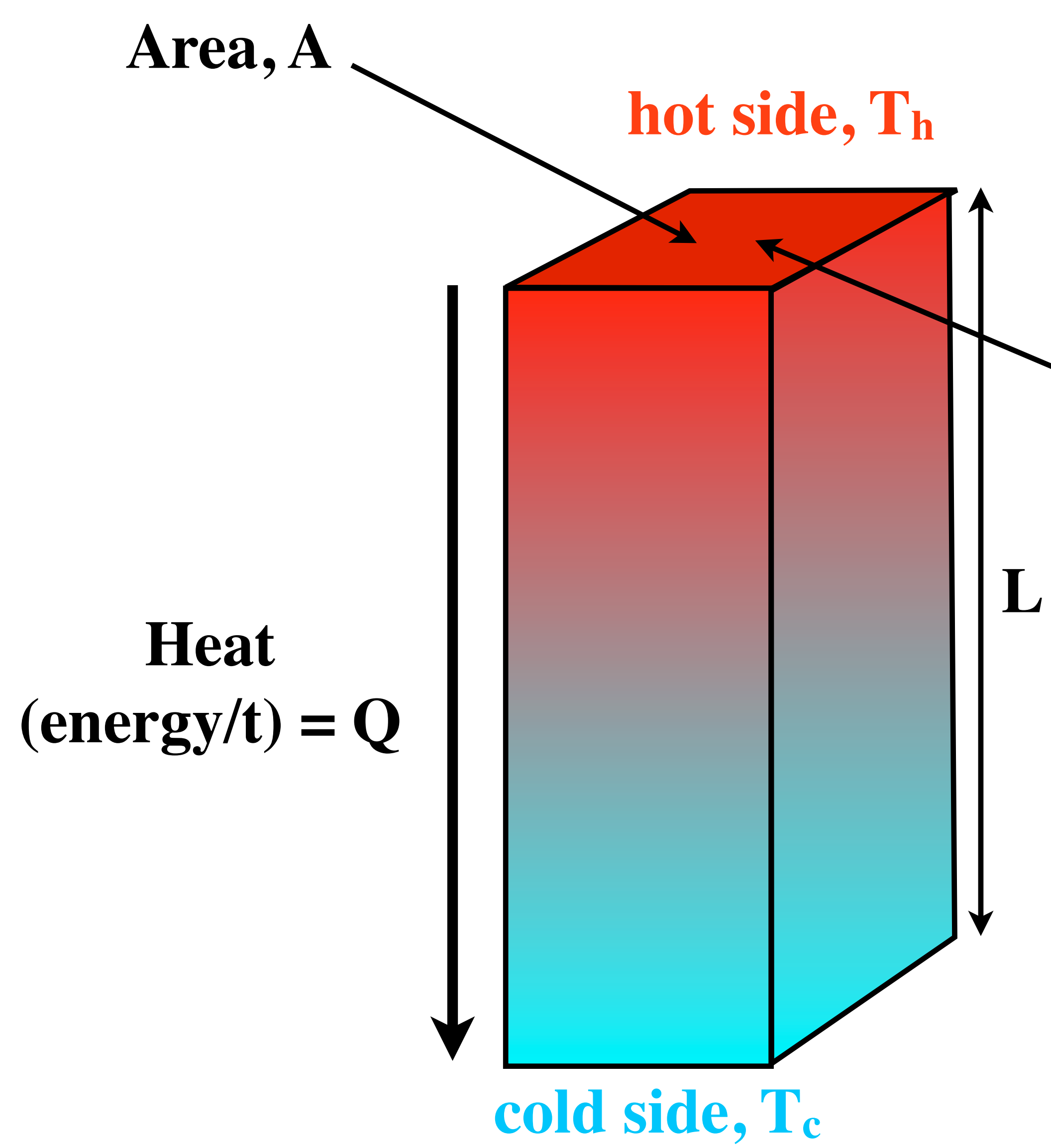
Fourier's Law of Heat Conduction



$$Q = -\kappa A \frac{T_h - T_c}{L}$$

negative since heat is removed from this end and conduction reduces thermoelectric effects

$$Q = -\kappa A \nabla T$$

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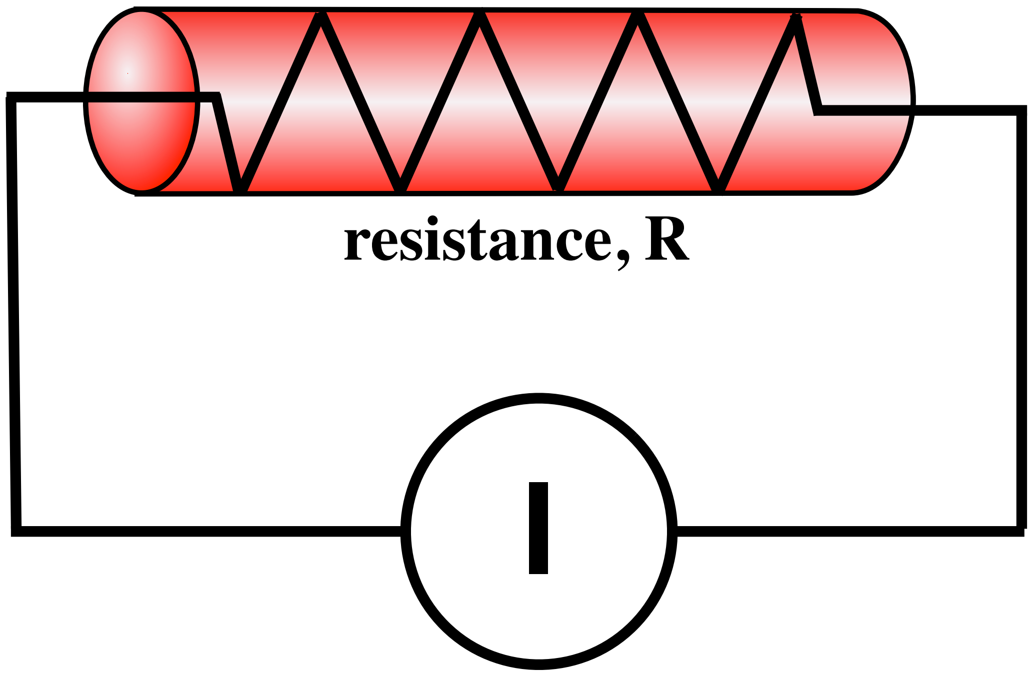
Joule Heating



$$Q = I^2R$$

Q = heat = power = energy / time

Background Physics

Fourier thermal transport

$$Q = -\kappa A \nabla T$$

Joule heating

$$Q = I^2 R$$

Q = heat (power i.e energy / time)

E_F = chemical potential

V = voltage

A = area

q = electron charge

g(E) = density of states

k_B = Boltzmann's constant

R = resistance

I = current (J = I/A)

κ = thermal conductivity

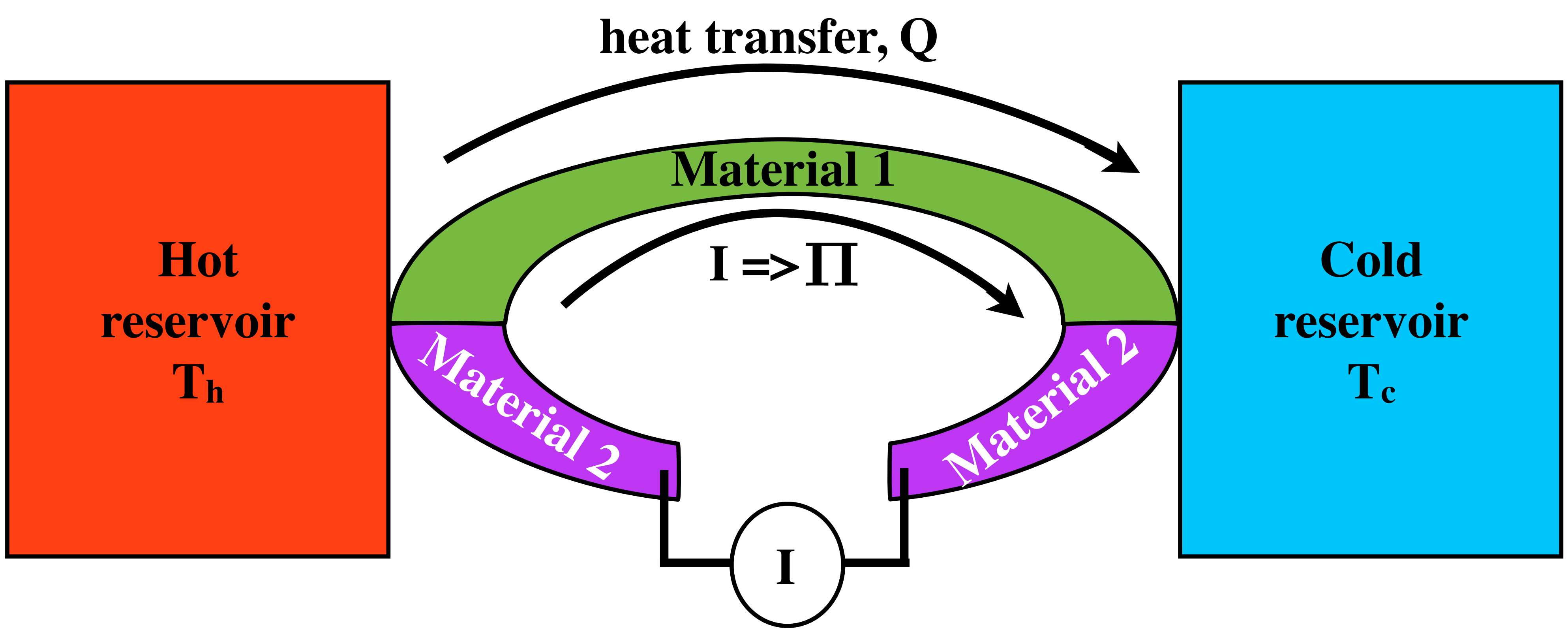
σ = electrical conductivity

α = Seebeck coefficient

f(E) = Fermi function

μ(E) = mobility

The Peltier Effect



Peltier coefficient, $\Pi = \frac{Q}{I}$

units: W/A = V

- Peltier coefficient is the energy carried by each electron per unit charge & time

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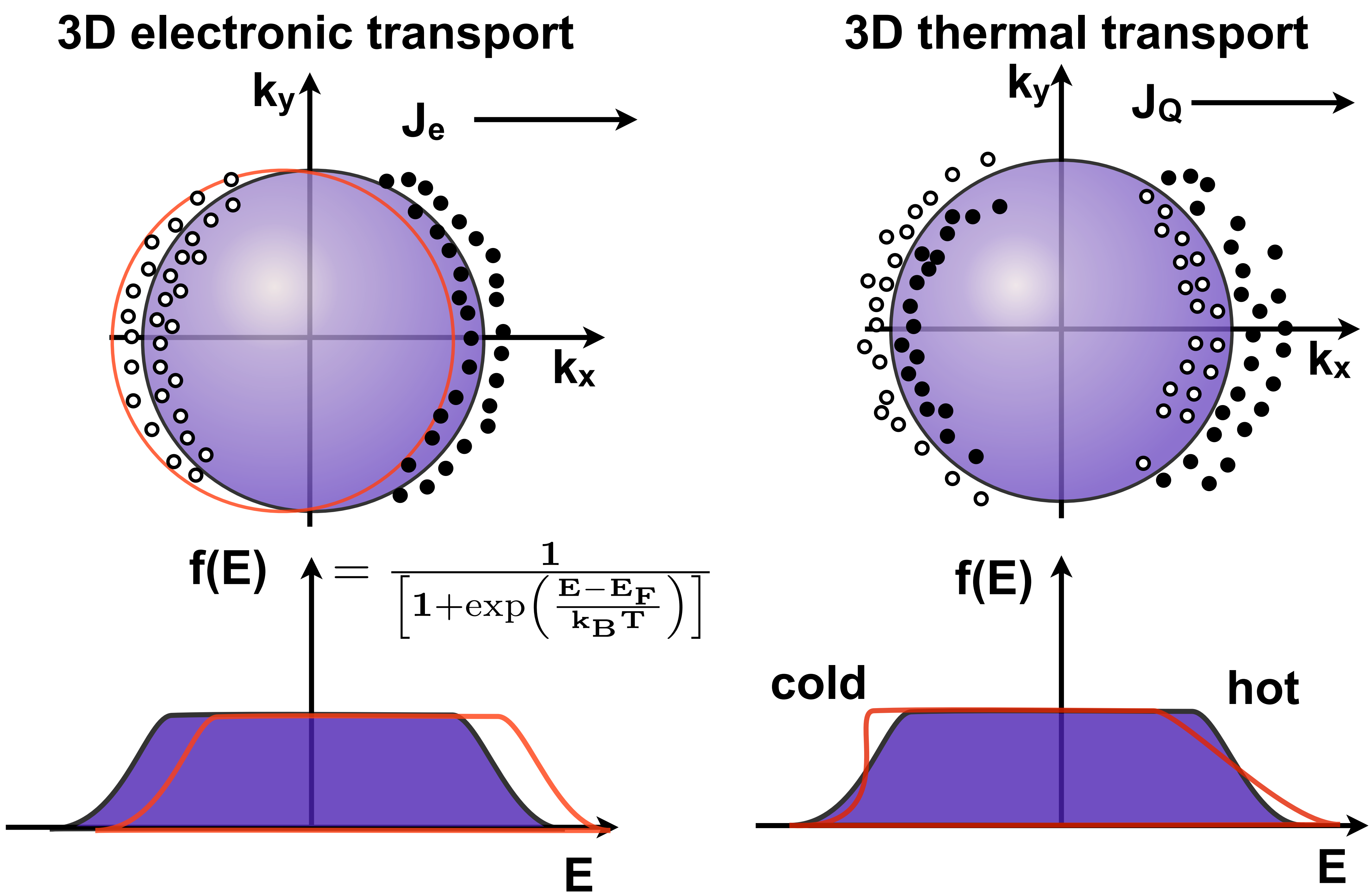
3D Electronic and Thermal Transport



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The Peltier Coefficient

- Full derivation uses relaxation time approximation & Boltzmann equation

- $$\Pi = -\frac{1}{q}\int (E - E_F)\frac{\sigma(E)}{\sigma}dE$$

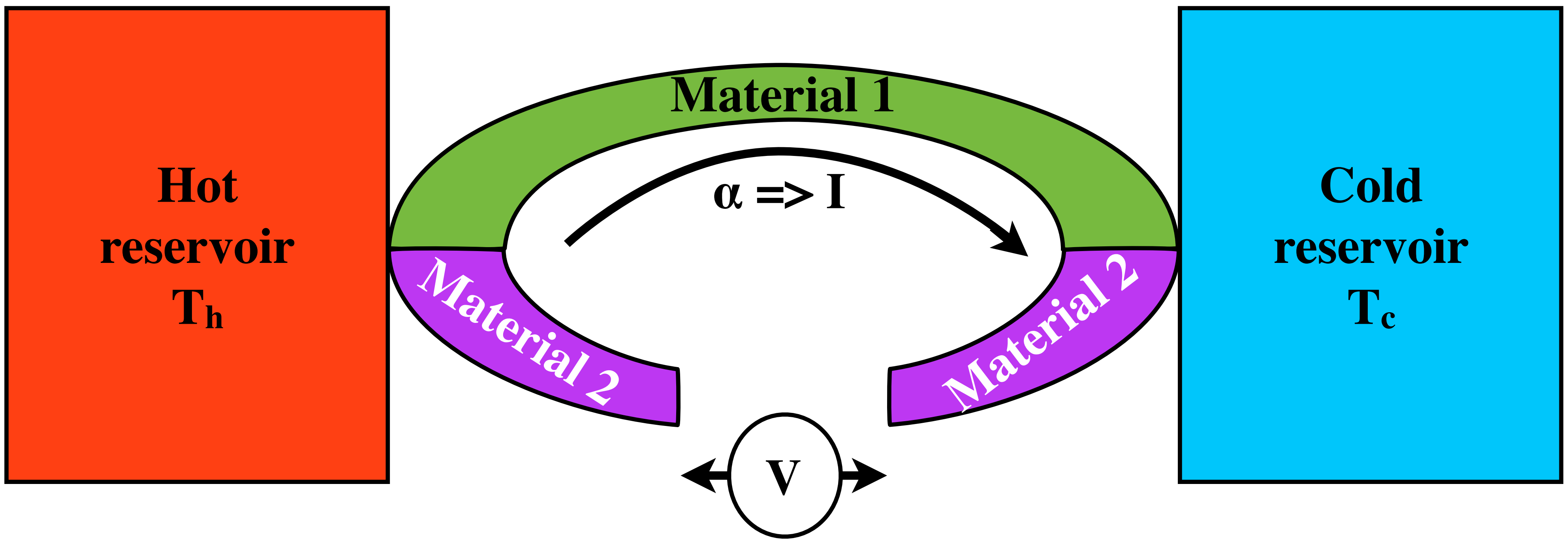
- $$\sigma = \int \sigma(E)dE = q\int g(E)\mu(E)f(E)[1 - f(E)]dE$$

- This derivation works well for high temperatures (> 100 K)

- At low temperatures phonon drag effects must be added

see H. Fritzsche, Solid State Comm. 9, 1813 (1971)

The Seebeck Effect



- Open circuit voltage, $V = \alpha (T_h - T_c) = \alpha \Delta T$

Seebeck coefficient, $$\alpha = \frac{dV}{dT}$$

units: V/K

- Seebeck coefficient = $\frac{1}{q}$ x entropy $\left(\frac{Q}{T}\right)$ transported with charge carrier

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The Seebeck Coefficient

- Full derivation uses relaxation time approximation, Boltzmann equation

- $$\alpha = \frac{1}{qT}\left[\frac{\langle E\tau\rangle}{\langle\tau\rangle} - E_F\right]$$

- $$\alpha = -\frac{k_B}{q}\int \frac{(E-E_F)}{k_B T}\frac{\sigma(E)}{\sigma}dE$$

$$\sigma = \int \sigma(E)dE = q\int g(E)\mu(E)f(E)[1-f(E)]dE$$

For electrons in the conduction band, E_c of a semiconductor

- $$\alpha = -\frac{k_B}{q}\left[\frac{E_c - E_F}{k_B T} + \frac{\int_0^\infty \frac{(E-E_c)}{k_B T}\sigma(E)dE}{\int_0^\infty \sigma(E)dE}\right] \quad \text{for } E > E_c$$

see Mott and Jones (1958) and H. Fritzsche, Solid State Comm. 9, 1813 (1971)

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The Seebeck Coefficient for Metals

- $$f(1-f) = -k_B T \frac{df}{dE}$$
- Expand $g(E)\mu(E)$ in Taylor's series at $E = E_F$
- $$\alpha = -\frac{\pi^2}{3q} k_B^2 T \left[\frac{d\ln(\mu(E)g(E))}{dE} \right]_{E=E_F}$$ (Mott's formula) Mott and Jones, 1958
- i.e. Seebeck coefficient depends on the asymmetry of the current contributions above and below E_F

Using the energy-independent scattering approximation:

- $$\alpha = -\frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{\frac{2}{3}} (1 + C)$$ n=carrier density

M. Cutler et al., Phys. Rev. 133, A1143 (1964)

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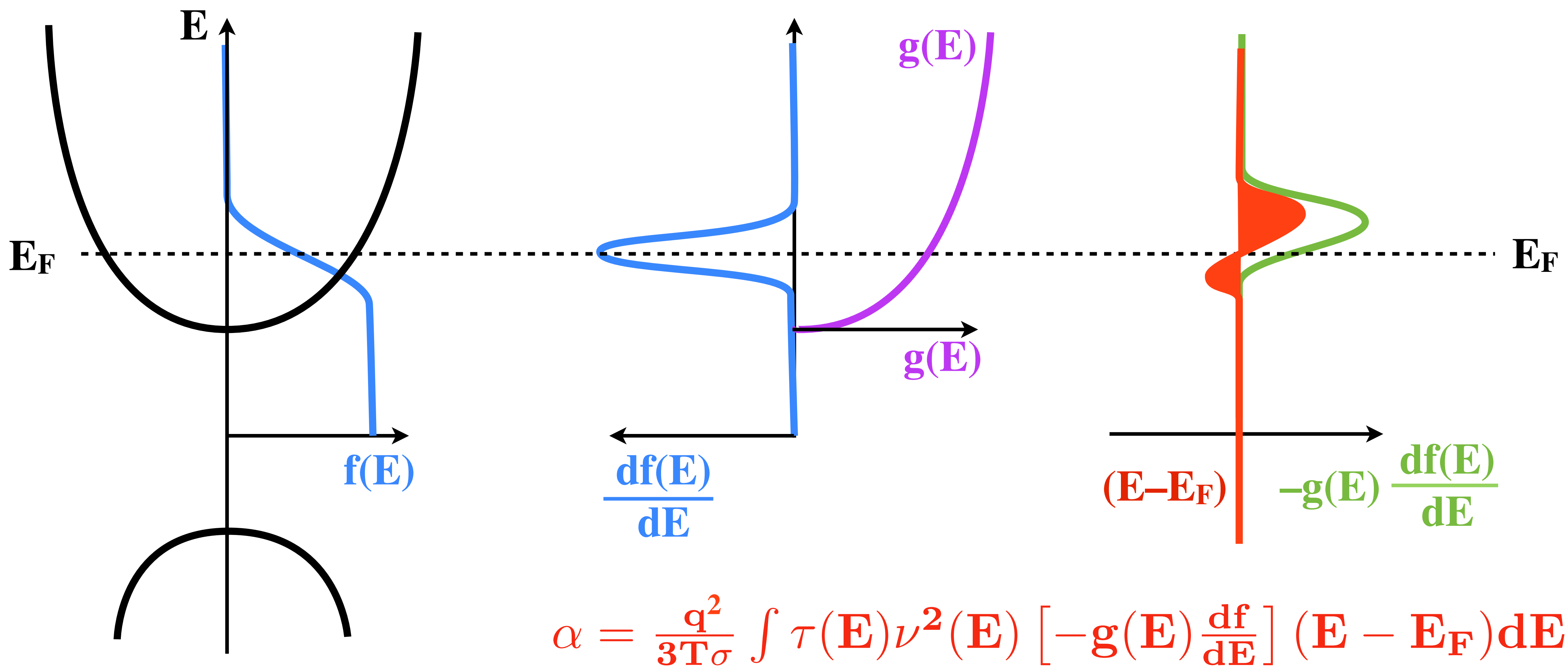
The Physics of the Thermoelectric Effect

- If we ignore energy dependent scattering (i.e. $\tau = \tau(E)$) then from Ziman

$$\sigma = \frac{q^2}{3}\int \tau(E)\nu^2(E)\left[-g(E)\frac{df}{dE}\right]dE$$



$$\alpha = \frac{q^2}{3T\sigma}\int \tau(E)\nu^2(E)\left[-g(E)\frac{df}{dE}\right](E - E_F)dE$$

- Thermoelectric power requires asymmetry in red area under curve

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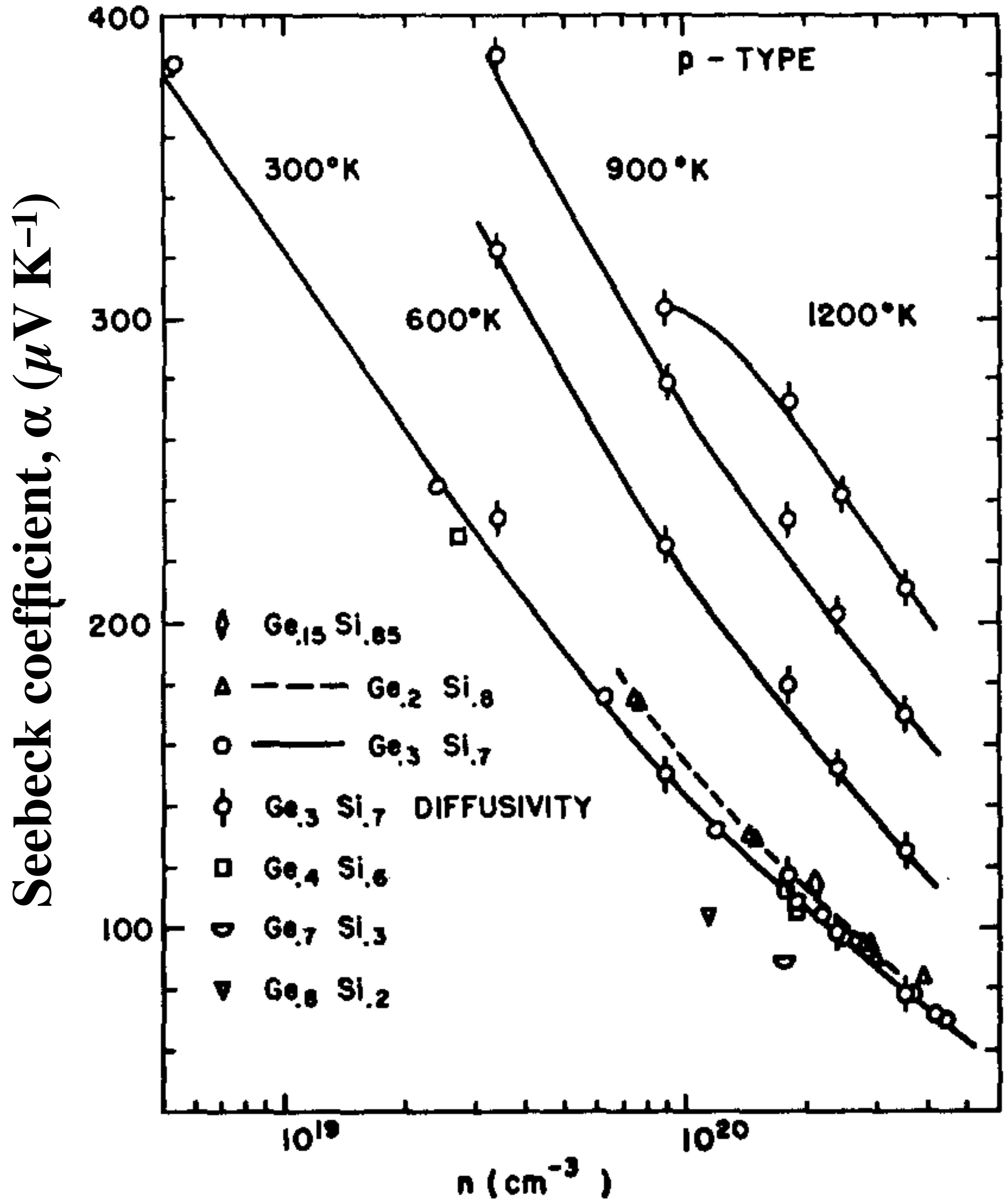
Semiconductor Example: SiGe Alloys



J.P. Dismukes et al., J. Appl. Phys. 35, 2899 (1964)

- Mott criteria ~ 2 x 10^{18} cm^{-3}
- Degenerately doped p-$Si_{0.7}Ge_{0.3}$
- α decreases for higher n
- For SiGe, α increases with T

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{\frac{2}{3}}$$

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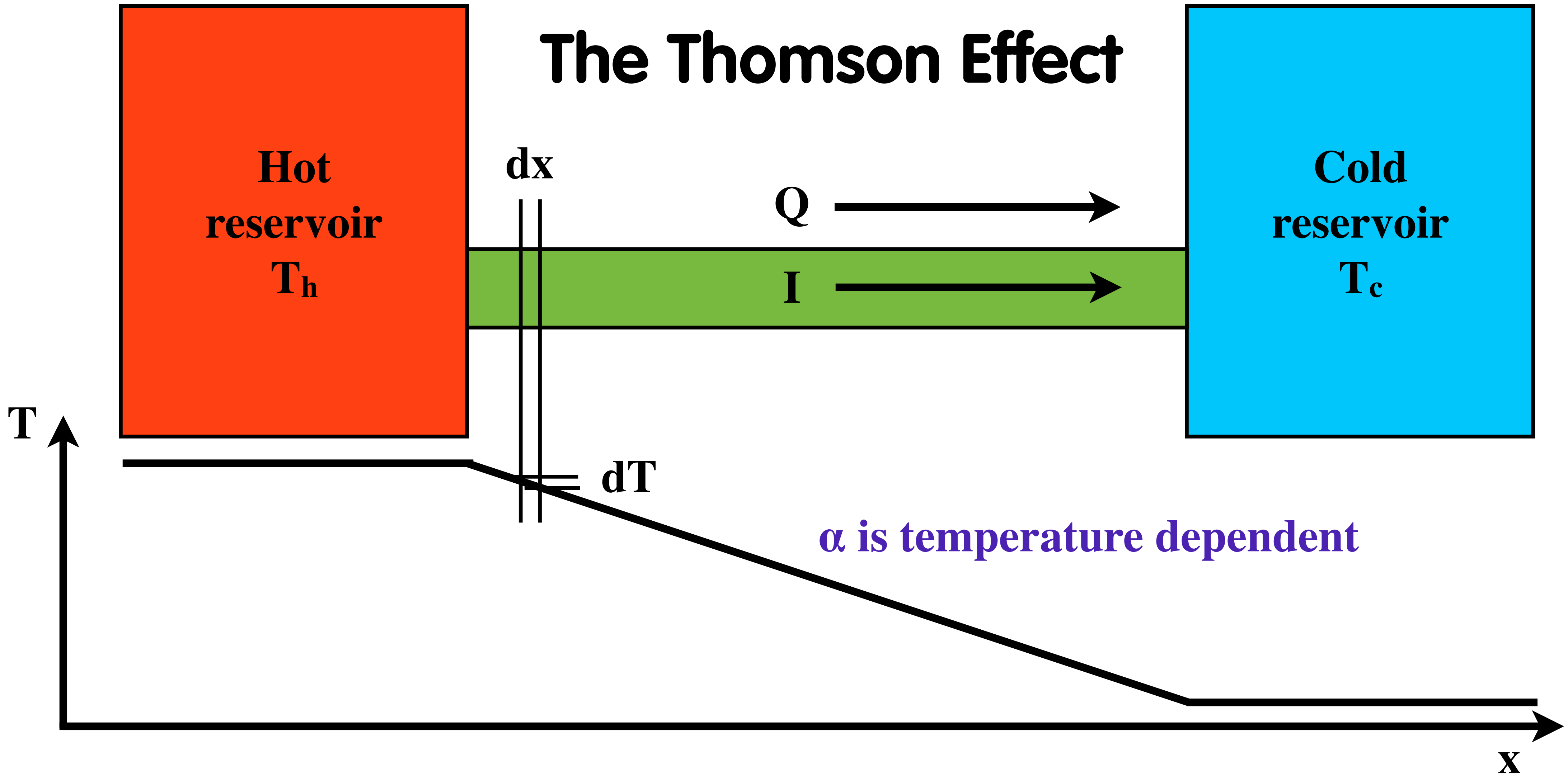
The Thomson Effect



- $$\frac{dQ}{dx} = \beta I \frac{dT}{dx}$$

Thomson coefficient, β	$dQ = \beta I dT$

units: V/K

The Kelvin Relationships

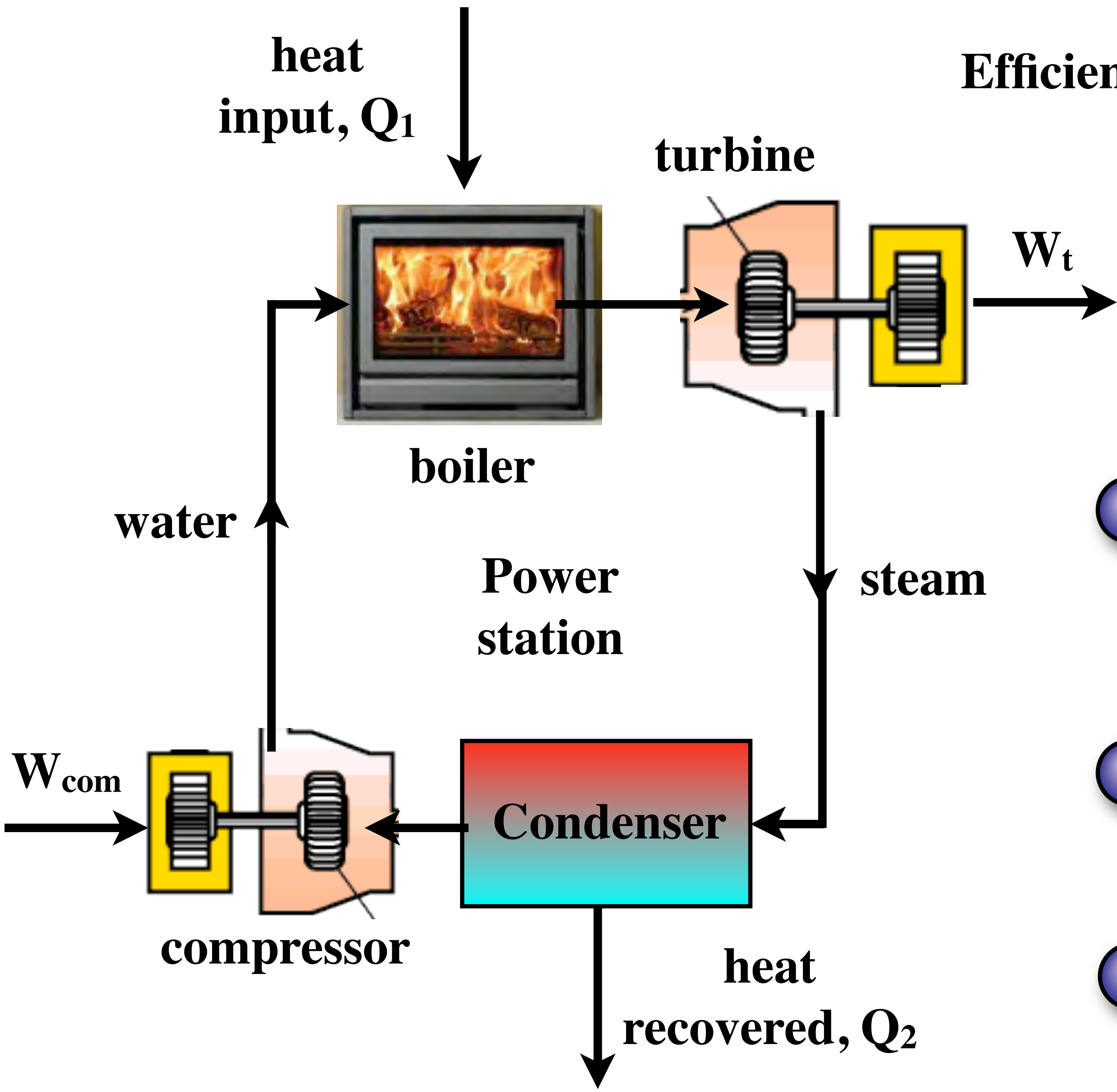
- Derived using irreversible thermodynamics

$$\Pi = \alpha T$$

$$\beta = T\frac{d\alpha}{dT}$$

- These relationships hold for all materials
- Seebeck, α is easy to measure experimentally
- Therefore measure α to obtain Π and β

Thermodynamic Efficiency for Power Stations



$$\text{Efficiency} = \eta = \frac{\text{net work output}}{\text{heat input}}$$

$$= \frac{W_t - W_{com}}{Q_1}$$

- 1^{st} law thermodynamics

  $(Q_1 - Q_2) - (W_t - W_{com}) = 0$

- $\eta = \frac{Q_1 - Q_2}{Q_1}$

- $\eta = 1 - \frac{Q_2}{Q_1}$

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Carnot Efficiency

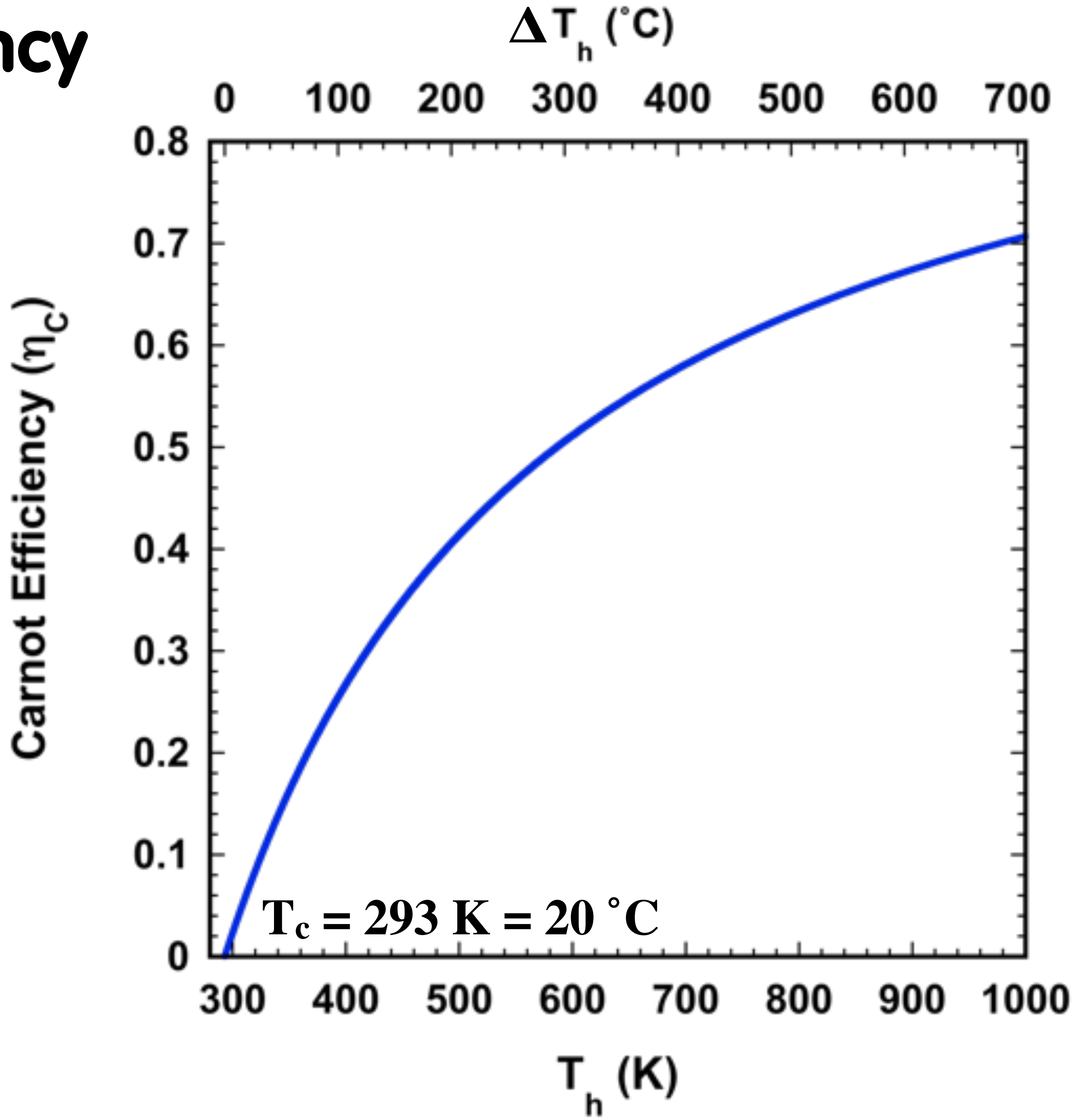
Efficiency =

$$\eta = \frac{\text{net work output}}{\text{heat input}}$$

$$\eta = 1 - \frac{Q_2}{Q_1}$$

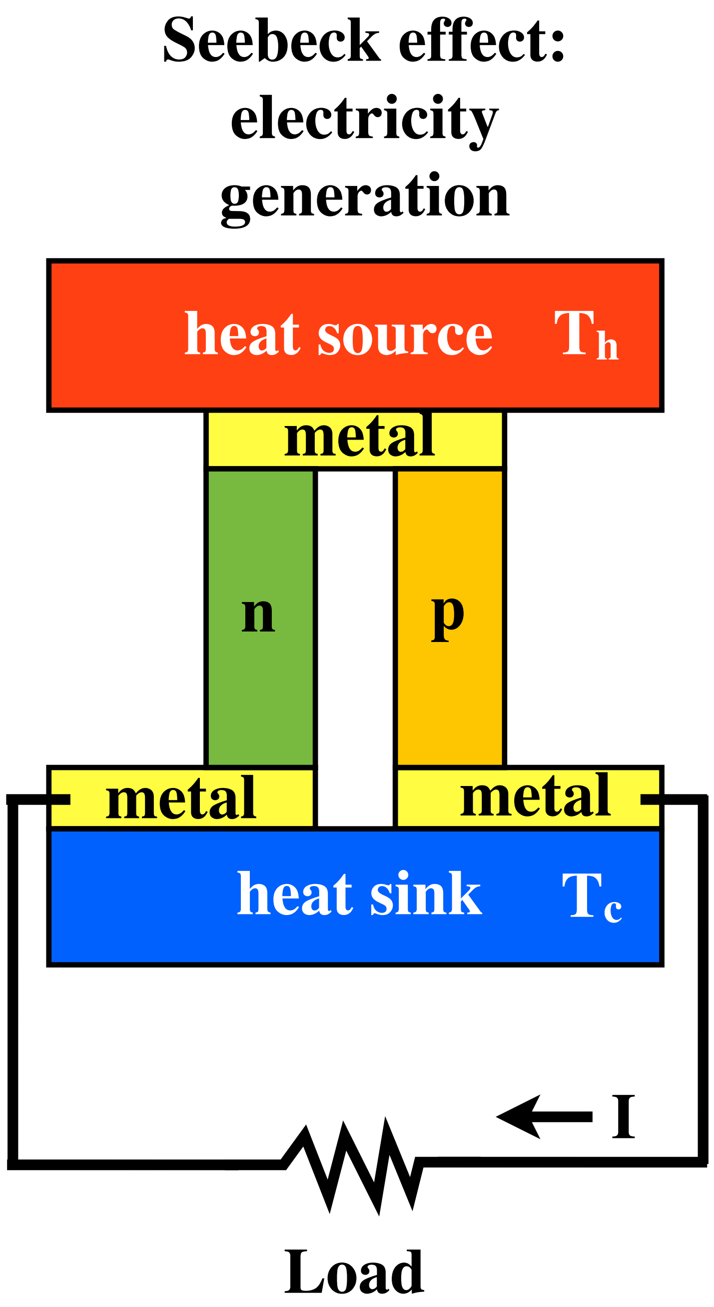
Carnot: maximum η only depends on T_c and T_h

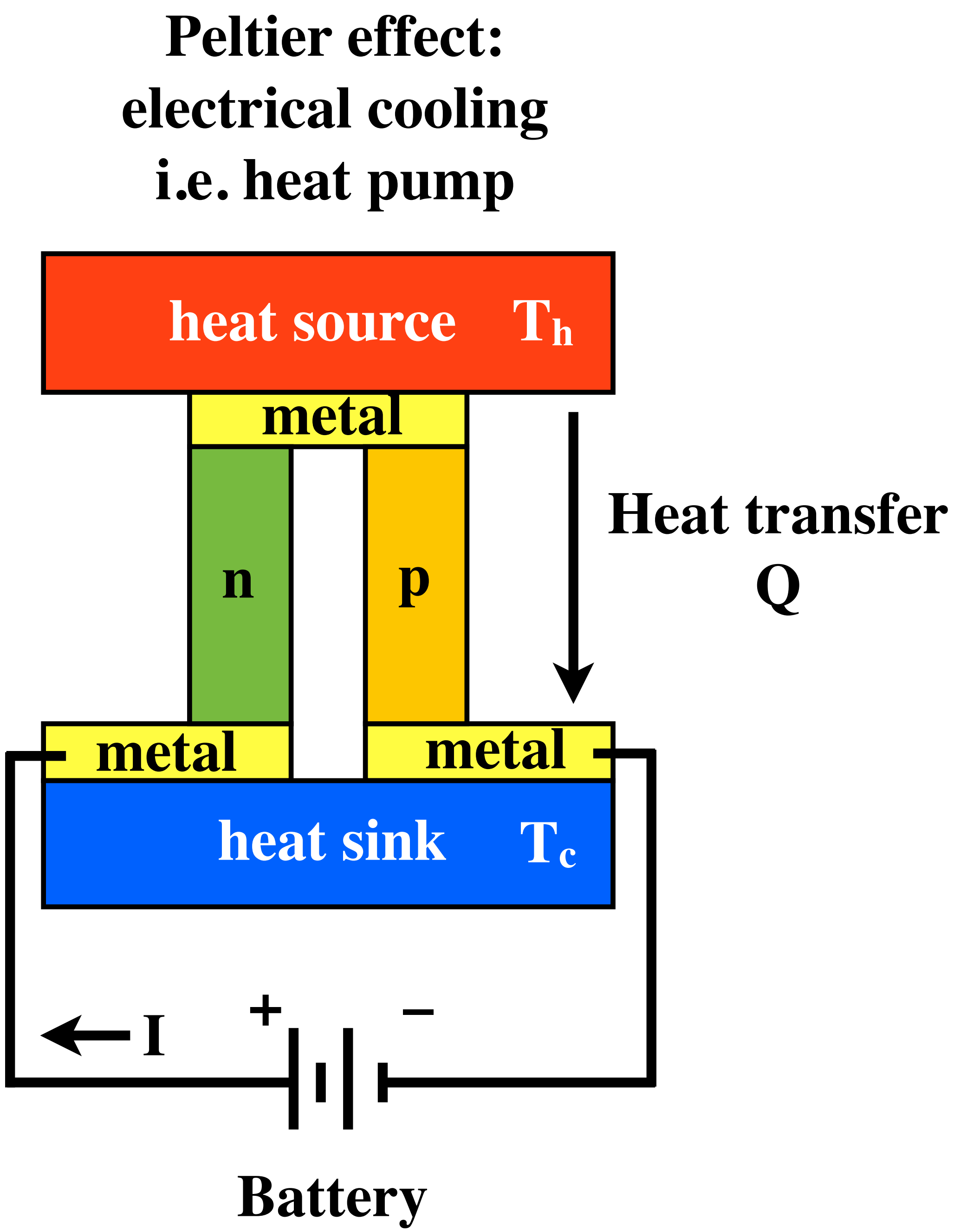
$$\eta_c = 1 - \frac{T_c}{T_h}$$



2nd law thermodynamics: no system operating in closed cycle can convert all the heat absorbed from a heat reservoir into the same amount of work

Semiconductors and Thermoelectrics





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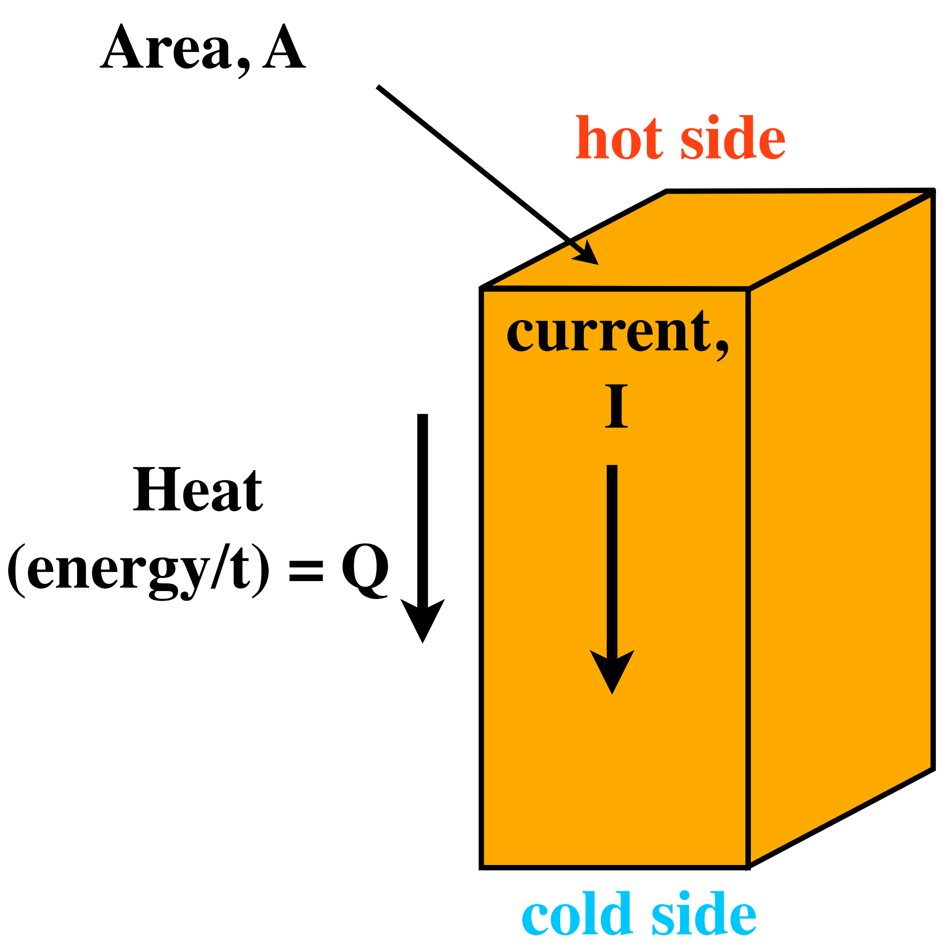
Peltier Effect, Heat Flux and Temperature

- **If a current of I flows through a thermoelectric material between hot and cold reservoirs:**



- **Heat flux per unit area =**

  (= Peltier + Fourier)

- $$\frac{\mathbf{Q}}{\mathbf{A}} = \mathbf{\Pi J} - \kappa \nabla \mathbf{T}$$

but $\mathbf{\Pi} = \alpha \mathbf{T}$ **and** $\mathbf{J} = \frac{\mathbf{I}}{\mathbf{A}}$

$$\mathbf{Q} = \alpha \mathbf{IT} - \kappa \mathbf{A} \nabla \mathbf{T}$$

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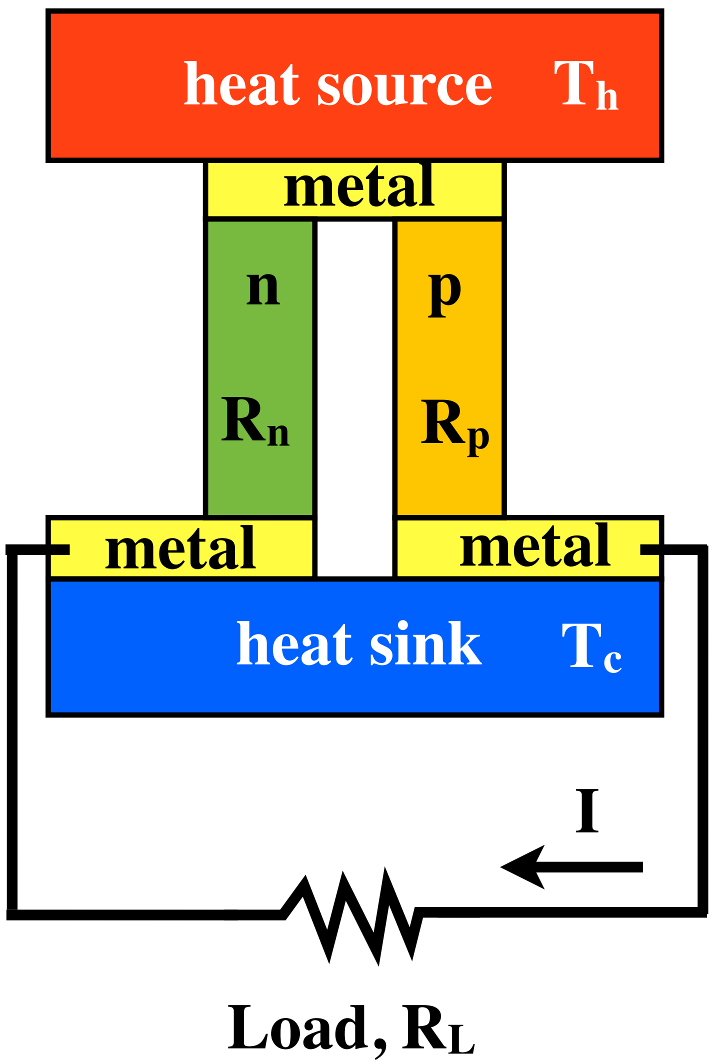
Conversion Efficiency



$R = R_n + R_p$

- $\eta = \dfrac{\text{power supplied to load}}{\text{heat absorbed at hot junction}}$
- Power to load (Joule heating) = I^2R_L
- Heat absorbed at hot junction = Peltier heat + heat withdrawn from hot junction
- Peltier heat $= \Pi I = \alpha I T_h$
- $I = \dfrac{\alpha(T_h - T_c)}{R + R_L}$ (Ohms Law)
- Heat withdrawn from hot junction $= \kappa A\,(T_h - T_c) - \frac{1}{2}I^2R$

NB half Joule heat returned to hot junction

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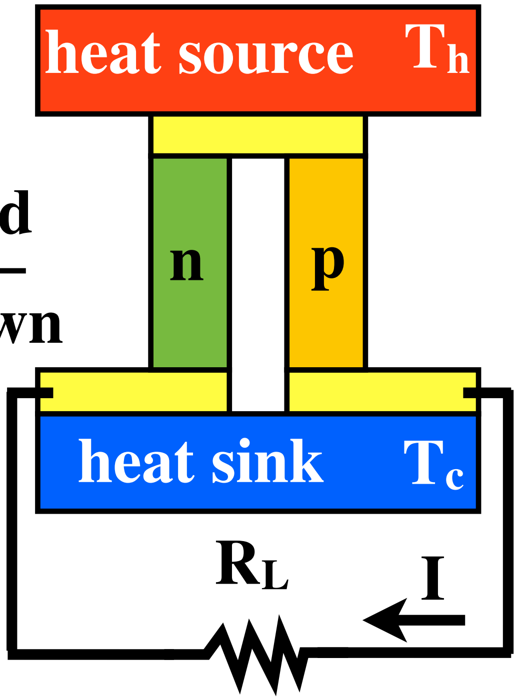
Conversion Efficiency

