Thermoelectric Energy Harvesting

Prof Douglas Paul

Director: James Watt Nanofabrication Centre
University of Glasgow
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