- $\eta = \frac{\text{power supplied to load}}{\text{heat absorbed at hot junction}} = \frac{\text{power supplied to load}}{\text{Peltier + heat withdrawn}}$



$$\eta = \frac{I^2 R_L}{\alpha I T_h + \kappa A (T_h - T_c) - \frac{1}{2} I^2 R}$$

For maximum value $\frac{d\eta}{d(\frac{R_L}{R})} = 0$ $\quad T = \frac{1}{2}(T_h + T_c)$

$$\eta_{max} = \frac{T_h - T_c}{T_h} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_c}{T_h}}$$

where $Z = \frac{\alpha^2}{R\kappa A} = \frac{\alpha^2 \sigma}{\kappa}$

= Carnot x Joule losses and irreversible processes

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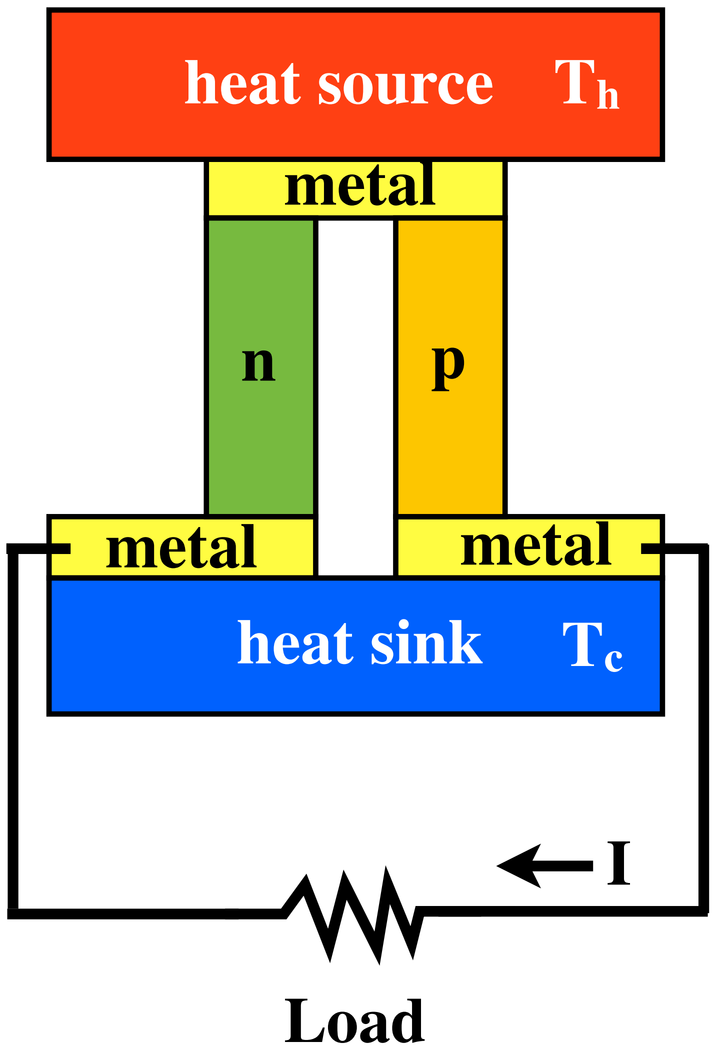
Thermoelectric Power Generating Efficiency



$$\eta = \frac{\Delta T}{T_h} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_c}{T_h}}$$

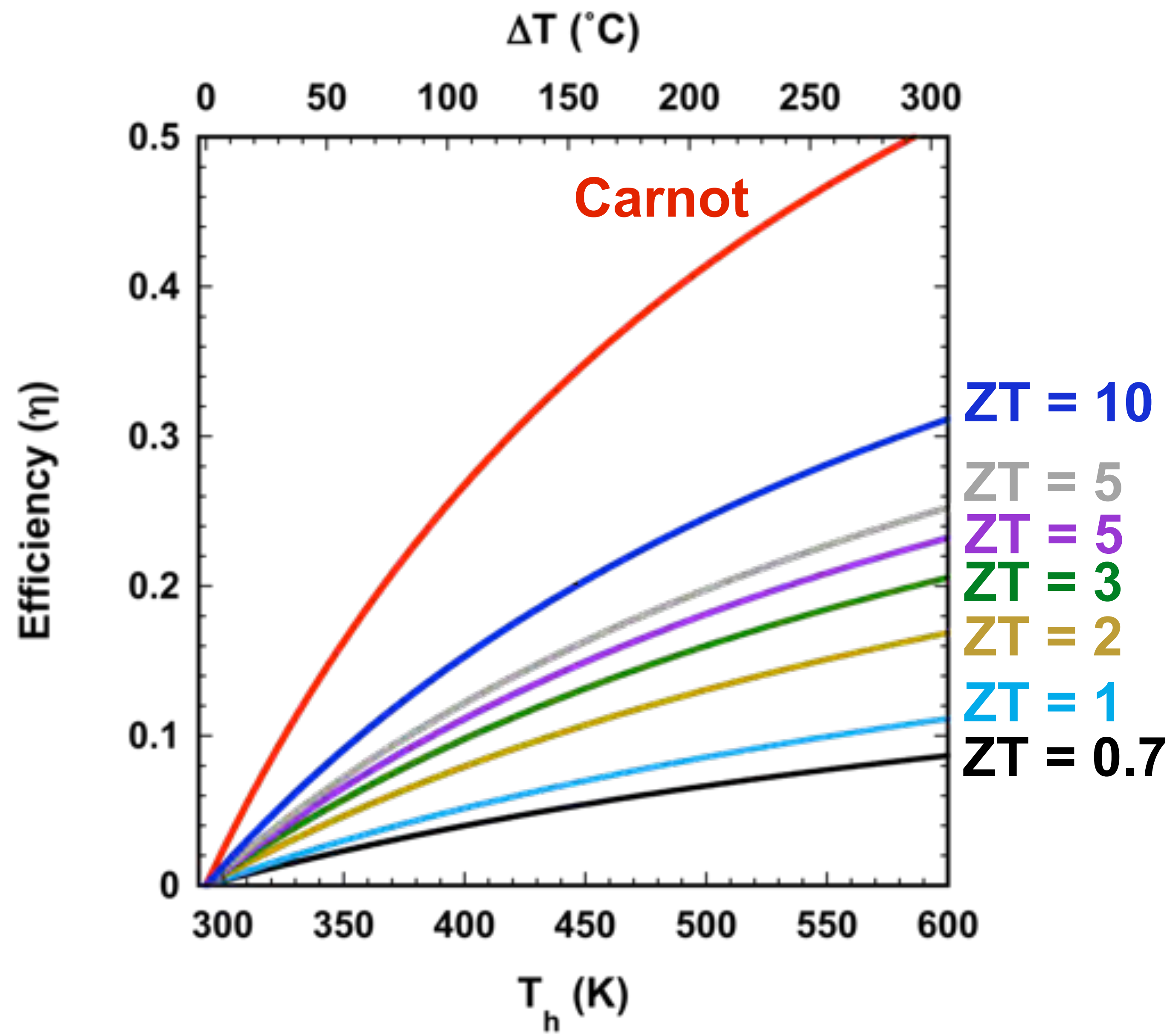


Figure of merit

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

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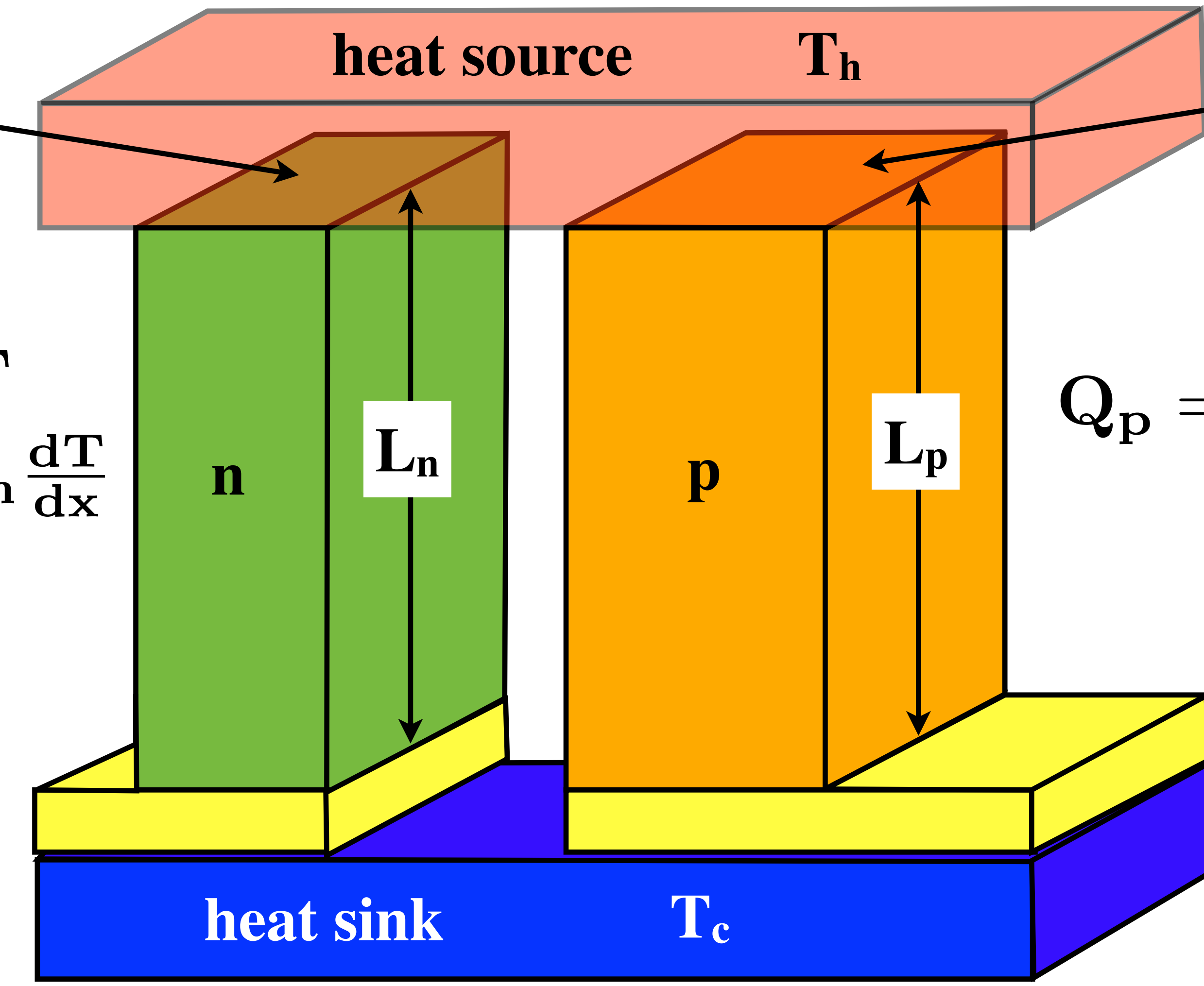
Heat Transfer in Thermoelectric Element

- But n-type and p-type materials are seldom identical



$$Q_n = -\alpha_n I T - \kappa_n A_n \frac{dT}{dx}$$

$$Q_p = \alpha_p I T - \kappa_p A_p \frac{dT}{dx}$$

- Z for a couple depends on relative dimensions

- Z is maximum for $$\frac{L_n A_p}{L_p A_n} = \sqrt{\frac{\sigma_n \kappa_n}{\sigma_p \kappa_p}}$$

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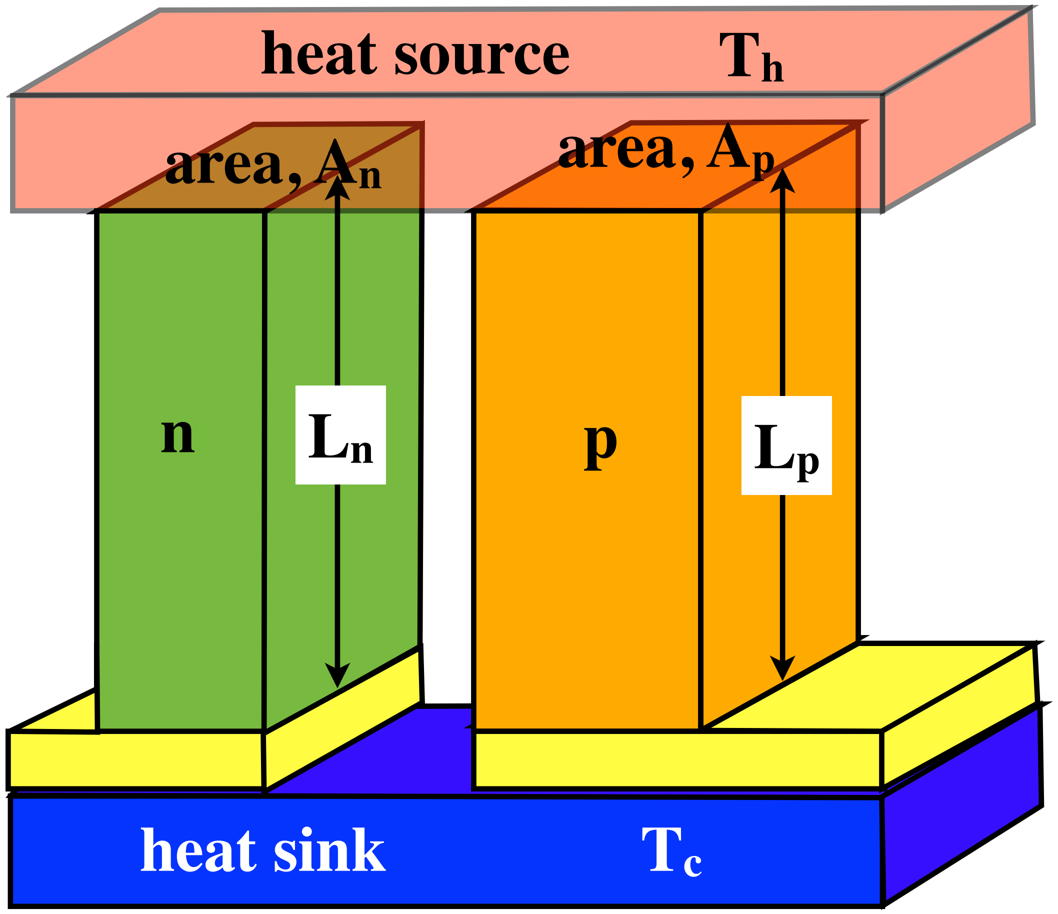
Maximising ZT for an Unbalanced Couple



$$\frac{L_n A_p}{L_p A_m} = \sqrt{\frac{\sigma_n \kappa_n}{\sigma_p \kappa_p}}$$

$$ZT = \frac{(\alpha_p - \alpha_n)^2 T}{\left[\sqrt{\frac{\kappa_p}{\sigma_p}} + \sqrt{\frac{\kappa_n}{\sigma_n}}\right]}$$

- We need good ZT for both n- and p-type semiconductors

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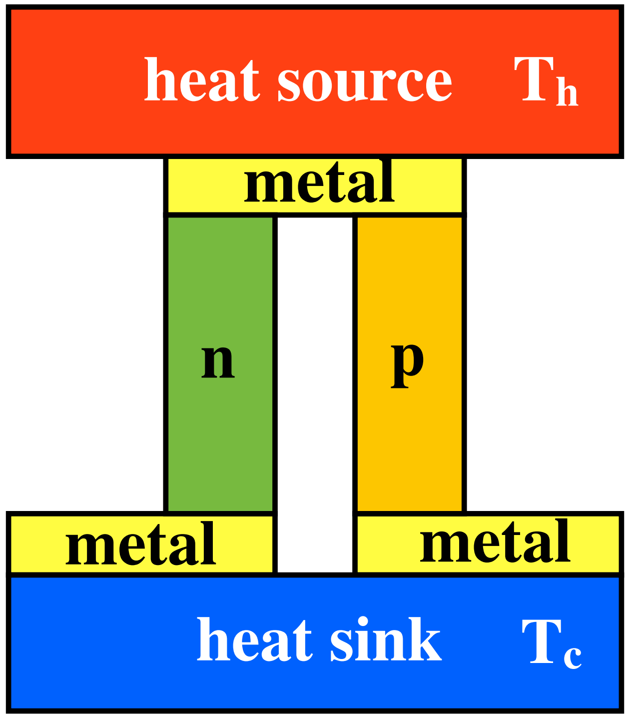
Maximum Temperature Drop

- As the system has thermal conductivity κ a maximum ΔT which can be sustained across a module is limited due to heat transport
- $$\Delta T_{max} = \frac{1}{2} Z T_c^2$$
- The efficiency cannot be increased indefinitely by increasing T_h
- The thermal conductivity also limits maximum ΔT in Peltier coolers
- Higher ΔT_{max} requires better Z materials



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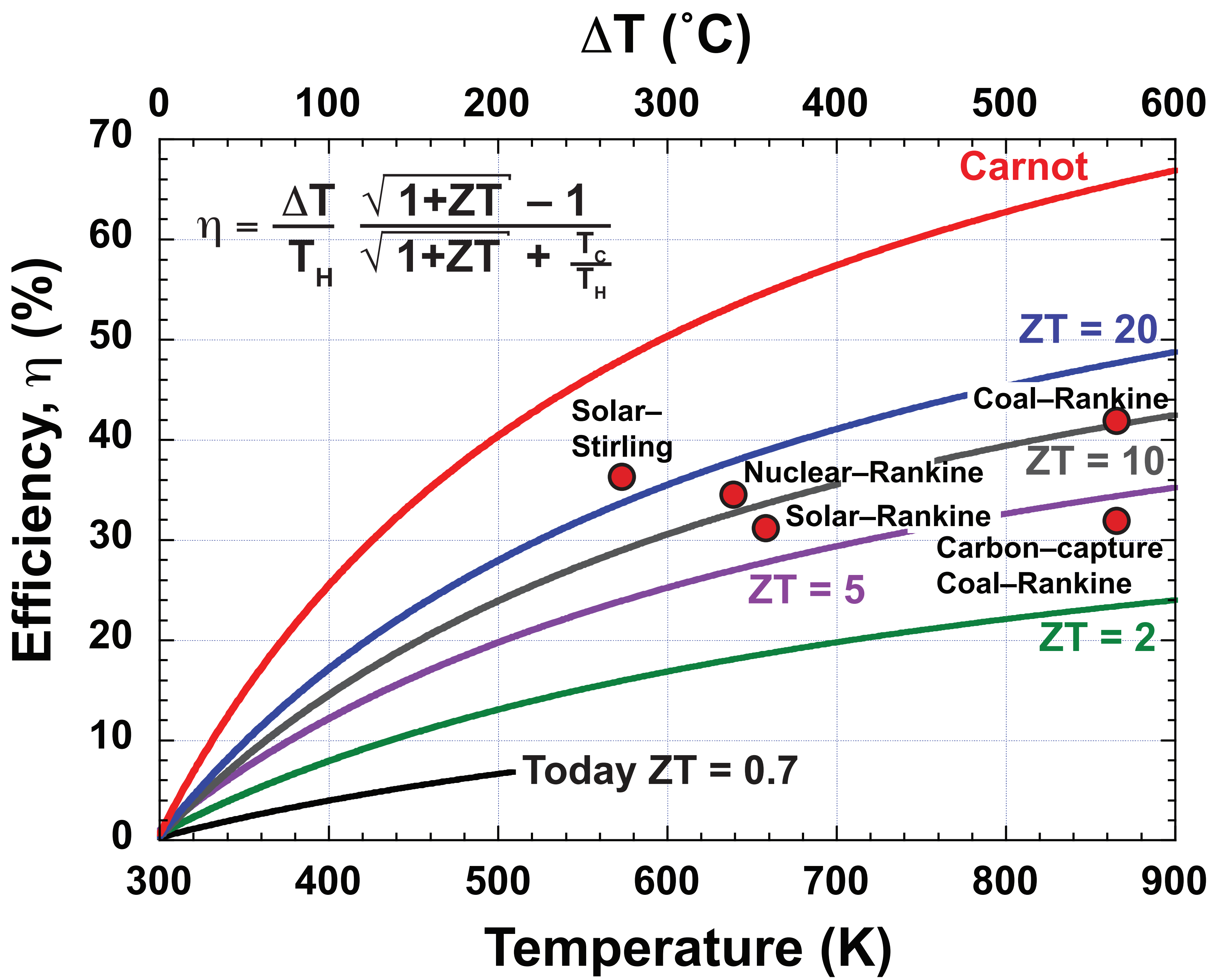
Thermodynamic Efficiency



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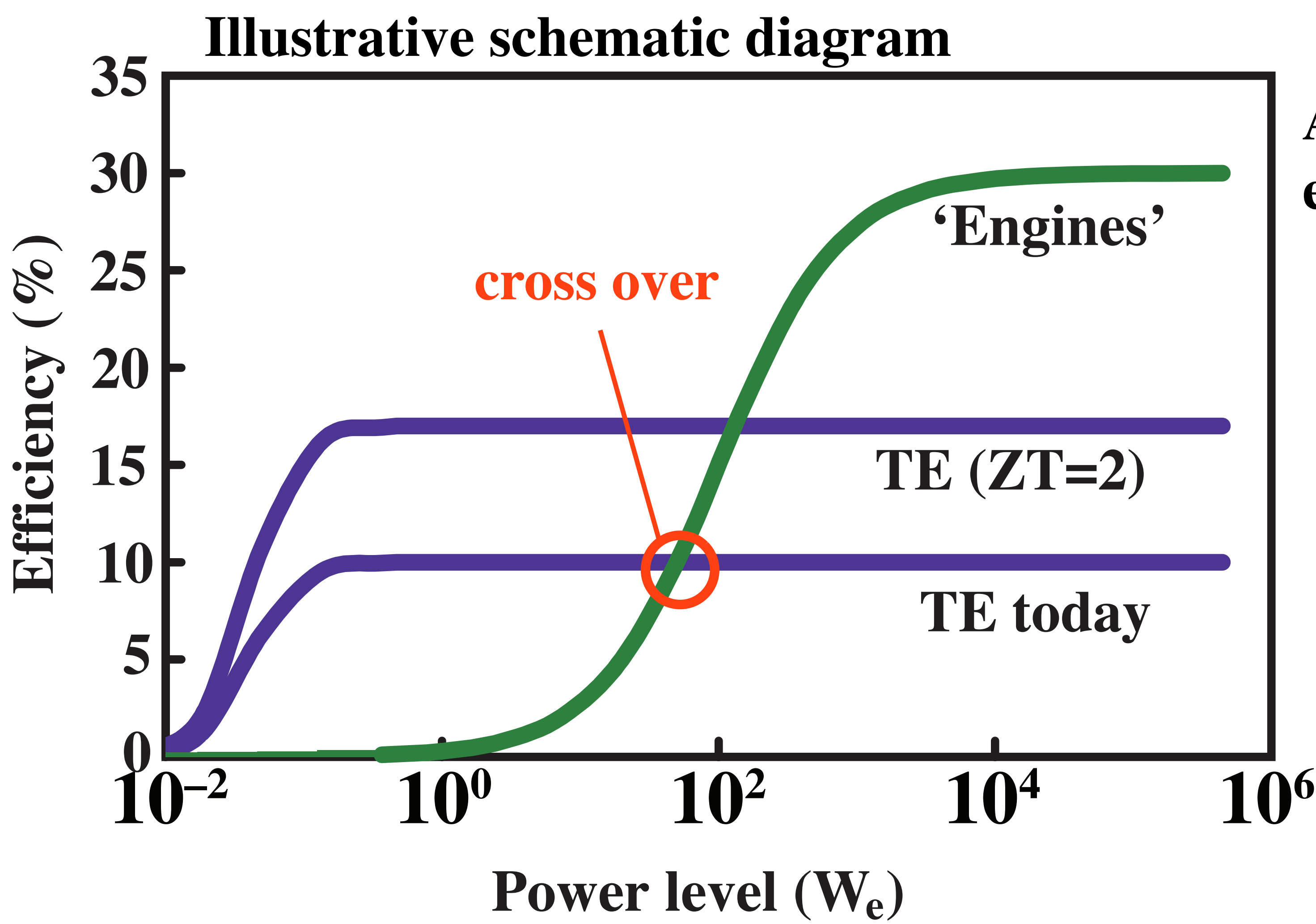
Power Generation From Macro to Micro



At large scale, thermodynamic engines more efficient than TE

ZT average for both n and p over all temperature range

Diagram assumes high T

- At the mm and μm scale with powers << 1W, thermoelectrics are more efficient than thermodynamic engines (Reynolds no. etc..)

C.B. Vining, Nature Mat. 8, 83 (2009)

Thermal Conductivity of Bulk Materials

- Both the lattice and electron current can contribute to heat transfer

thermal conductivity = electron contribution + phonon contribution
= (electrical conductivity) + (lattice contributions)

$$\kappa = \kappa_{\mathrm{el}} + \kappa_{\mathrm{ph}}$$

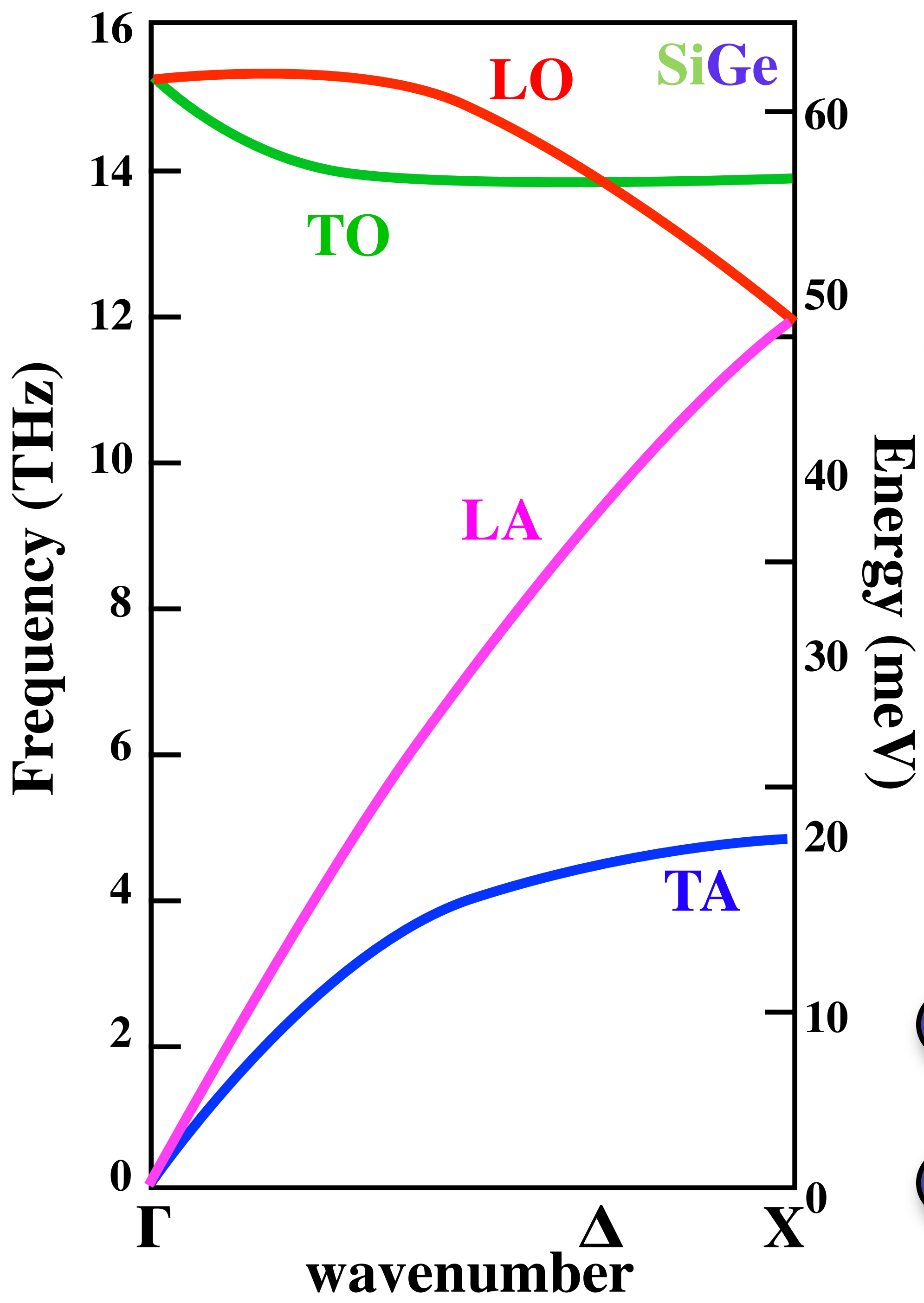
- For low carrier densities in semiconductors (non-degenerate) $\kappa_{\mathrm{el}} \ll \kappa_{\mathrm{ph}}$

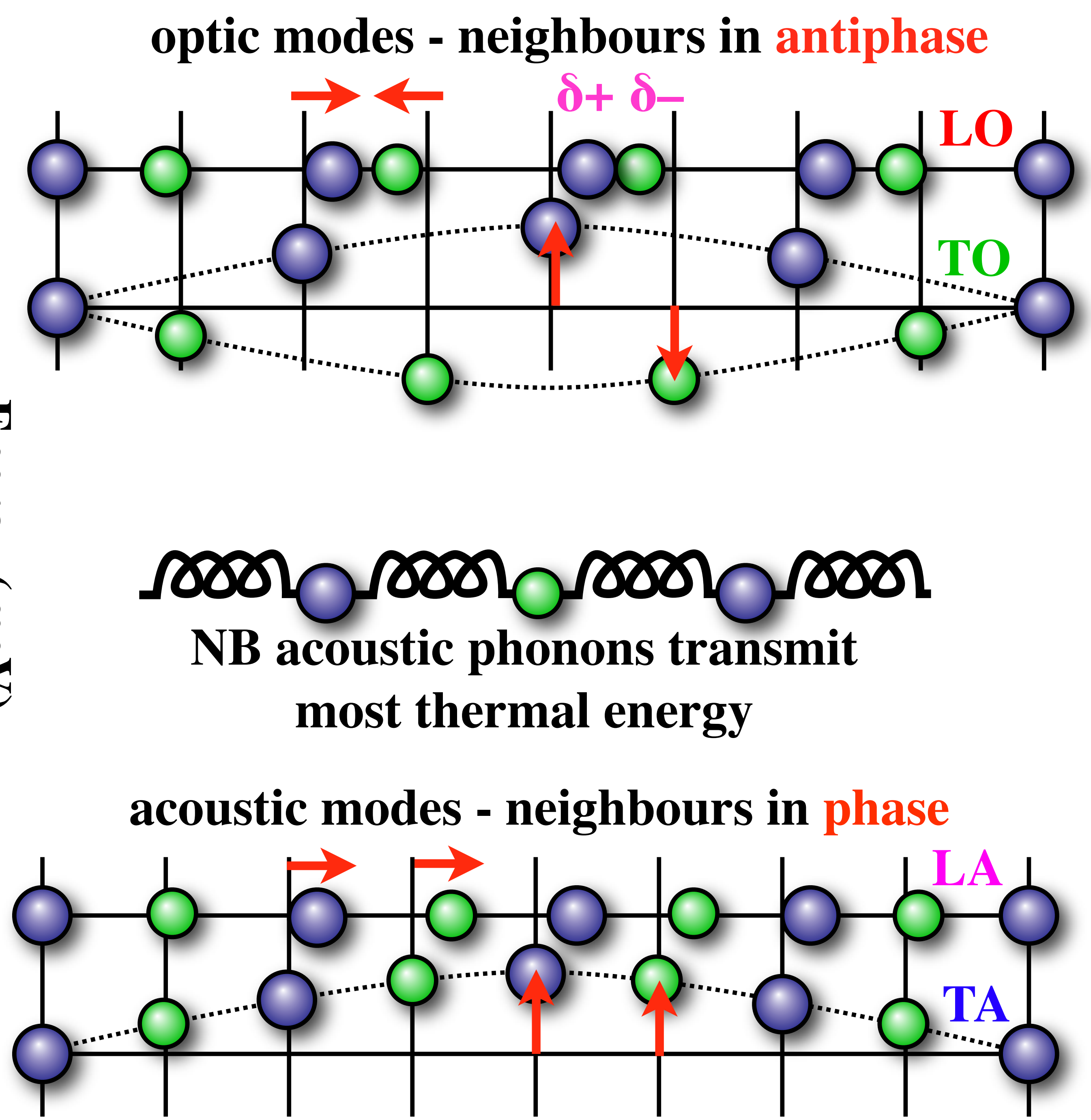
- For high carrier densities in semiconductors (degenerate) $\kappa_{\mathrm{el}} \gg \kappa_{\mathrm{ph}}$

- Good thermoelectric materials should ideally have $\kappa_{\mathrm{el}} \ll \kappa_{\mathrm{ph}}$

  i.e. electrical and thermal conductivities are largely decoupled

Phonons: Lattice Vibration Heat Transfer





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Thermal Conductivity

Lattice contribution:

- $$\kappa_{ph} = \frac{k_B}{2\pi^2}\left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\frac{\theta_D}{T}} \frac{\tau_c(x)x^4e^x}{\upsilon(x)(e^x-1)^2}dx$$

θ_D = Debye temperature (640 K for Si)

$x = \frac{\hbar\omega}{k_B T}$

τ_c = combined phonon scattering time

$\upsilon(x)$ = velocity

J. Callaway, Phys. Rev. 113, 1046 (1959)

Electron (hole) contribution:

- $$\kappa_{el} = \frac{\sigma}{q^2 T}\left[\frac{\langle\tau\rangle\left\langle E^2\tau\right\rangle - \langle E\tau\rangle^2}{\langle\tau^3\rangle}\right]$$

$\tau(E)$ = total electron momentum relaxation time

B. R. Nag, Electron Transport in Compound Semiconductors, (Springer-Verlag, New York USA, 1980)

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Wiedemann-Franz Law

- **Empirical law from experimental observation that $\frac{\kappa}{\sigma T}$ = constant for metals**
- **Drude model's great success was an explanation of Wiedemann-Franz**
- **Drude model assumes bulk of thermal transport by conduction electrons in metals**
- **Success fortuitous: two factors of 100 cancel to produce the empirical result from the Drude theory**
- **Incorrect assumption: classical gas laws cannot be applied to electron gas**

Wiedemann-Franz Law for Metals

- In metals, the thermal conductivity is dominated by κ_{el}

$$\therefore \quad \frac{\sigma T}{\kappa} = \frac{3}{\pi^2}\left(\frac{q}{k_B}\right)^2 = \frac{1}{L}$$

L = Lorentz number
= 2.45 x 10^{-8} W-ΩK^{-2}

$$ZT = \frac{3}{\pi^2}\left(\frac{q\alpha}{k_B}\right)^2 = 4.09 \times 10^7 \, \alpha^2$$

for $\kappa_{el} \gg \kappa_{ph}$

Exceptions:

- most exceptions systems with $\kappa_{el} \ll \kappa_{ph}$
- some pure metals at low temperatures
- certain alloys where small κ_{el} results in significant κ_{ph} contribution
- certain low dimensional structures where κ_{ph} can dominate

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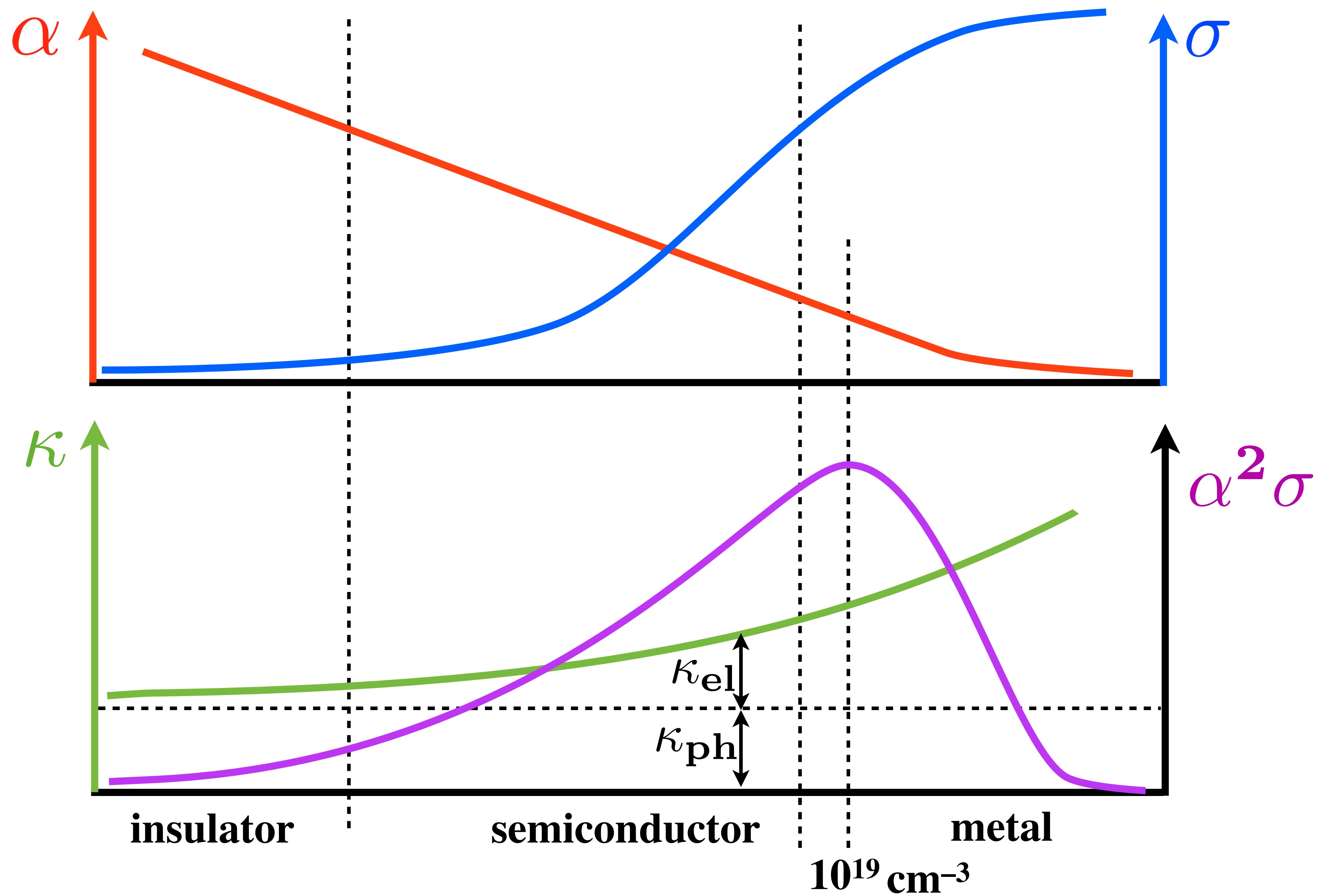
Thermoelectric Effect vs Doping of Semiconductors



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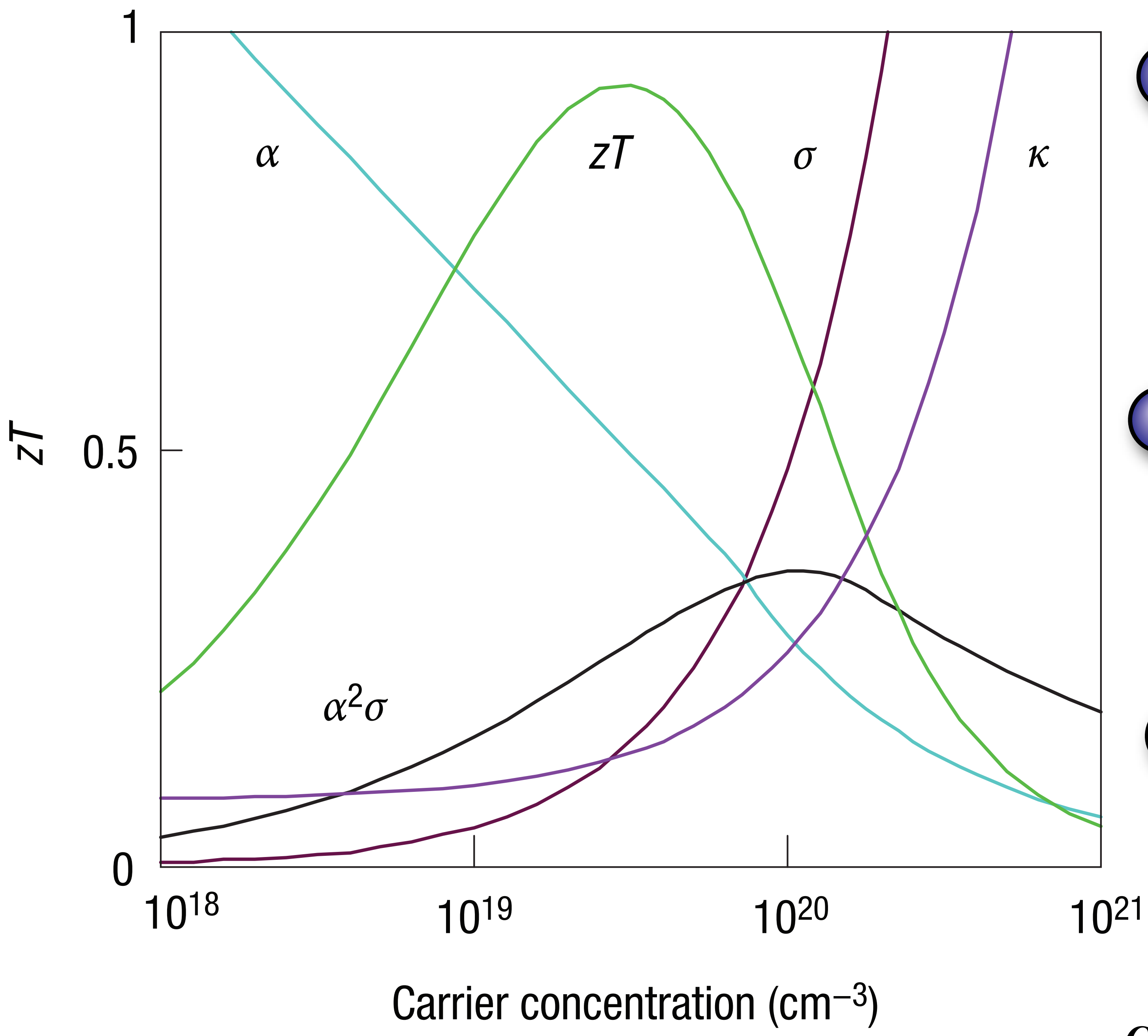
Bi_2Te_3 ZT Optimisation Through Doping



- **Maximum ZT requires compromises with α, σ & κ**
- **Limited by Wiedemann-Franz Law**
- **Maximum ZT ~ 1 at ~100 ˚C**

G.J. Snyder et al., Nature Mat. 7, 105 (2008)

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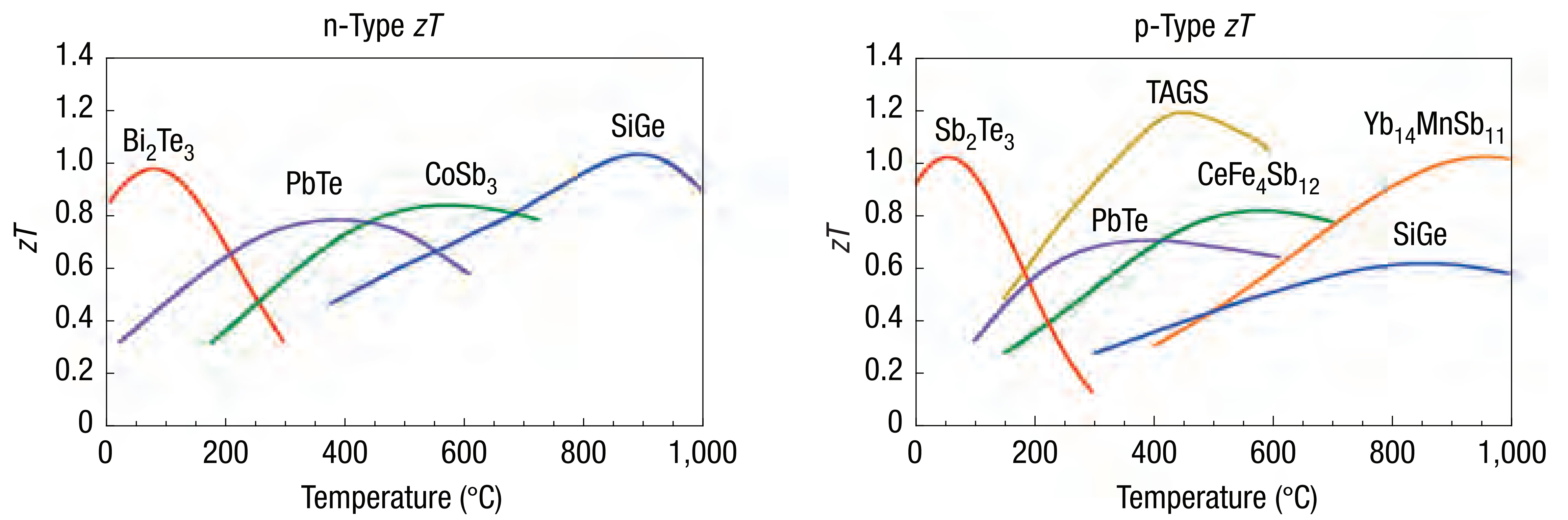
Bulk Thermoelectric Materials Performance



Nature Materials 7, 105 (2008)

- **Bulk n-Bi_2Te_3 and p-Sb_2Te_3 used in most commercial Peltier coolers**
- **Bulk $Si_{1-x}Ge_x$ (x~0.2 to 0.3) used for high temperature satellite applications**
- **ZT in bulk materials limited by Wiedemann-Franz law**

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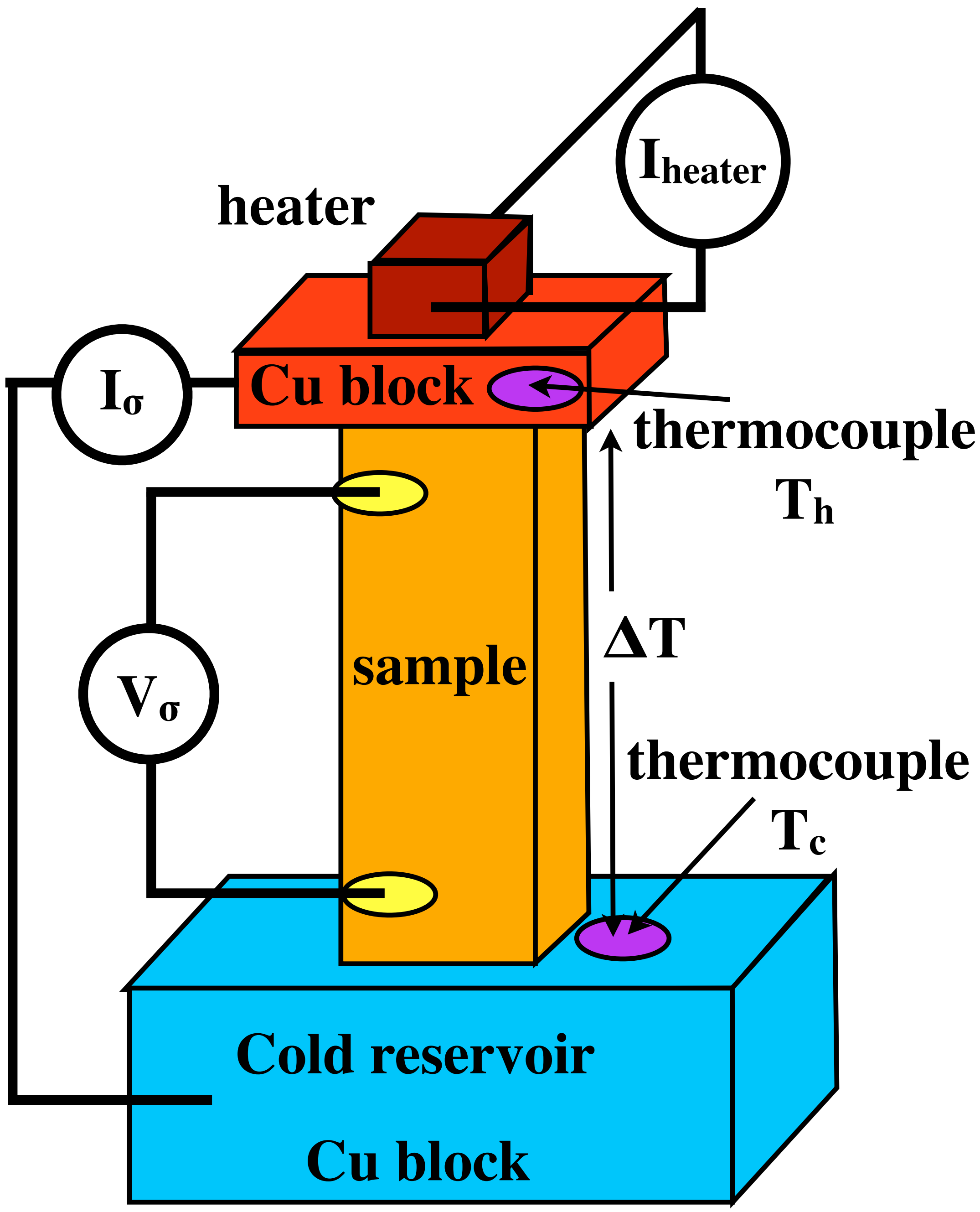
Measuring α, κ, σ and ZT

- σ can be determined to > 4 significant figures without difficulty
- Seebeck voltage can be measured to > 4 significant figures but temperature is more difficult
- Measuring heat flow accurately is extremely difficult i.e. κ
- The result is that measurements of ZT can have large uncertainties
- Care needs to be taken in measuring α, σ, κ and ZT

Measuring Seebeck Coefficient



- Physically heat one side of sample
- Cold sink at the other side of sample
- Thermocouples top and bottom to measure ΔT
- 4 terminal electrical measurements

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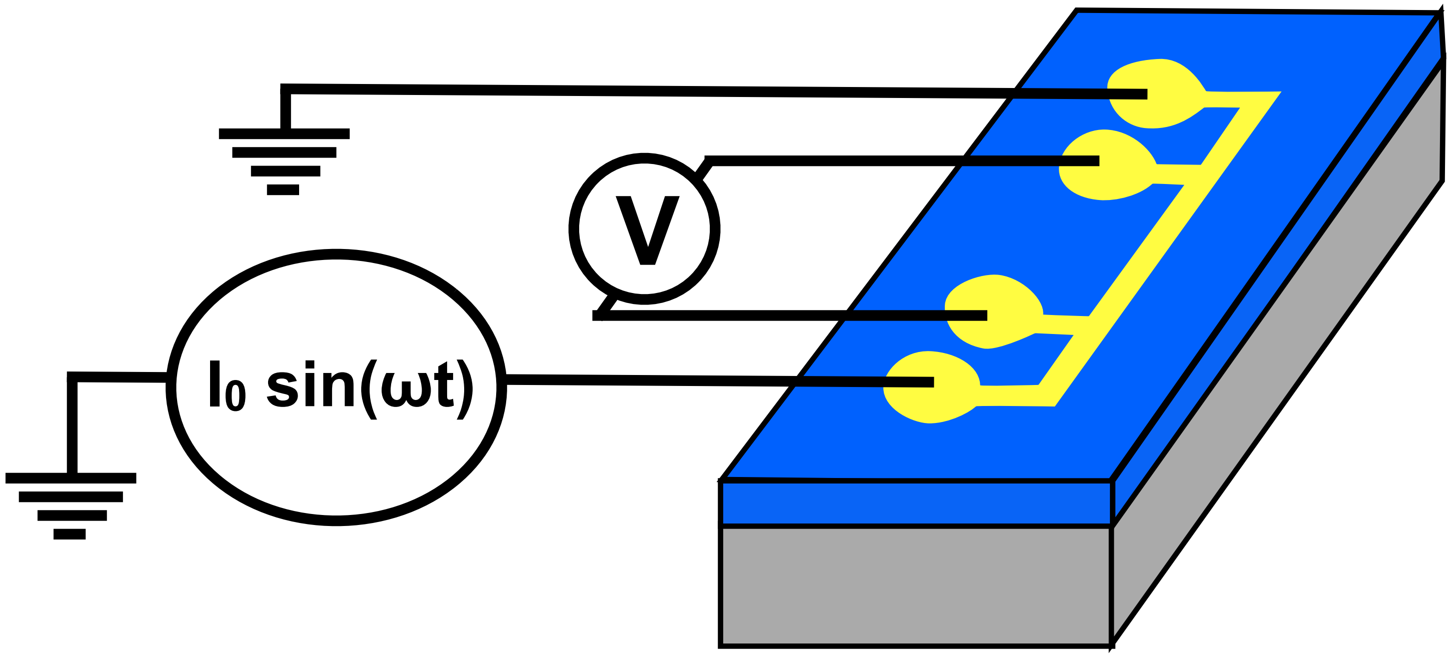
3ω Thermal Conductivity Measurements



$I \sim \omega$

$T \sim I^2 \sim 2\omega$

$R \sim T \sim 2\omega$

$V = IR \sim 3\omega$

- AC current of frequency ω will produce Joule heating = I^2R at frequency 2ω
- Measured voltage, V = IR will have both an ω and 3ω component
- $$V = IR = I_0 e^{i\omega t}\left[R_0 + \frac{\delta R}{\delta T}\Delta T\right]$$

$$V = I_0 e^{i\omega t}\left(R_0 + C_0 e^{i2\omega t}\right)$$

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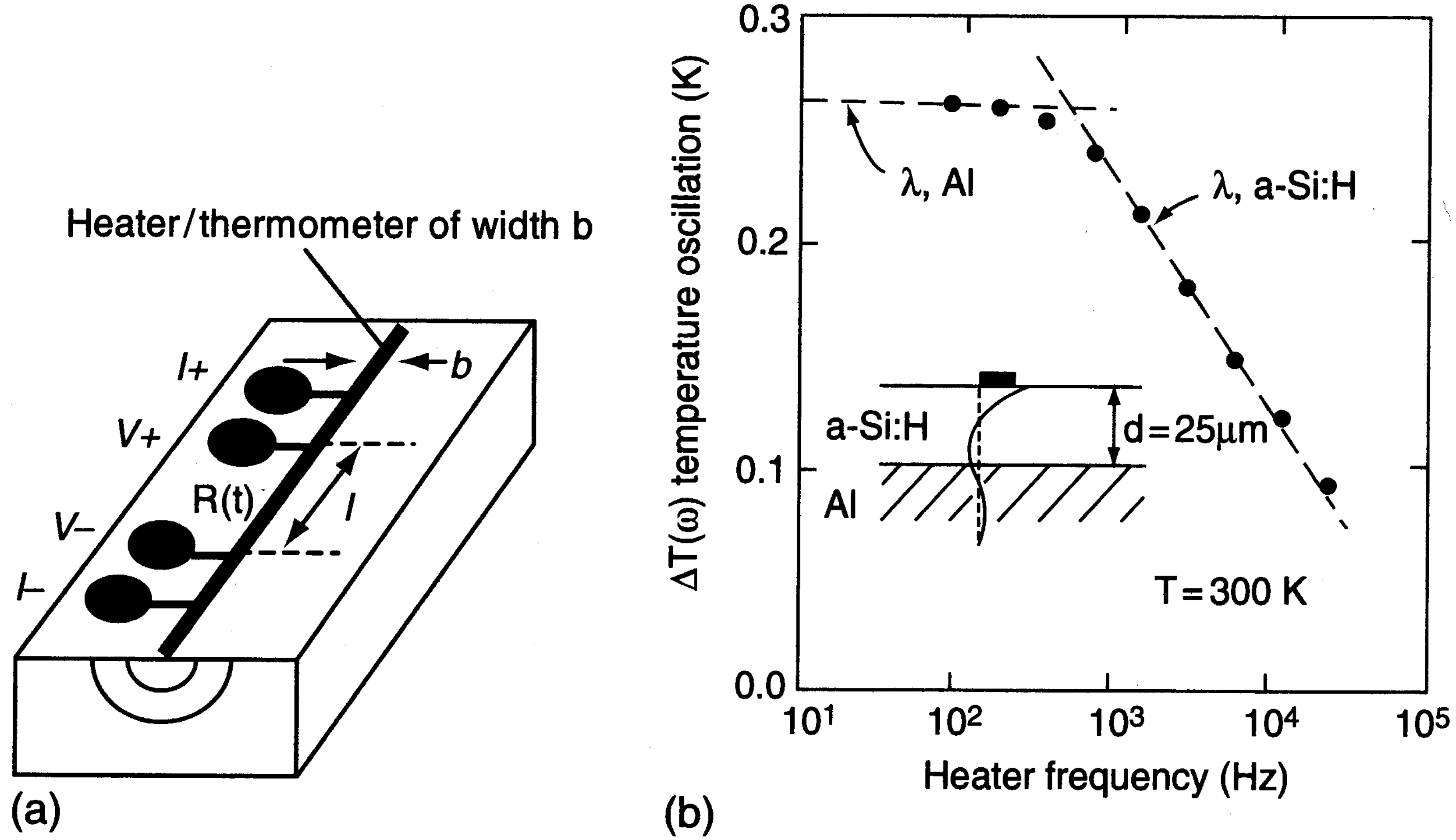
3ω Technique for Measuring Thermal Conductivity

V applied at frequency ω



$$\kappa = \frac{V^3 \ln(\frac{\omega_1}{\omega_2})}{4\pi l R^2 [V_3(\omega_2) - V_3(\omega_1)]} \frac{dR}{dT}$$

- $V_3(\omega_1)$ and $V_3(\omega_2)$ are voltages at 3rd harmonic frequencies ω_1 and ω_2

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3ω Issues and Limitations

- 3ω technique uses 1st term from Taylor expansion i.e. approximation

- 3ω technique only works for uniform bulk layers

- Superlattices and quantum dots are seldom valid in the approximation

- Other techniques required for accurate thermal conductivity measurements

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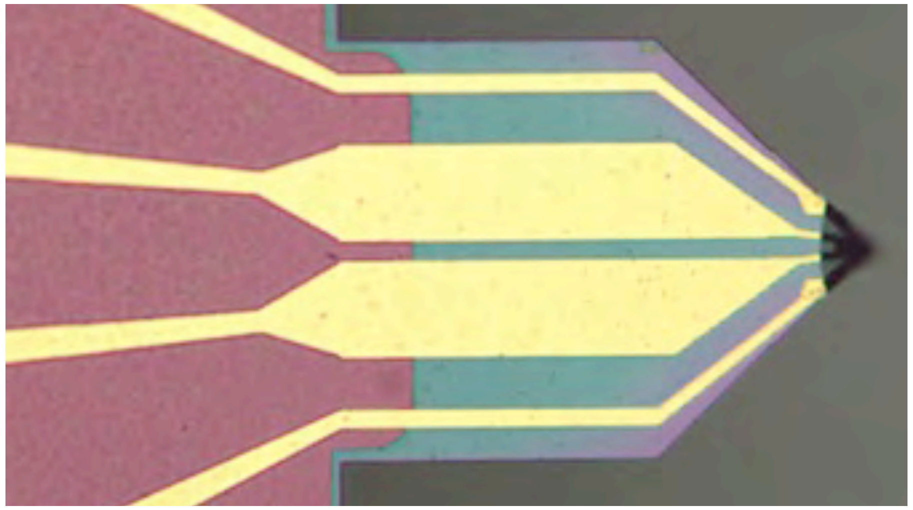
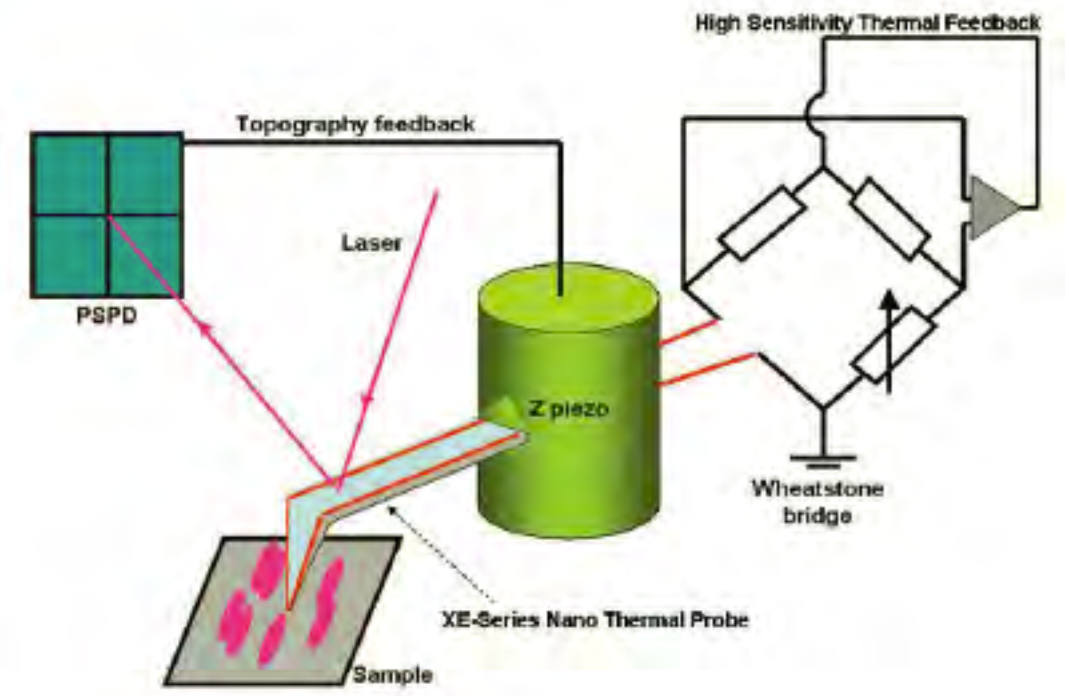
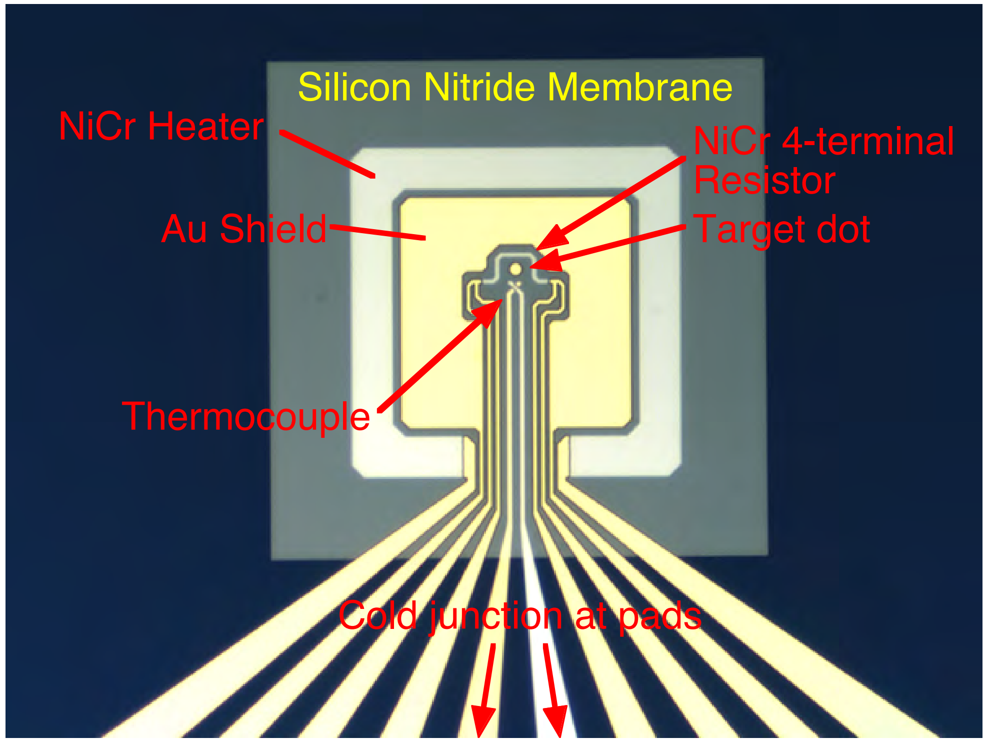
Thermal Conductivity using Thermal AFM

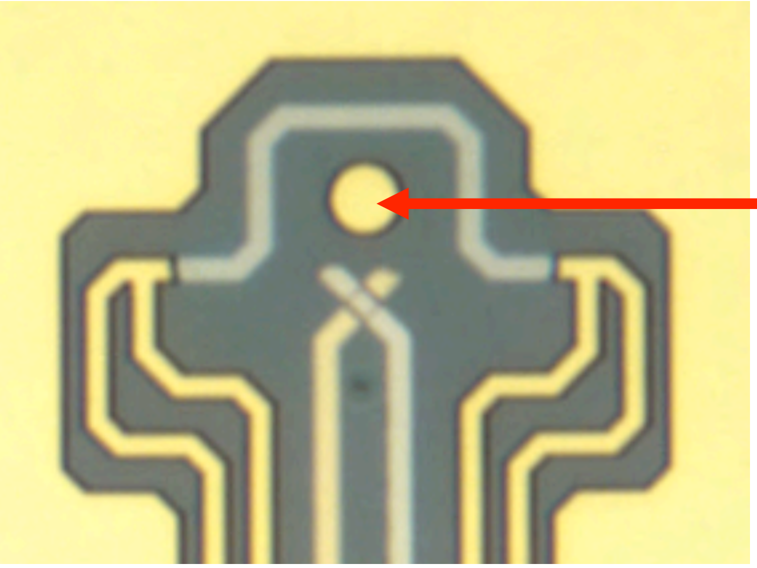




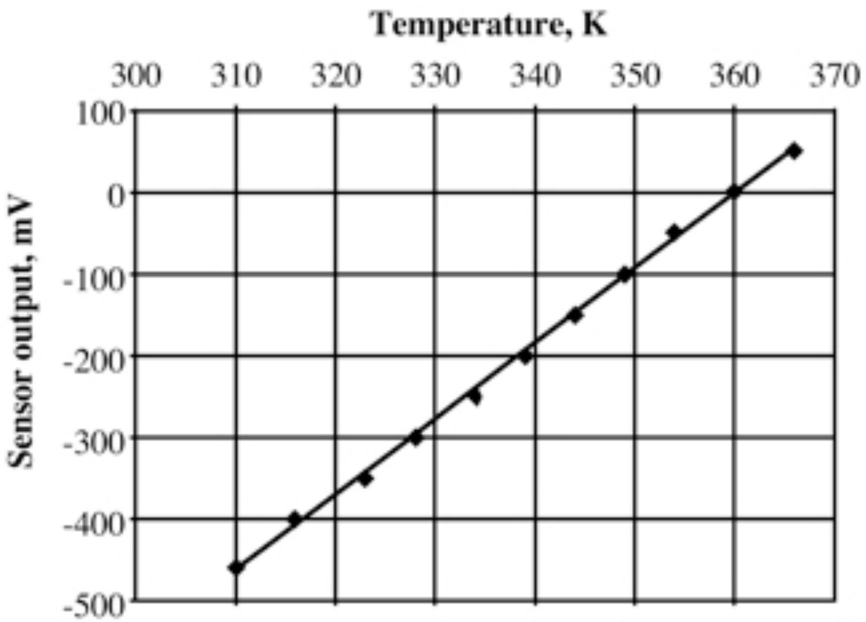
- Spatial resolution < 100 nm (ideal for micro and nano structures)
- Temperature resolution to 0.1 K
- Direct temperature measurements and 3ω

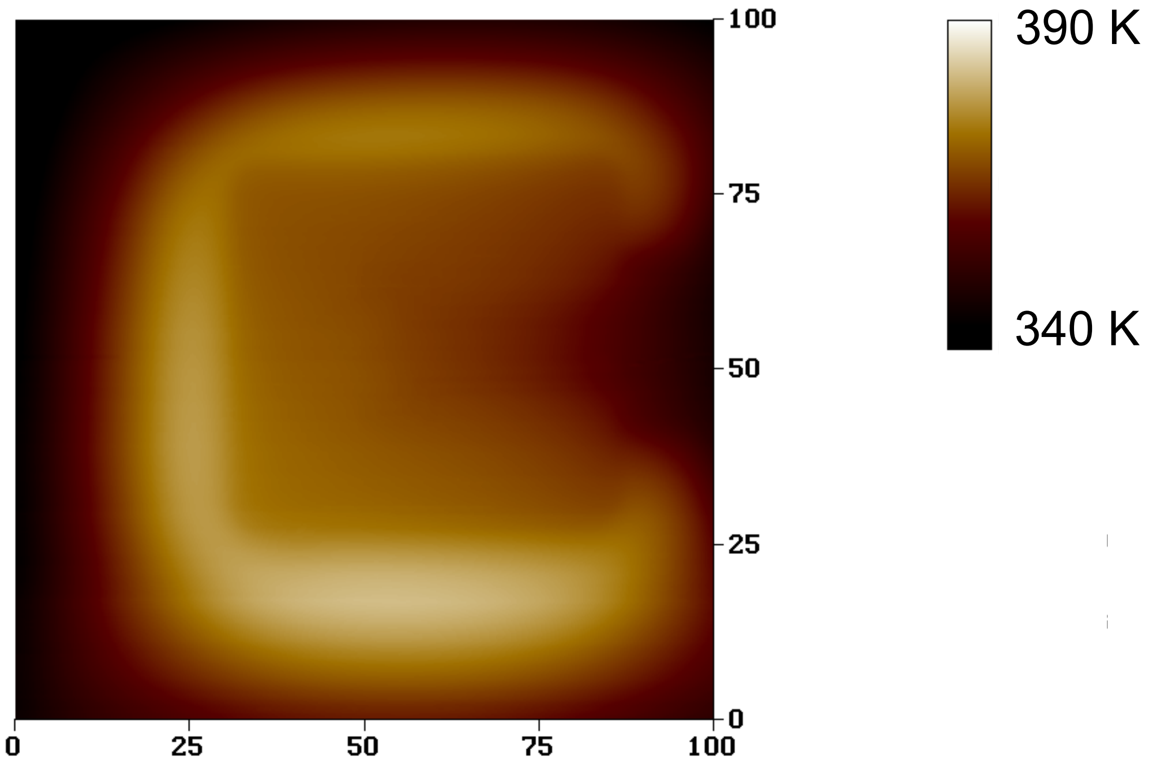
Thermal Calibration





Electrically isolated Au spot: isothermal with resistor





P. S. Dobson, et al., Rev. Sci. Inst. 76, 054901 (2006)

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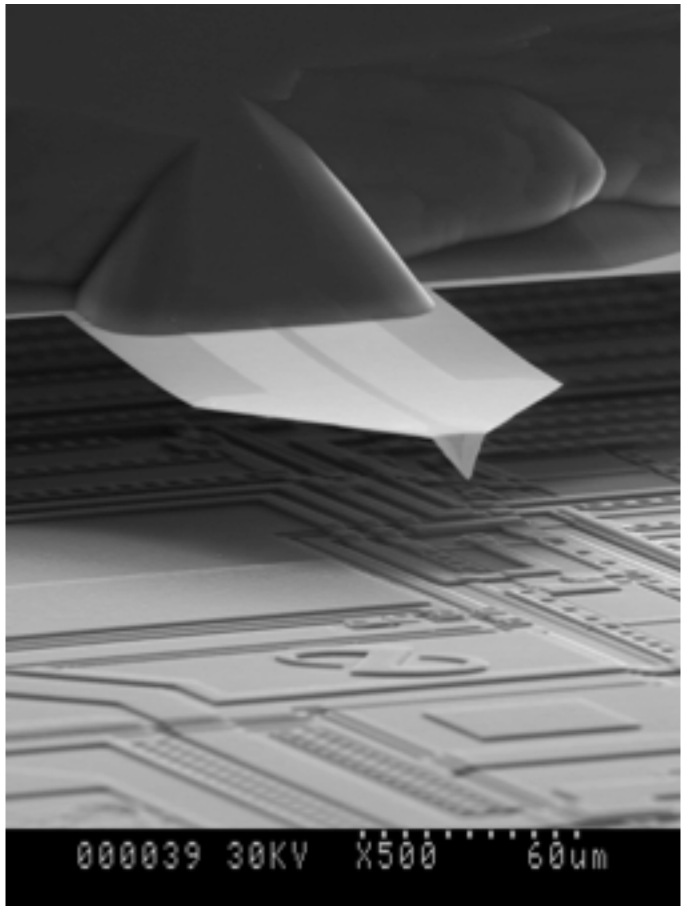
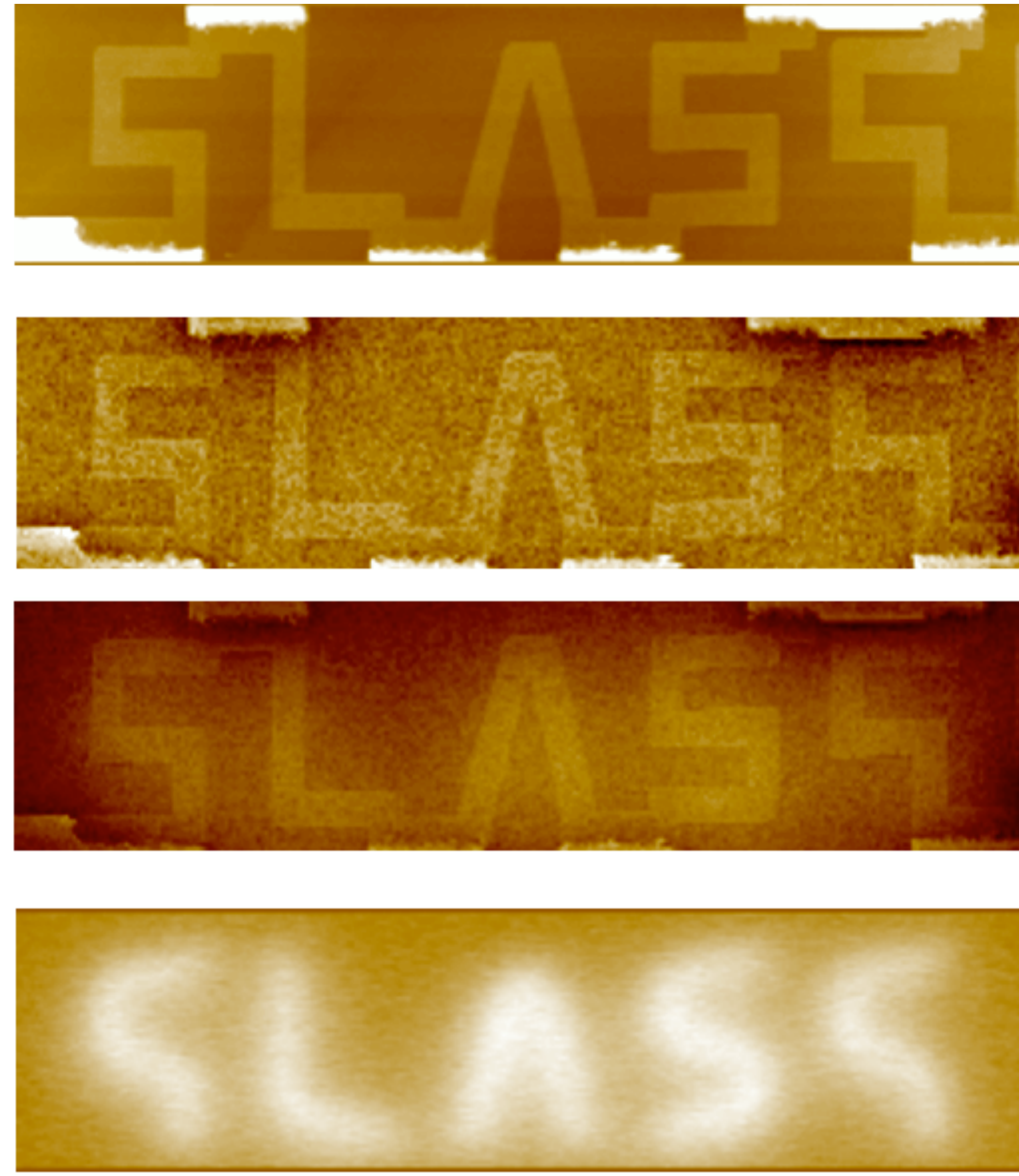
AFM Thermal Measurements

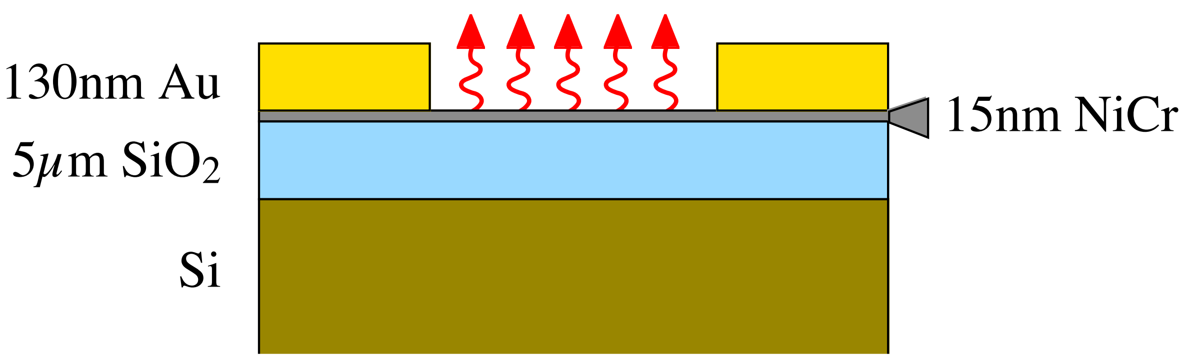


Topography

Thermal conduction

Temperature

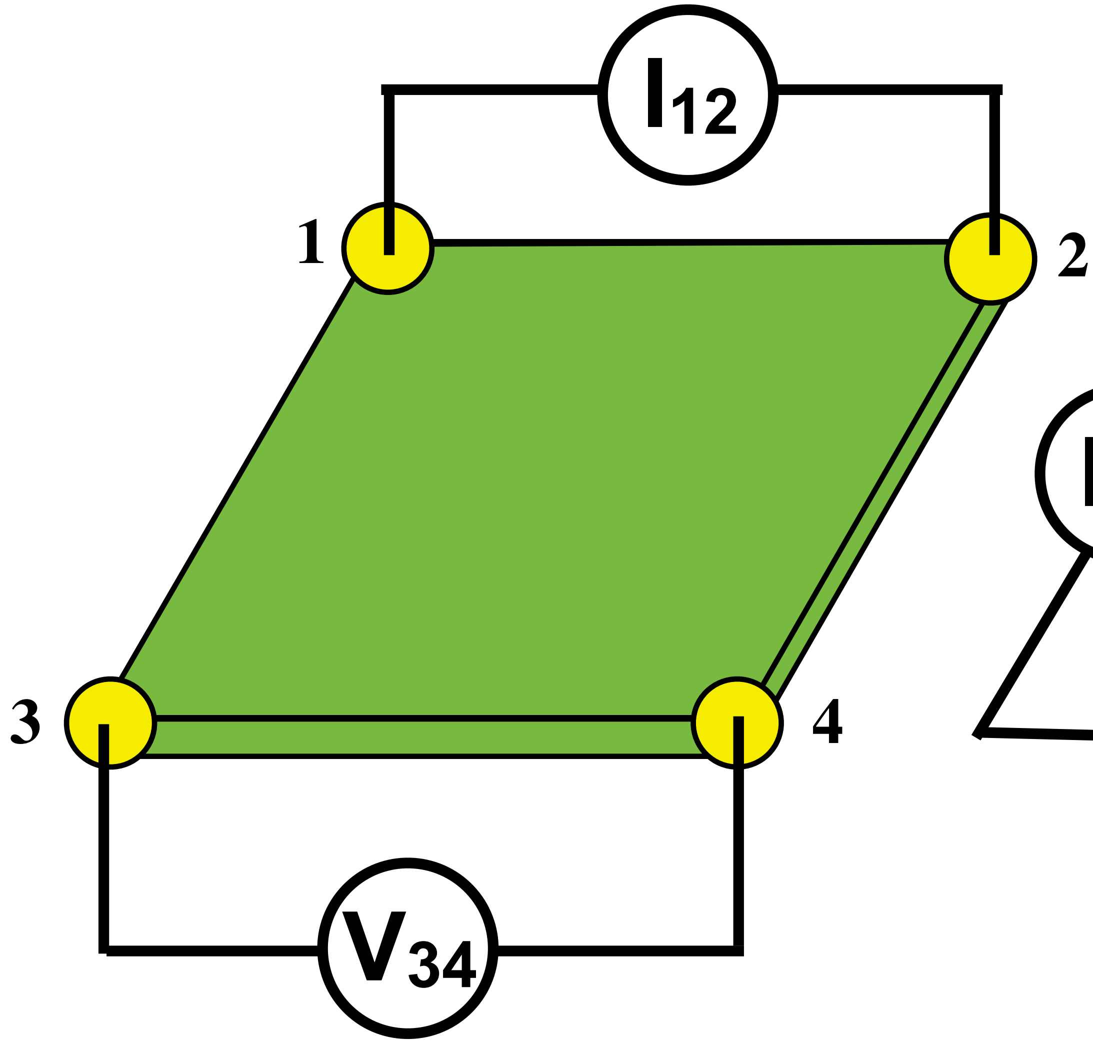


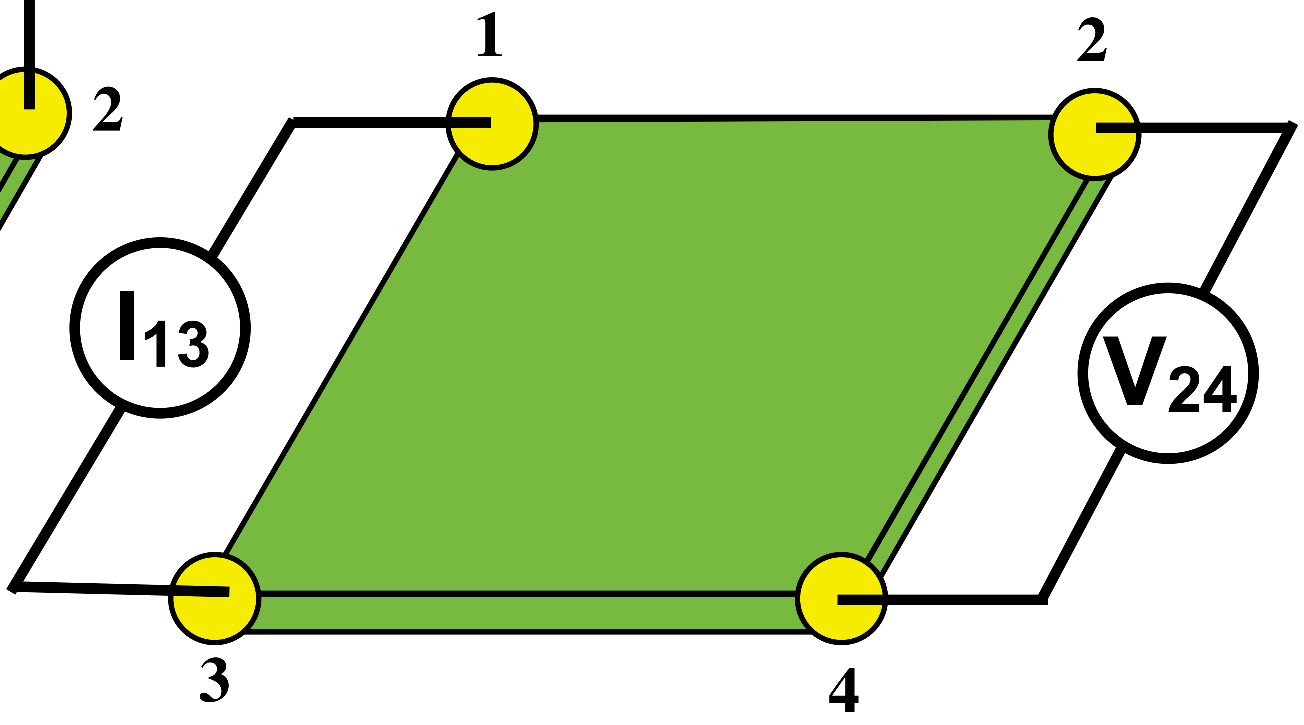


Lock in signal 35 kHz 2ω

P.D. Dobson, J.M.R. Weaver et al.

Electrical Measurements: Van der Pauw





For a square

$$\sigma = \frac{I_{12}}{V_{34}} = \frac{I_{13}}{V_{24}}$$

If contact area large then Δσ > 50%

Δσ increases for smaller devices and larger contacts

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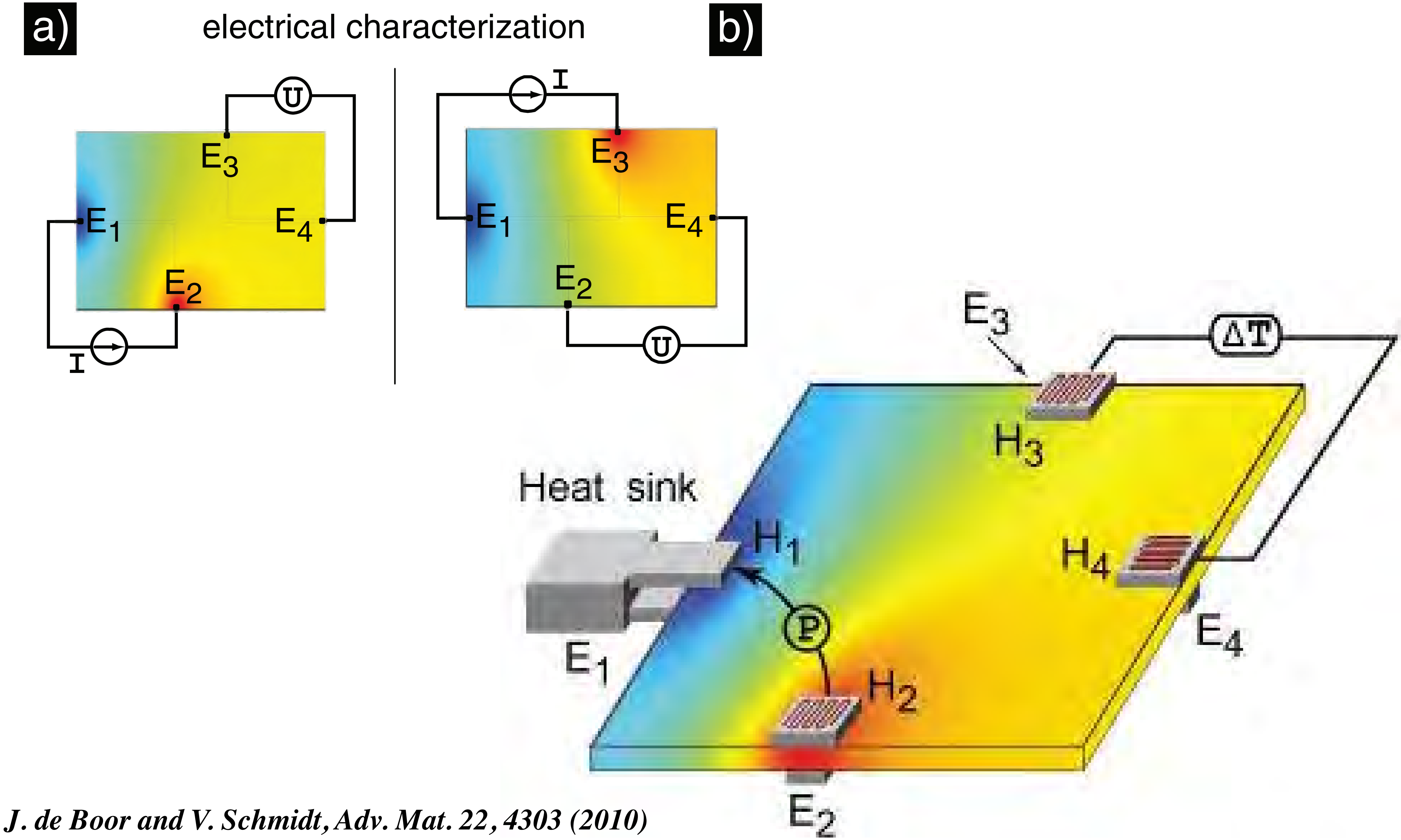
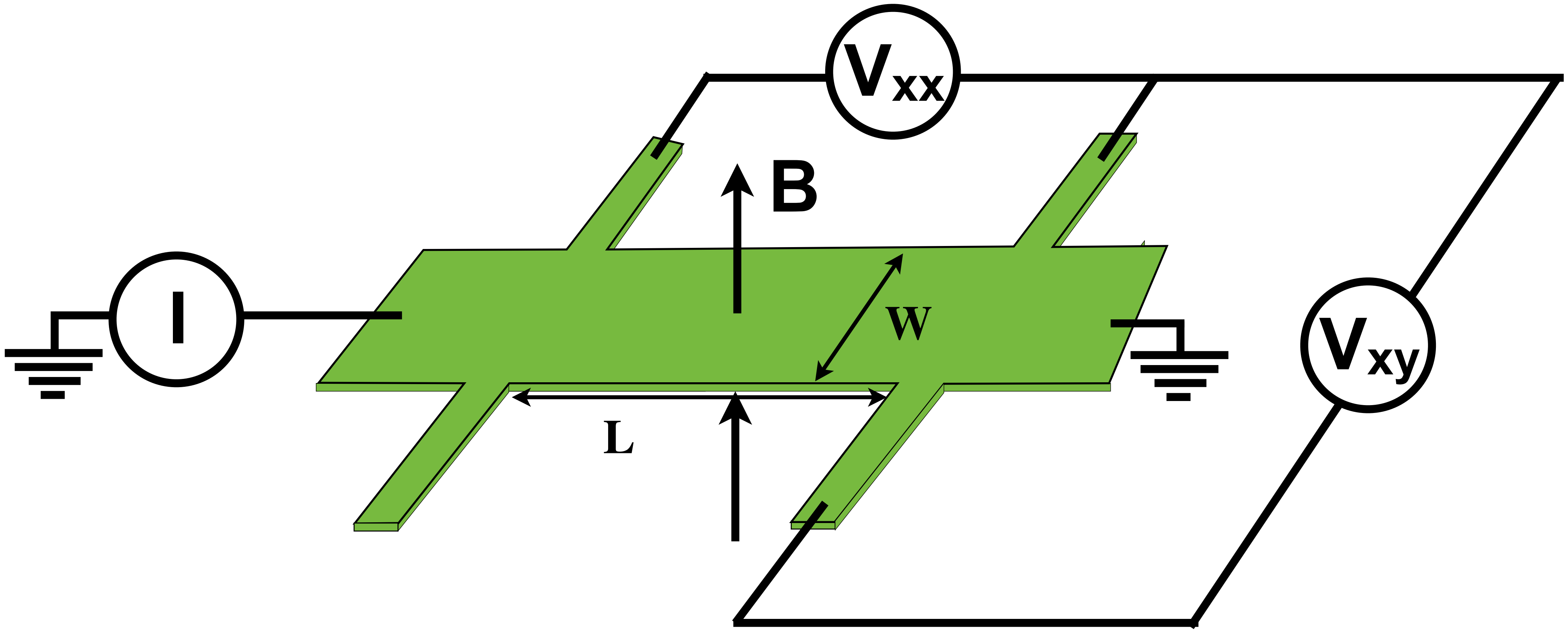
Combined σ and κ from van der Pauw



J. de Boor and V. Schmidt, Adv. Mat. 22, 4303 (2010)

Electrical Measurements: Hall Measurements

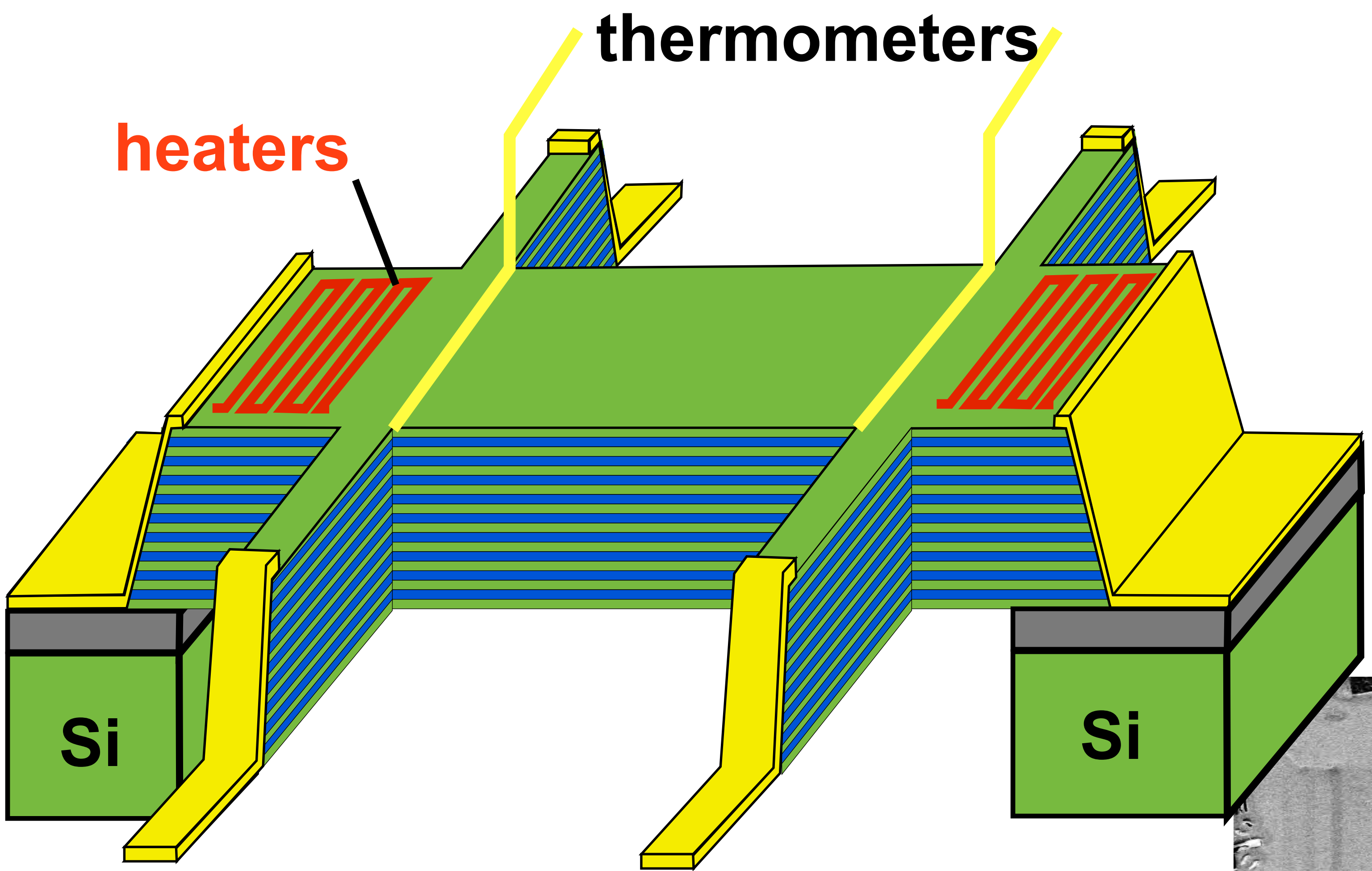


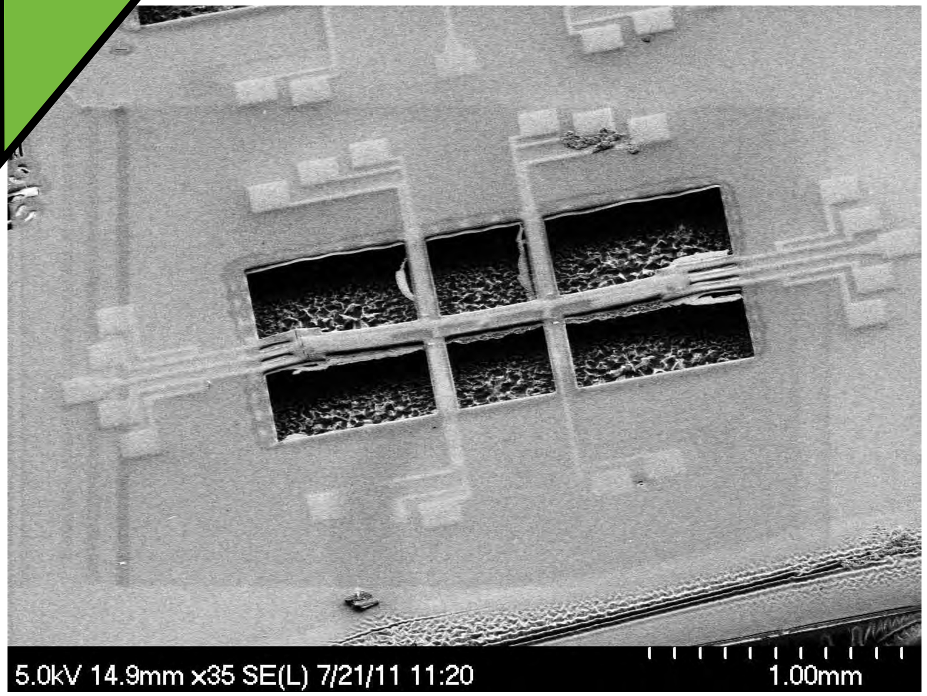
$$\sigma = \frac{IW}{V_{xx}L}$$

If $L > 3W$ then $\Delta\sigma < 10^{-3}$

Application of magnetic field, B gives carrier density and mobility through V_{xy} measurement

α, κ, σ and ZT Measurements in Single Device





The Uncertainty in Measuring ZT

- Many materials with ZT > 1.5 reported but few confirmed by others
- No devices demonstrated with such high efficiencies
- Due to: measurement uncertainty & complexity of fabricating devices
- $$\frac{\Delta(\mathrm{ZT})}{\mathrm{ZT}} = 2\frac{\Delta\alpha}{\alpha} + \frac{\Delta\sigma}{\sigma} + \frac{\Delta\kappa}{\kappa} + \frac{\Delta \mathrm{T}}{\mathrm{T}}$$

  Δx = uncertainty in x = standard deviation in x
- Measurements are conceptually simple but results vary considerably due to thermal gradients in the measurements –> systematic inaccuracies
- Total ZT uncertainty can be between 25% to 50%

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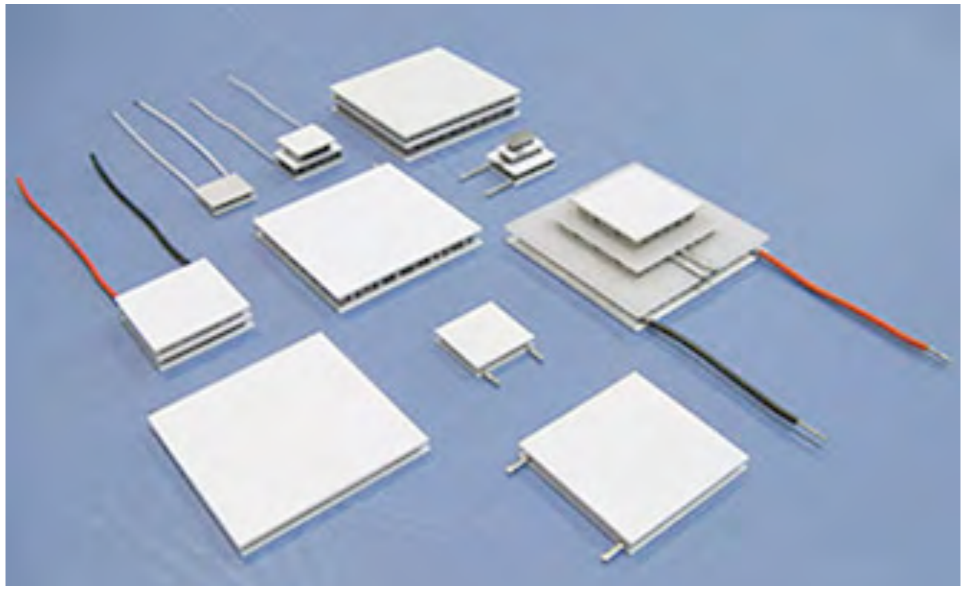
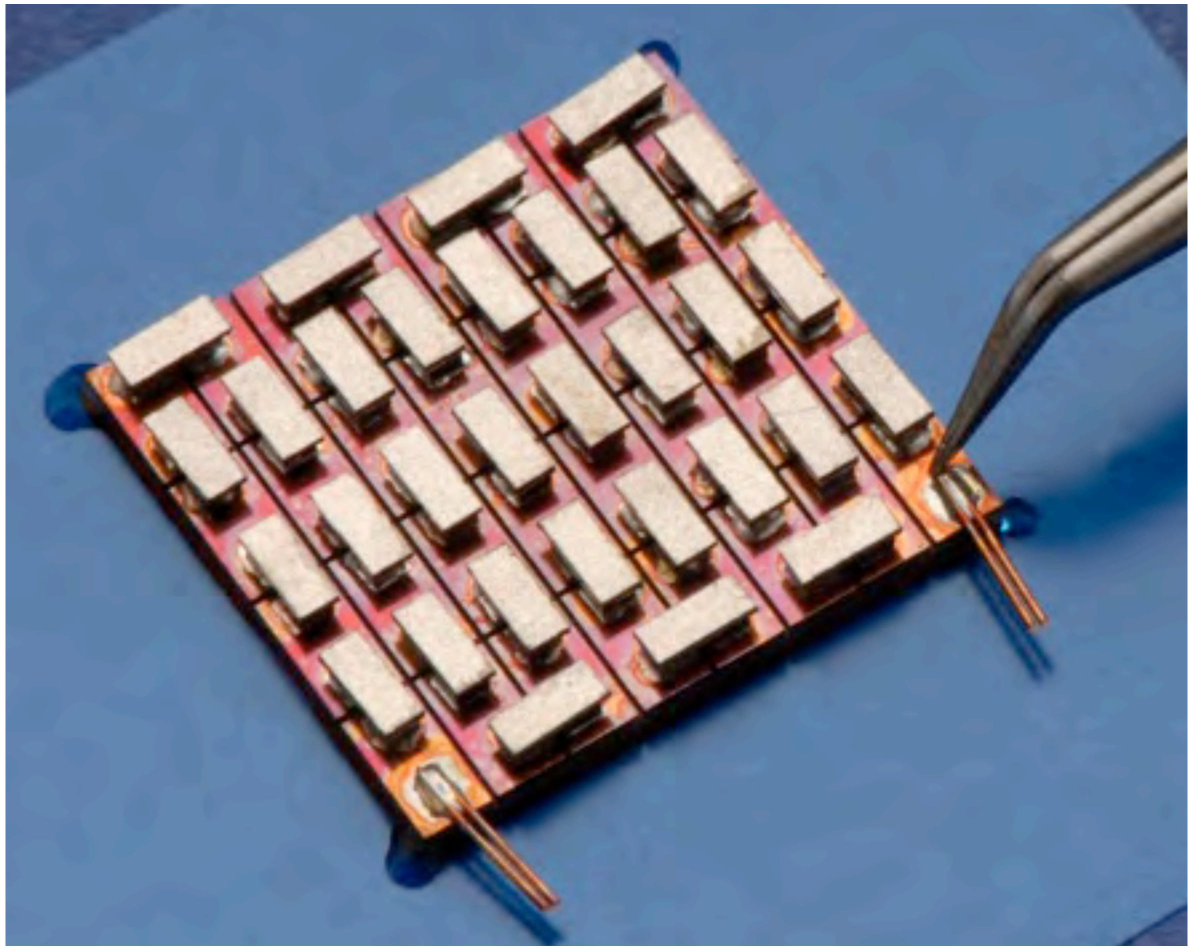
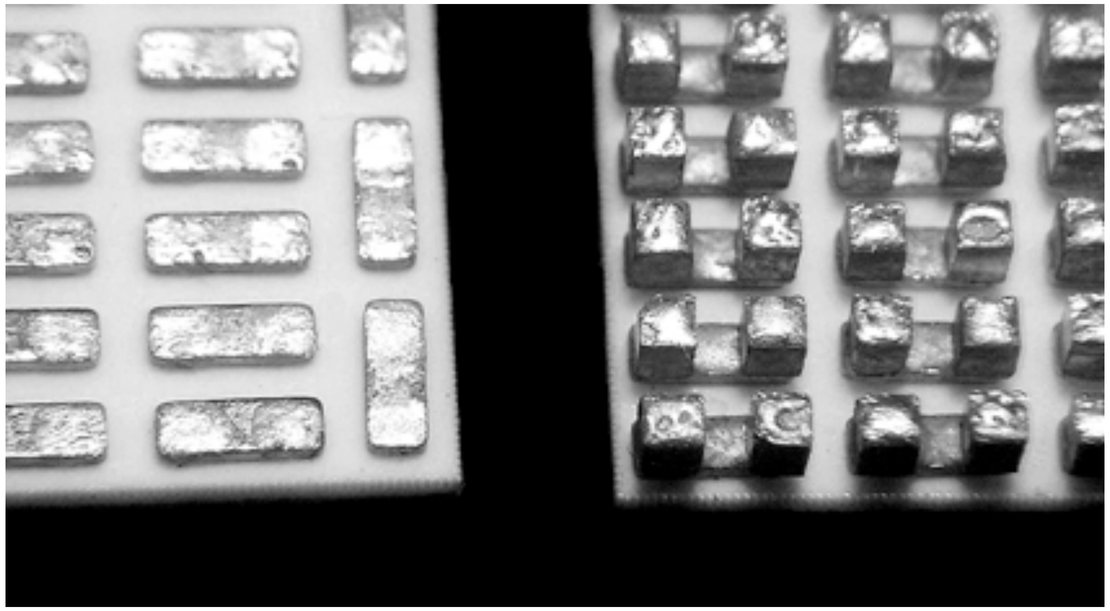
Thermoelectric Generators / Peltier Coolers

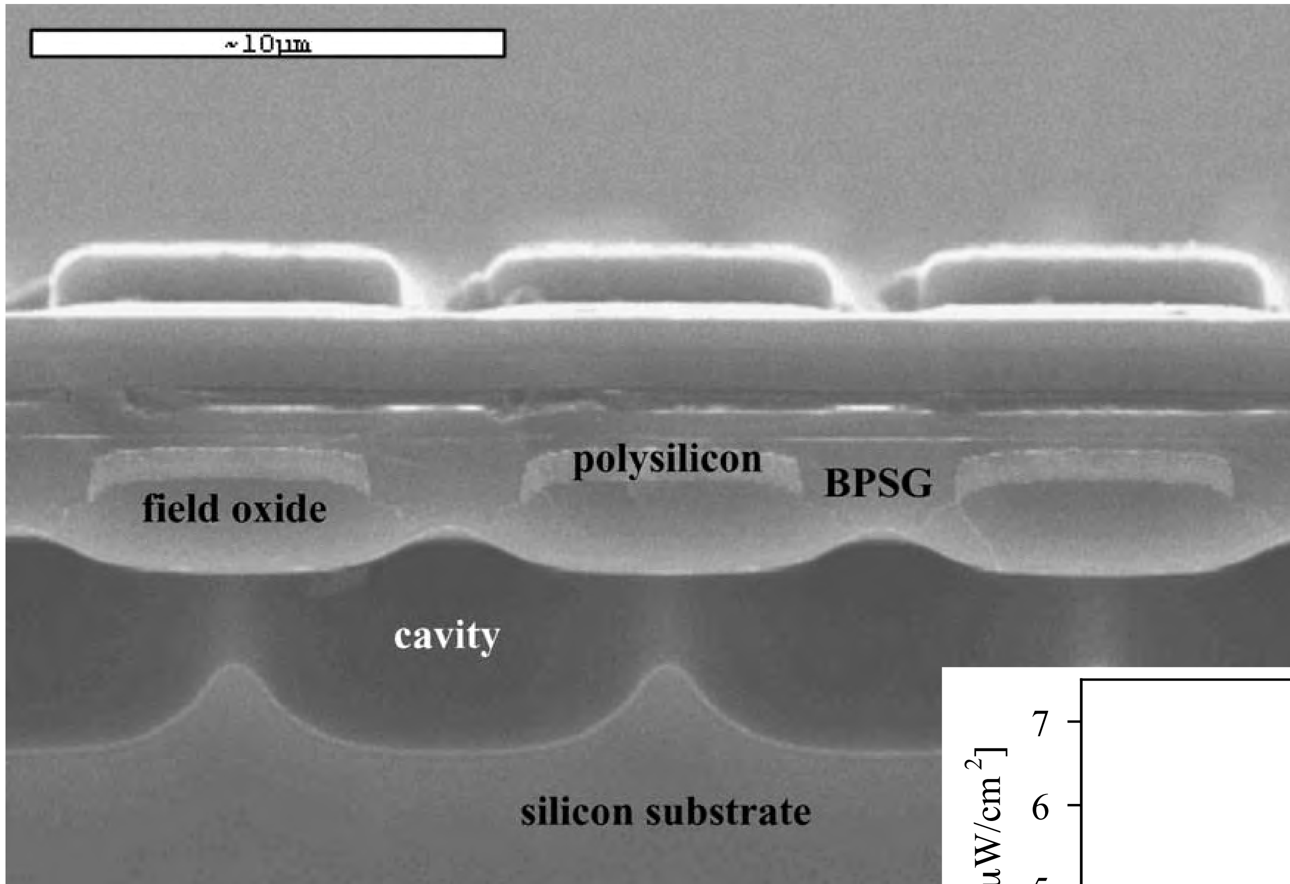


Bulk n-Bi_2Te_3 and p-Sb_2Te_3 devices

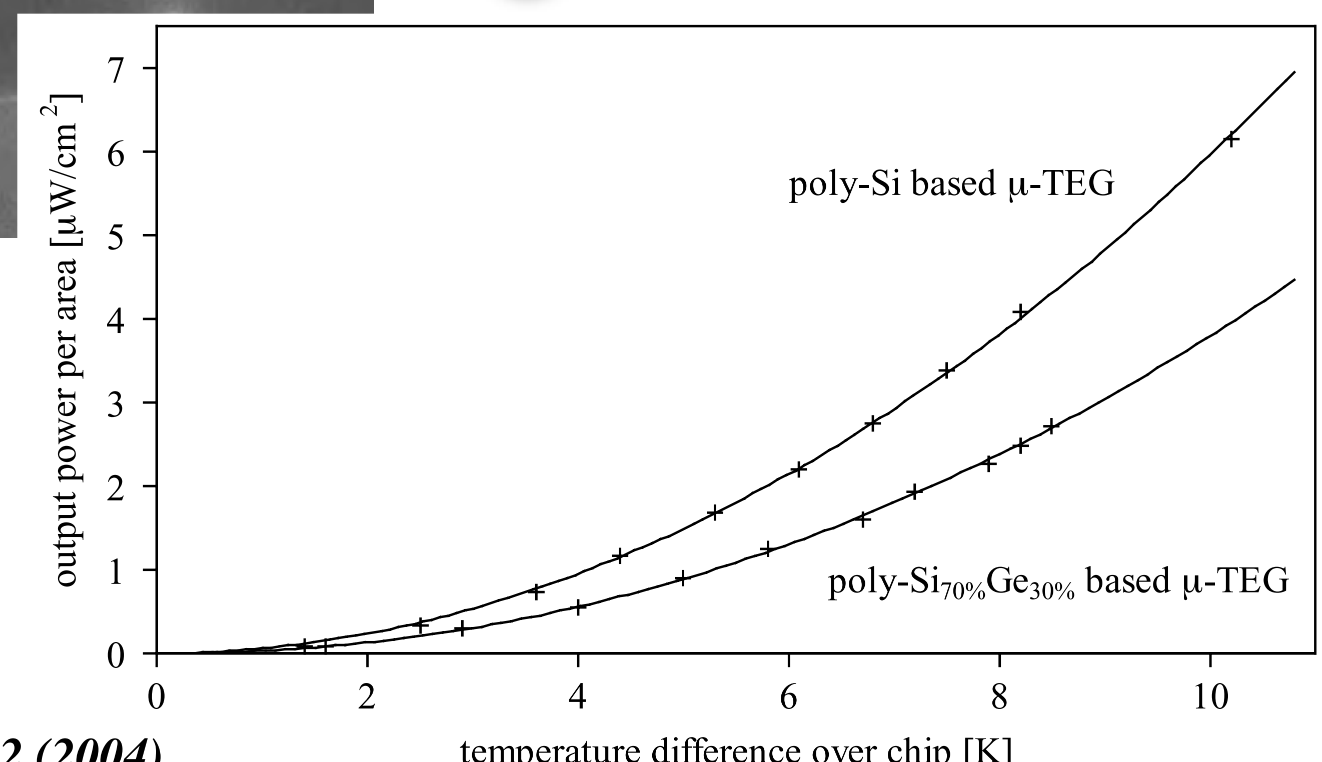




Small Scale Microfabricated Energy Harvesting



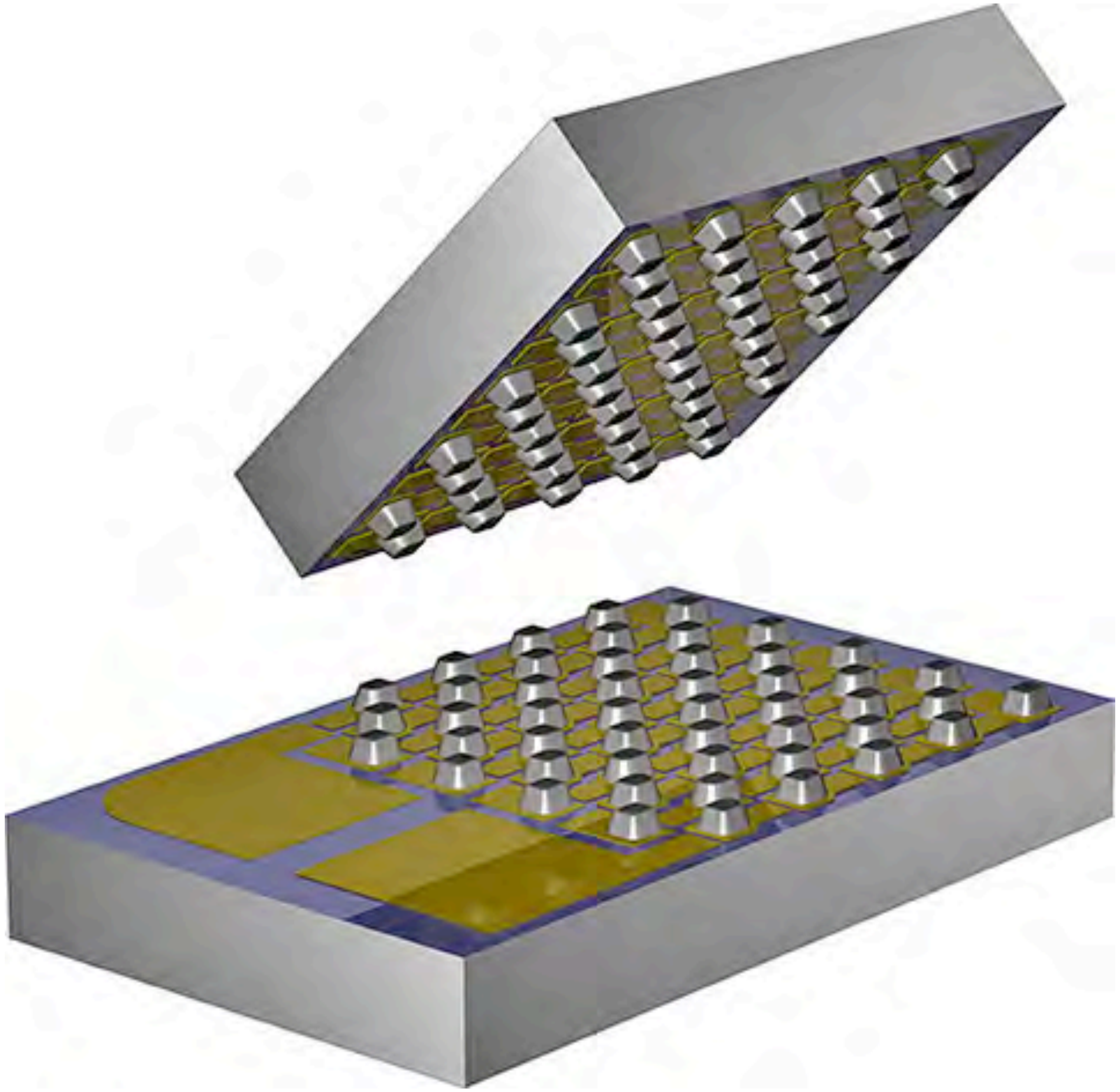
- Si process: poly-Si
- α_{n+p} = 160 μV/K
- κ = 31.4 $Wm^{-1}K^{-1}$
- ϱ = 1.5 mΩ-cm

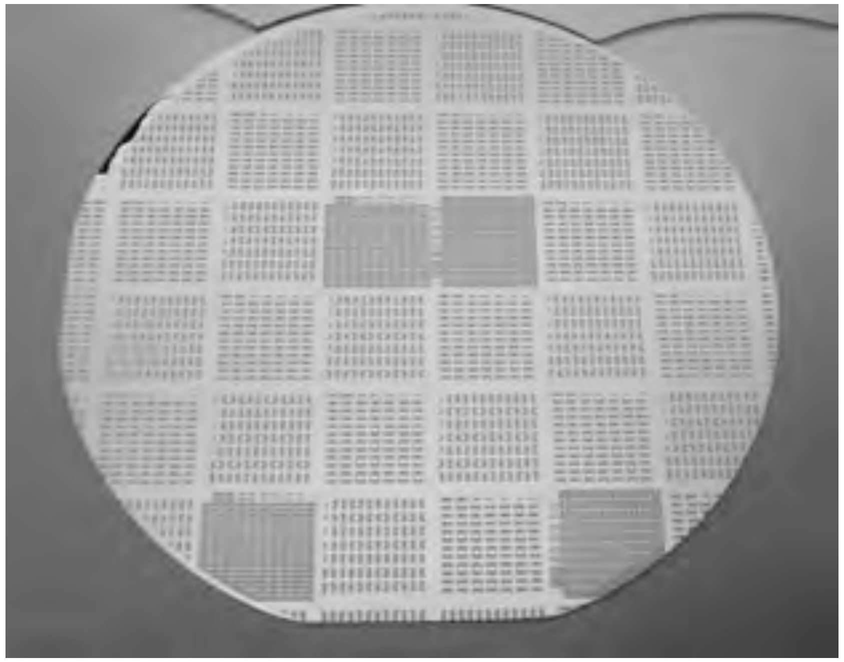


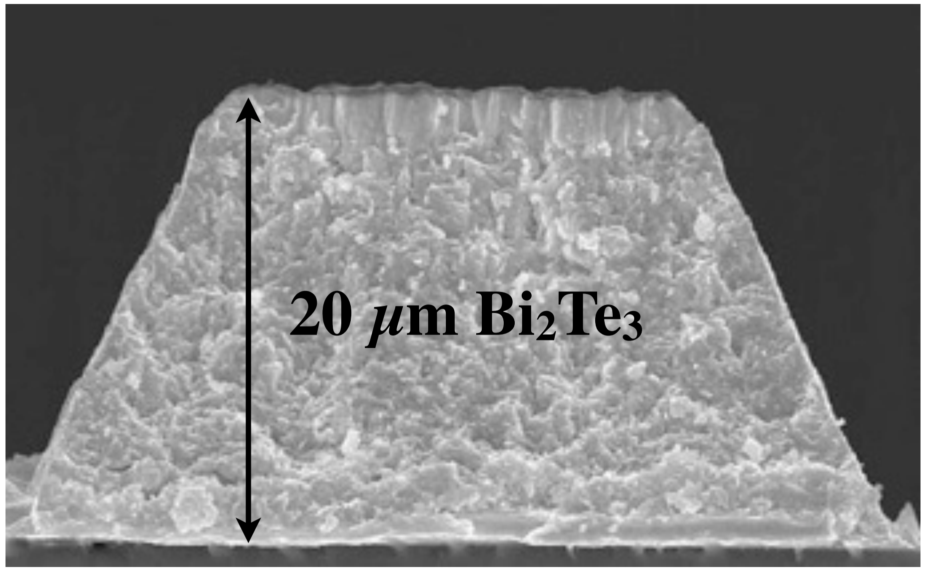
ΔT = 5 K –> 5 V and 1 μW

M. Strasser et al., Sensors Actuators A 114, 362 (2004)

Micropelt: Microfabricated Bi_2Te_3 Technology







http://www.micropelt.com/

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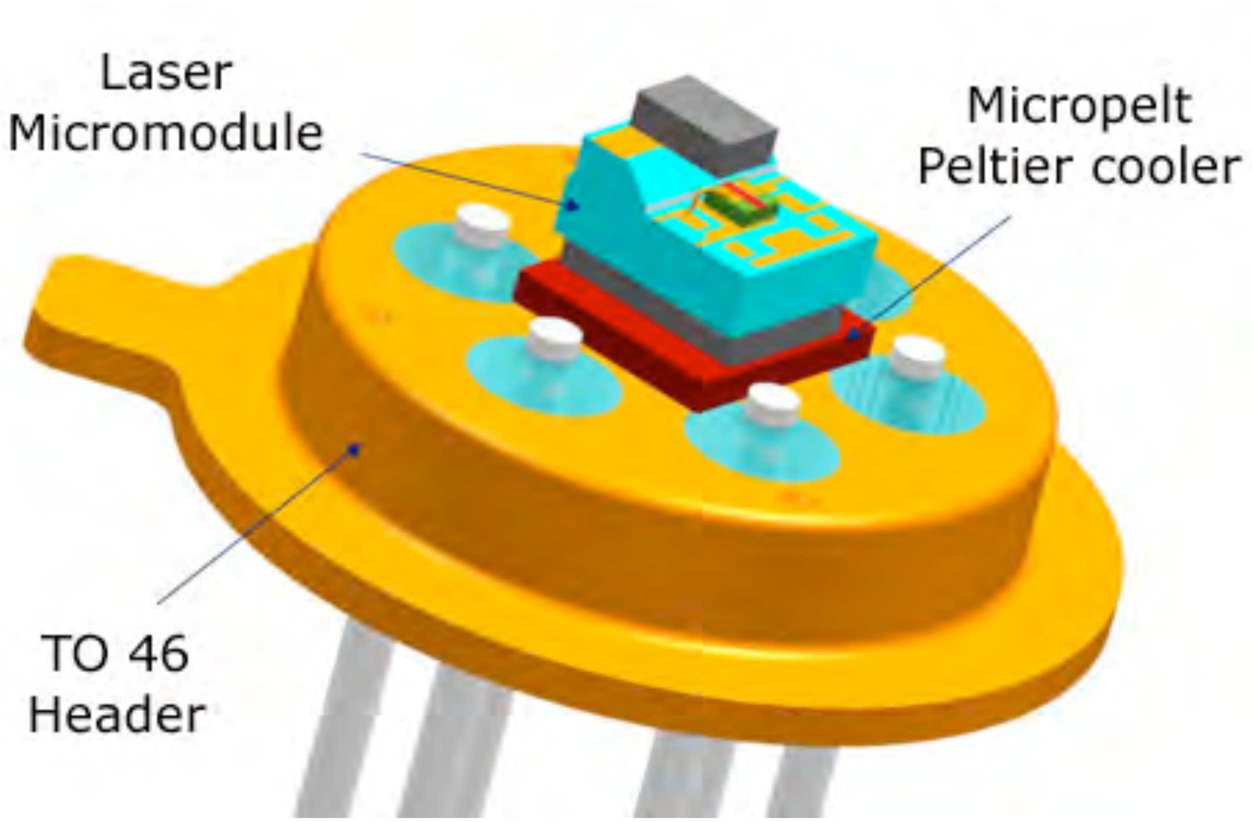
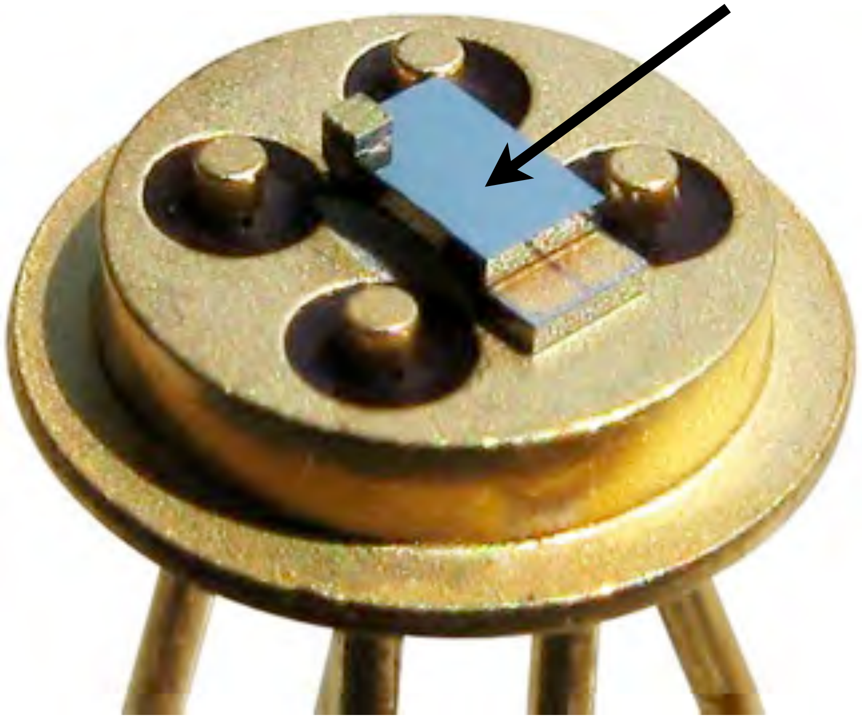
Micropelt Peltier Coolers for Lasers

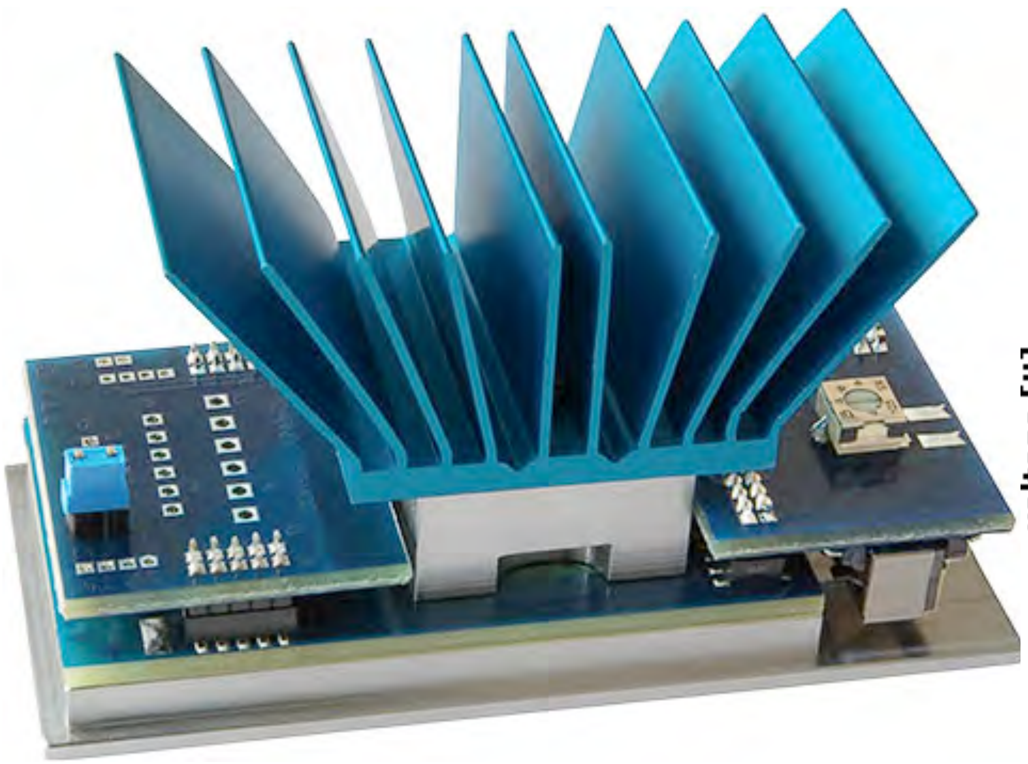
- Microfabricated Bi_2Te_3 thermoelectric devices



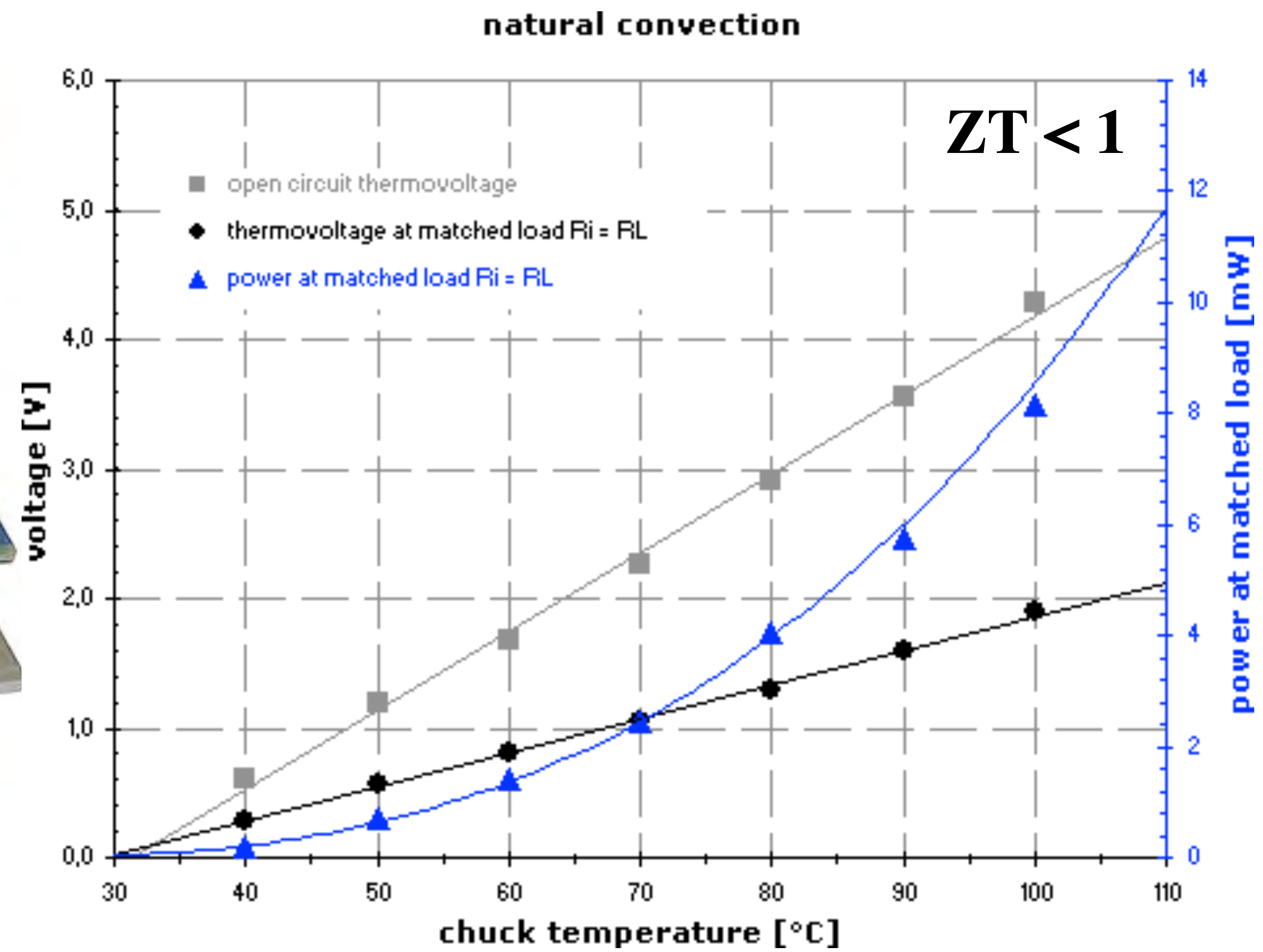


http://www.micropelt.com/

Micropelt Bi_2Te_3 Thermoelectric Energy Harvester



3.4 mm x 3.4 mm
thermoelectric chip



http://www.micropelt.com/

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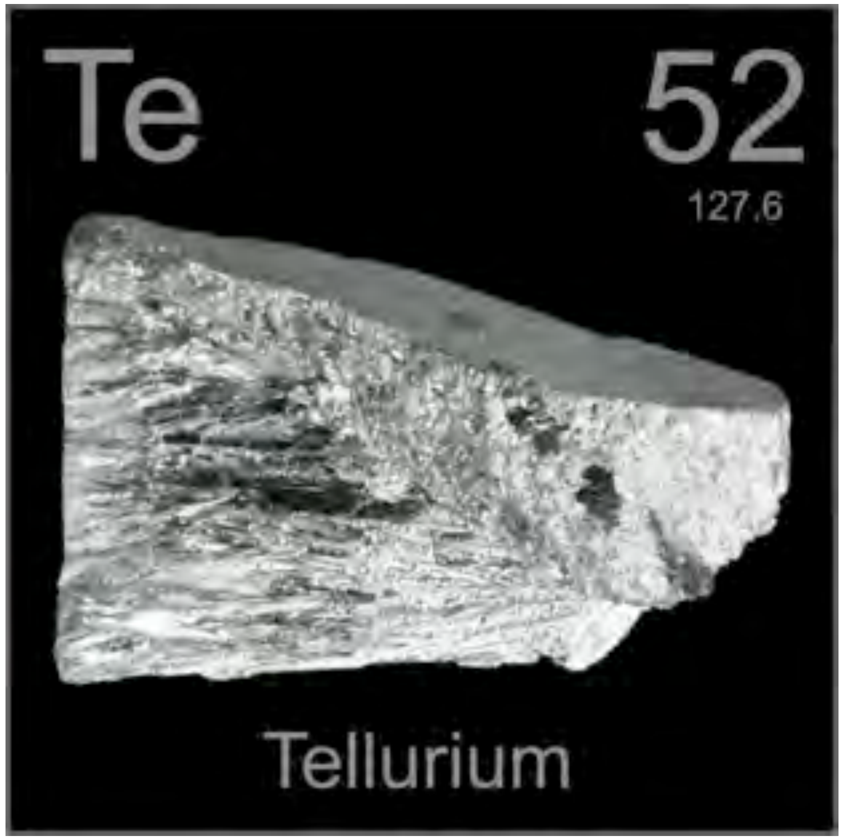
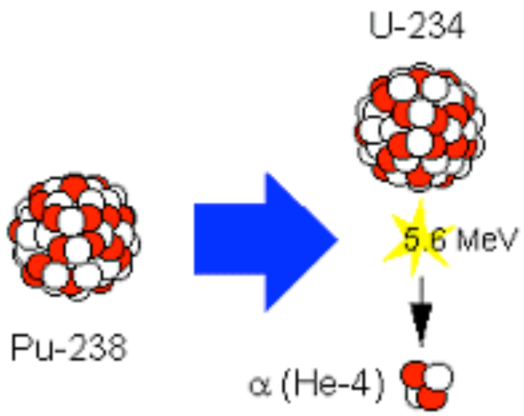
Rare Elements !!!!!

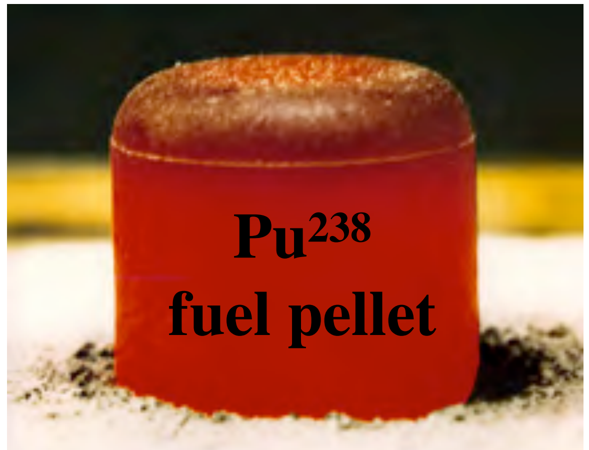


- Tellurium is the 7th rarest element on planet earth
- Supply is limited and price fluctuations are enormous on a weekly basis
- Te based materials are unlikely to be available in the (near) future!
- Sustainable thermoelectrics needs new sustainable or plentiful materials and not Bi_2Te_3 or PbTe

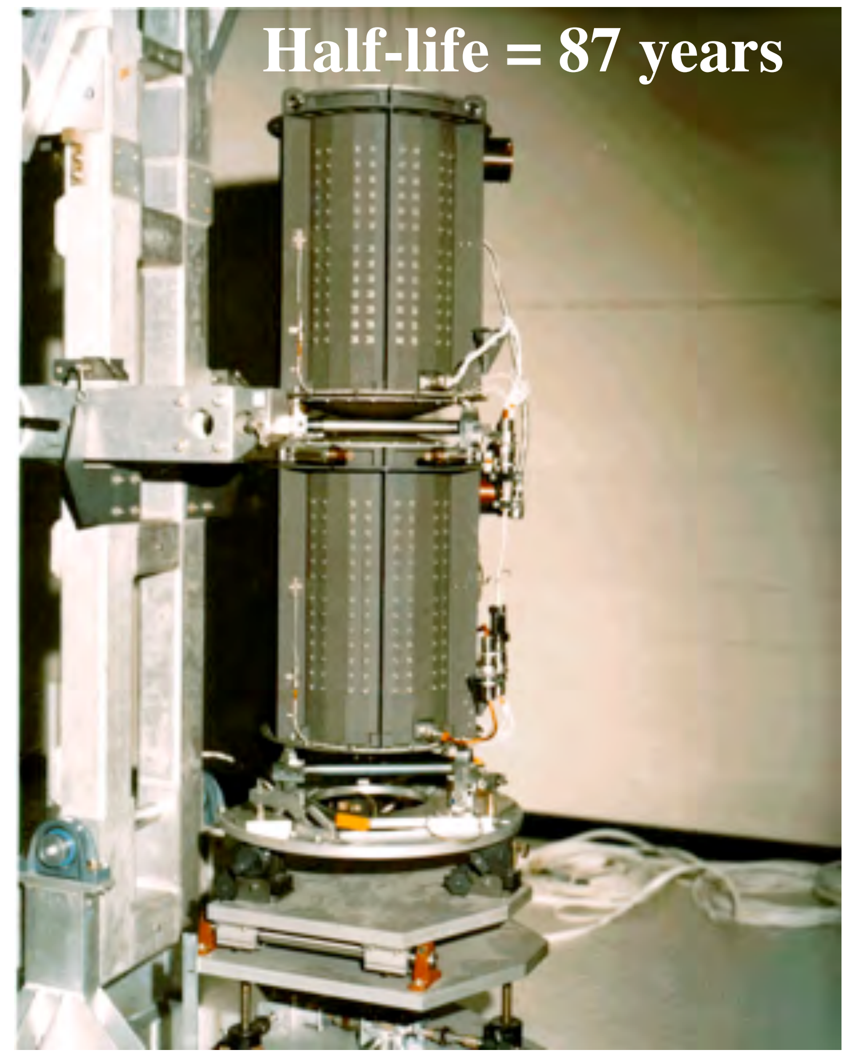
NASA Radioisotope Thermoelectric Generator

Radioisotope heater –> thermoelectric generator –> electricity

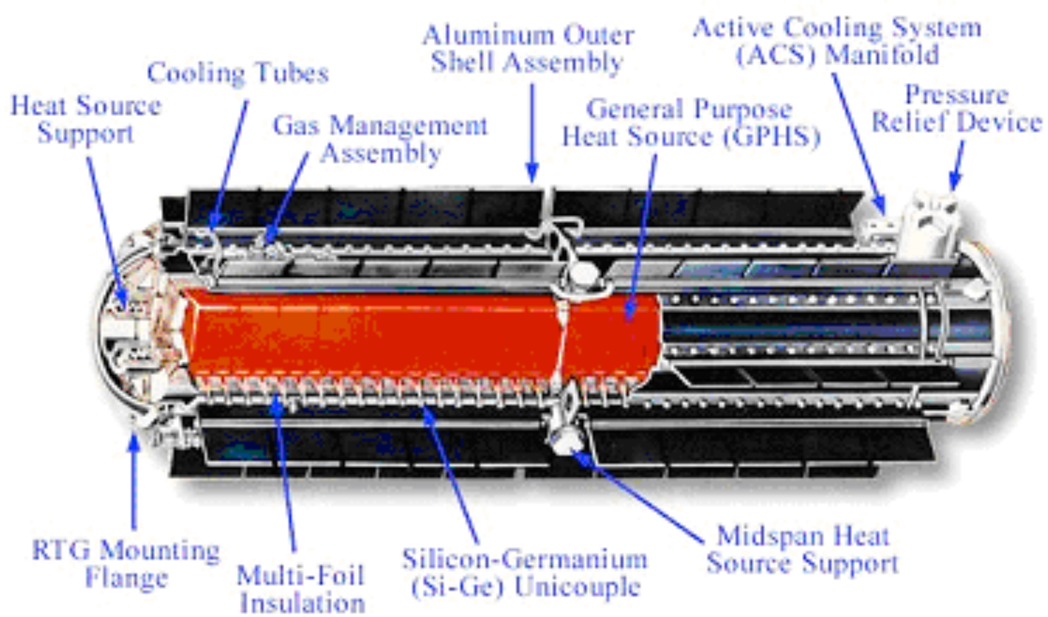




Voyager – Pu^{238}



GPHS-RTG



- 470 W @ 30 V on launch, after 33 years power = $470 \times 2^{-\frac{33}{87}}$ = 361 W

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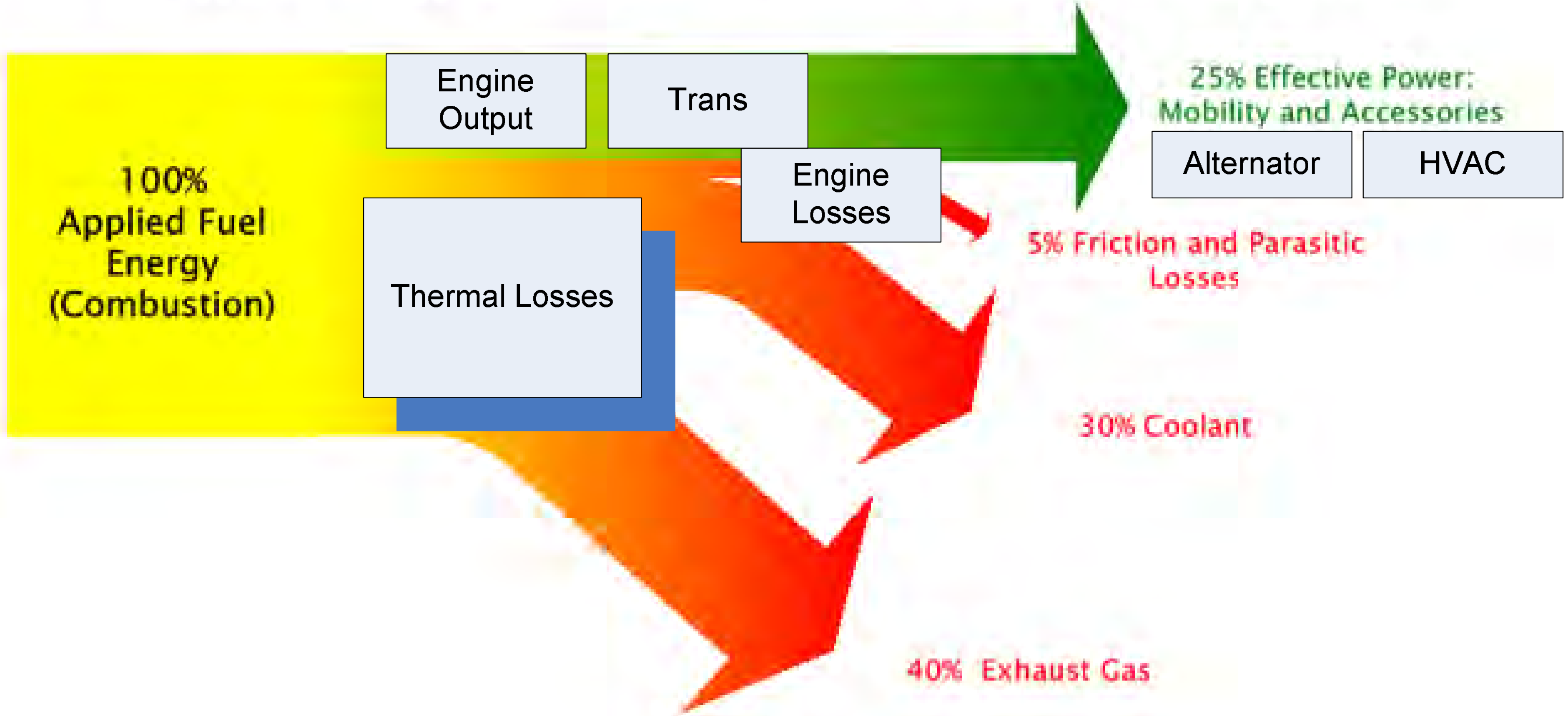
Thermoelectrics in Cars



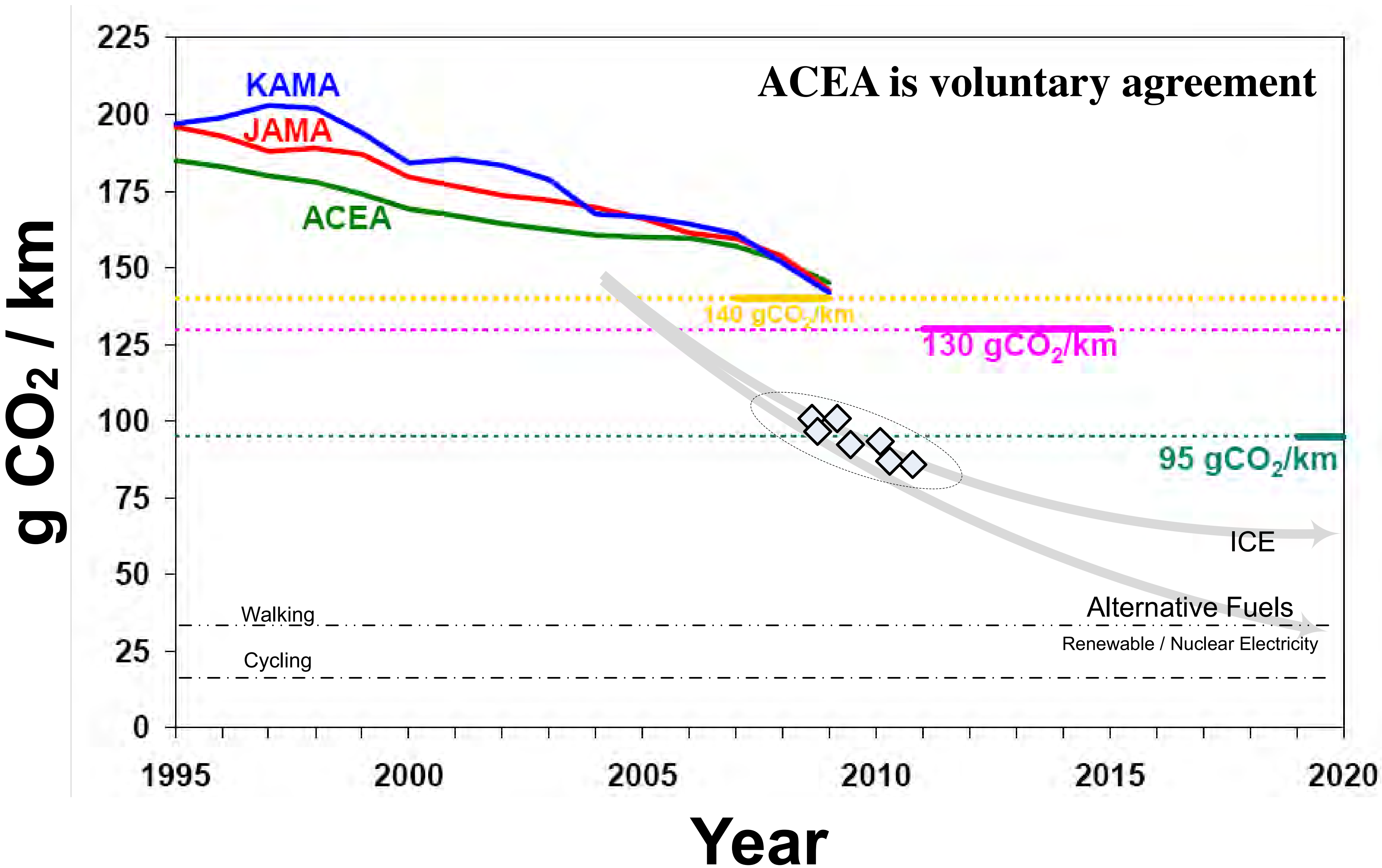
$$\text{Fuel Consumption} \propto \eta_{\text{powertrain}} \times (\tfrac{1}{2}\rho \mathbf{V}^2 \mathbf{C_d} \mathbf{A} + \mu_{\mathbf{r}} \times \text{mpg}) + \mathbf{E}_{\text{amenities}}$$

Thermoelectrics in Cars:

- **Increase electrical supply**
- **Use waste heat energy (45% of fuel!)**
- **Provide efficient local cooling**

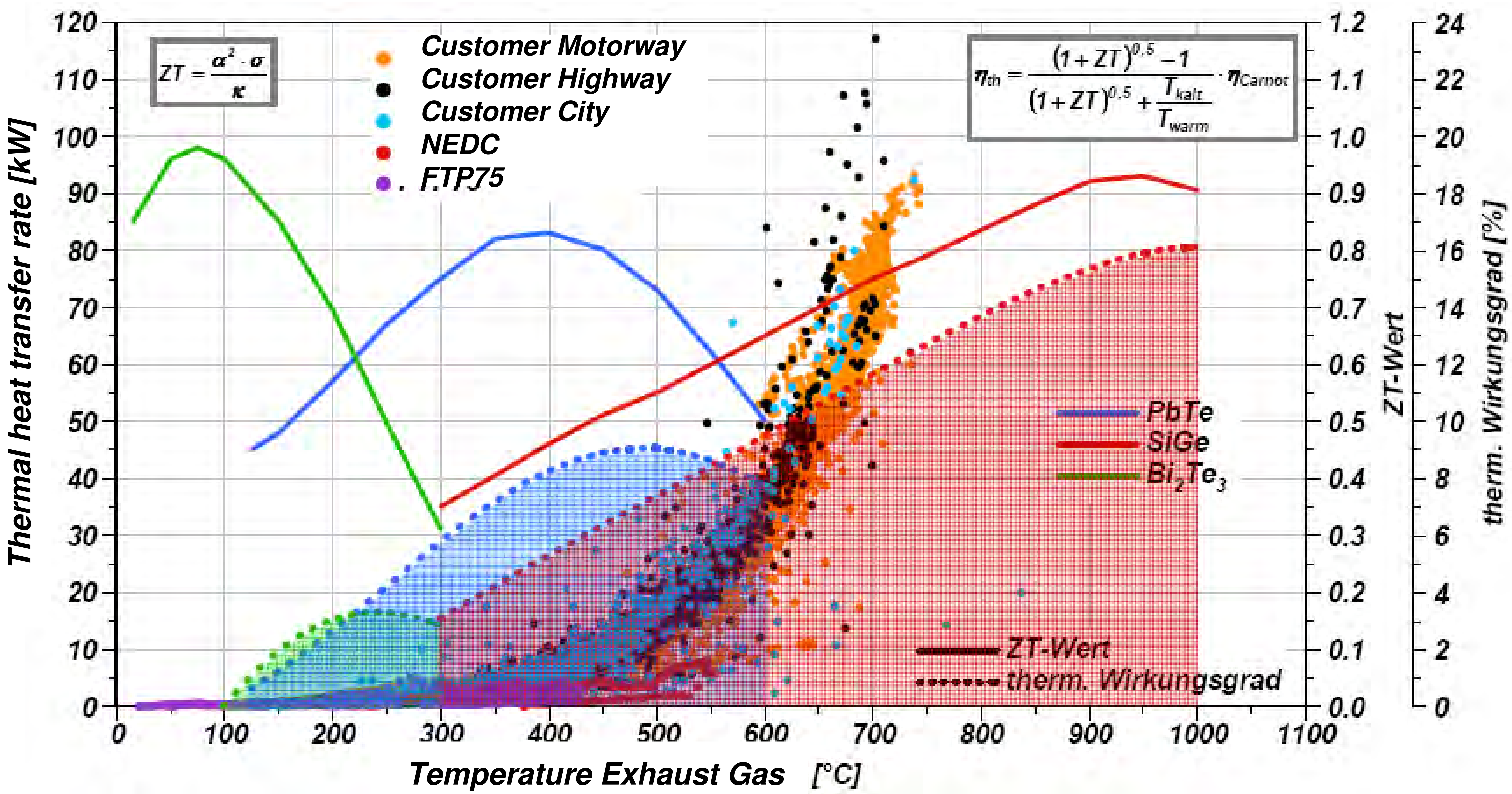
M. Ellis, Jaguar-Land Rover

Cars: CO_2 Emissions Legislation



M. Ellis, Jaguar-Land Rover

Heat from Car Exhaust



M. Ellis, Jaguar-Land Rover

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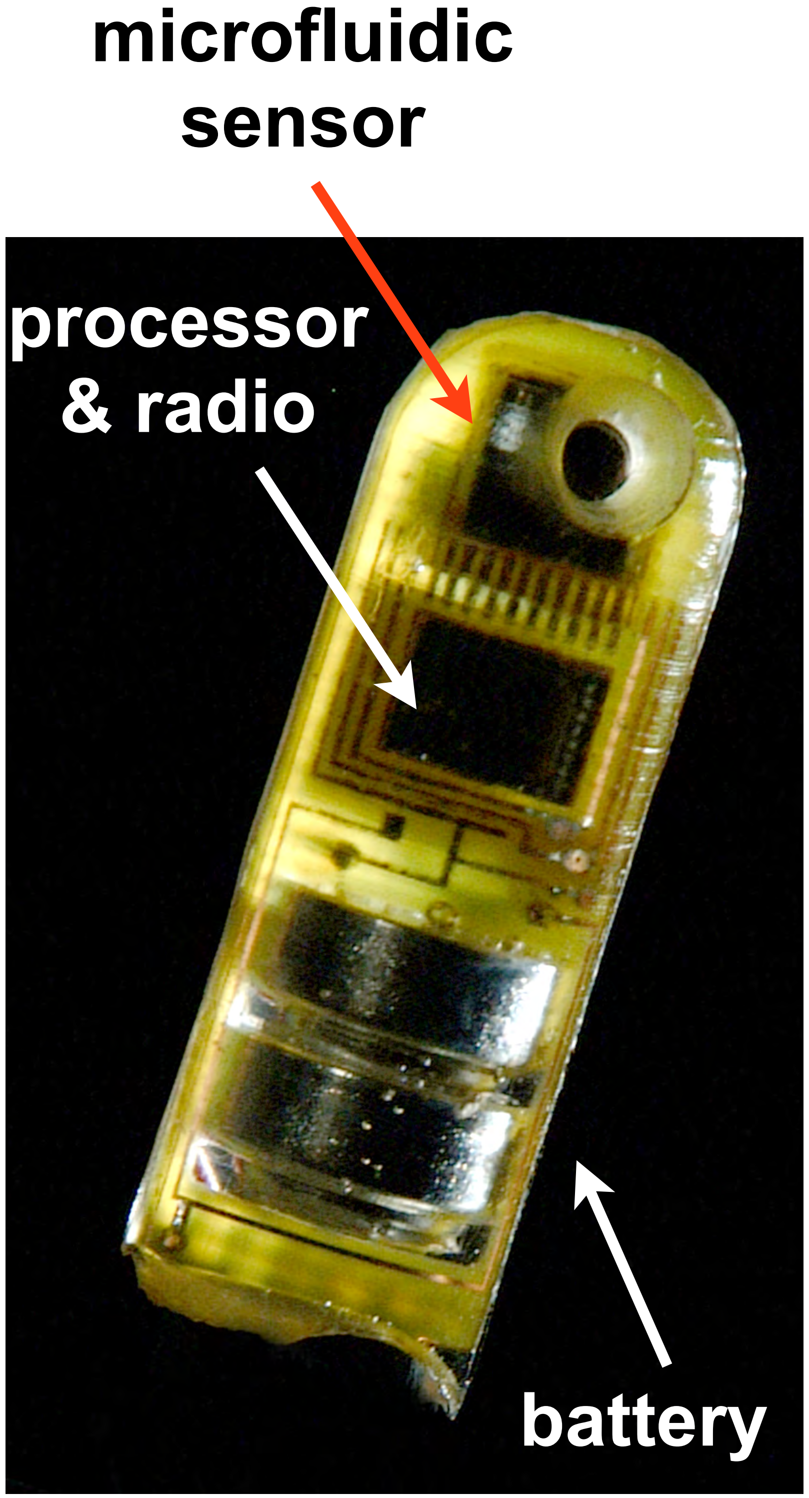
Present Thermoelectric Energy Harvesting

- VW and BMW announced TE on exhaust in 2008: 24 Bi_2Te_3 modules
- 600 W under motorway driving –> ~10% of car's electrical requirement
- 5% reduction in fuel consumption through removing alternator

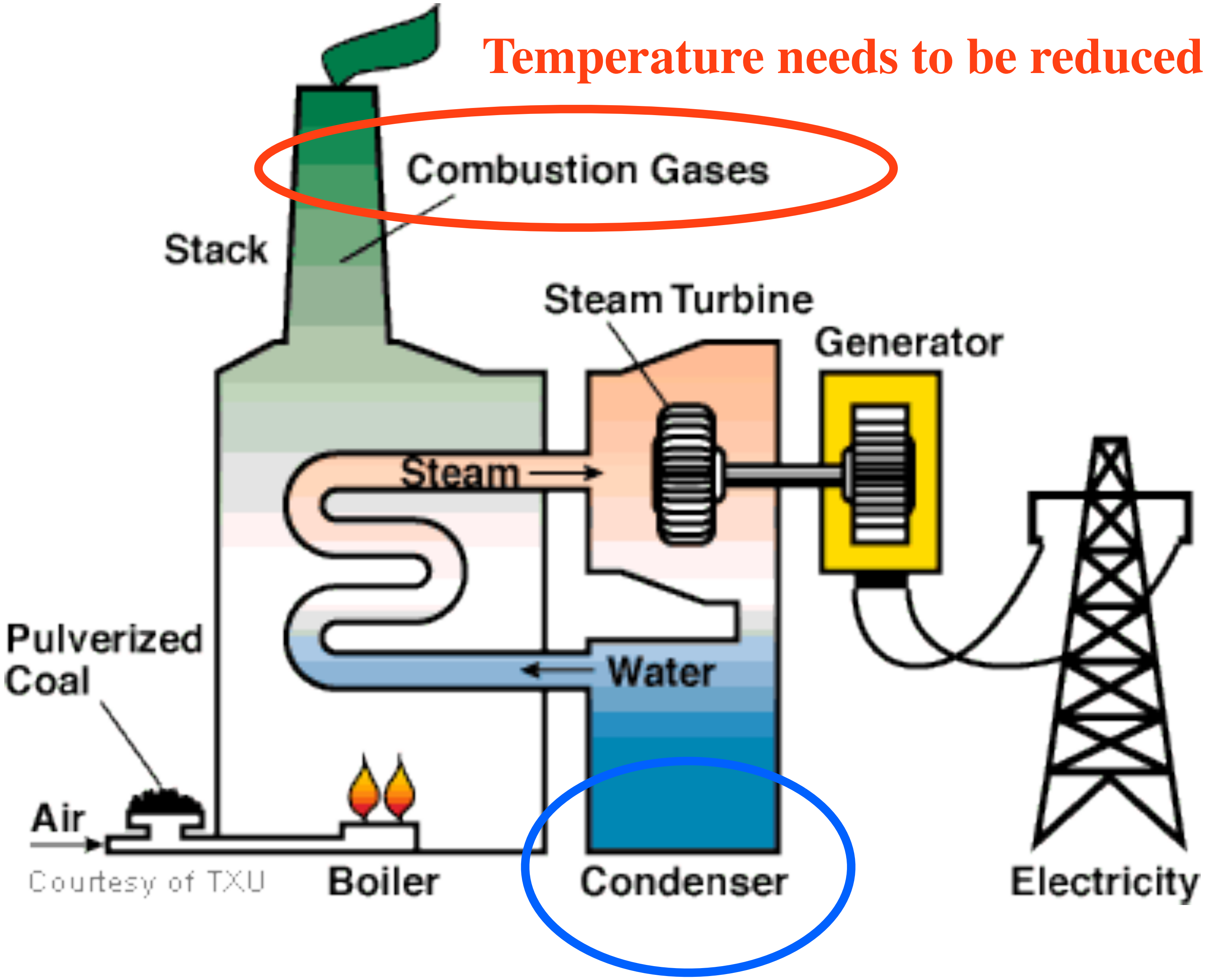
Mode Diagnostic: Lab-on-a-pill

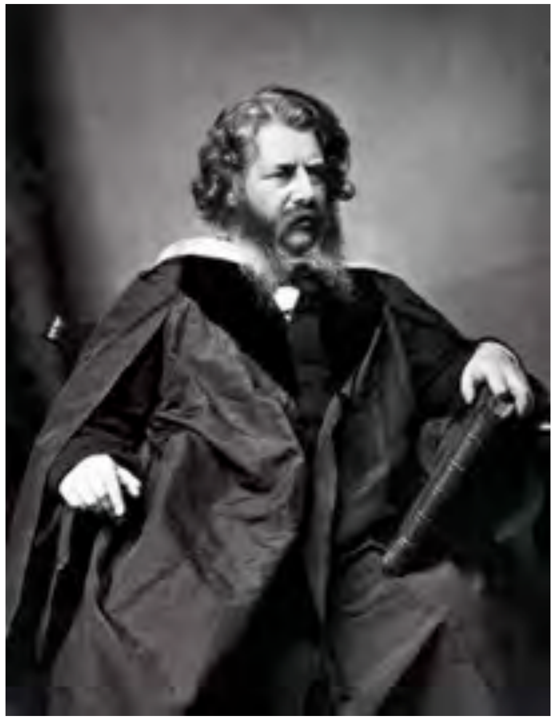


- Spin out from Glasgow: Mode Diagnostic
- Microfluidic lab-on-a-chip for blood analysis in the gut with integrated wireless readout
- Battery powered but issue of toxic materials in batteries and limited lifetime
- Can thermoelectrics be used in the future?

Energy Conversion: Electricity: The Rankine Cycle

Temperature needs to be reduced by 80 ˚C for carbon capture





Cooling towers –> throw heat away –> added losses

Energy stored in fuel → heat → kinetic energy → electric energy

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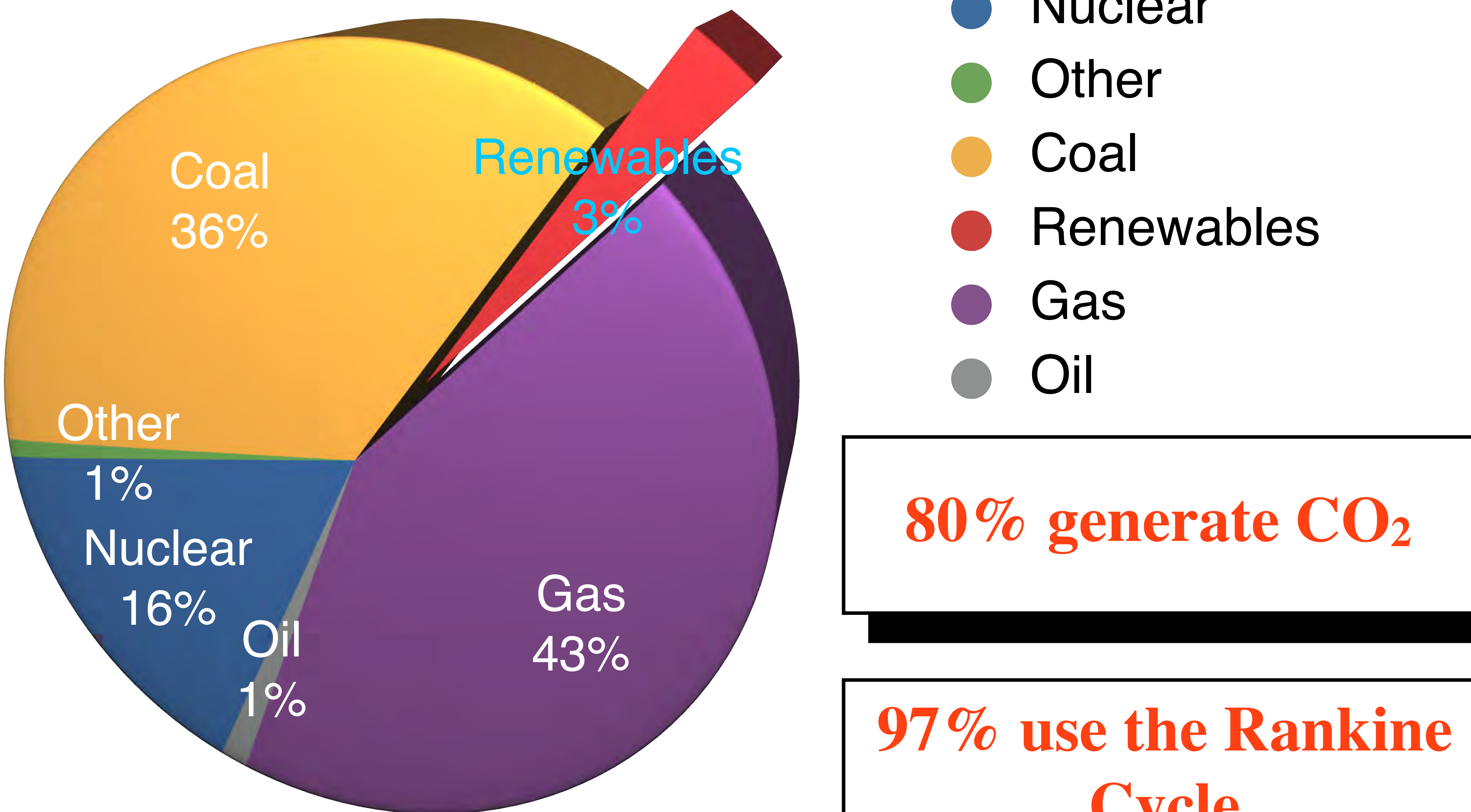
U.K. Electricity Generation 2007



80% generate CO_2

97% use the Rankine Cycle

http://www.berr.gov.uk/energy/statistics/

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Energy Density for Materials

Substance	Energy Density (MJ/kg)
$E = \Delta m\, c^2$	89,876,000,000
H_2 fusion	645,000,000
^{235}U fission	88,250,000
Hydrogen	143
Petrol	50
Beech tree	5
TNT	4.61
Lithium ion battery	0.72
Ultra capacitor	0.02
Water in 100 m height dam	0.001
1.75 m wind turbine @ 5 ms^{-1}	0.00006

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Main Strategies for Optimising ZT

Reducing thermal conductivity faster than electrical conductivity:

- e.g. skutterudite structure: filling voids with heavy atoms

Low-dimensional structures:

- Increase α through enhanced DOS $\left(\alpha = -\frac{\pi^2}{3q} k_B^2 T \left[\frac{d\ln(\mu(E)g(E))}{dE}\right]_{E=E_F}\right)$
- Make κ and σ almost independent
- Reduce κ through numerous interfaces to increase phonon scattering

Energy filtering:

enhance

- $$\alpha = -\frac{k_B}{q}\left[\frac{E_c - E_F}{k_B T} + \frac{\int_0^\infty \frac{(E-E_c)}{k_B T}\sigma(E)dE}{\int_0^\infty \sigma(E)dE}\right]$$

Y.I. Ravich et al., Phys. Stat. Sol. (b) 43, 453 (1971)

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Length Scales: Mean Free Paths

3D electron mean free path $\ell = v_F \tau_m = \frac{\hbar}{m^*}(3\pi^2 n)^{\frac{1}{3}} \frac{\mu m^*}{q}$

$$\ell = \frac{\hbar\mu}{q}(3\pi^2 n)^{\frac{1}{3}}$$

3D phonon mean free path

$$\Lambda_{ph} = \frac{3\kappa_{ph}}{C_v \langle v_t \rangle \rho}$$

- C_v = specific heat capacity
- $<v_t>$ = average phonon velocity
- ϱ = density of phonons

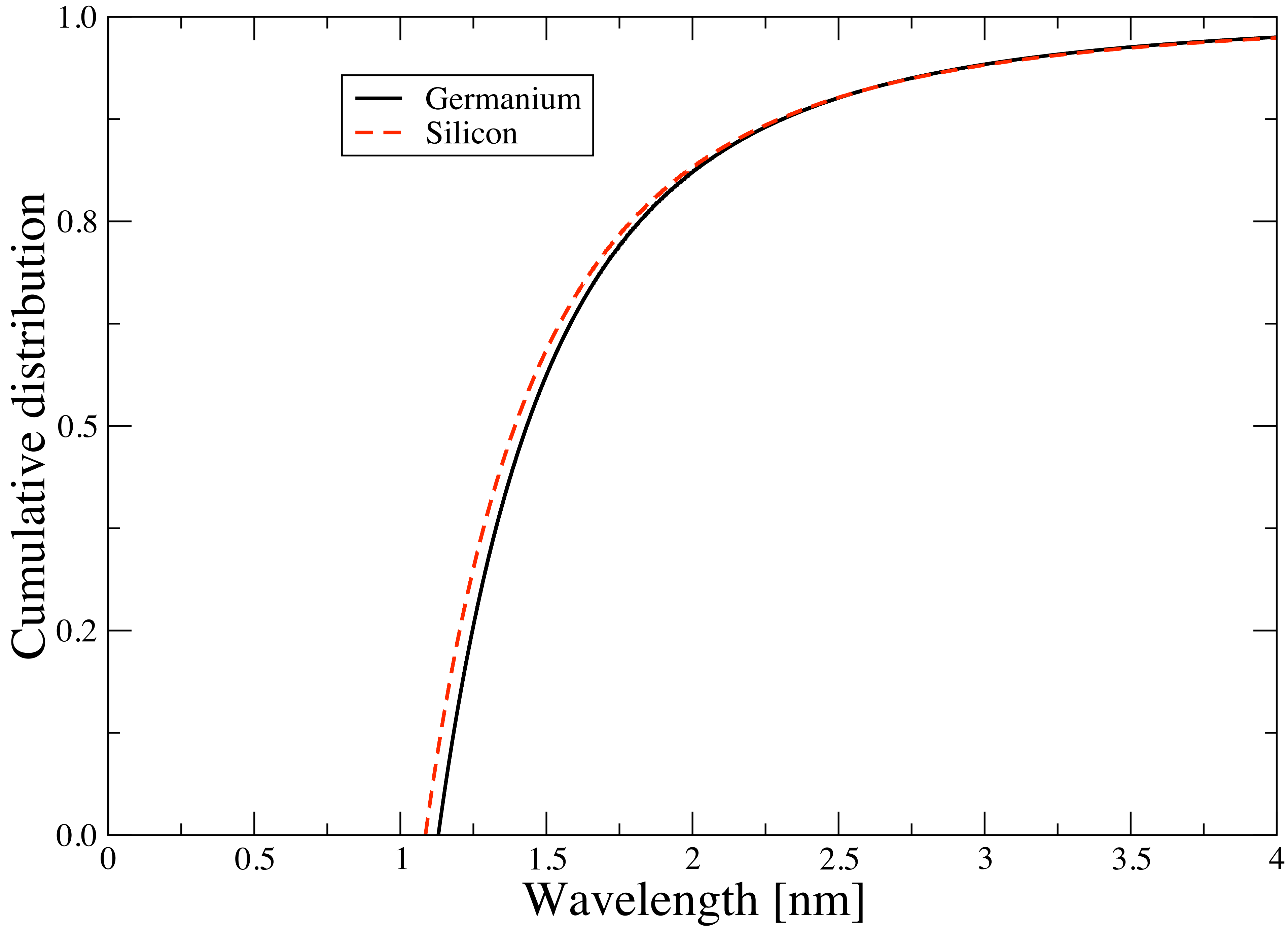
- A structure may be 2D or 3D for electrons but 1 D for phonons (or vice versa!)

Phonon Mean Free Paths

Material	Model	Specific Heat (x10^6 $Jm^{-3}K^{-1}$)	Group velocity (ms^{-1})	Phonon mean free path, Λ_{ph} (nm)
Si	Debye	1.66	6400	40.9
Si	Dispersion	0.93	1804	260.4
Ge	Debye	1.67	3900	27.5
Ge	Dispersion	0.87	1042	198.6

G. Chen, Phys. Rev. B 57, 14958 (1998)

Phonon Wavelengths that Carry Heat



- **Greater than 95% of heat conduction in Si / Ge from phonons with wavelengths between 1.2 and 3.5 nm**

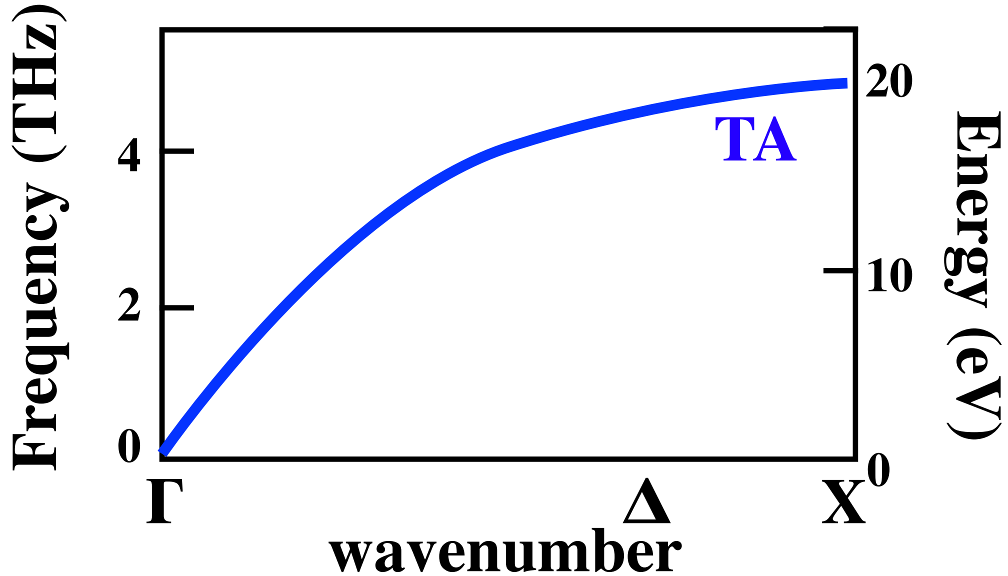
Phonon Enhancements

Phonon scattering:

- Require structures below the phonon mean free path

Phonon Bandgaps:

- Change the acoustic phonon dispersion –> stationary phonons or bandgaps
- Require structures with features at the phonon wavelength (< 5 nm)
- Phonon group velocity $\propto \frac{dE}{dk_q}$



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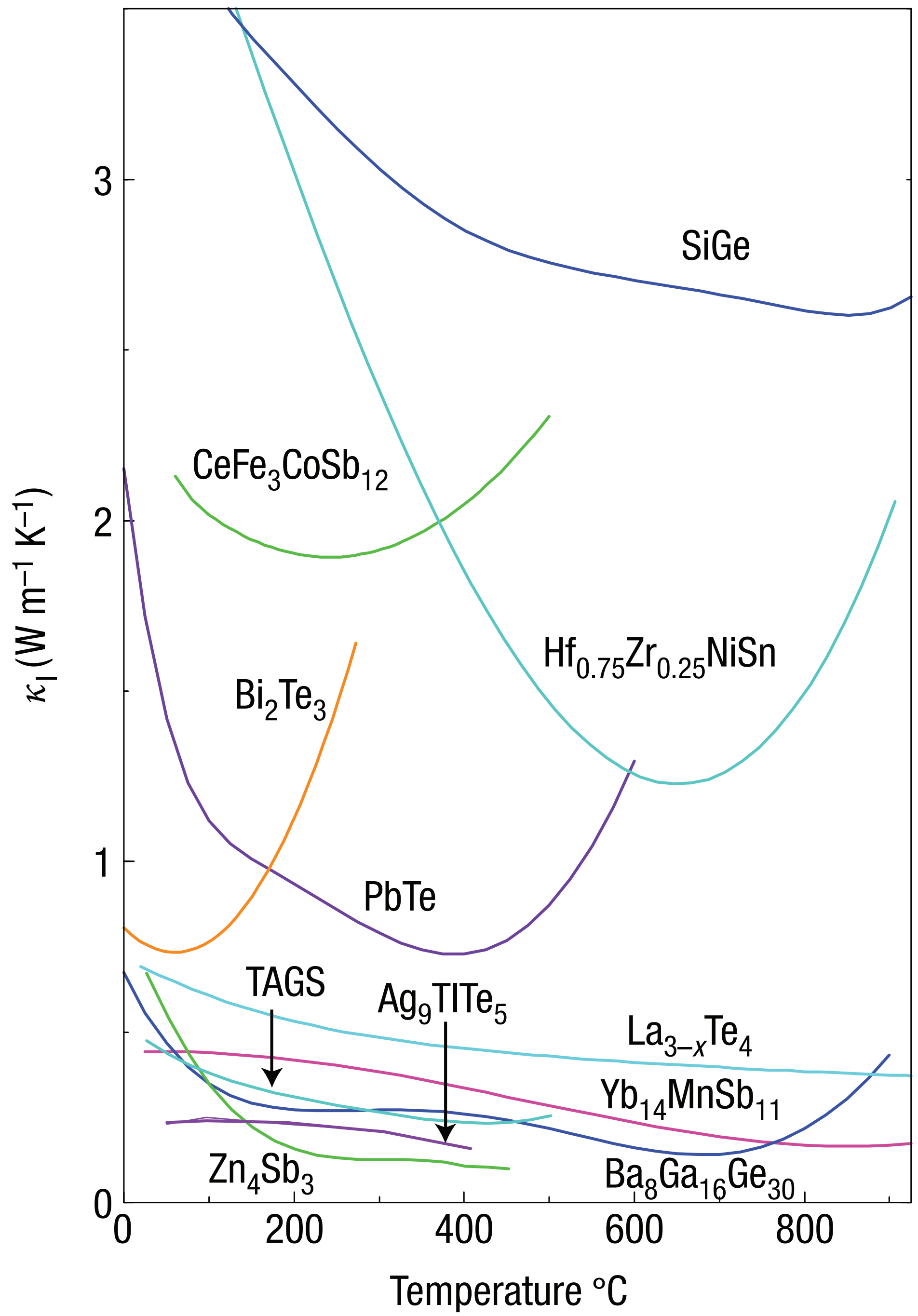
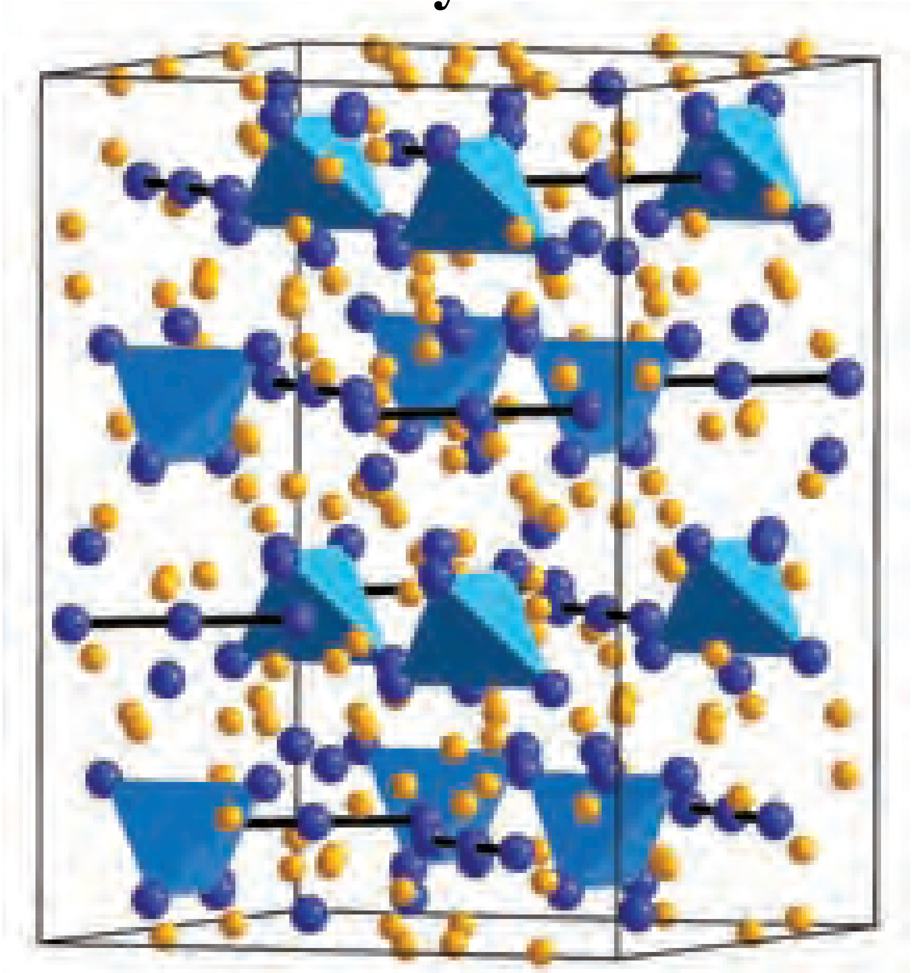
Complex Crystal Structures: Reducing κ_{ph}



Skutterudite structure: filling voids with heavy atoms

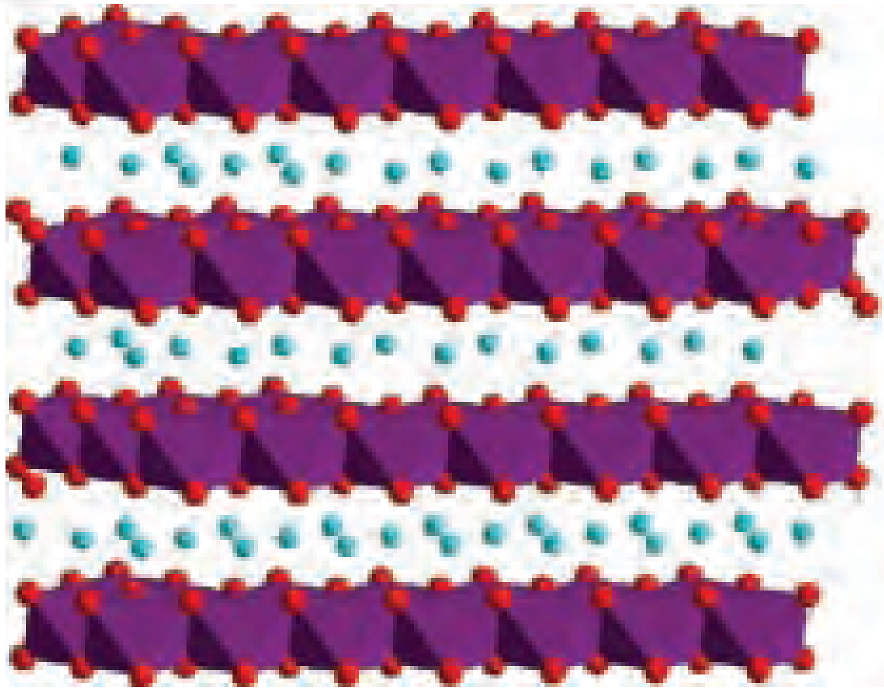


p-Yb$_{14}$MnSb$_{11}$ – ZT ~ 1 @ 900 ˚C

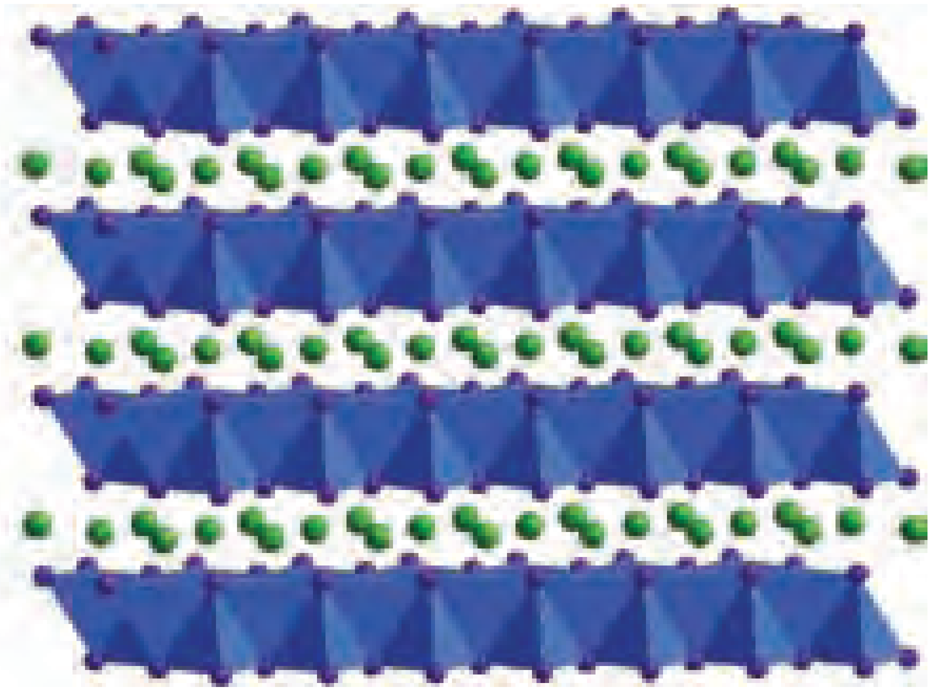
G.J. Snyder et al., Nat. Mat. 7, 105 (2008)

Electron Crystal – Phonon Glass Materials

- Principle: trying to copy "High T_c" superconductor structures
- Heavy ion / atom layers for phonon scattering
- High mobility electron layers for high electrical conductivity



Na_xCoO_2

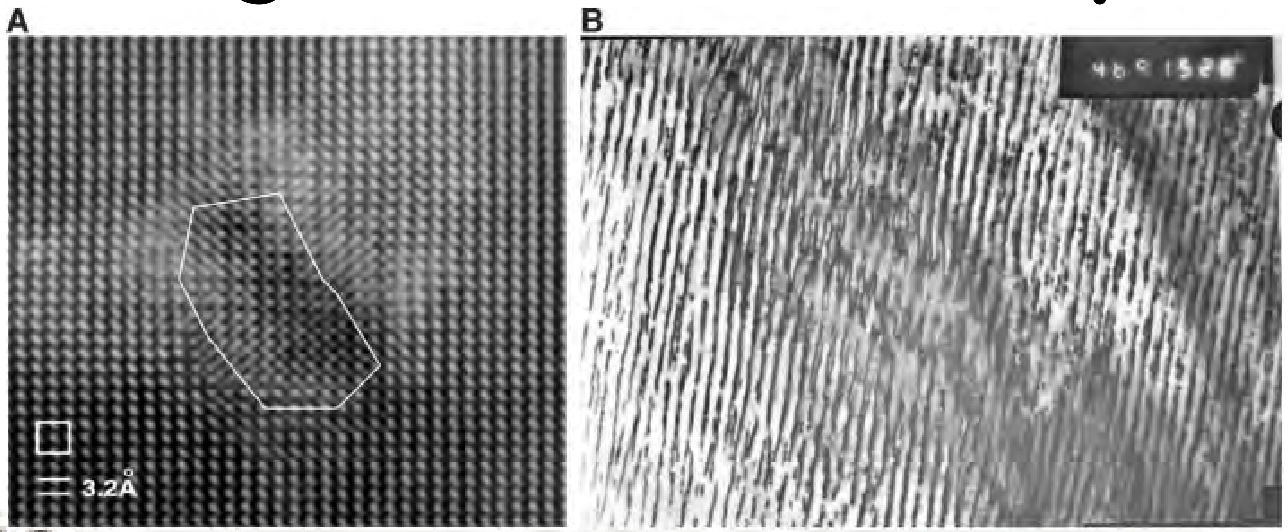


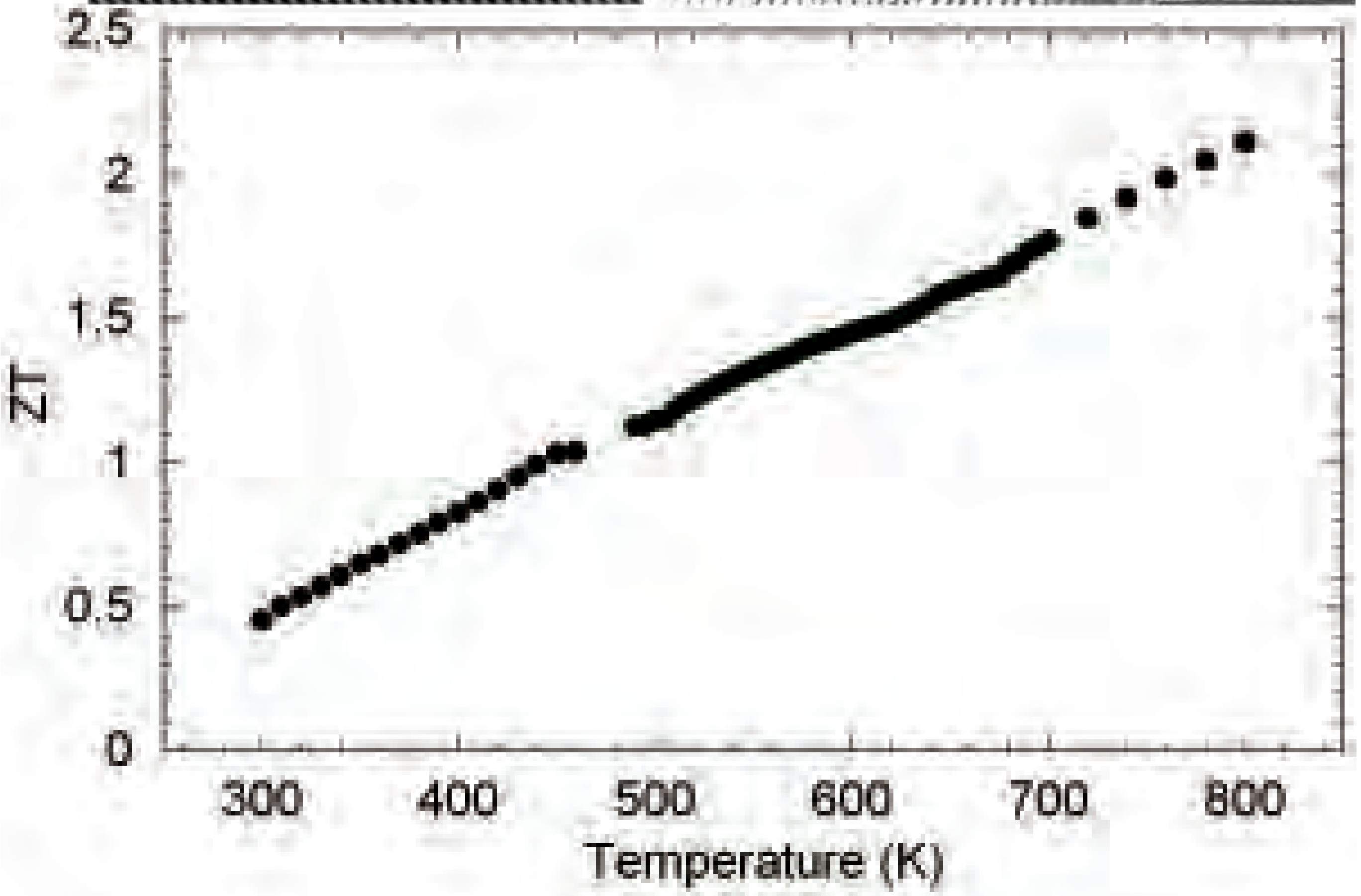
$Ca_xYb_{1-x}Zn_2Sb_2$

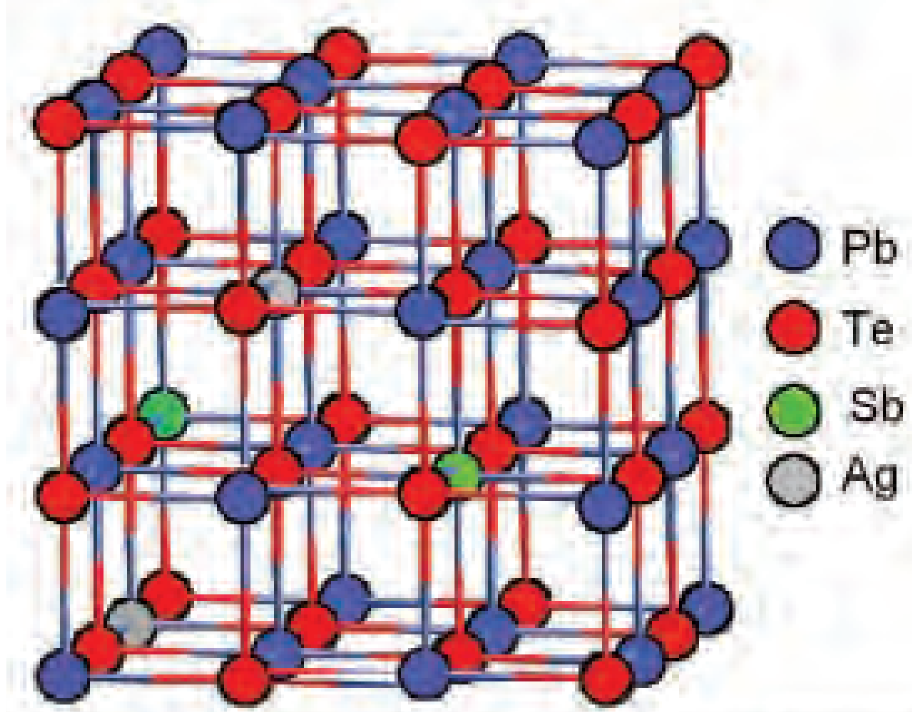
- Only small improvements to ZT observed

G.J. Snyder et al., Nat. Mat. 7, 105 (2008)

$AgPb_{18}SbTe20$ – Nanoparticle Scattering?







α = –335 μVK^{-1}
σ = 30,000 S/m
κ = 1.1 $Wm^{-1}K^{-1}$
at 700 K

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

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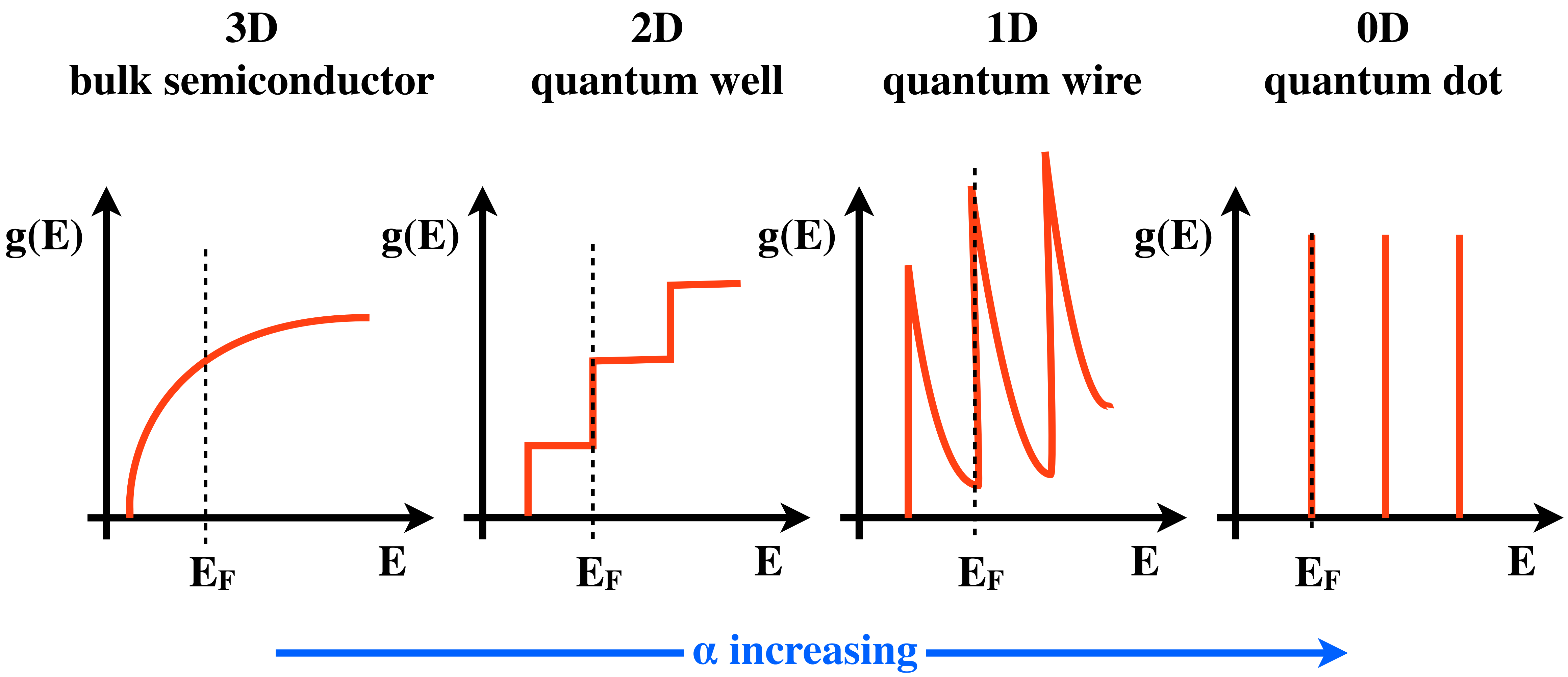
Seebeck Enhancement at Low Dimensions

- **Increase α through enhanced DOS:**

$$\alpha = -\frac{\pi^2}{3q} k_B^2 T \left[\frac{d\ln(\mu(E)g(E))}{dE} \right]_{E=E_F}$$



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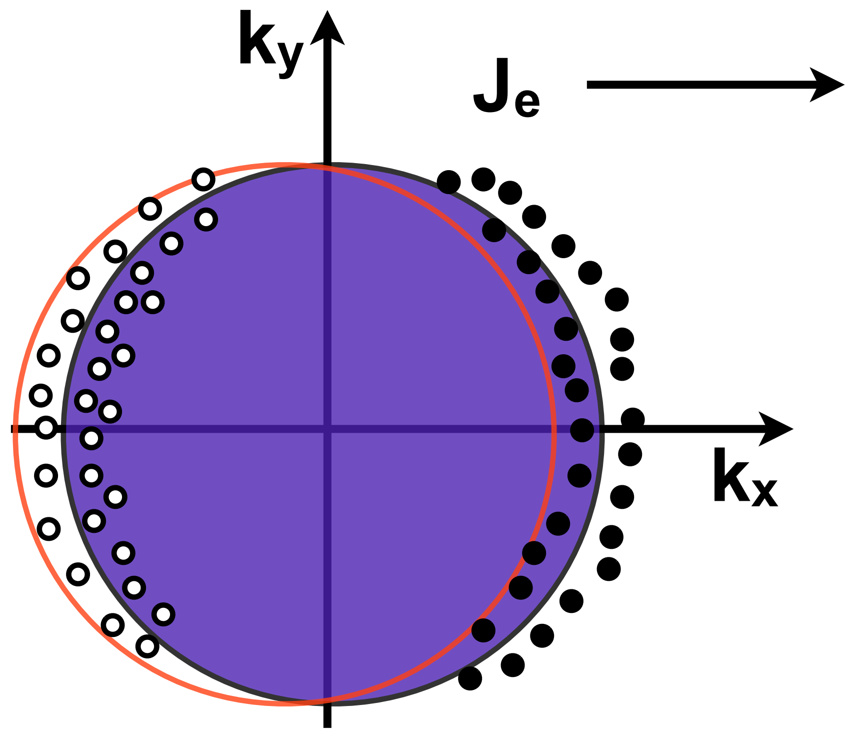
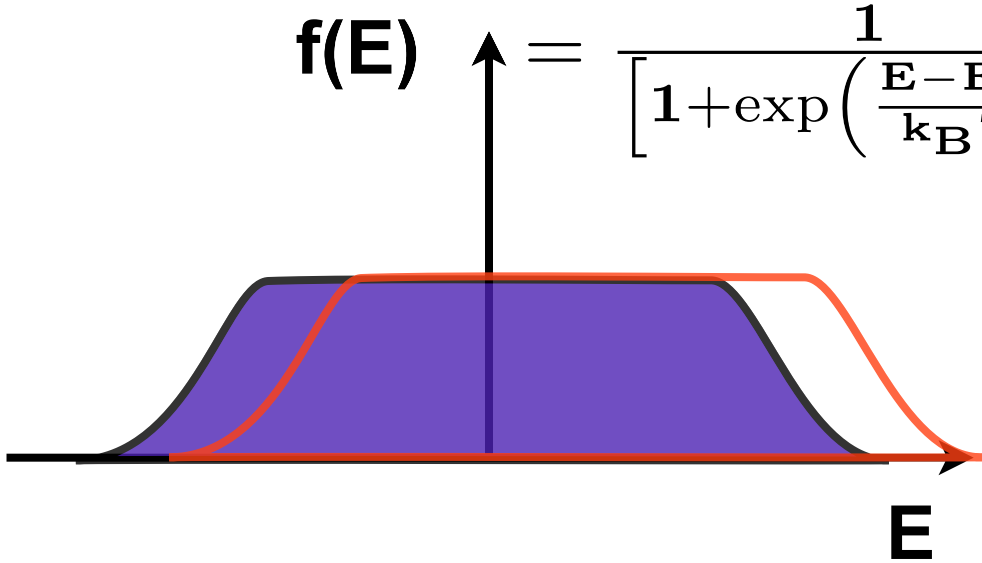
2D Electronic and Thermal Transport

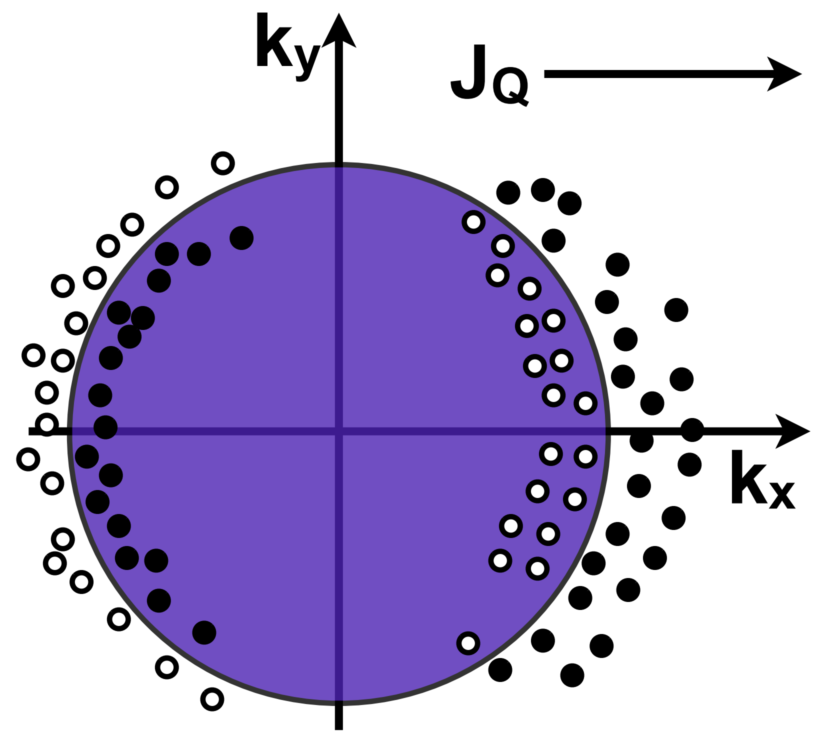
2D electronic transport

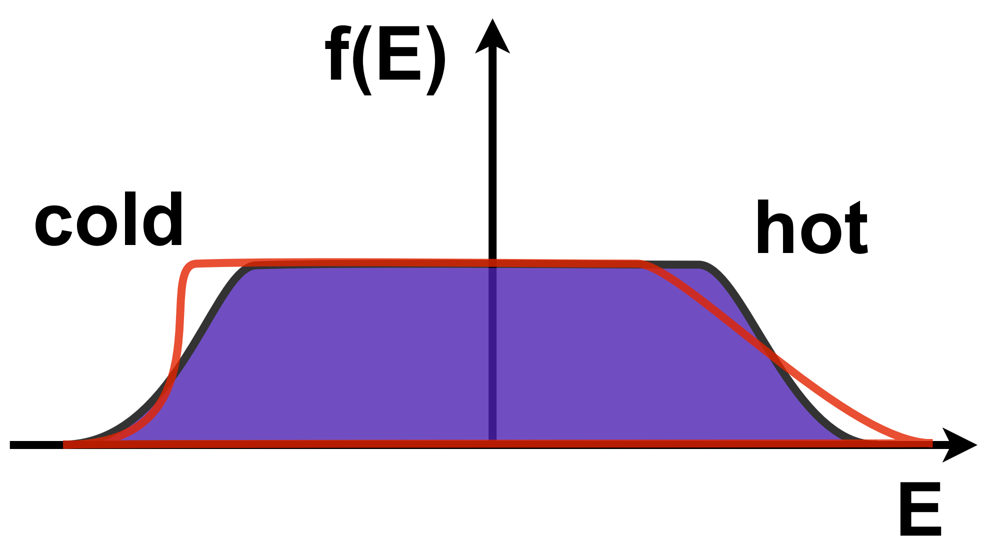




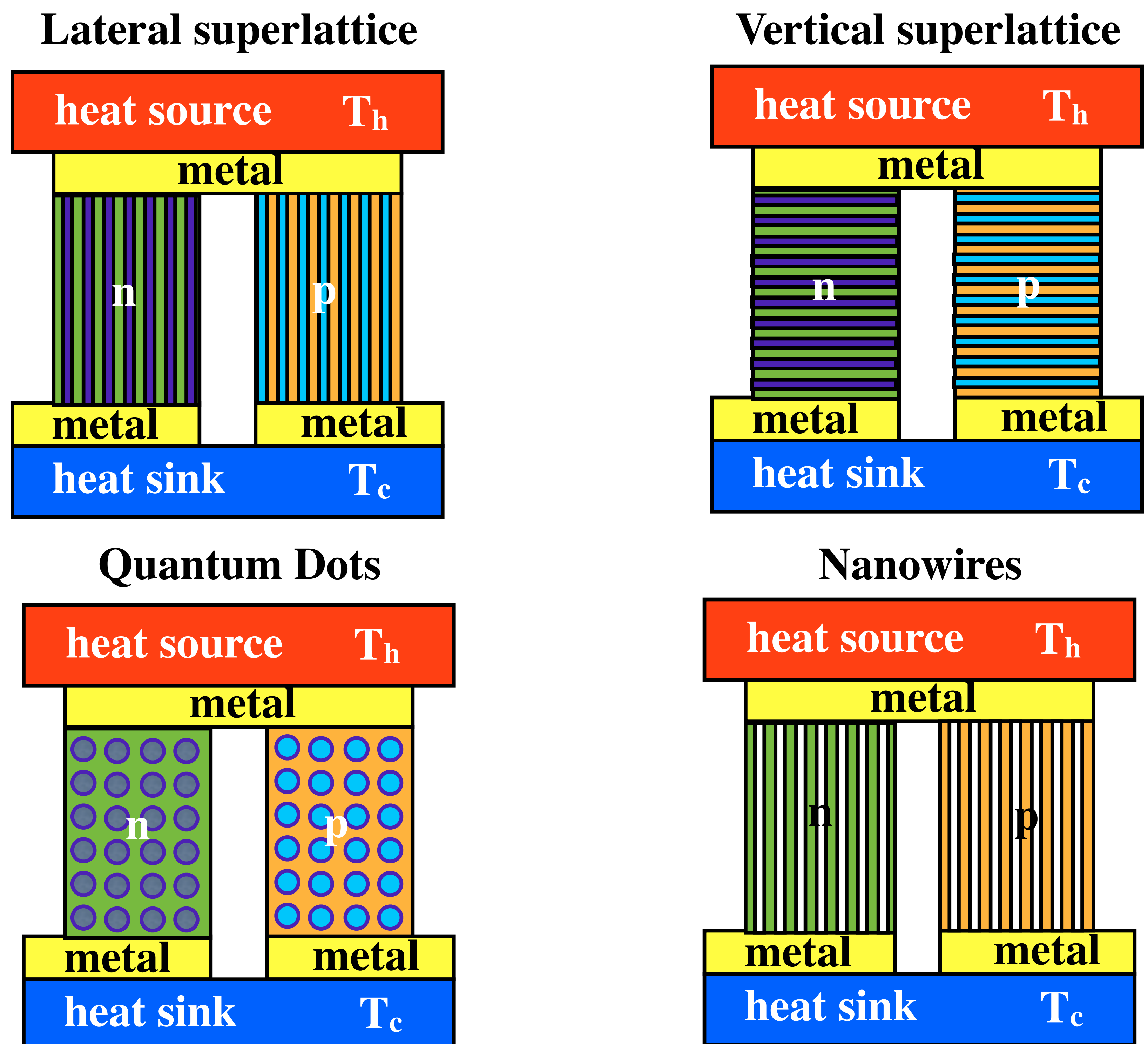
$$= \frac{1}{\left[1+\exp\left(\frac{E-E_F}{k_B T}\right)\right]}$$

2D thermal transport





Thermoelectric Low Dimensional Structures



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Low Dimensional Structures: 2D Superlattices

- Use of transport along superlattice quantum wells
- Higher α from the higher density of states
- Higher electron mobility in quantum well –> higher σ
- Lower κ_{ph} through additional phonon scattering from heterointerfaces
- Disadvantage: higher κ_{el} with higher σ (but layered structure can reduce this effect)
- Overall Z and ZT should increase

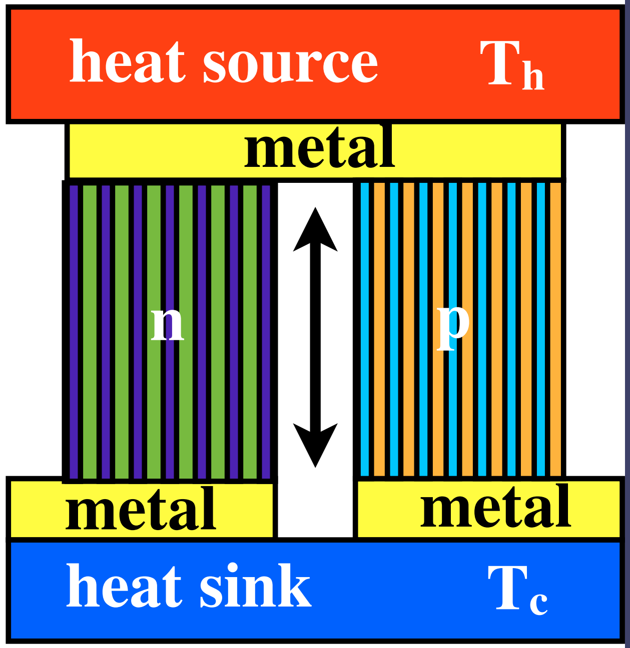


Figure of merit

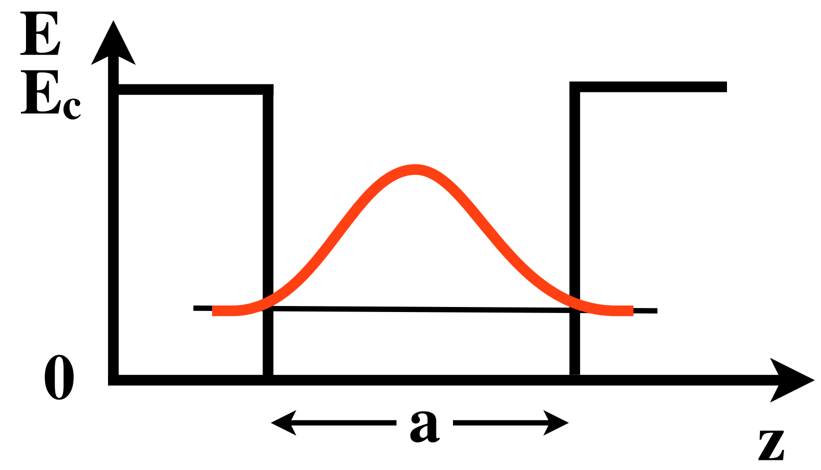
$$ZT = \frac{\alpha^2 \sigma}{\kappa} T$$

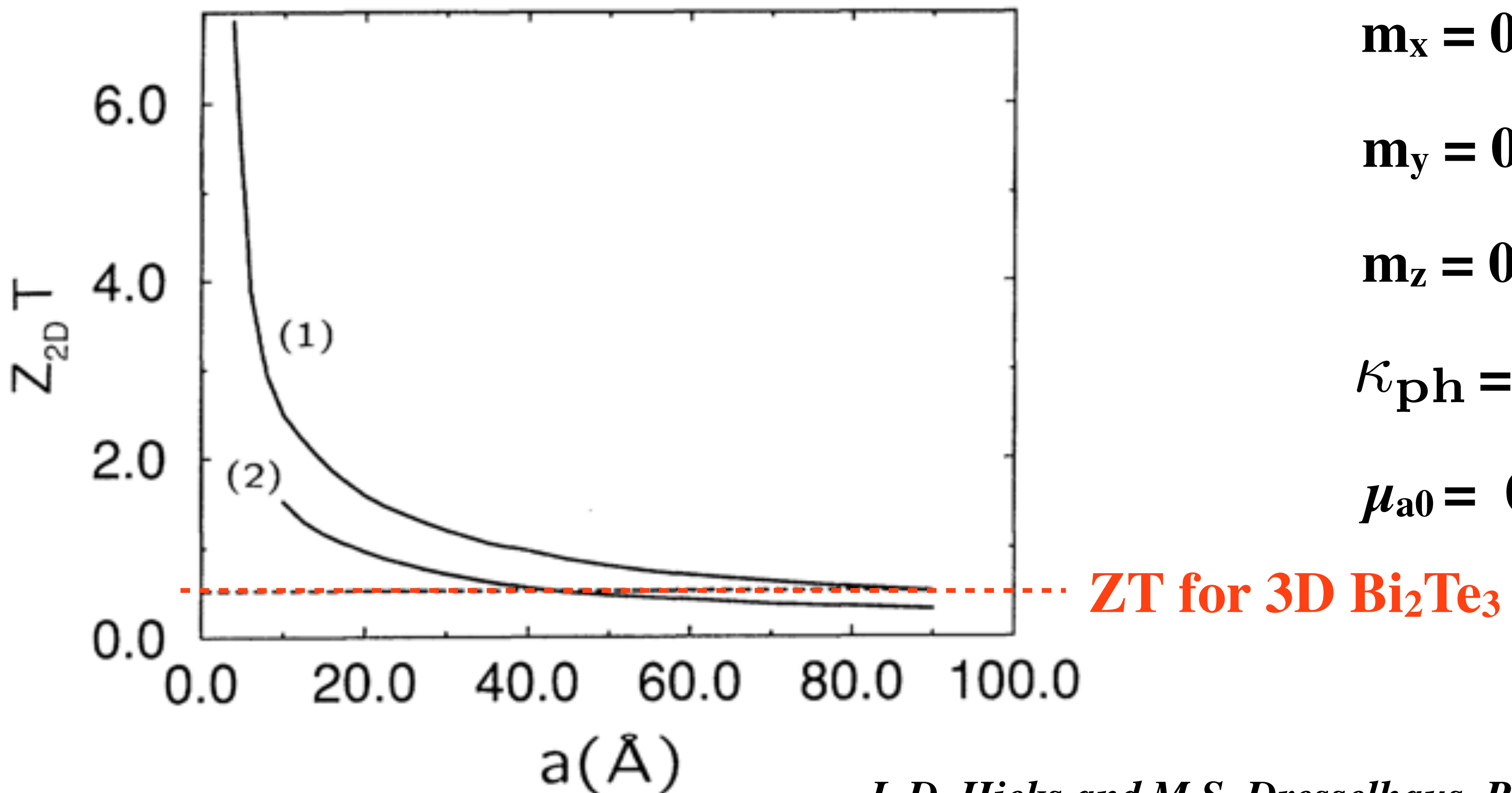
EHC Parker and TE Whall, 1987

L.D. Hicks and M.S. Dresselhaus, Phys. Rev. B 47, 12737 (1993)

2D Bi_2Te_3 Superlattices

- $$E_{F2D} = E_{F3D} - \frac{\hbar^2 \pi^2}{2 m_z^* a^2}$$
- Both doping and quantum well width, a can now be used to engineer ZT





$m_x = 0.021\ m_0$

$m_y = 0.081\ m_0$

$m_z = 0.32\ m_0$

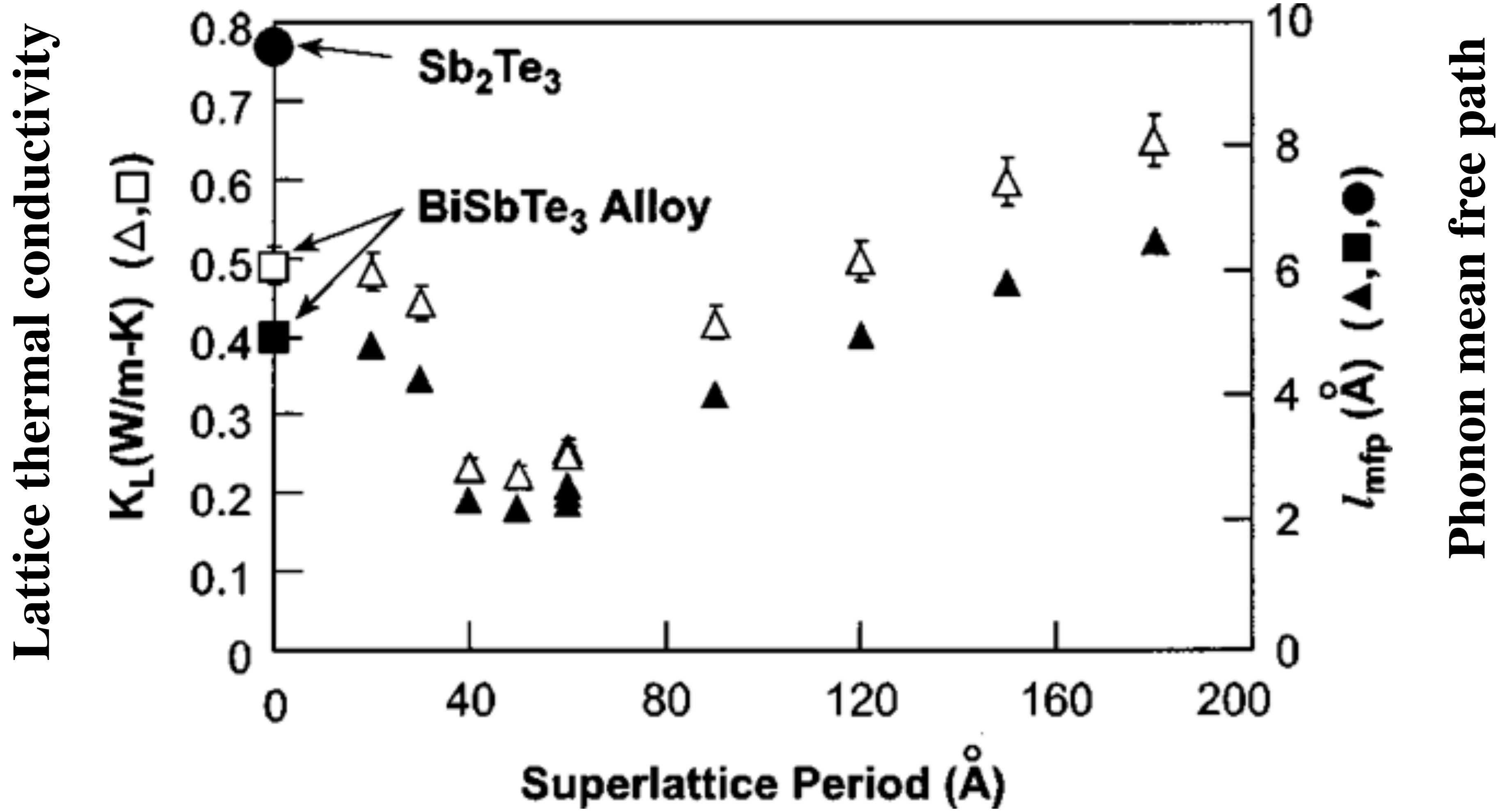
$\kappa_{ph} = 1.5\ Wm^{-1}K^{-1}$

$\mu_{a0} = 0.12\ m^2V^{-1}s^{-1}$

L.D. Hicks and M.S. Dresselhaus, Phys. Rev. B 47, 12737 (1993)

p-Bi_2Te_3 / Sb_2Te_3 Superlattices

- Bi_2Te_3 κ_{ph} = 1.05 $Wm^{-1}K^{-1}$

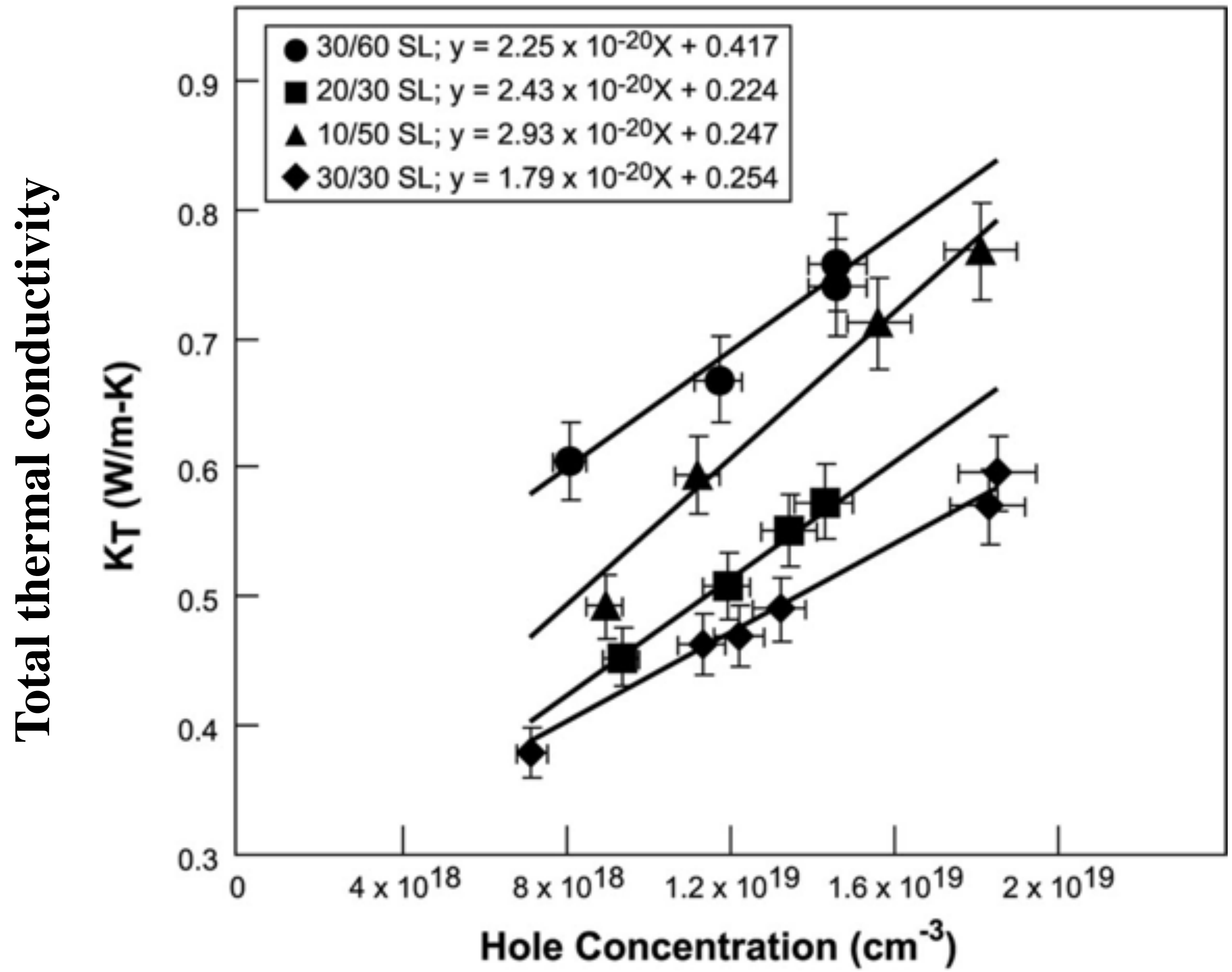


- 3/3 nm, 1/5 nm, 2/4 nm Bi_2Te_3 / Sb_2Te_3 periods almost identical κ_{ph}

R. Venkatasubramanium Phys. Rev. B 61, 3091 (2000)

p-Bi_2Te_3 / Sb_2Te_3 Superlattices

- Bi_2Te_3 κ_{ph} = 1.2 $Wm^{-1}K^{-1}$ *C.B. Satterthwaite, et al. Phys. Rev. 108: 1164 (1957)*



R. Venkatasubramanium Phys. Rev. B 61, 3091 (2000)

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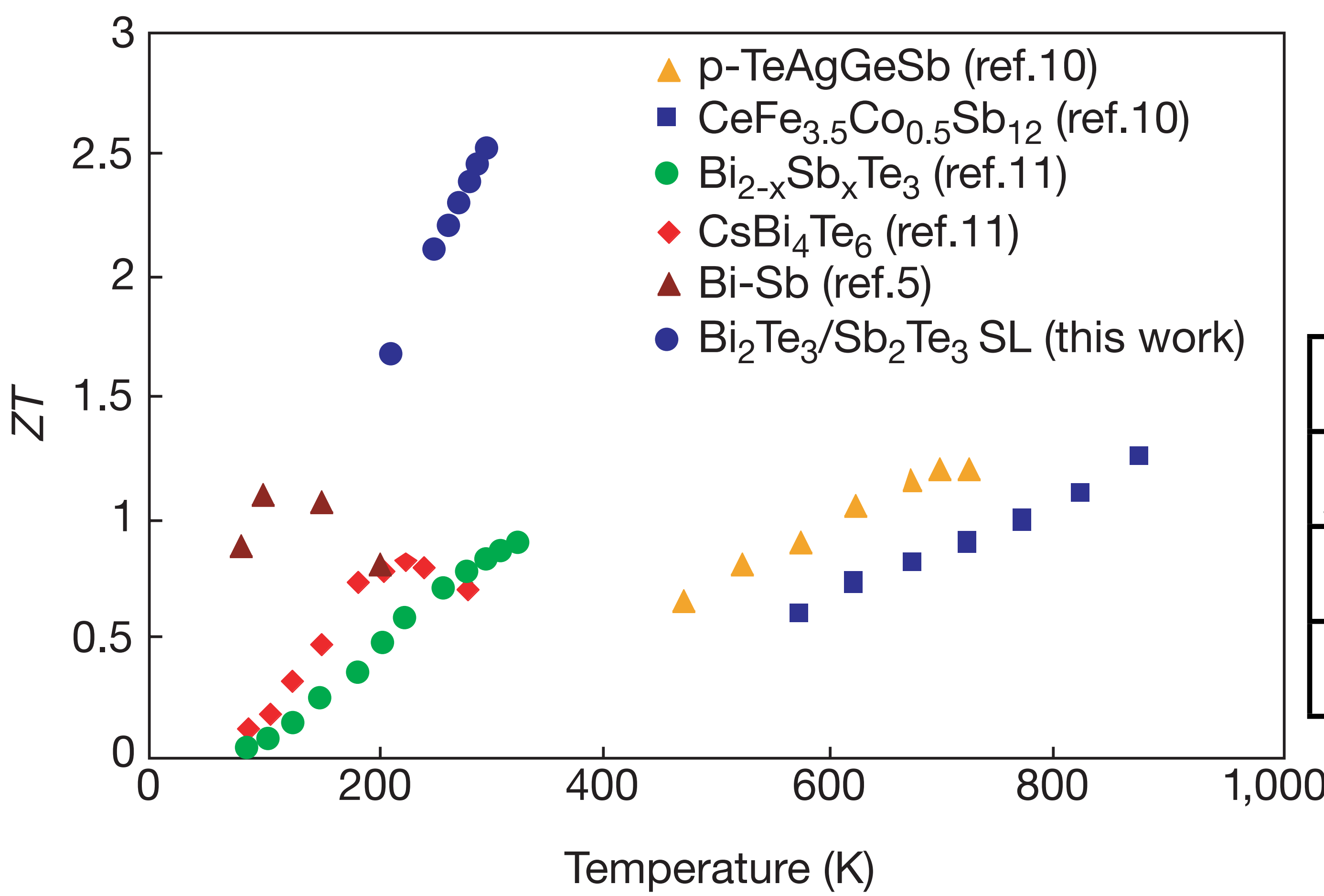
p-Bi_2Te_3 / Sb_2Te_3 Superlattices



Bulk Bi_2Te_3 ZT ~ 1.0

Superlattice ZT = 2.6

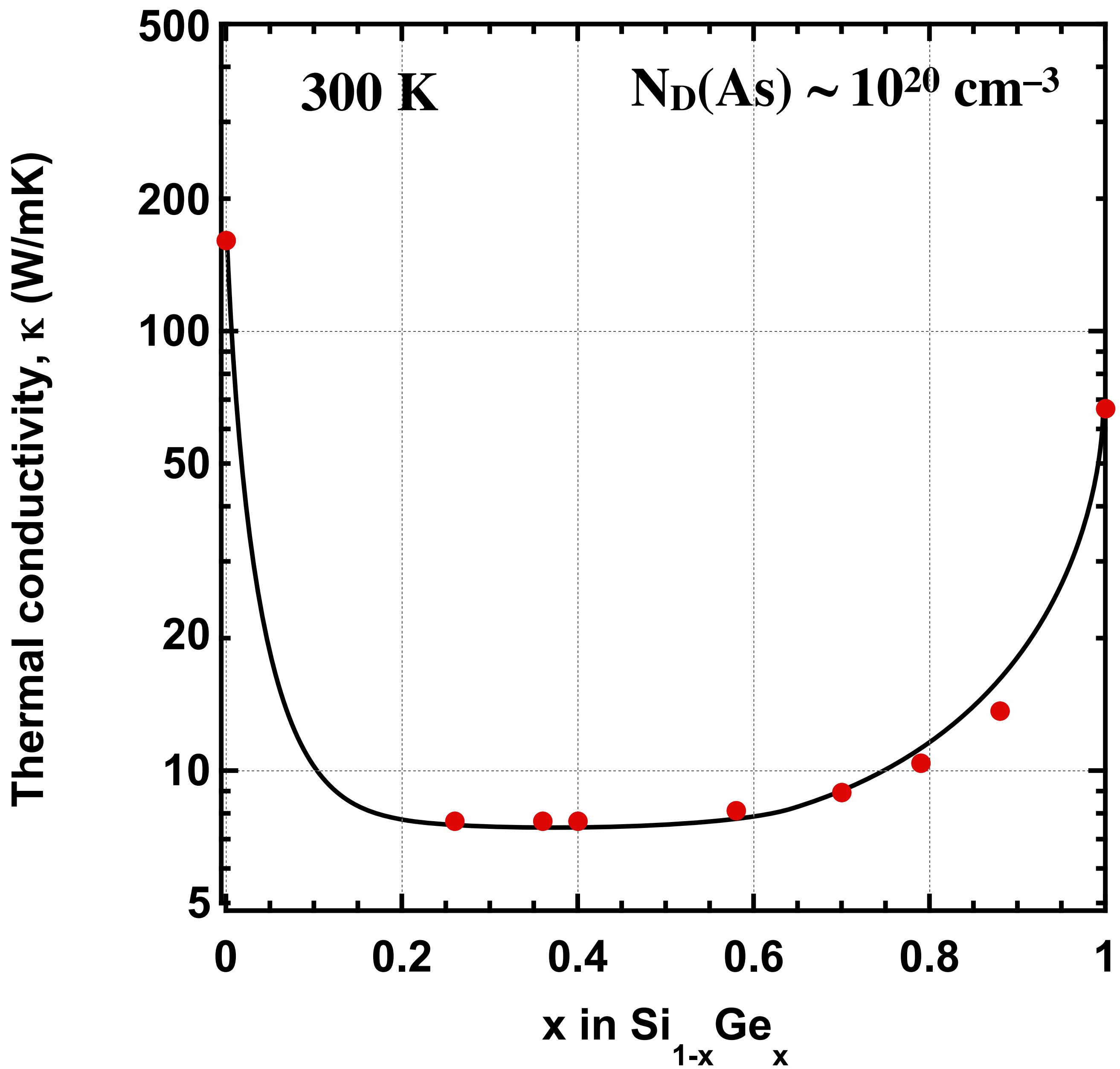
Electrons	Phonons
μ=383 cm^{2}V^{-1}s^{-1}	
ℓ = 11.4 nm	Λ_{ph} = 3 nm
$k_{el}\ell$ ~ 7.6	$k_{ph}\Lambda$ ~ 0.5

=> Phonon blocking

- **1 nm: 5 nm p-Bi_2Te_3 QW / Sb_2Te_3 barrier superlattices**
- **Thermal conductivity reduced more than electrical conductivity**

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

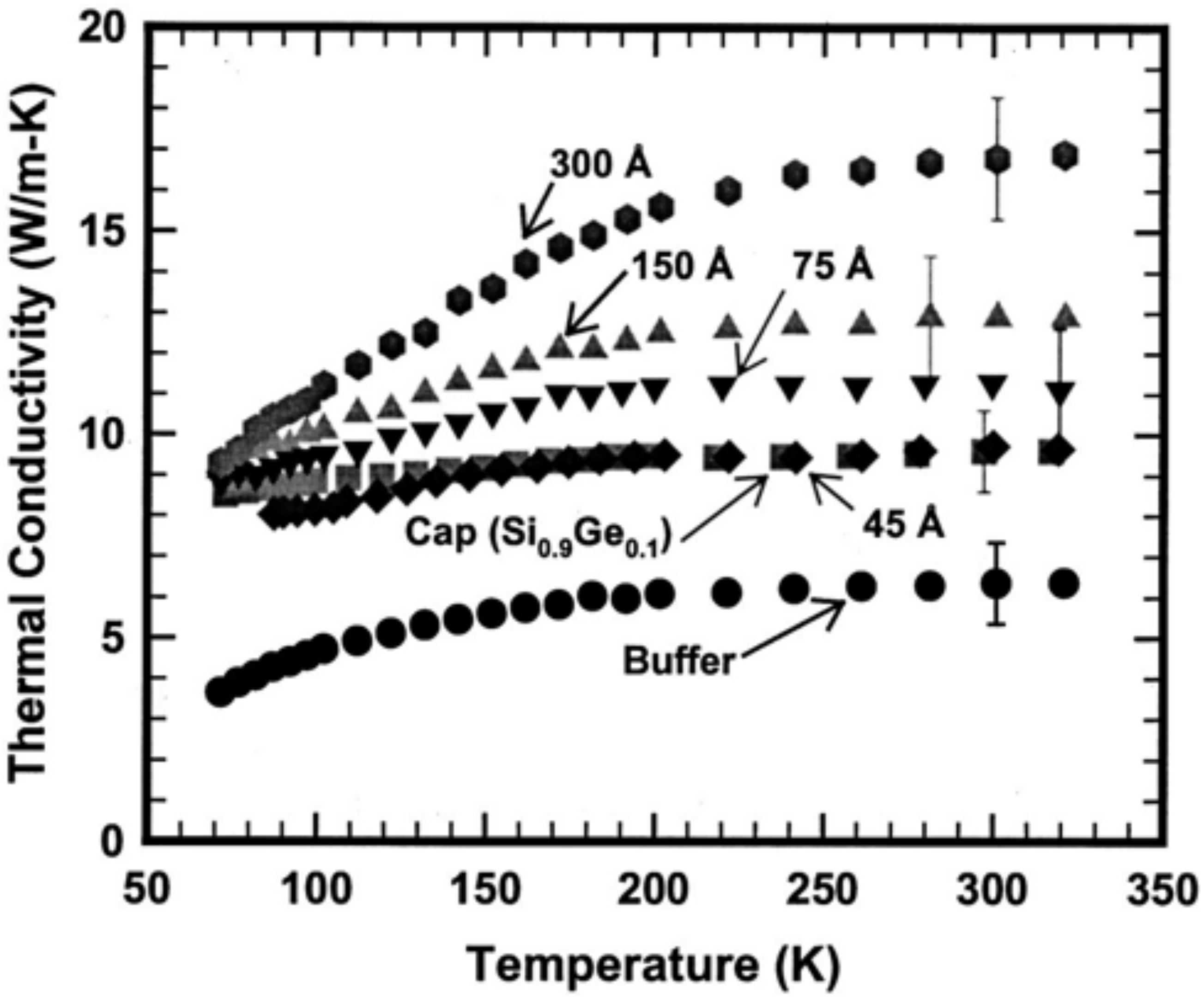
SiGe Thermal Conductivity



- Lower κ in alloy through additional phonon scattering
- Electron / hole mobility - small reduction by alloy scattering
- Effect ideal for engineering thermoelectric materials

J.P. Dismukes et al., J. Appl. Phys. 35, 2899 (1964)

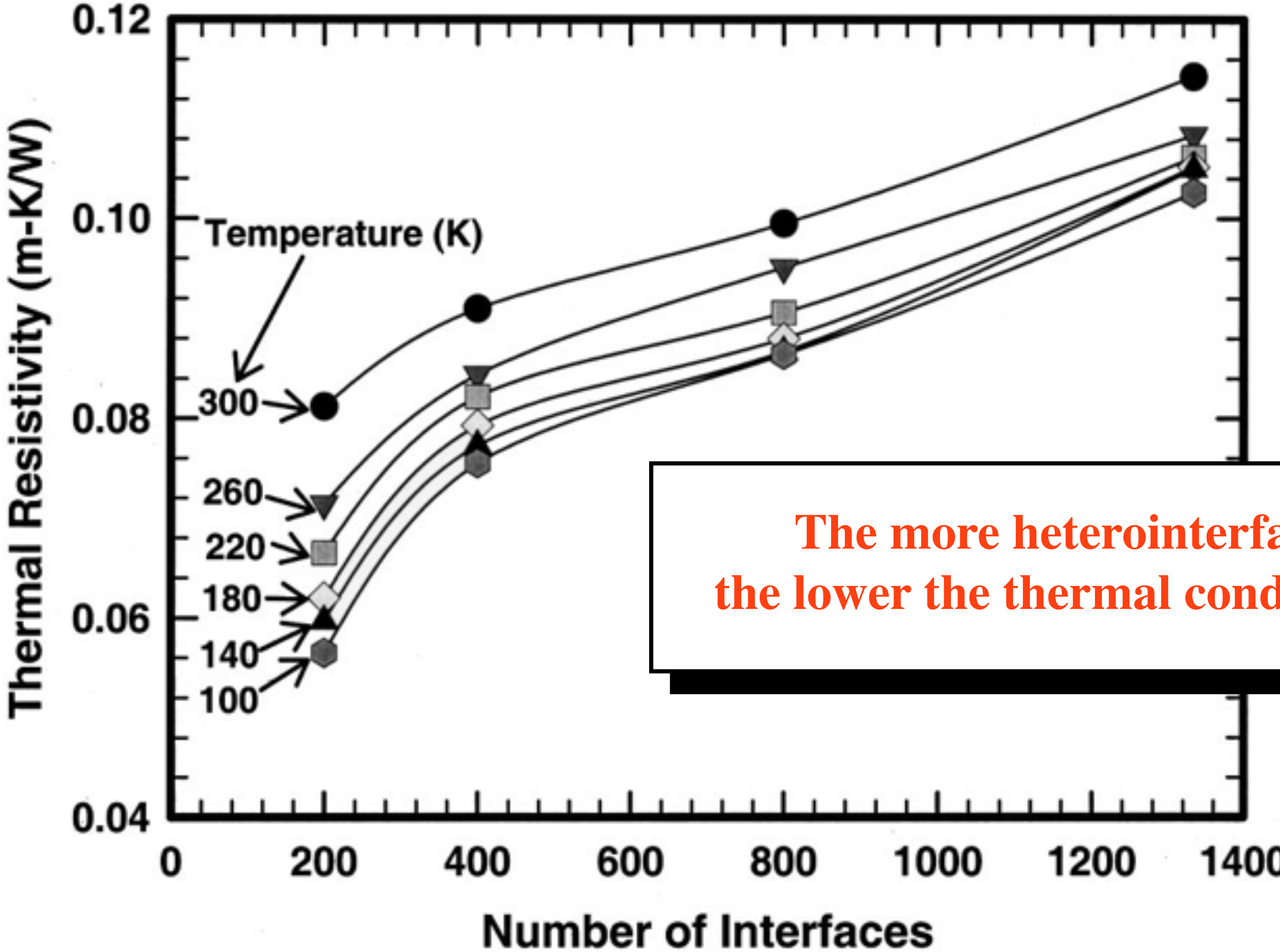
Thermal Conductivity Si/$Si_{0.7}Ge_{0.3}$ Superlattices



- 2:1 Si to $Si_{0.7}Ge_{0.3}$
- Buffer is 1 μm $Si_{0.9}Ge_{0.1}$
- κ reduces as heterolayer thickness reduces

S. Huxtable et al., Appl. Phys. Lett. 80, 1737 (2002)

Thermal Conductivity Si/$Si_{0.7}Ge_{0.3}$ Superlattices

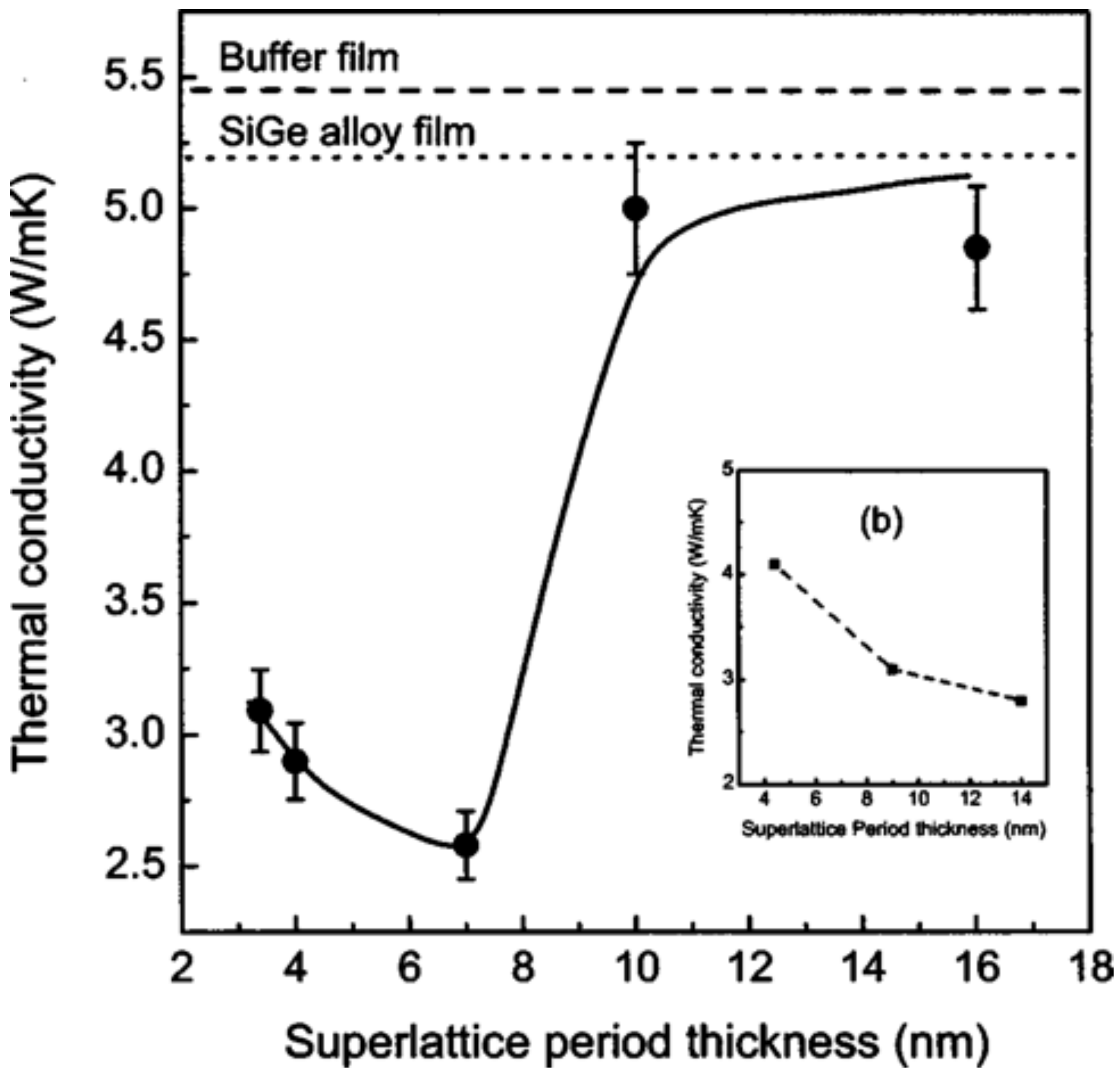


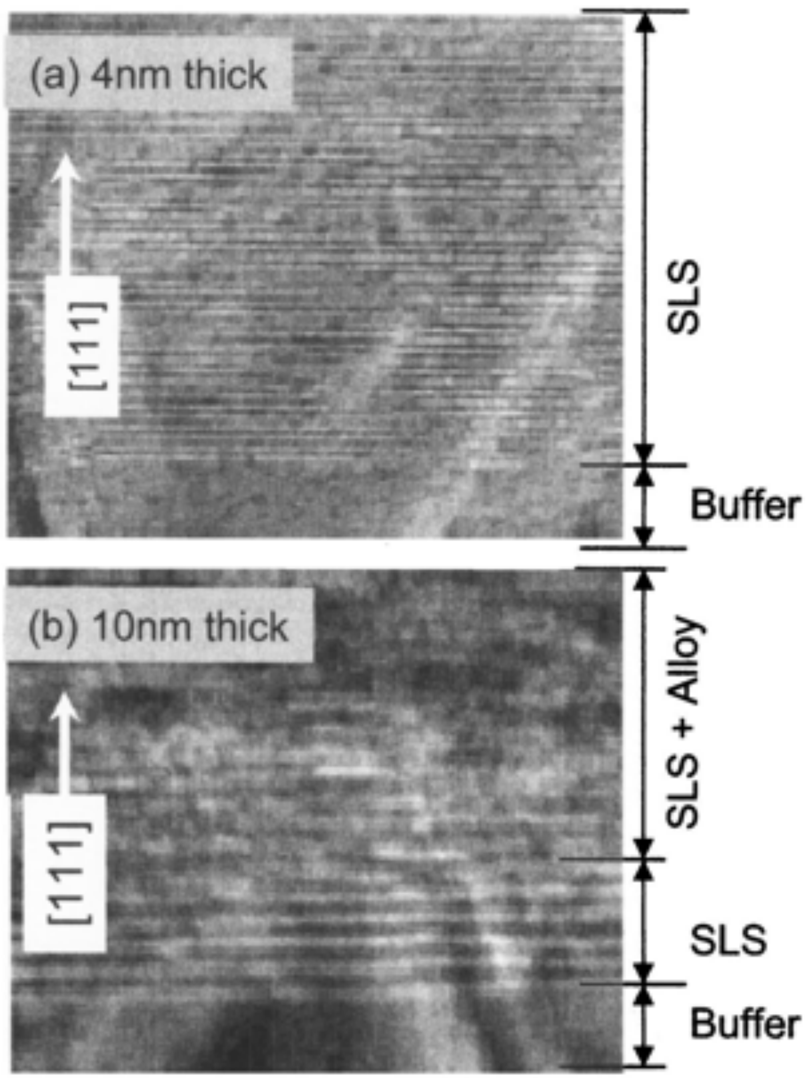
The more heterointerfaces, the lower the thermal conductivity

- Physically: more heterointerfaces –> more phonon scattering

S. Huxtable et al., Appl. Phys. Lett. 80, 1737 (2002)

Si/Ge Superlattice Reduced Thermal Conductivity

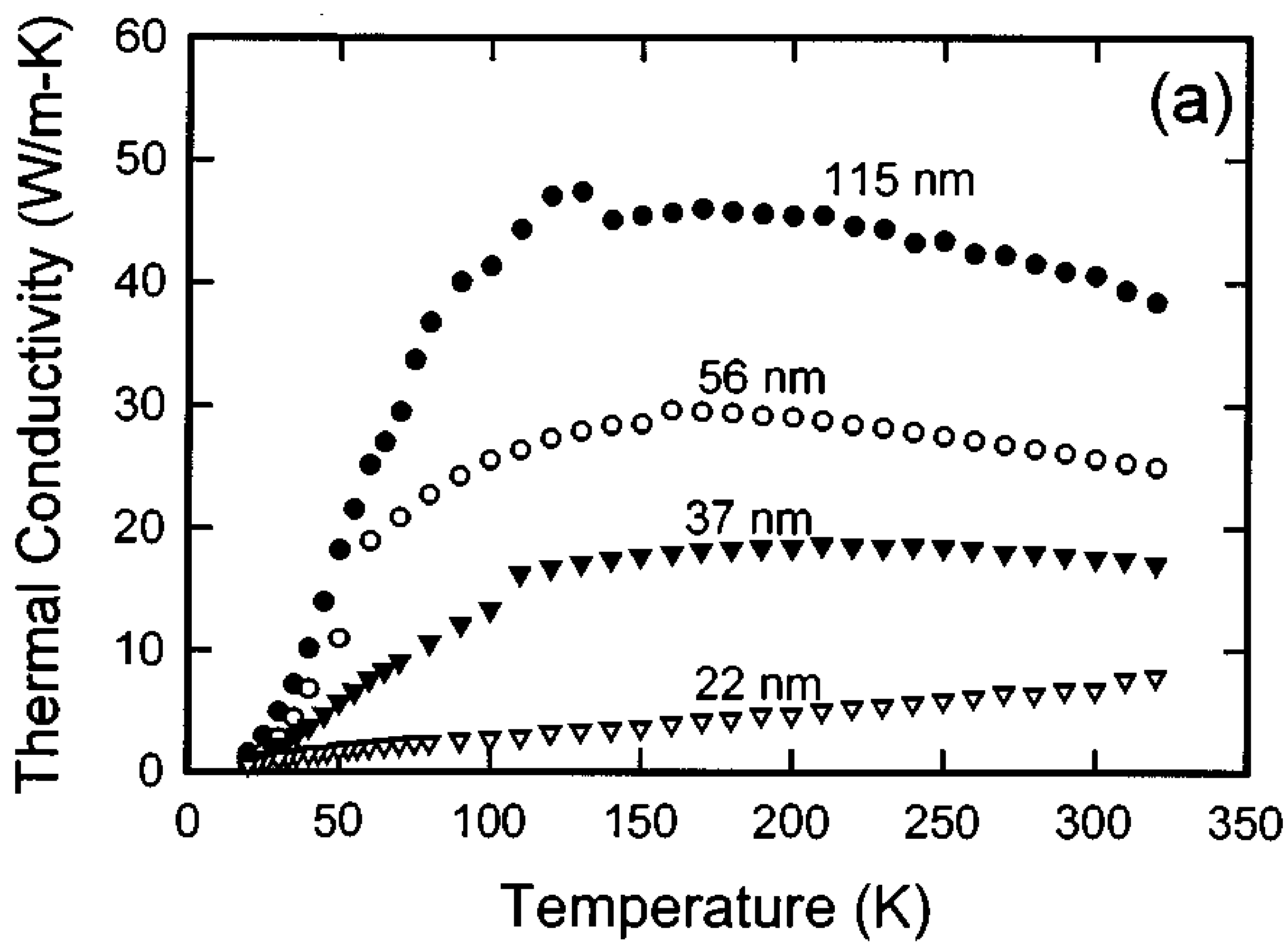




$Si_{0.5}Ge_{0.5}$ buffer

S. Chakraborty et al., Appl. Phys. Lett. 83, 4184 (2003)

Thermal Conductivity of Silicon Nanowires



- For bulk Si

  κ ~149 Wm^{-1}K^{-1} at 300 K

- For bulk Si

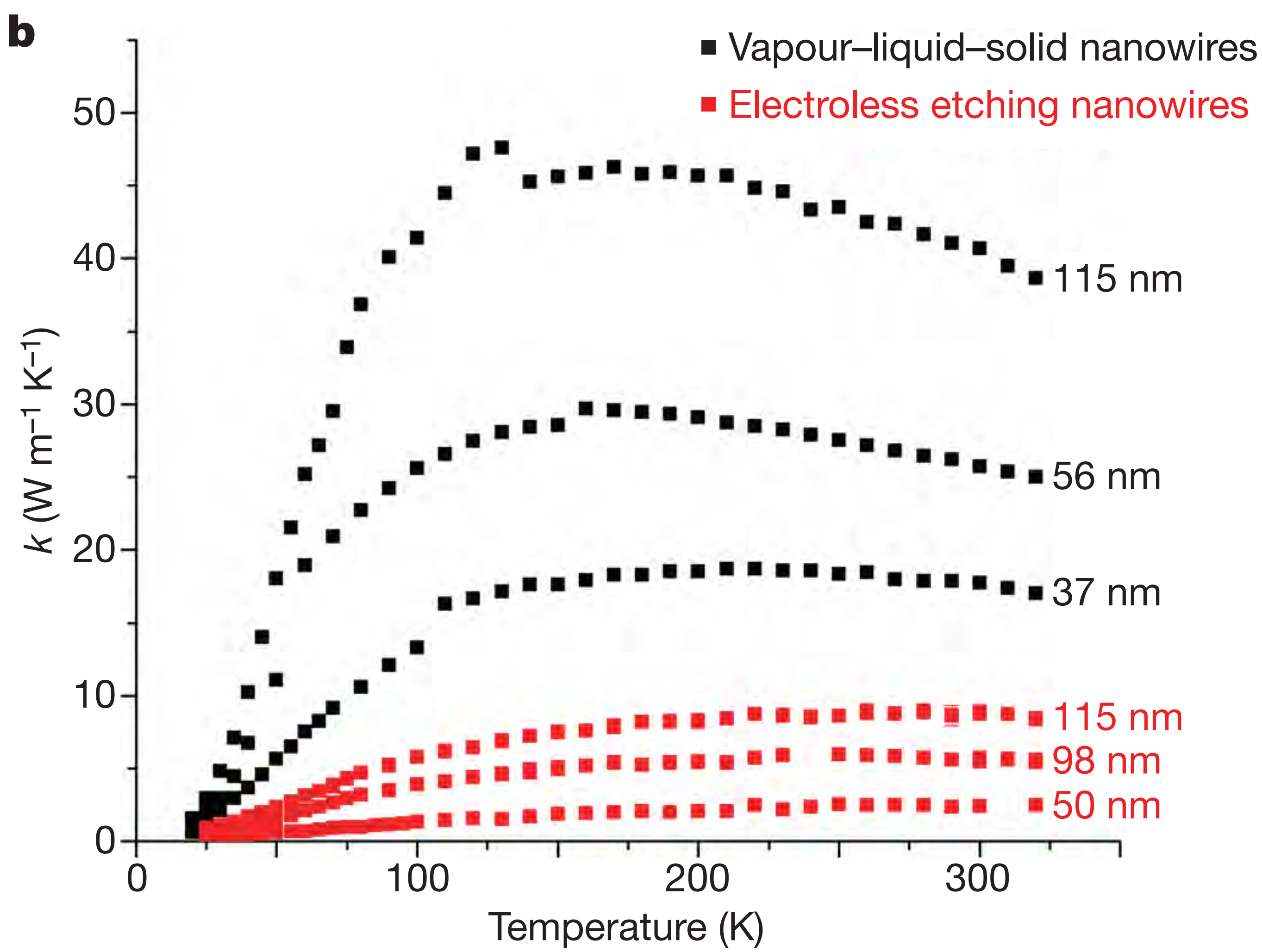
$$\Lambda_{ph} = \frac{3\kappa_{ph}}{C_v \langle v_t \rangle \rho}$$

  ~300 nm

- Phonon scattering at boundaries increases for smaller diameter wires

D.Y. Li et al. Appl. Phys. Lett. 83, 2934 (2003)

Thermal Conductivity of 1D Silicon Nanowires



Red data from nanowires with rough boundaries

- $$\Lambda_{ph} = \frac{3\kappa_{ph}}{C_v \langle v_t \rangle \rho}$$

  ~ 300 nm

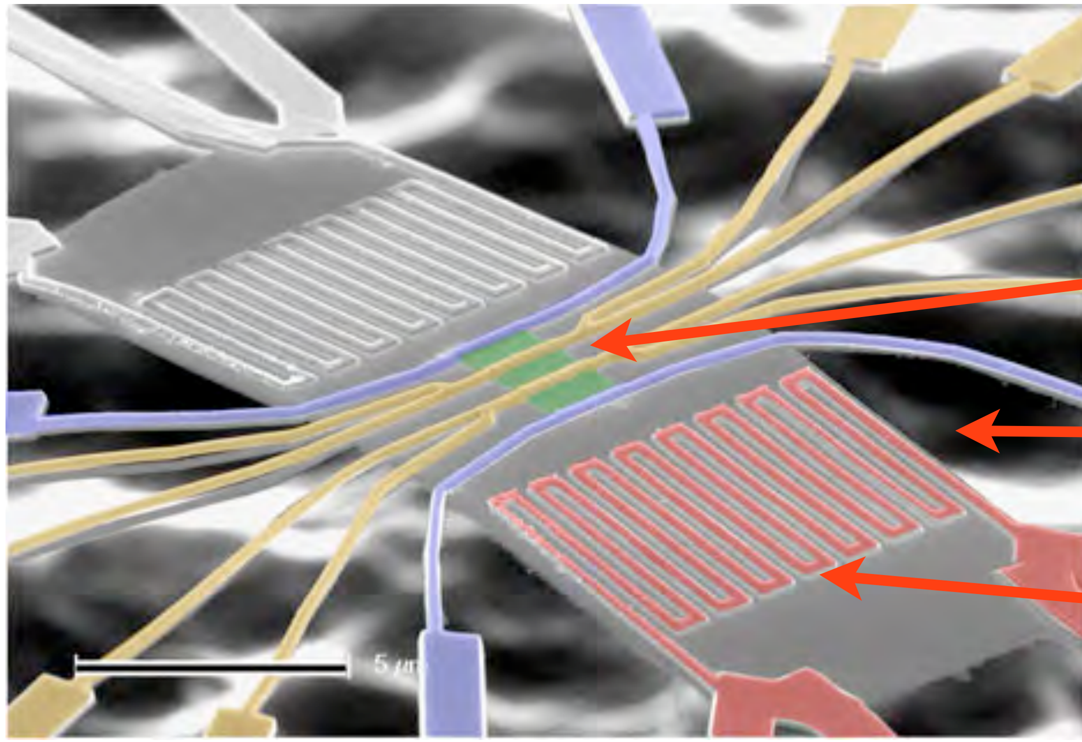
- ℓ **= 110 nm**

- **Phonon scattering >> electron scattering**

- **reduces faster than σ**

A.I. Hochbaum et al., Nature 451, 163 (2007)

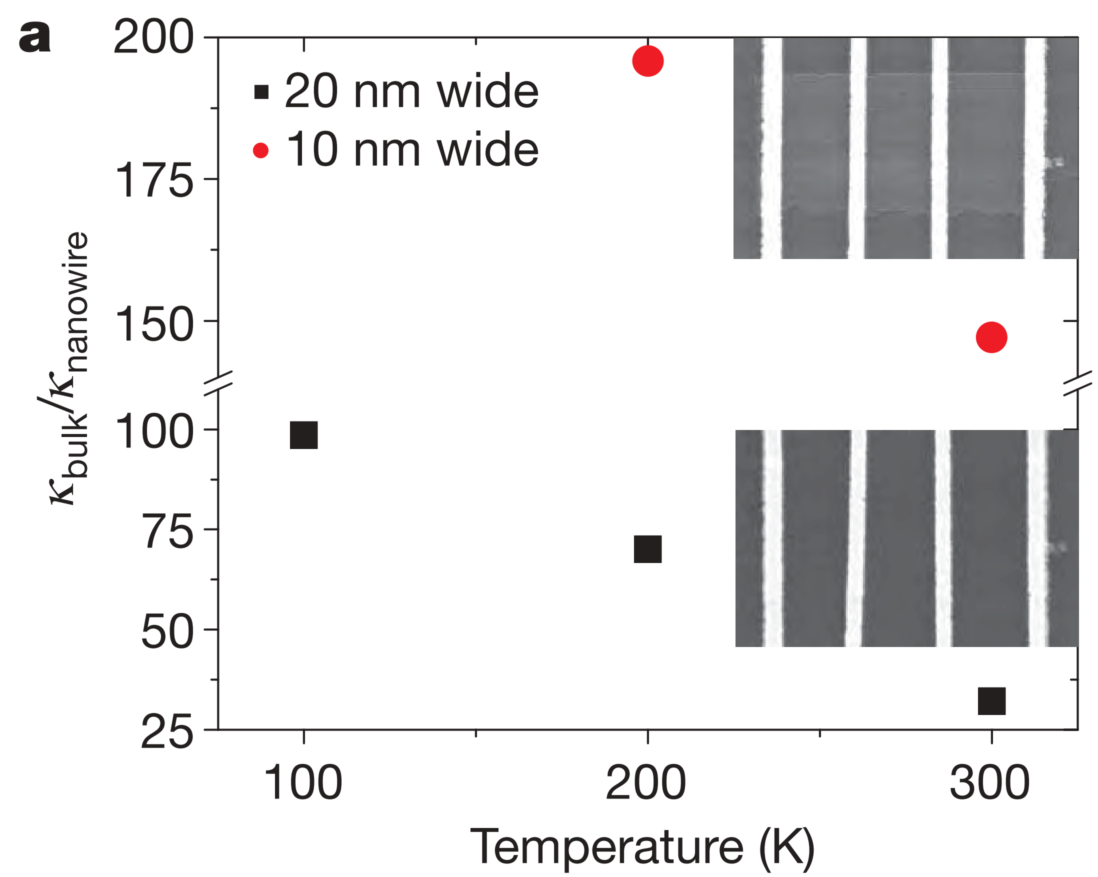
1D Nanowires



4 terminal Si nanowires

Substrate removed by etching

Heaters



A.I. Boukai et al., Nature 451, 168 (2007)

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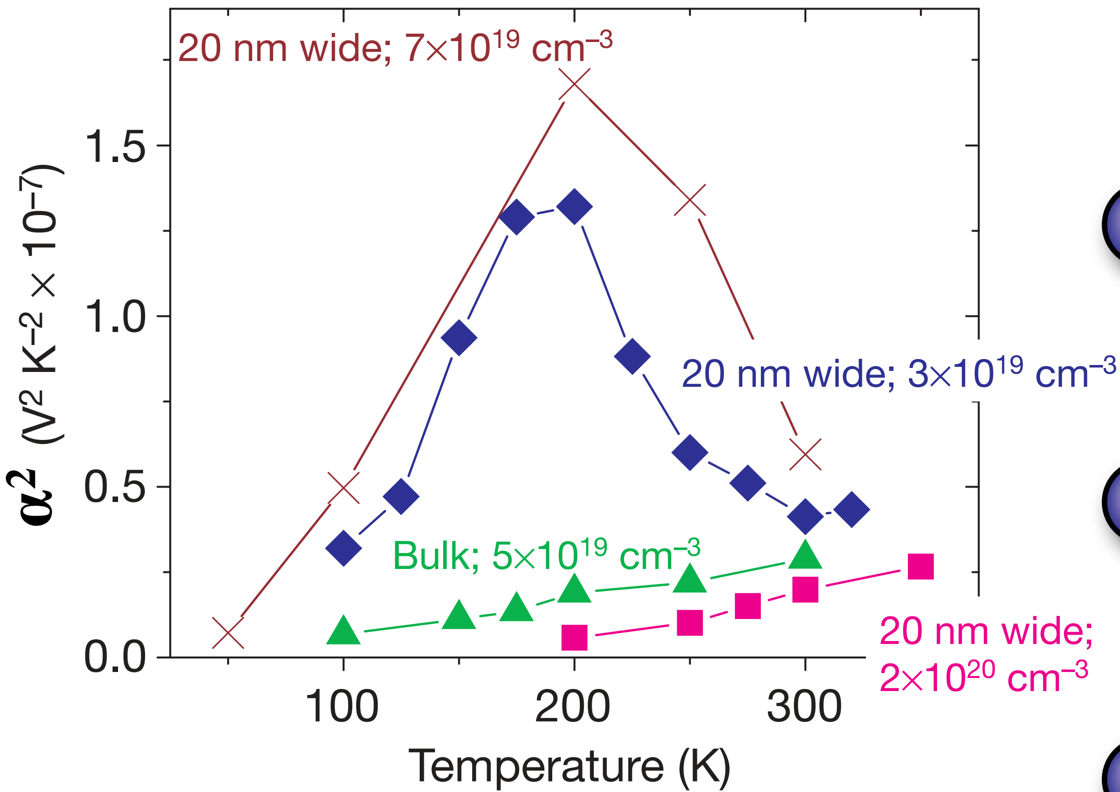
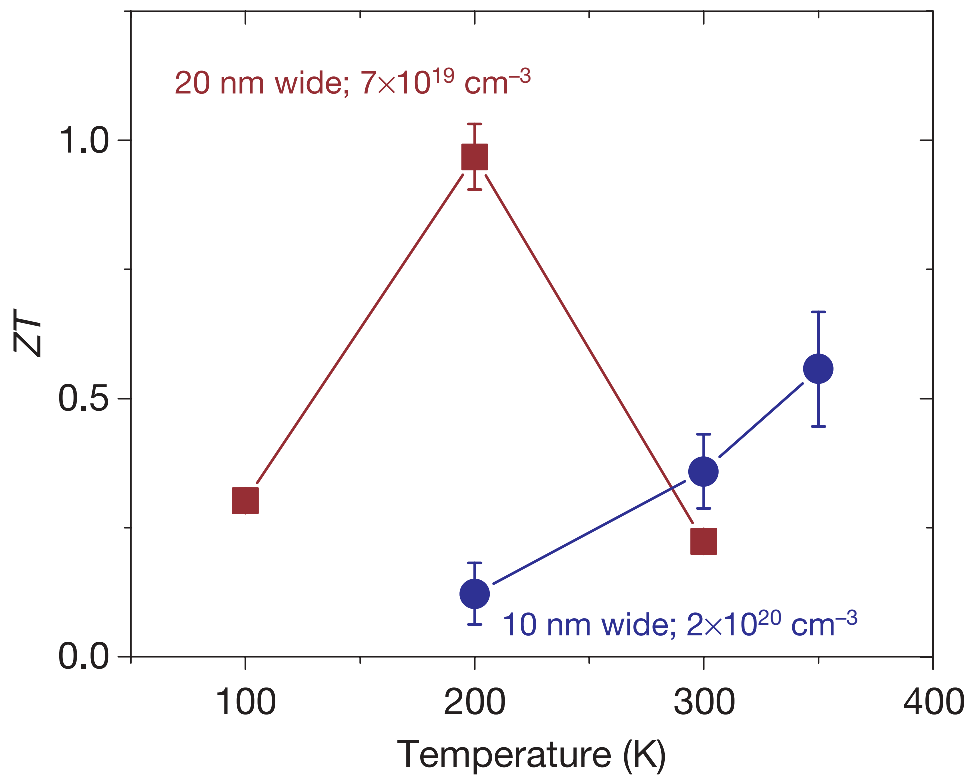


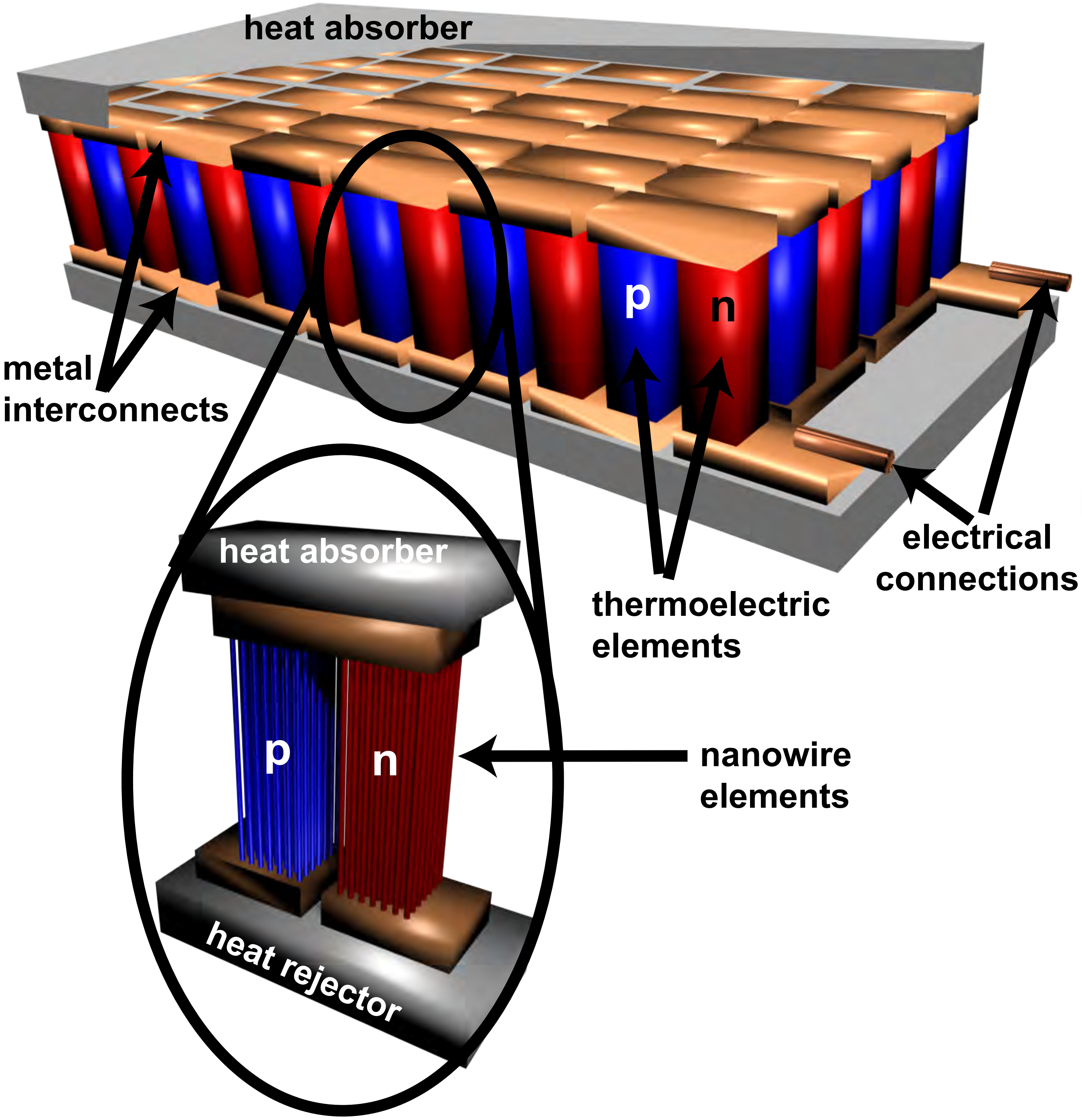


1D Silicon Nanowires

- **Higher α from the higher DOS, g(E)**
- **α increased by ~ 2**
- **κ reduced by factor ~150**
- **ZT increased by factor 600**
- **Thermal conductivity reduced more than electrical conductivity**

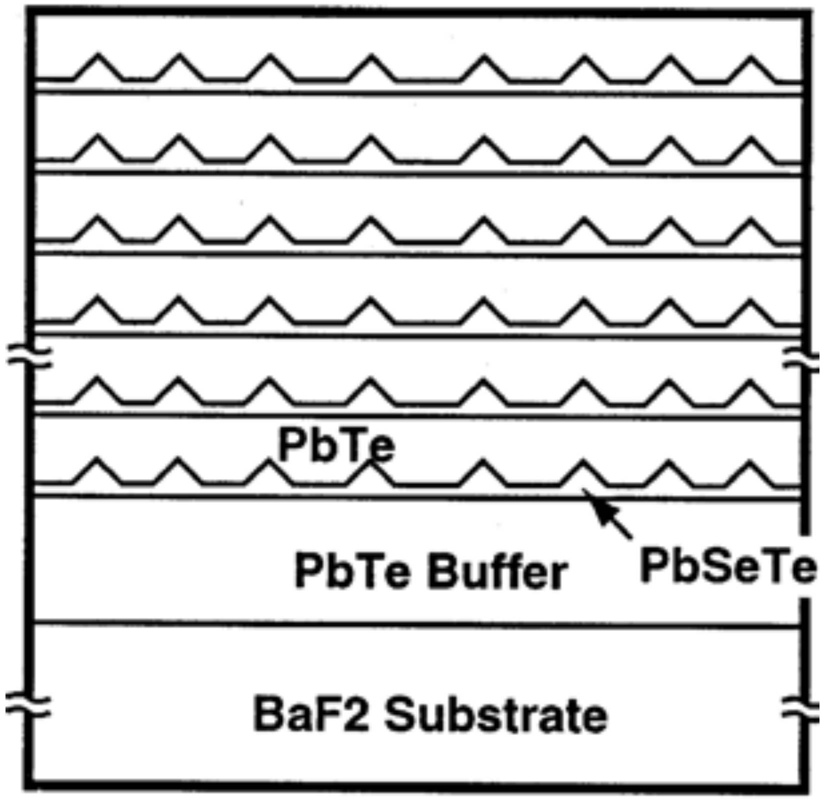
A.I. Boukai et al., Nature 451, 168 (2007)

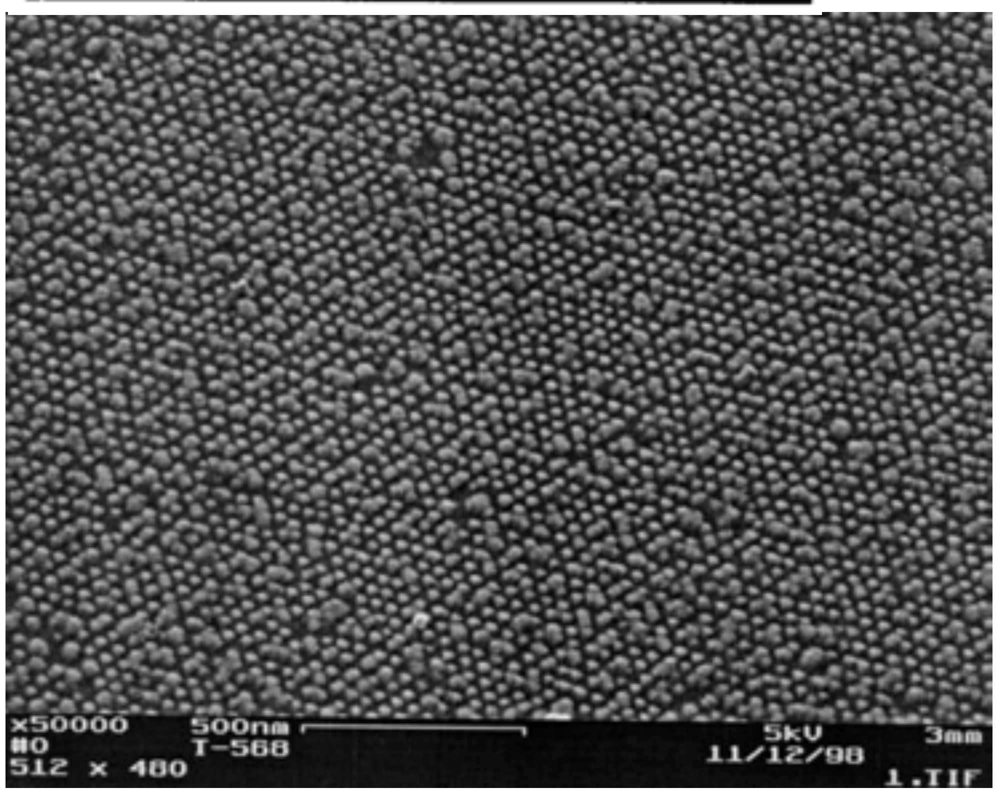
For Module Require Vertical Nanowires

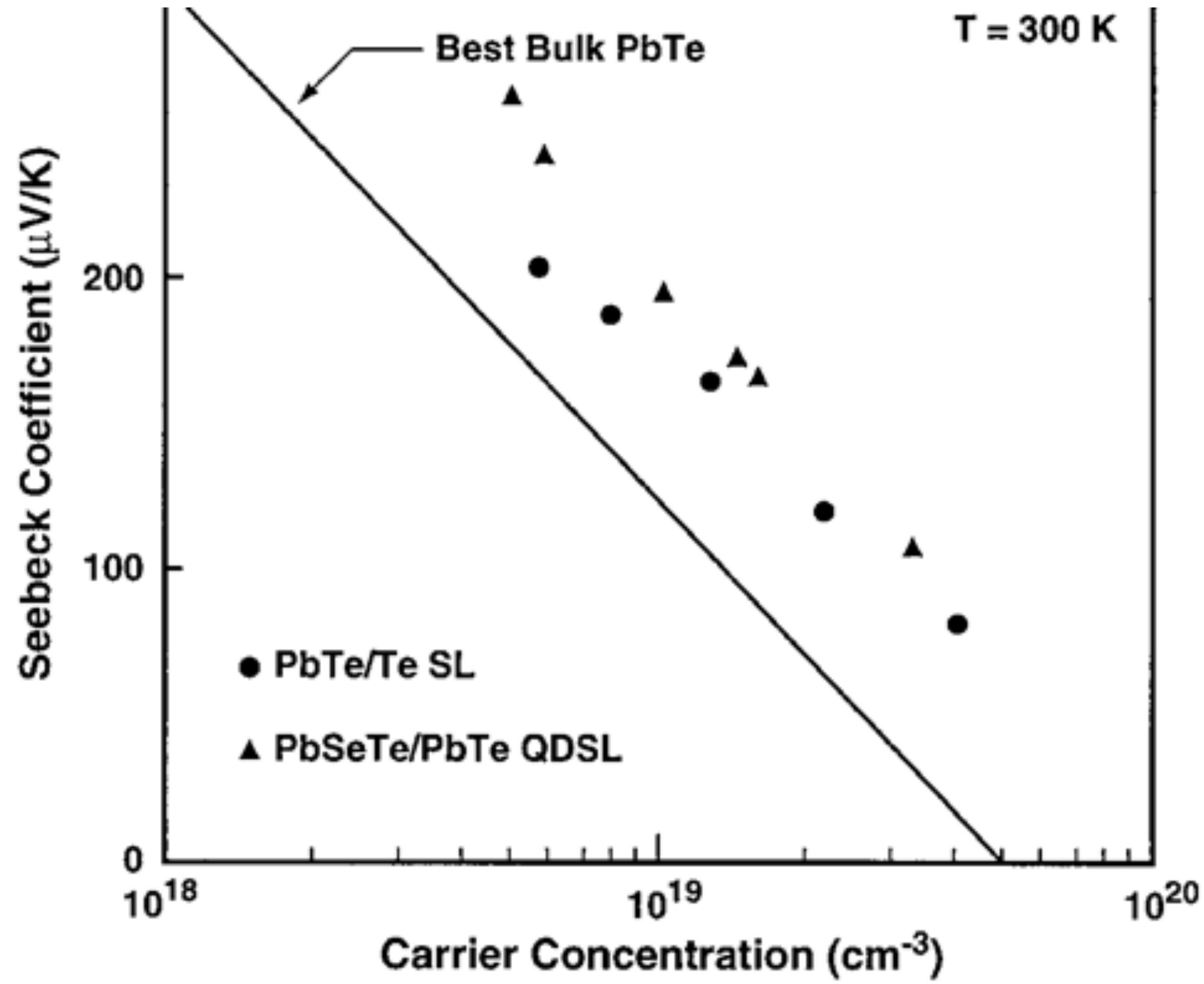


- 20nm vertical Si nanowires >> 5 μm height required
- High aspect ratio nanowires difficult to etch
- Also difficult to grow

0D Quantum Dots



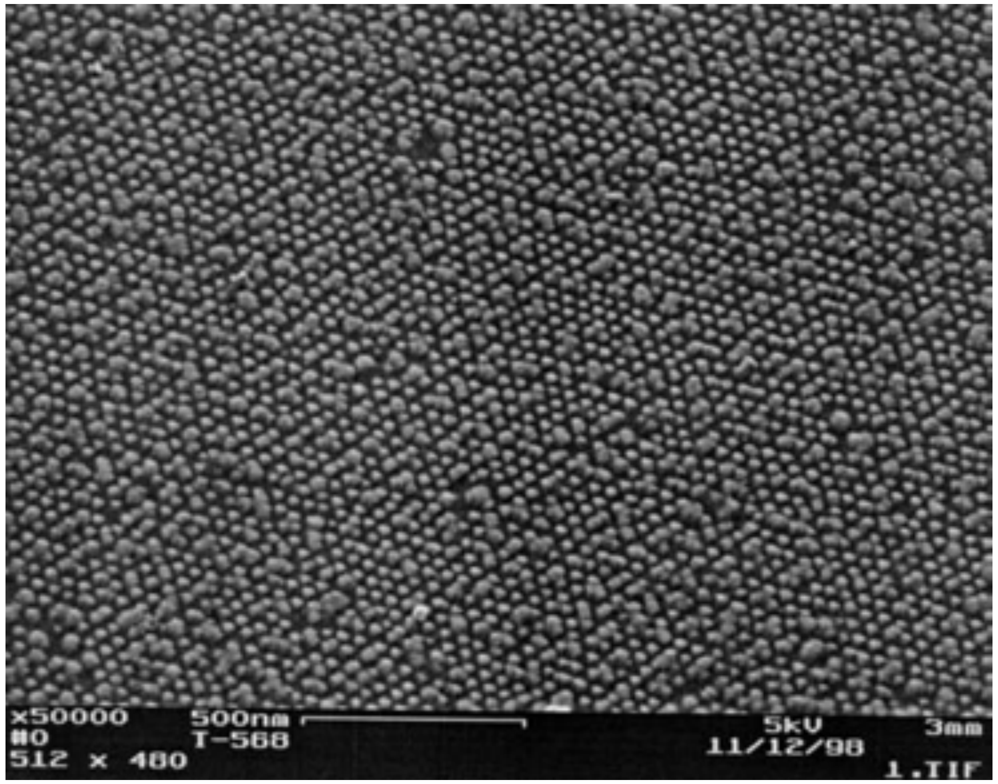


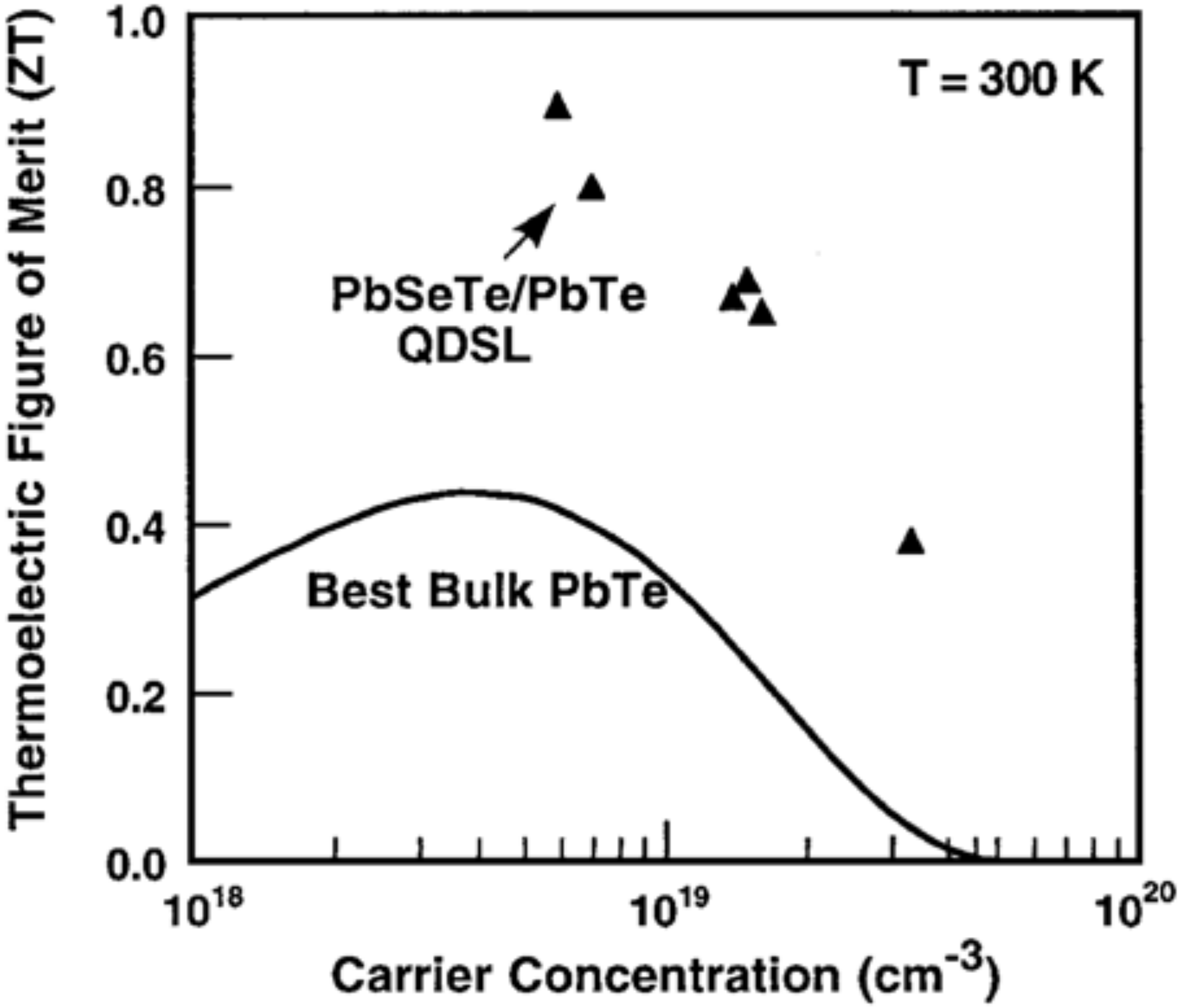


- Seebeck α: bulk < superlattice < QD

T.C. Harman et al., J. Elec. Mat. 29, L1 (2000)

0D Quantum Dots

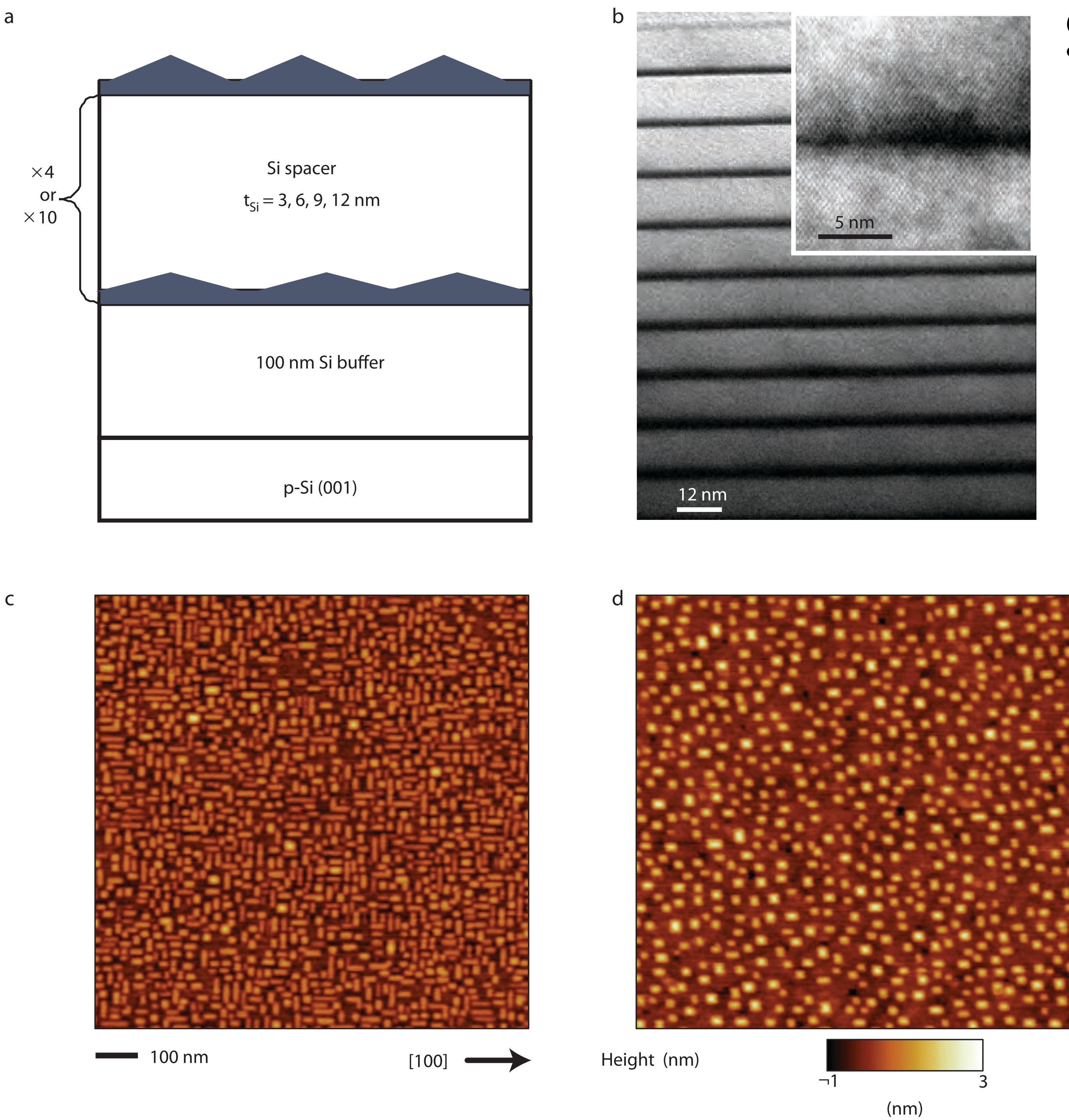


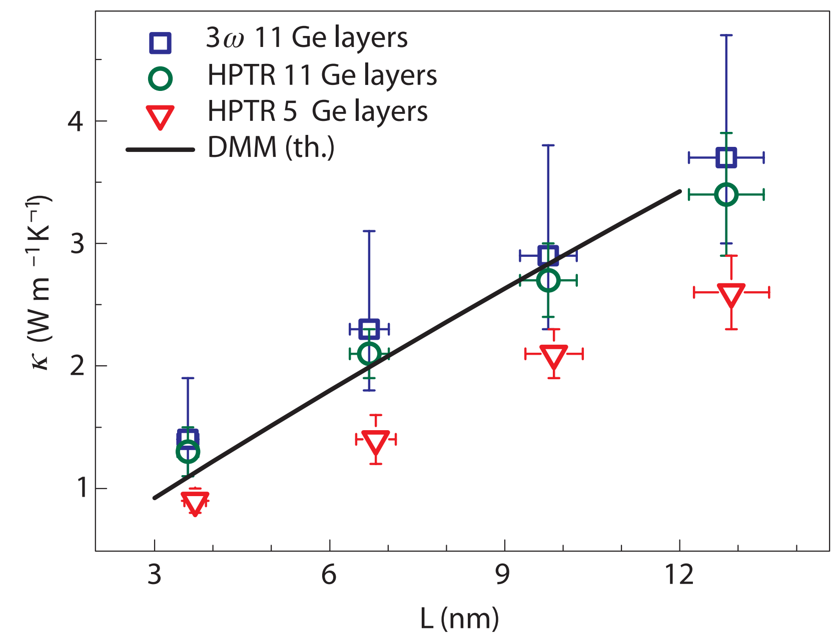


- Thermal conductivity reduced more than electrical conductivity

T.C. Harman et al., J. Elec. Mat. 29, L1 (2000)

SiGe Quantum Dots





Lowest reported κ for SiGe materials but no doping!

G. Perot et al., Nat. Mat. 9, 491 (2010)

Nanoparticle Engineering

Advantages:

- **Potentially cheap, mass manufacturable technology (hot press)**
- **Periodic structures not required to reduce thermal conductivity**
- **In SiGe material, particles below 50 nm demonstrate improved ZT**

Disadvantages:

- **Many orders of magnitude change in ZT for small change in density (few %) –> voids in material**
- **Technology immature and process dependent**

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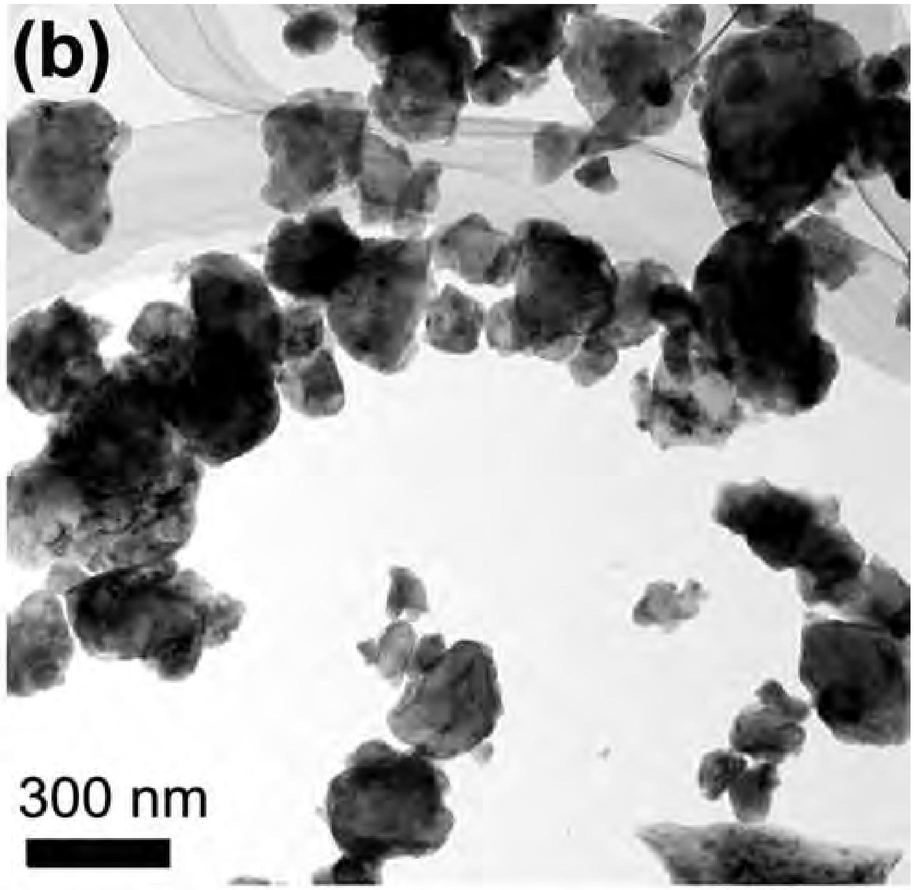
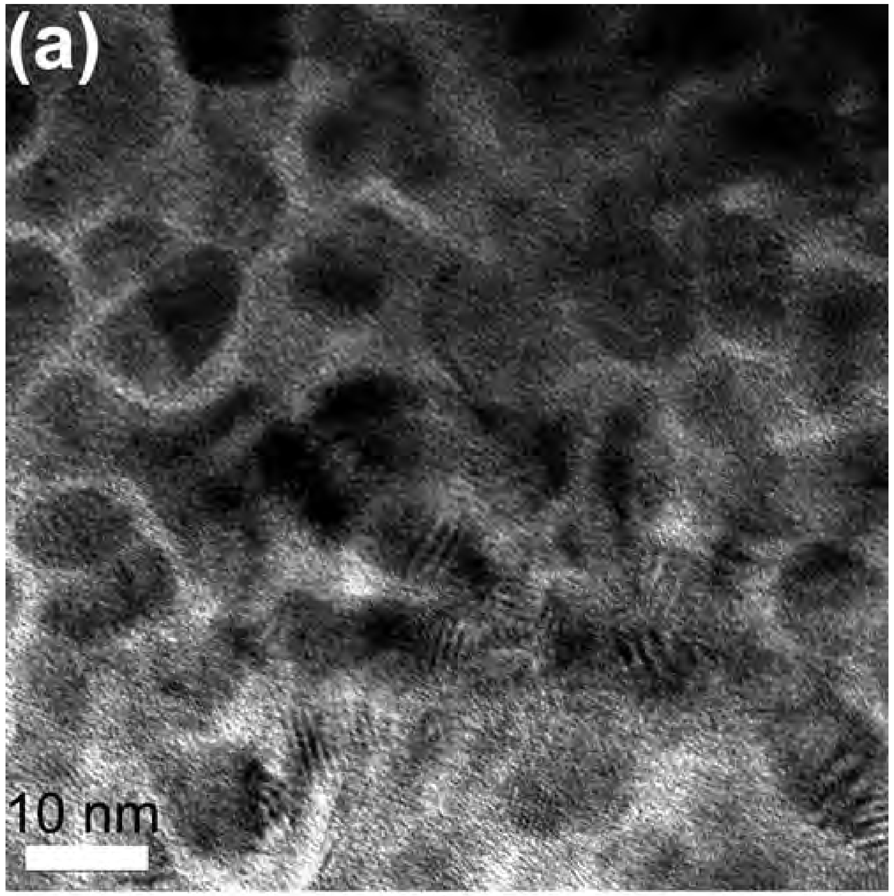
Nanoparticle / Quantum Dot Materials



Ball milled bulk SiGe alloy



Hot pressed material with ~ 10 nm nanoparticles

X.W. Wang et al. Appl. Phys. Lett. 93, 193121 (2008)

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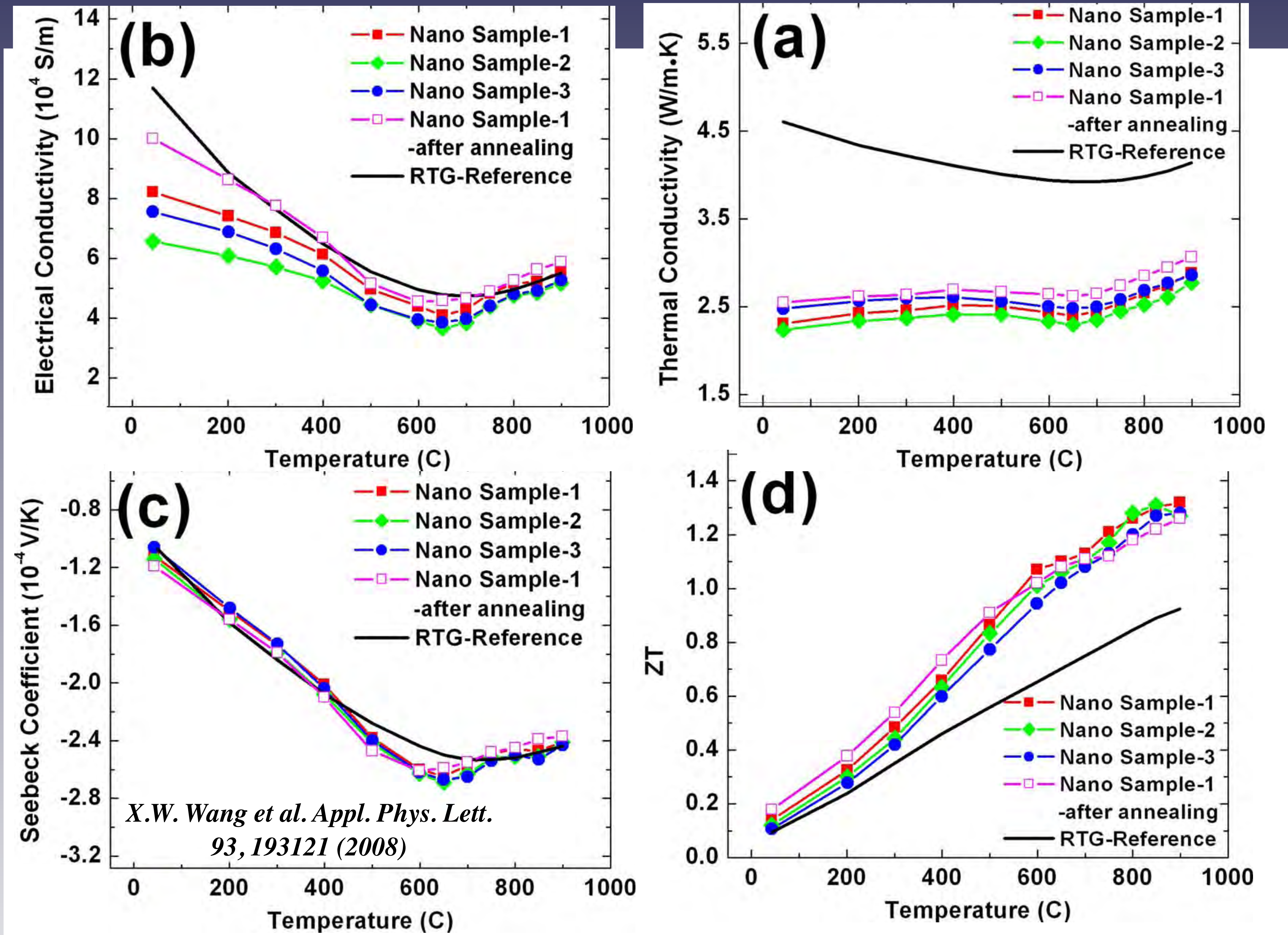


(b)
Nano Sample-1
Nano Sample-2
Nano Sample-3
Nano Sample-1
-after annealing
RTG-Reference
Electrical Conductivity (10^4 S/m)
Temperature (C)
(a)
Thermal Conductivity (W/m.K)
(c)
Seebeck Coefficient (10^-4 V/K)
X.W. Wang et al. Appl. Phys. Lett.
93, 193121 (2008)
(d)
ZT

Thermoelectric Power Generating Efficiency

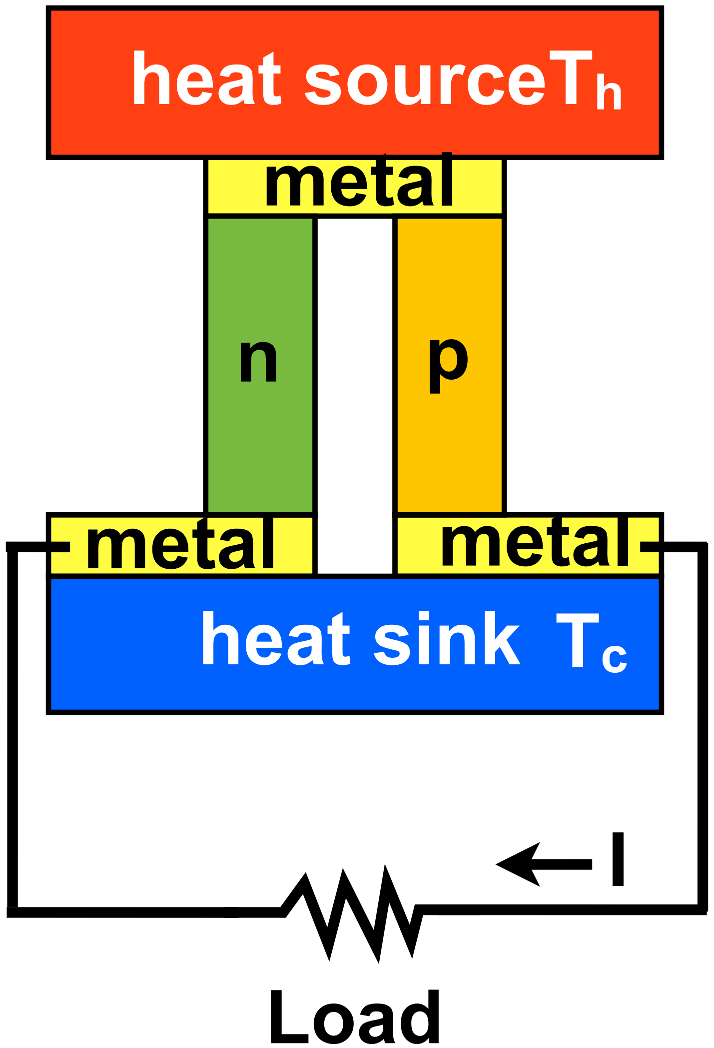
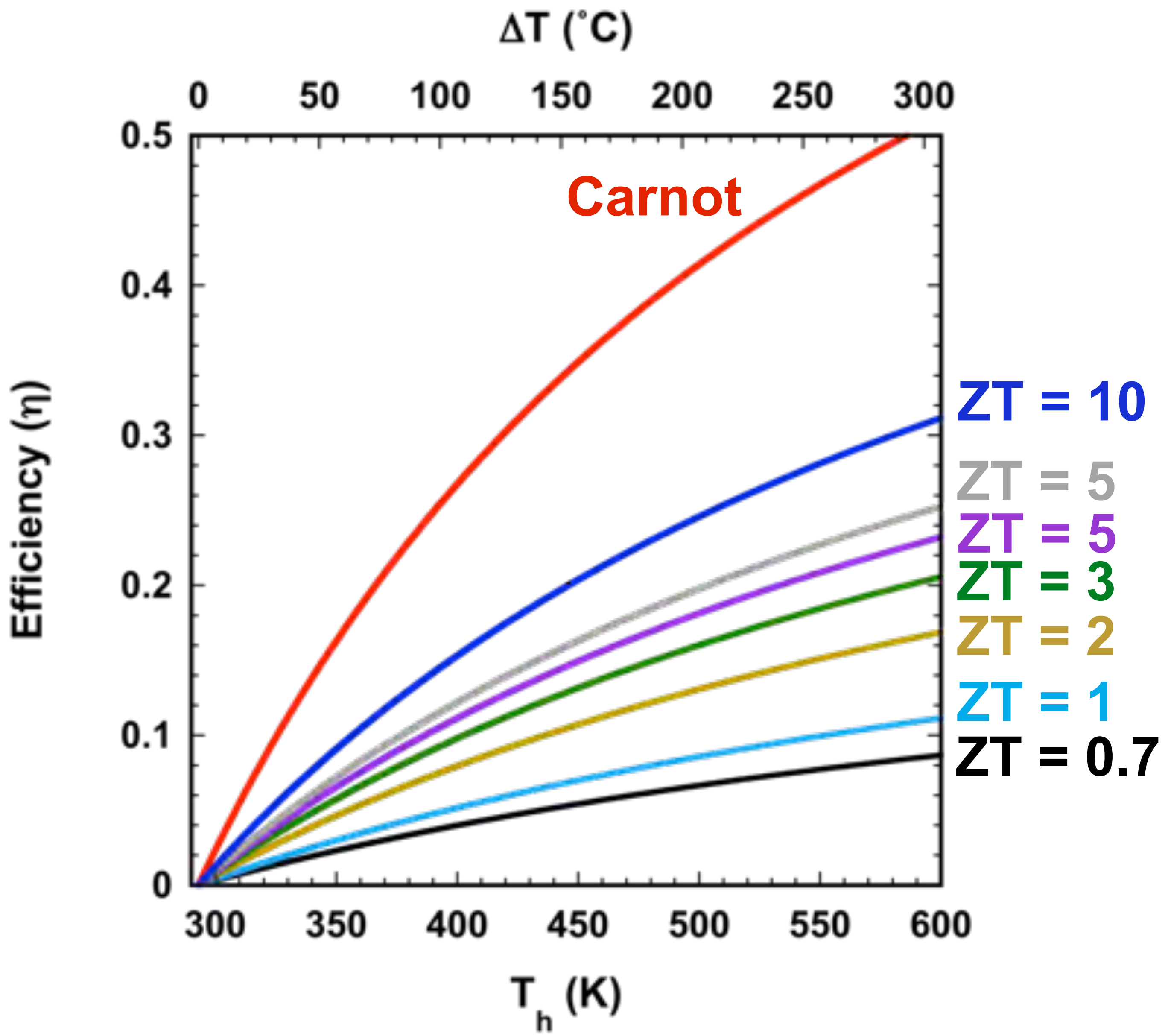


Figure of merit

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

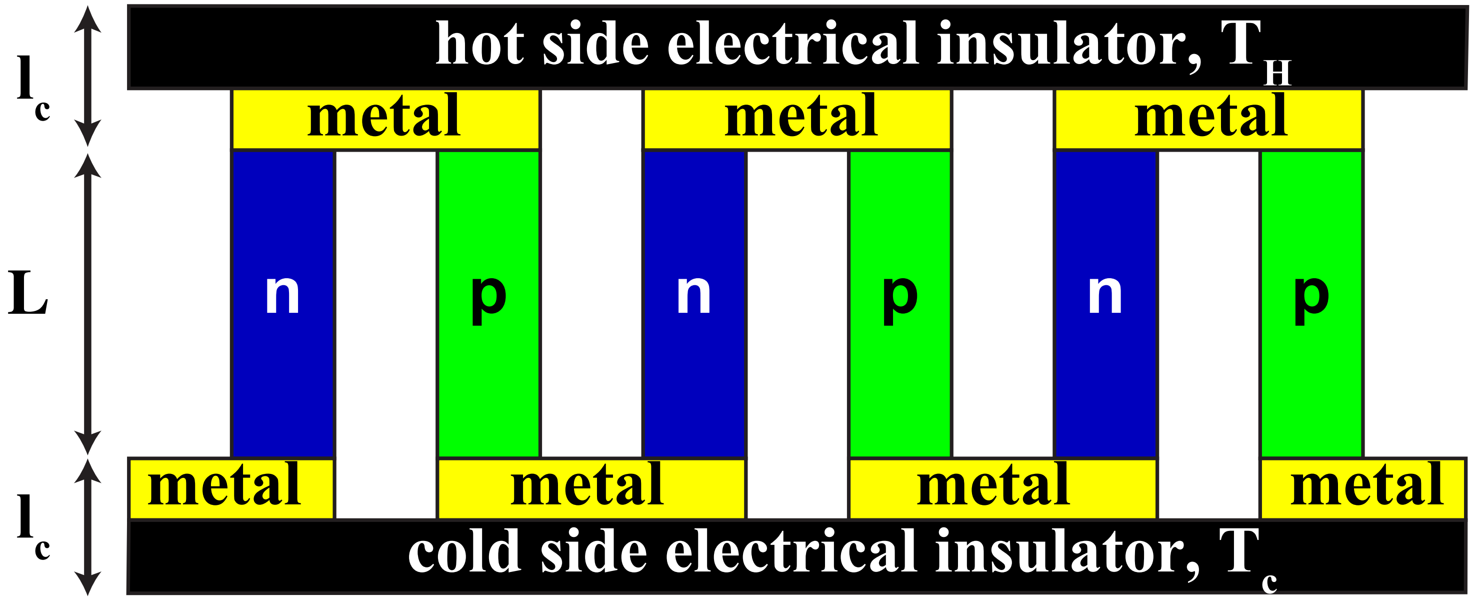
$$\eta = \frac{\Delta T}{T_h} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_c}{T_h}}$$



Power factor = $\alpha^2\sigma$

Impedance matching and maximum power point tracking are key for thermoelectrics

Voltage / Current from Real Thermoelectric Modules



A = module leg area

L = module leg length

N = number of modules

κ_c = thermal contact conductivity

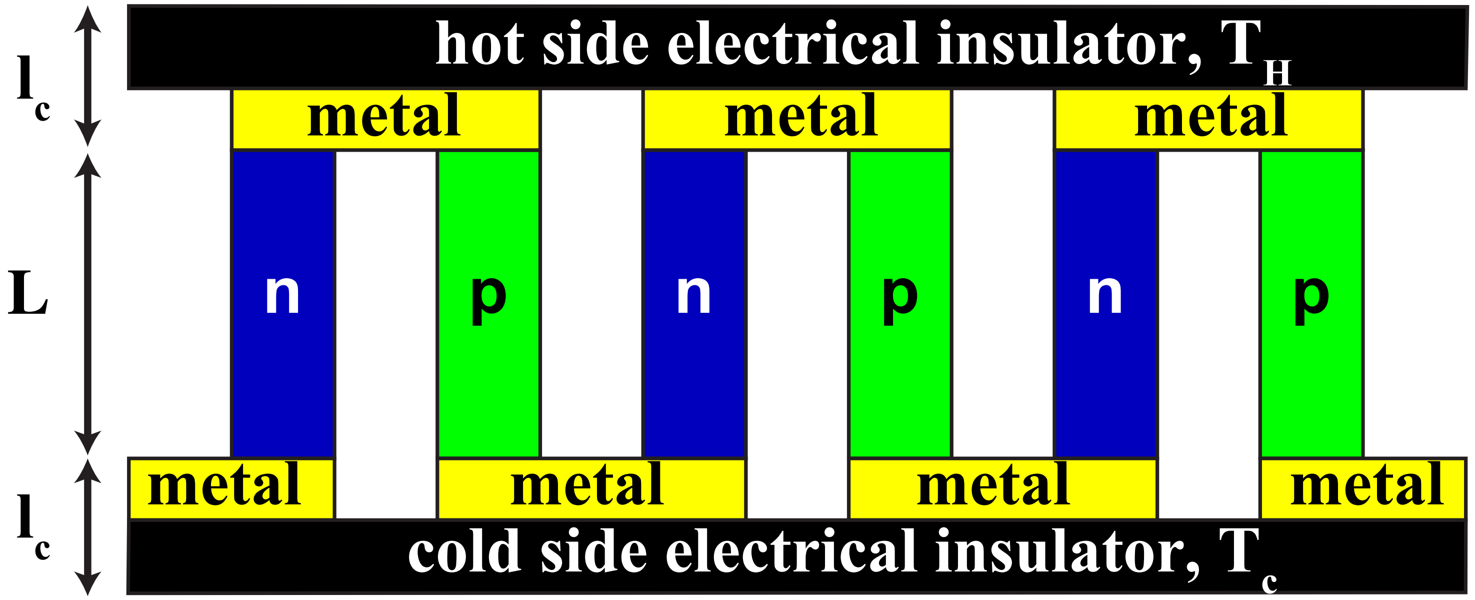
ρ_c = electrical contact resistivity

$$V = \frac{N\alpha\Delta T}{1+2\frac{\kappa l_c}{\kappa_c L}}$$

$$I = \frac{A\alpha\sigma\Delta T}{2(\rho_c\sigma+L)(1+2\frac{\kappa l_c}{\kappa_c L})}$$

D.M. Rowe (Ed.), 'Thermoelectrics Handbook: Macro to Nano' CRC Taylor and Francis (2006)

Power from Real Thermoelectric Modules



A = module leg area

L = module leg length

N = number of modules

κ_c = thermal contact conductivity

ρ_c = electrical contact resistivity

$$P = \frac{\alpha^2 \sigma A N \Delta T^2}{2(\rho_c \sigma + L)\left(1 + 2\frac{\kappa l_c}{\kappa_c L}\right)}$$

D.M. Rowe (Ed.), 'Thermoelectrics Handbook: Macro to Nano' CRC Taylor and Francis (2006)

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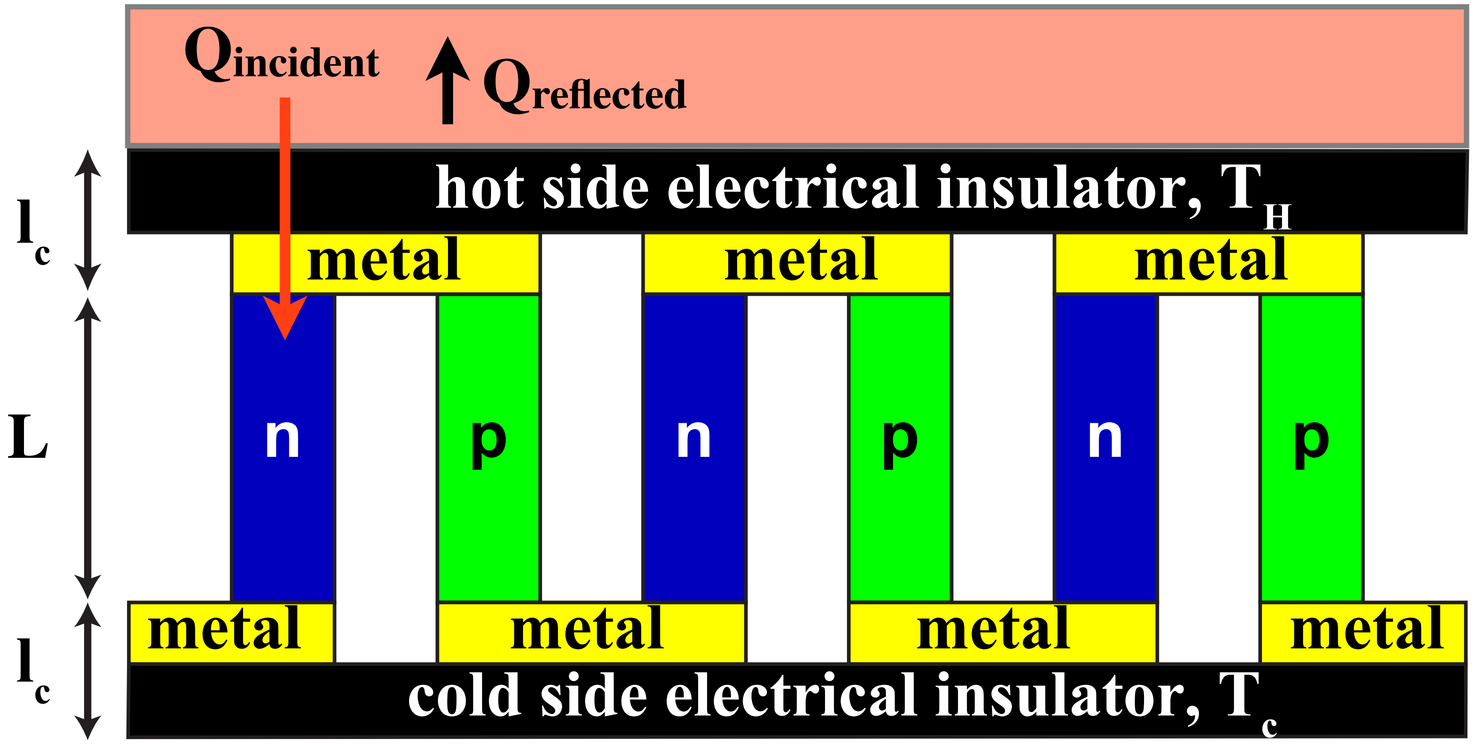
Maximum Output Power



A = module leg area

L = module leg length

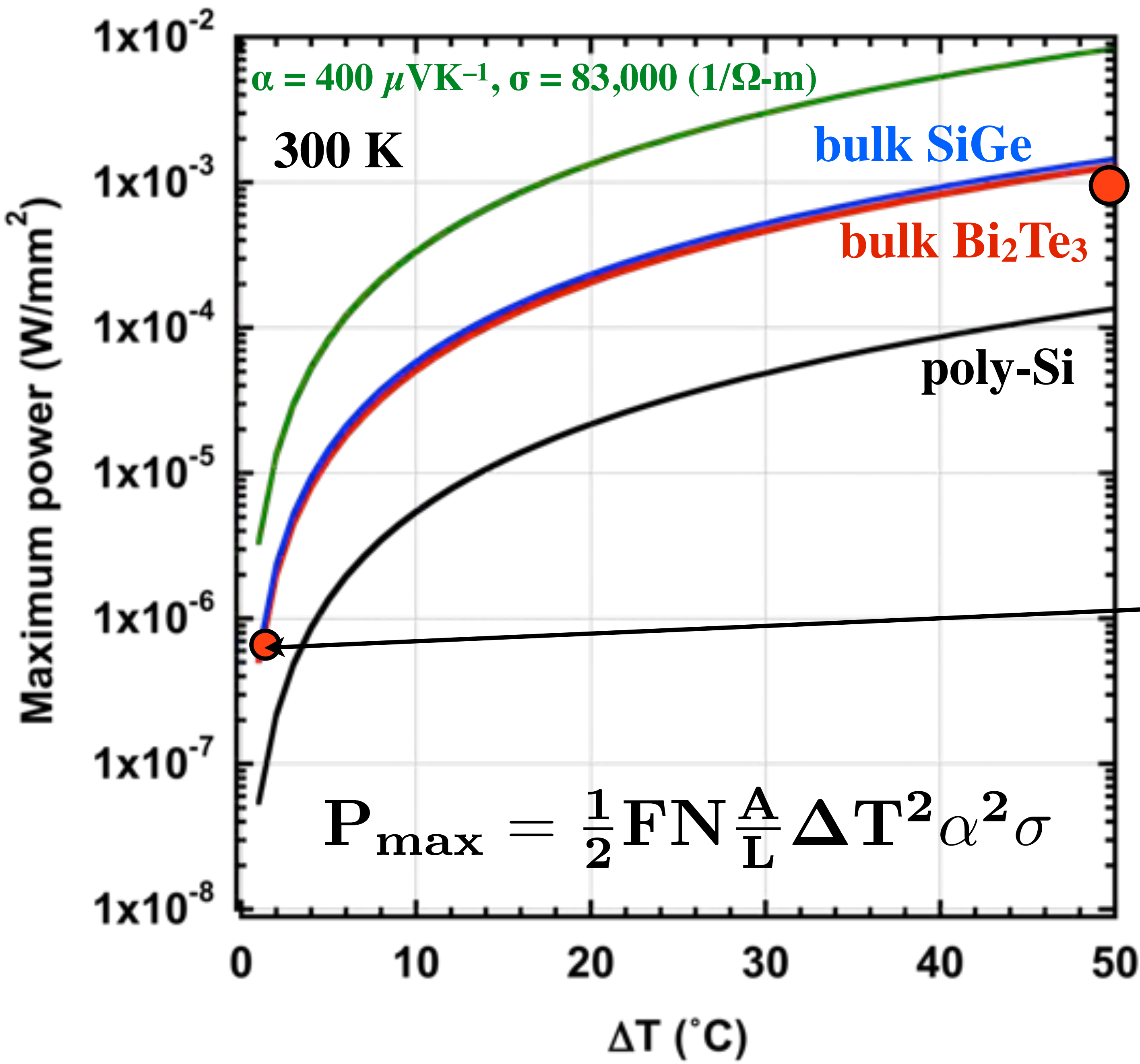
N = number of modules

- F = fabrication factor = perfect system – $R_{contact}$ – R_{series} – Lost heat
- Practical systems: both electrical and thermal impedance matching is required

$$P_{max} = \frac{1}{2} F N \frac{A}{L} \Delta T^2 \alpha^2 \sigma$$

D.M. Rowe (Ed.), 'Thermoelectrics Handbook: Macro to Nano' CRC Taylor and Francis (2006)

Maximum Power Examples



Dense microfabricated module

N = 2500

L = 10 μm

l_c = 1 μm

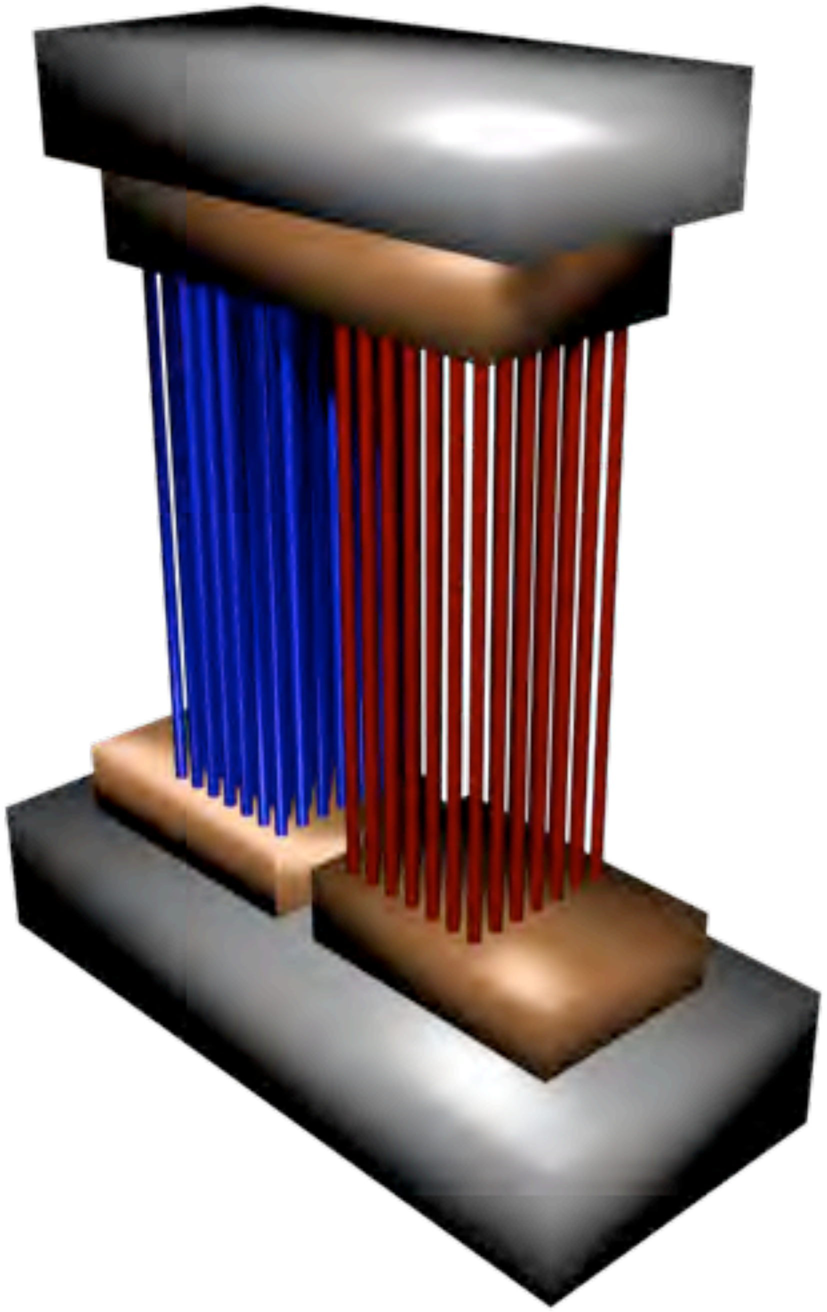
A = 10 x 10 μm^2

F = 0.2

bulk Bi_2Te_3 experiment
Nat. Mat. 2, 528 (2003)
(scaled from L = 20 –> 10 μm)

N.B. The thermal conductivity must also be considered for ΔT_{max}!

Generate Renewable Energy Efficiently using Nanofabricated Silicon (GREEN Silicon)



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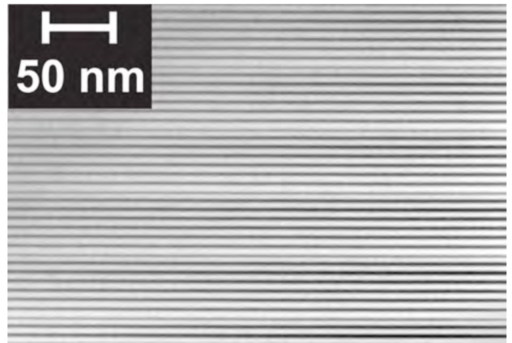
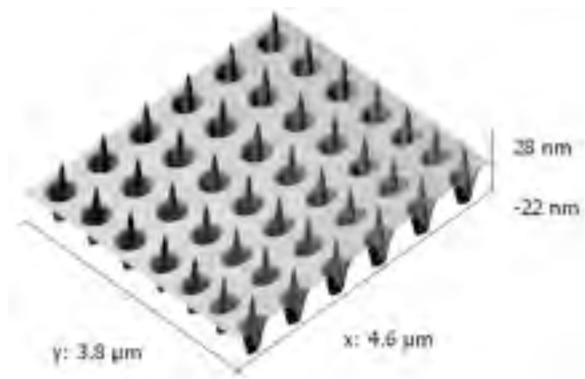
EC FP7 ICT FET
"2ZeroPowerICT" No.: 257750

GREEN Silicon Approach

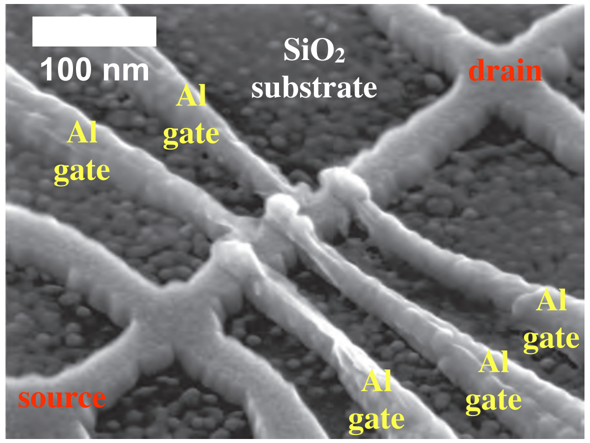
Low dimension technology



superlattice

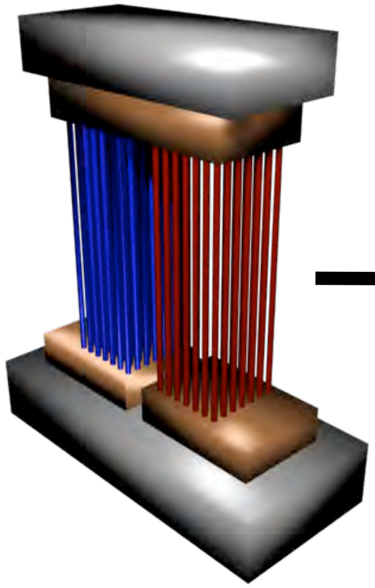


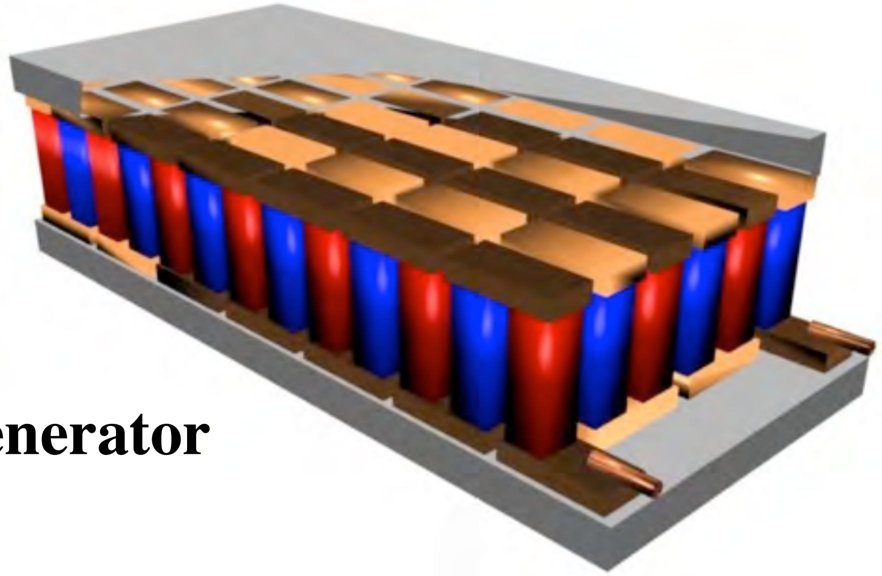
quantum dot



nanowires

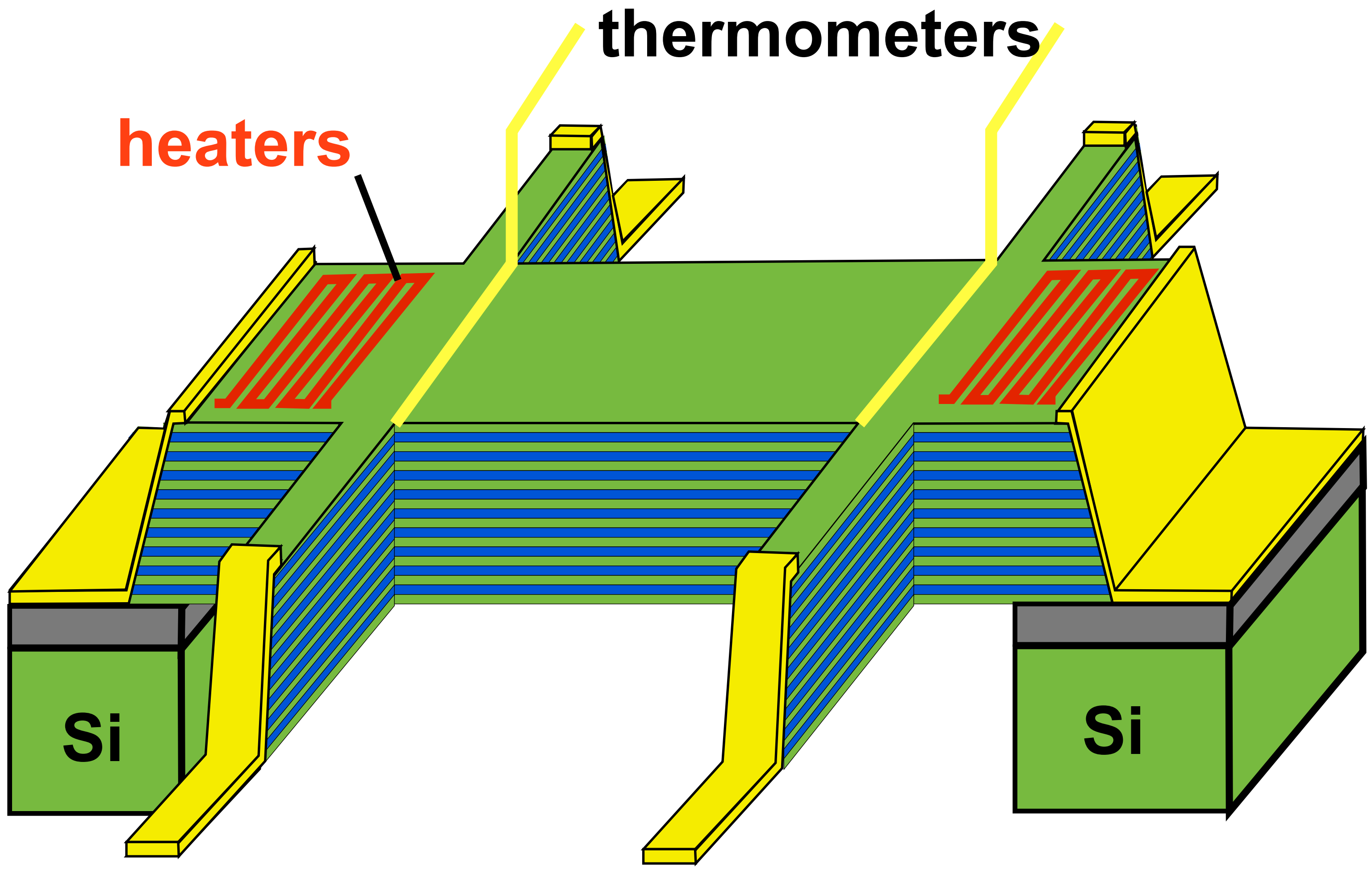
Module

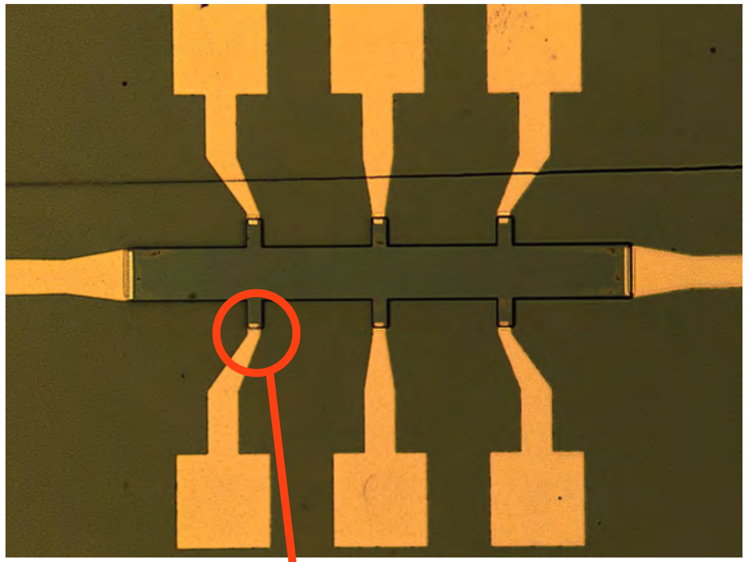


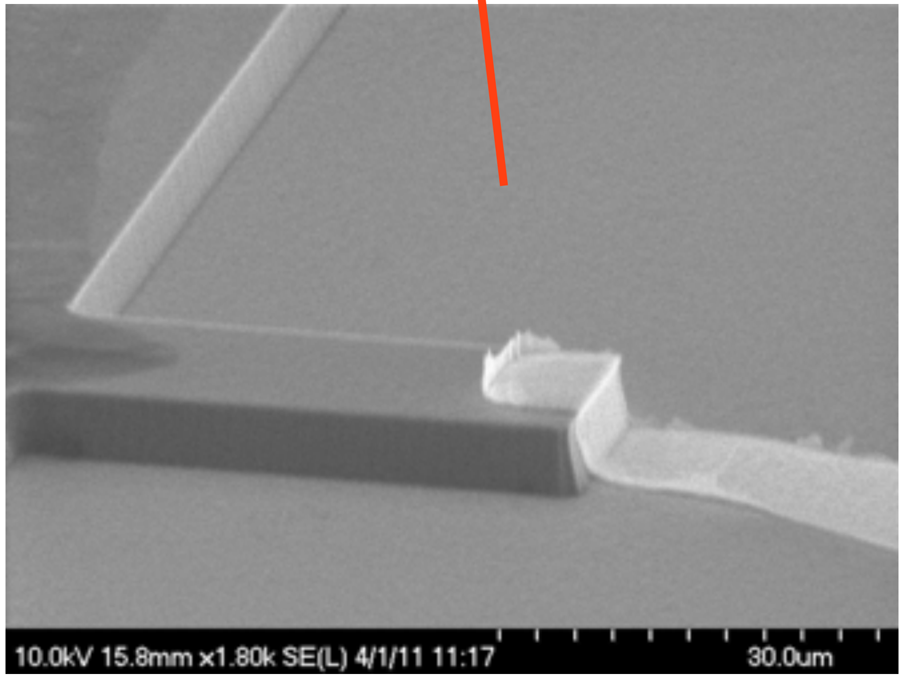


Generator

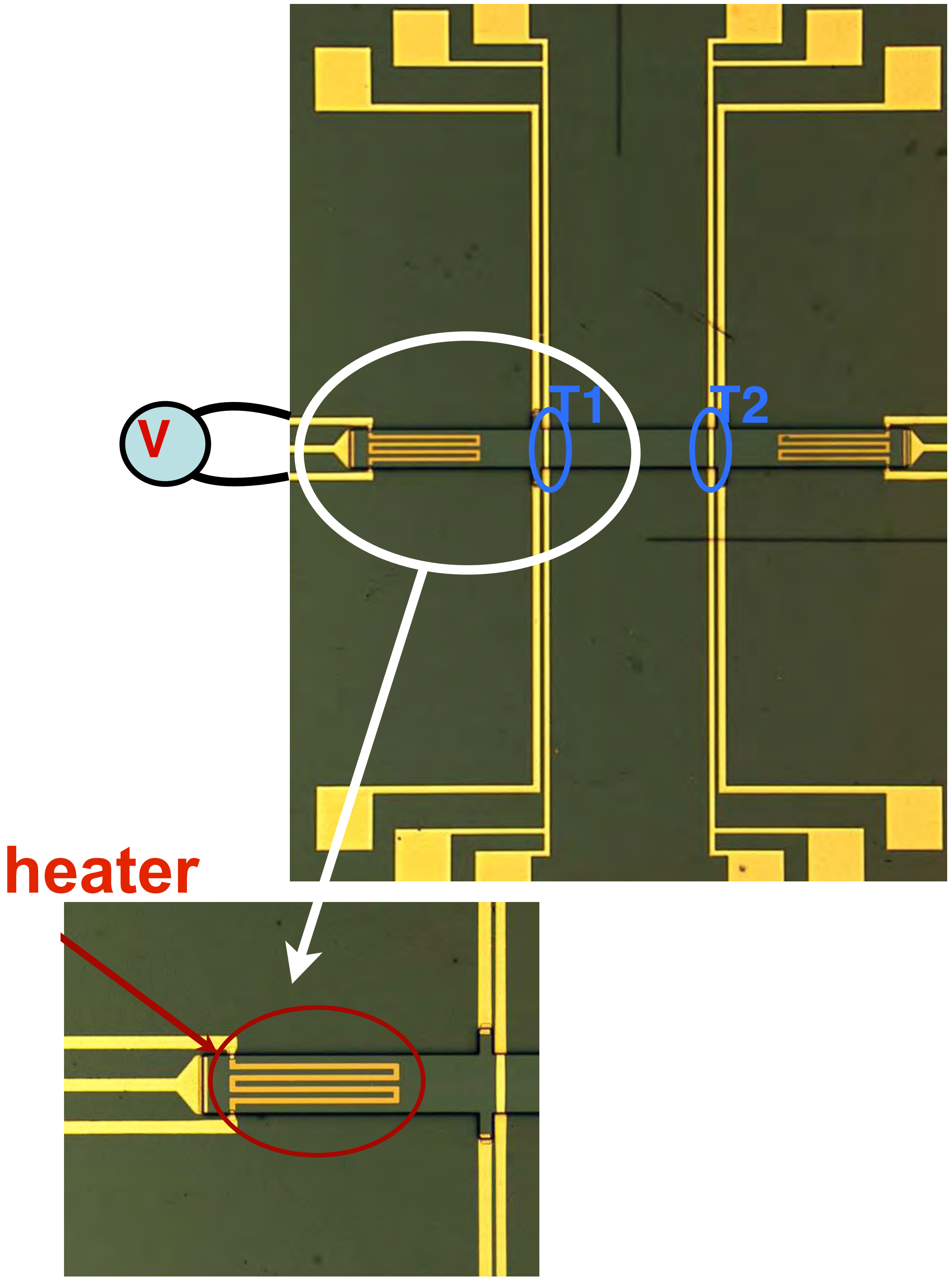
Present GREEN Silicon Position





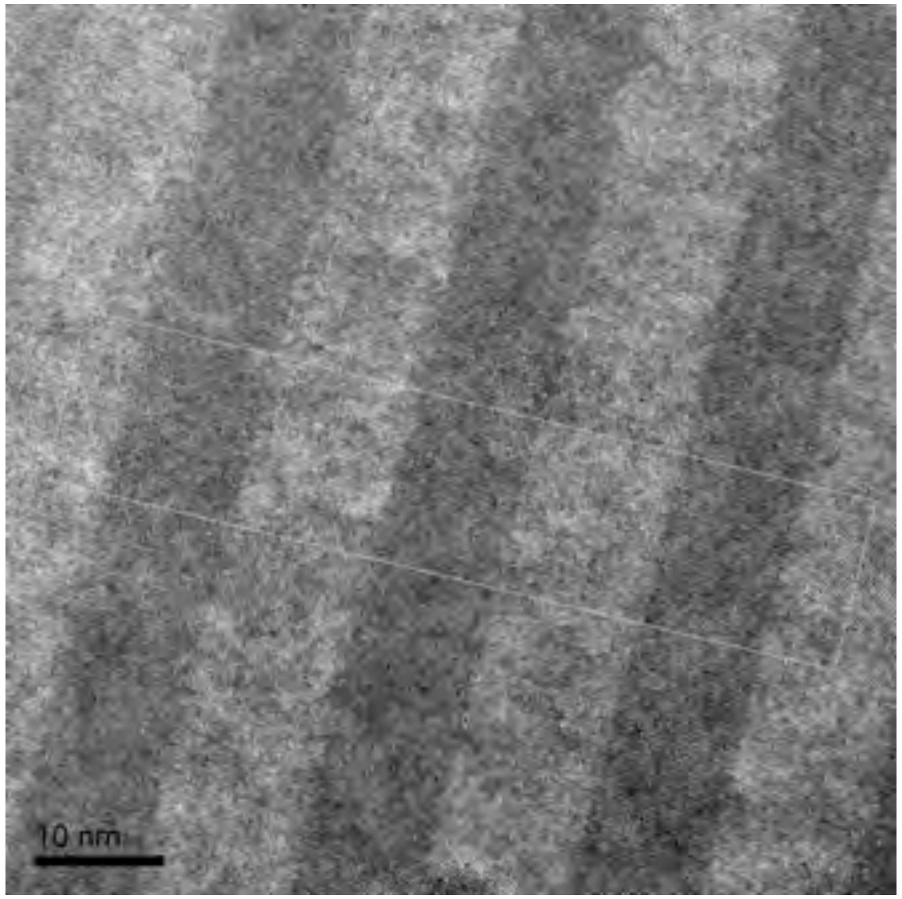


ZT Hall Bar Devices

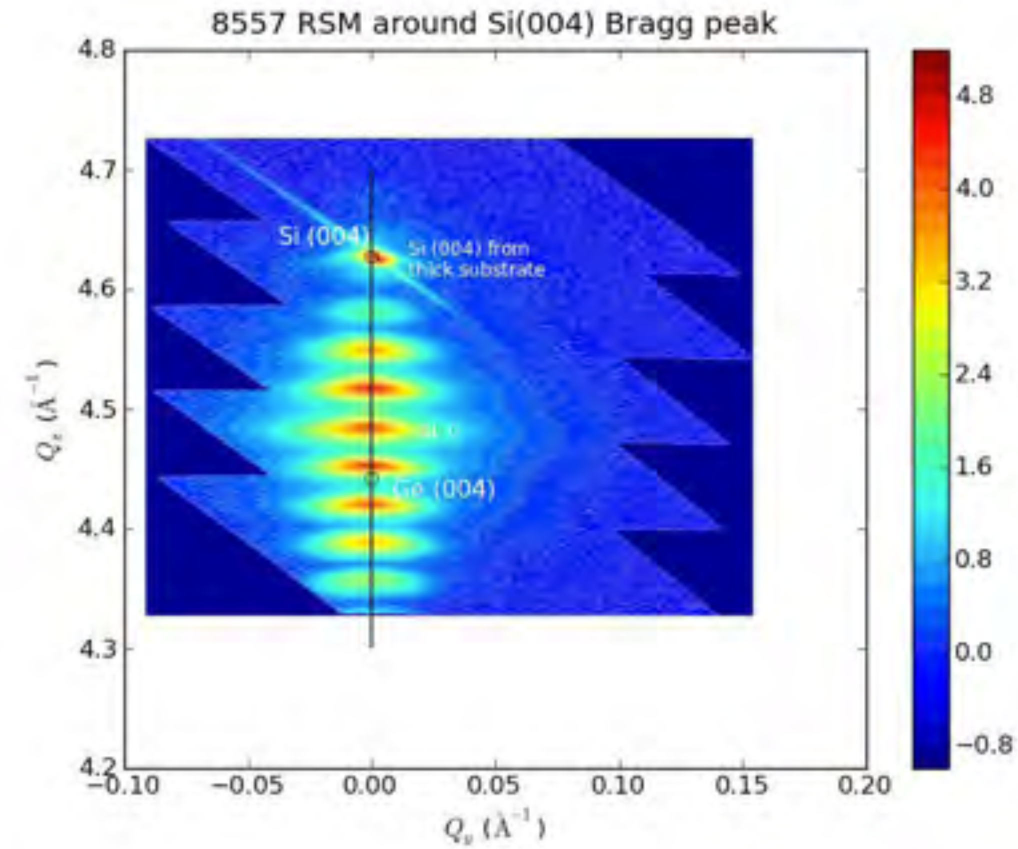


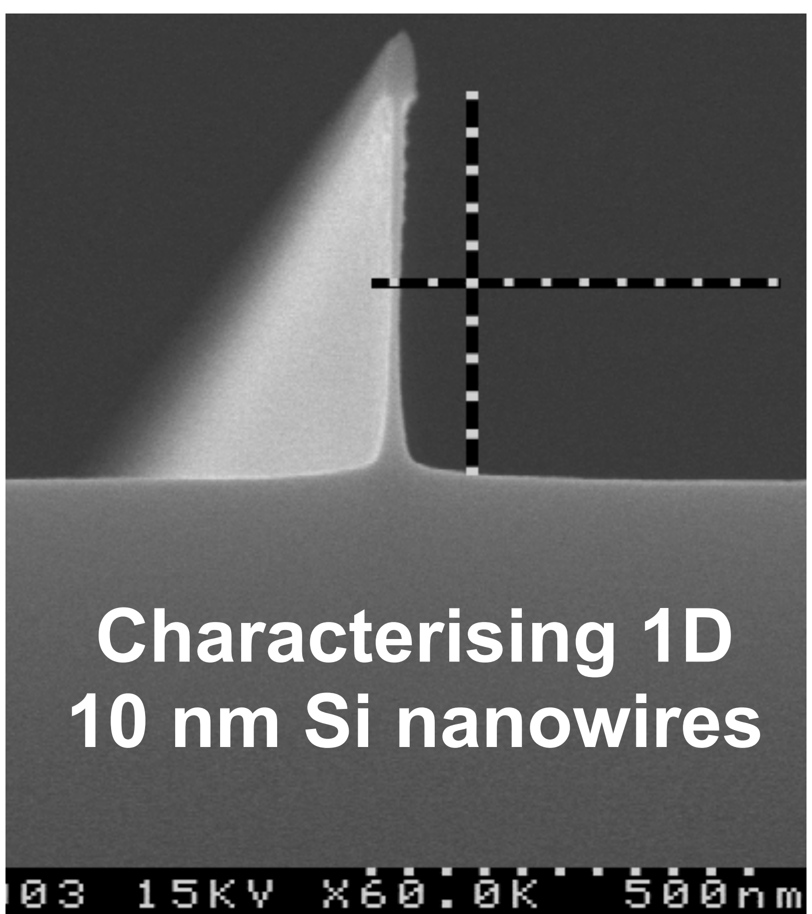
Substrate removed

2D, 1D and 0D structures

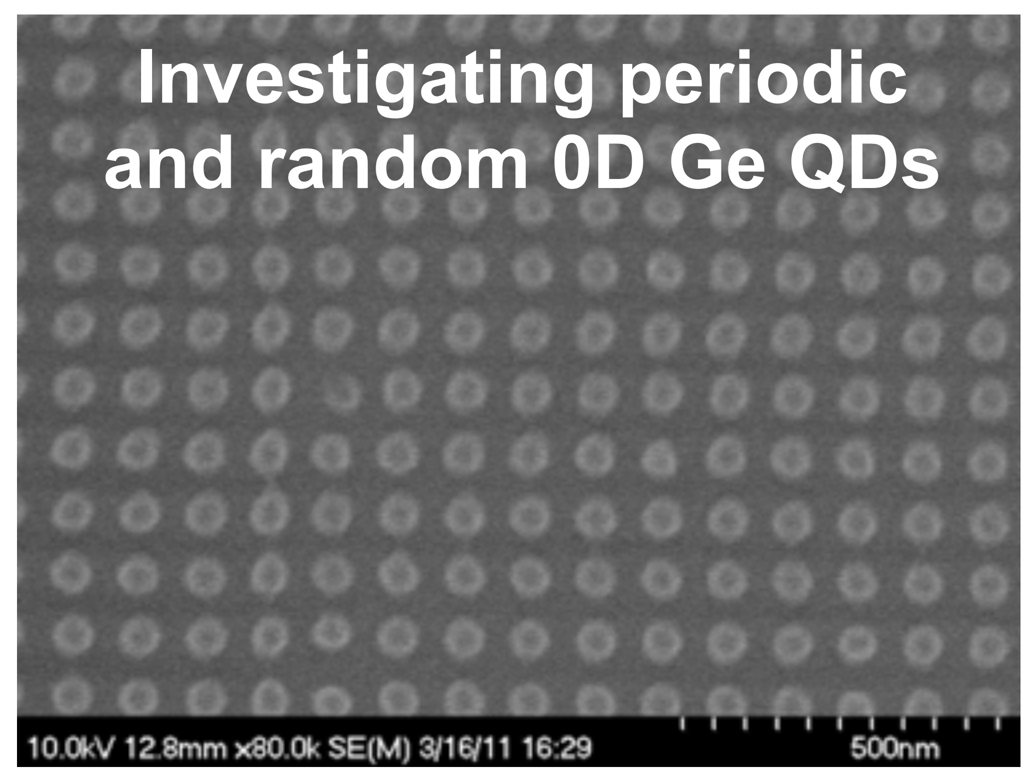


TEM & XRD characterisation of 2D superlattice designs





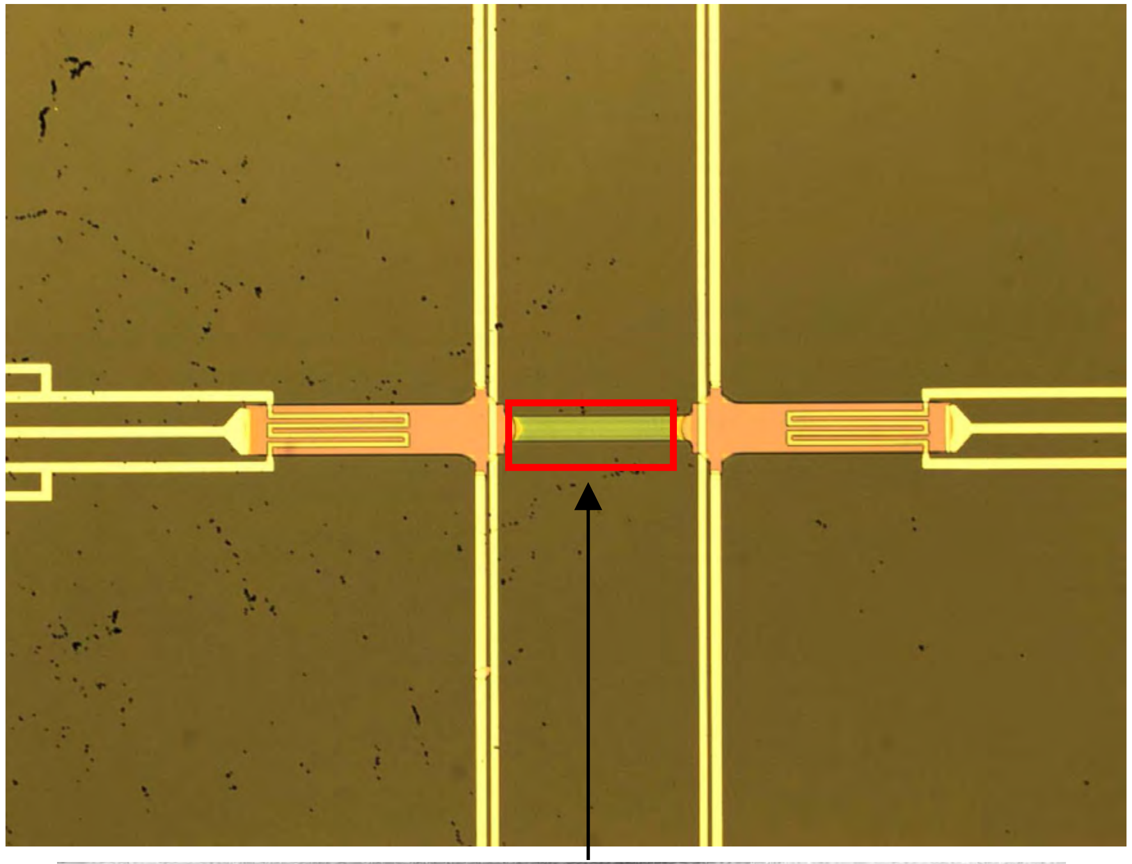
Characterising 1D 10 nm Si nanowires

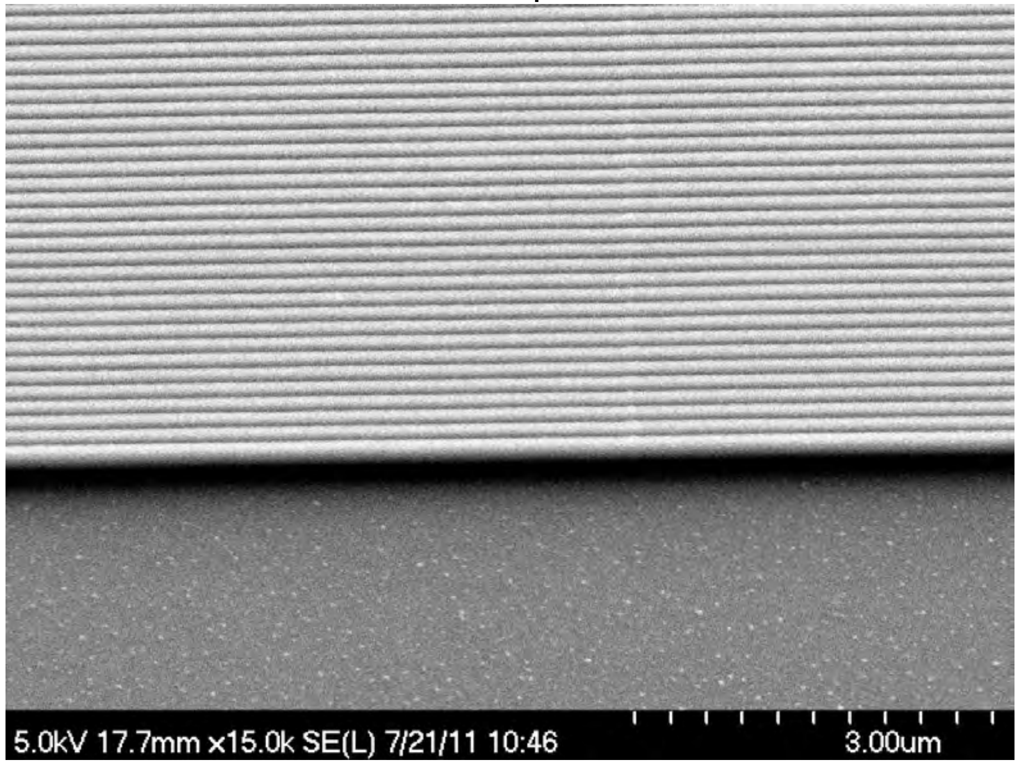


Investigating periodic and random 0D Ge QDs

1D Nanowires

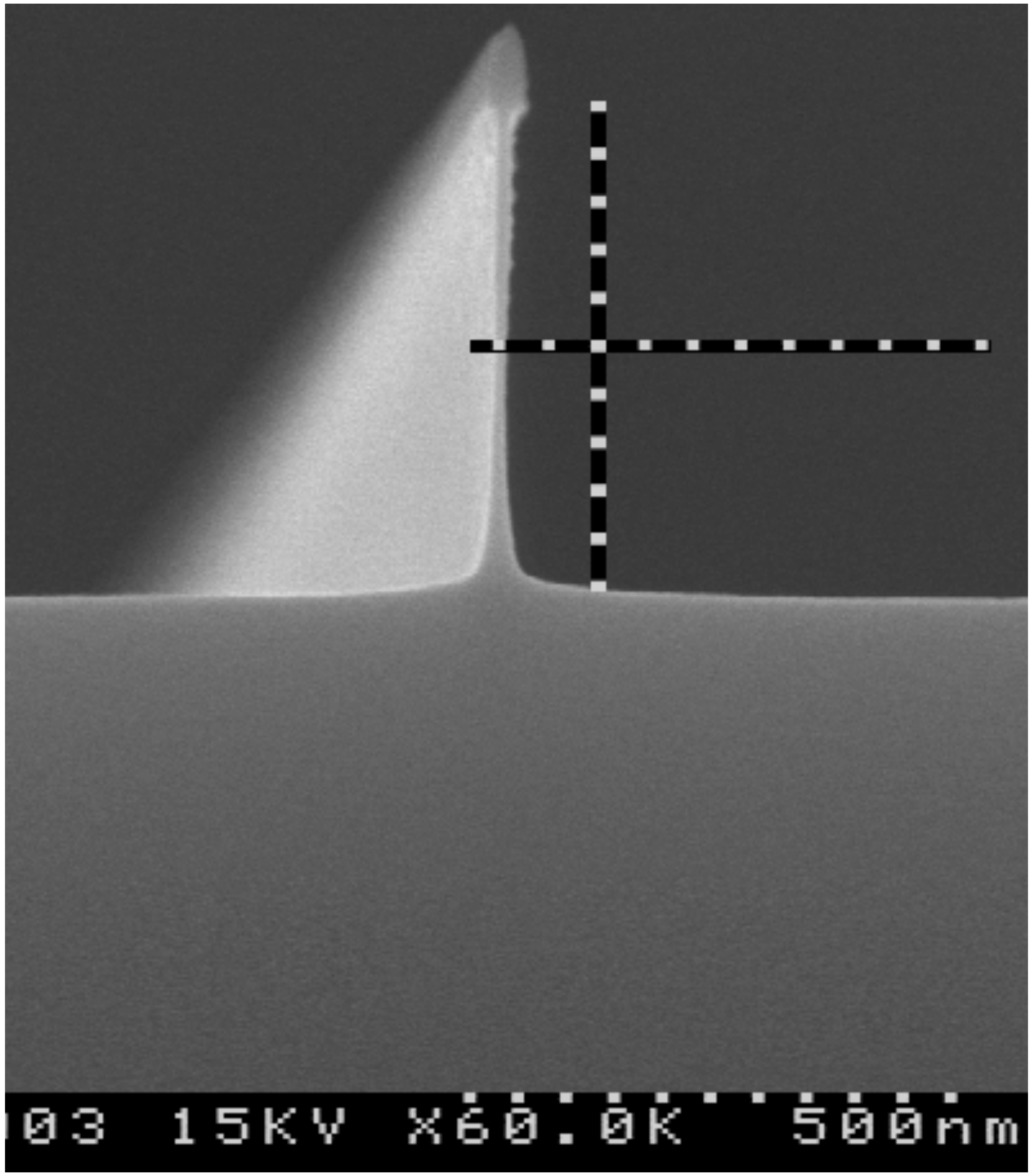
Lateral Nanowires





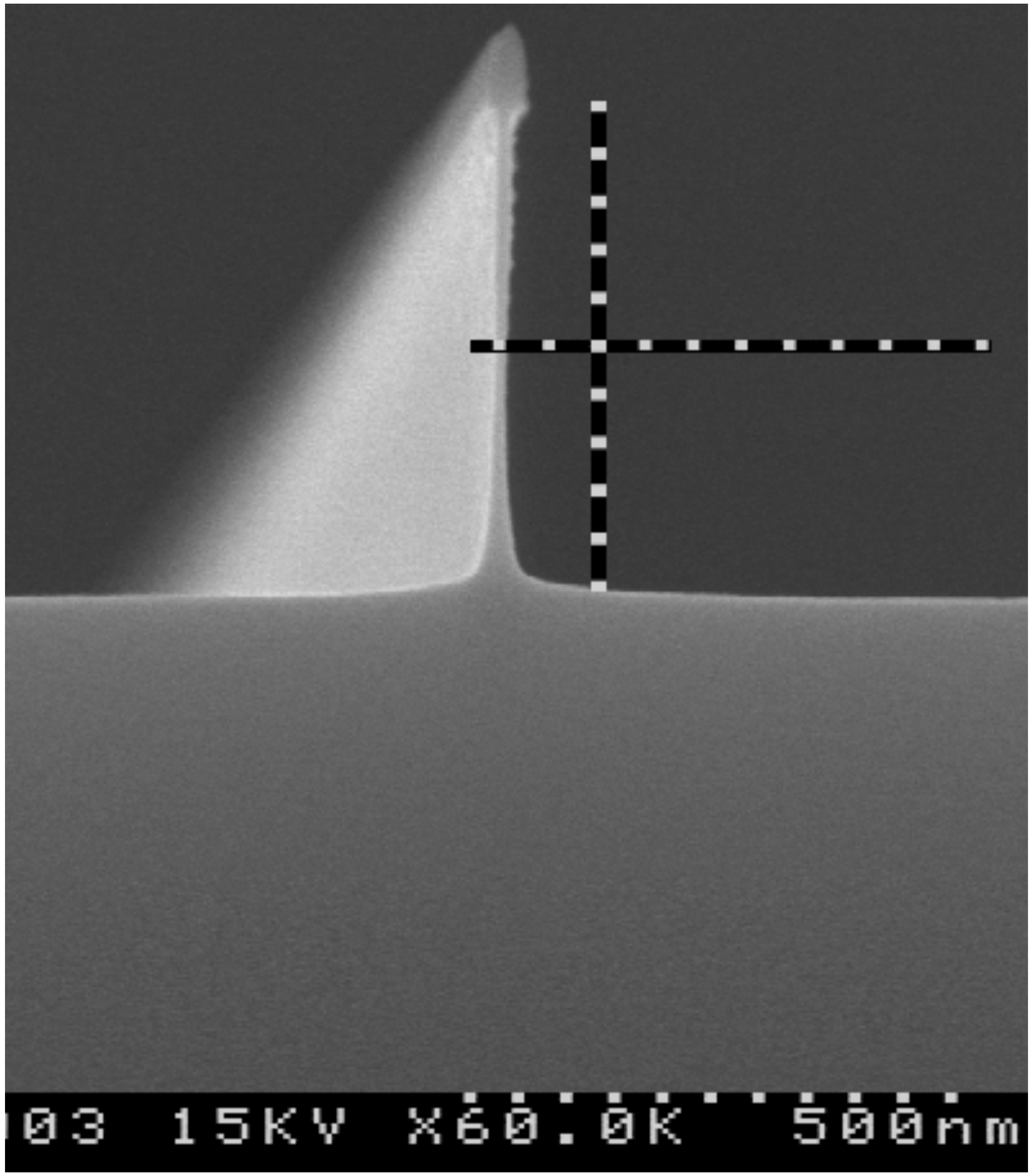
Vertical Nanowires

10 nm wide
500 nm tall
Si nanowire

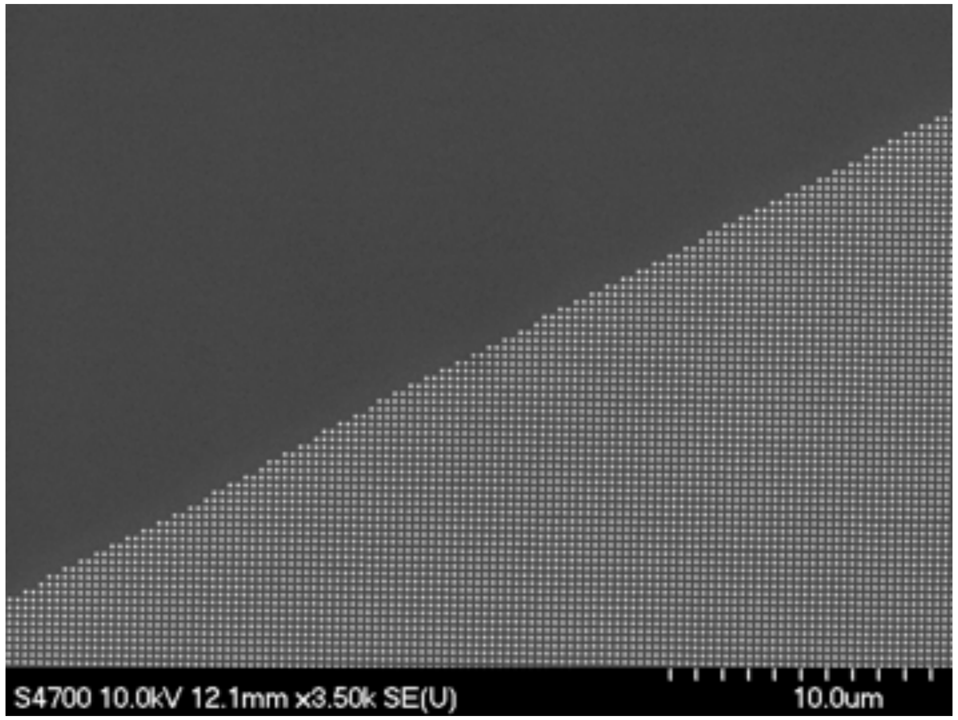


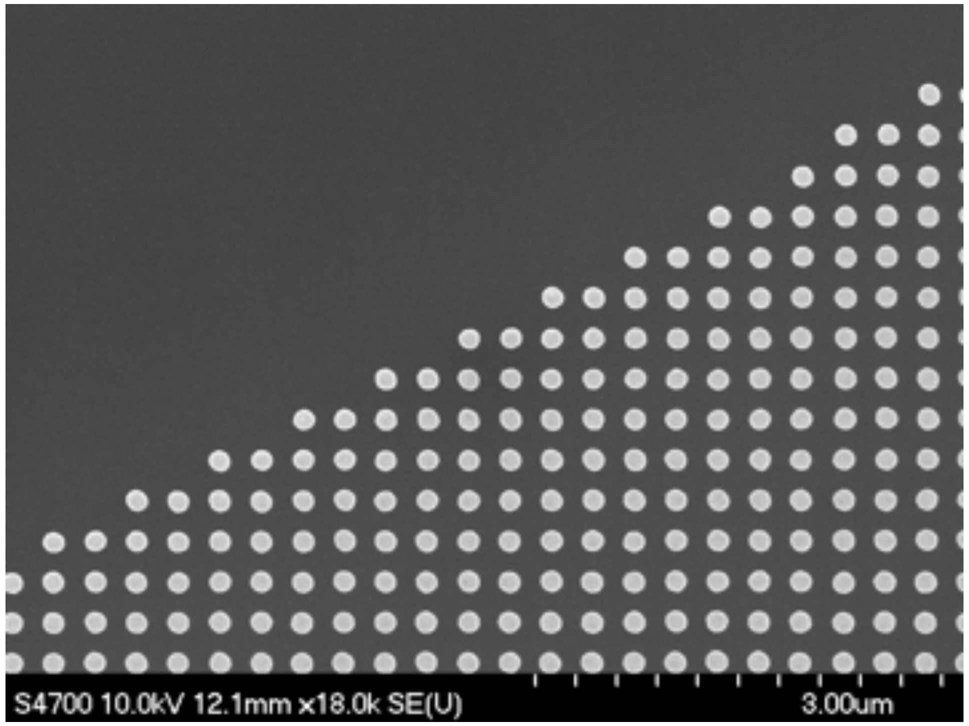
Si Nanowires: Practical 1D enhancements?

**10 nm wide
500 nm tall
Si nanowire**



57,600,000,000 Si pillars of 40 nm diameter





- **Techniques towards cheap manufacture also being investigated**

Summary

- Waste heat is everywhere –> enormous number of applications
- Low dimensional structures are yet to demonstrate the predicted increases in α due to DOS
- Reducing κ_{ph} faster than σ has been the most successful approach to improving ZT to date
- Heterointerface scattering of phonons has been successful in reducing κ
- TE materials and generators are not optimised –> there is plenty of room for innovation

Further Reading

- D.M. Rowe (Ed.), "*Thermoelectrics Handbook: Macro to Nano*" CRC Taylor and Francis (2006) ISBN 0-8494-2264-2

- G.S. Nolas, J. Sharp and H.J. Goldsmid "*Thermoelectrics: Basic Principles and New Materials Development*" (2001) ISBN 3-540-41245-X

- M.S. Dresselhaus et al. "*New directions for low-dimensional thermoelectric materials*" Adv. Mat. 19, 1043 (2007)

Further Information

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http://www.greensilicon.eu/GREENSilicon/index.html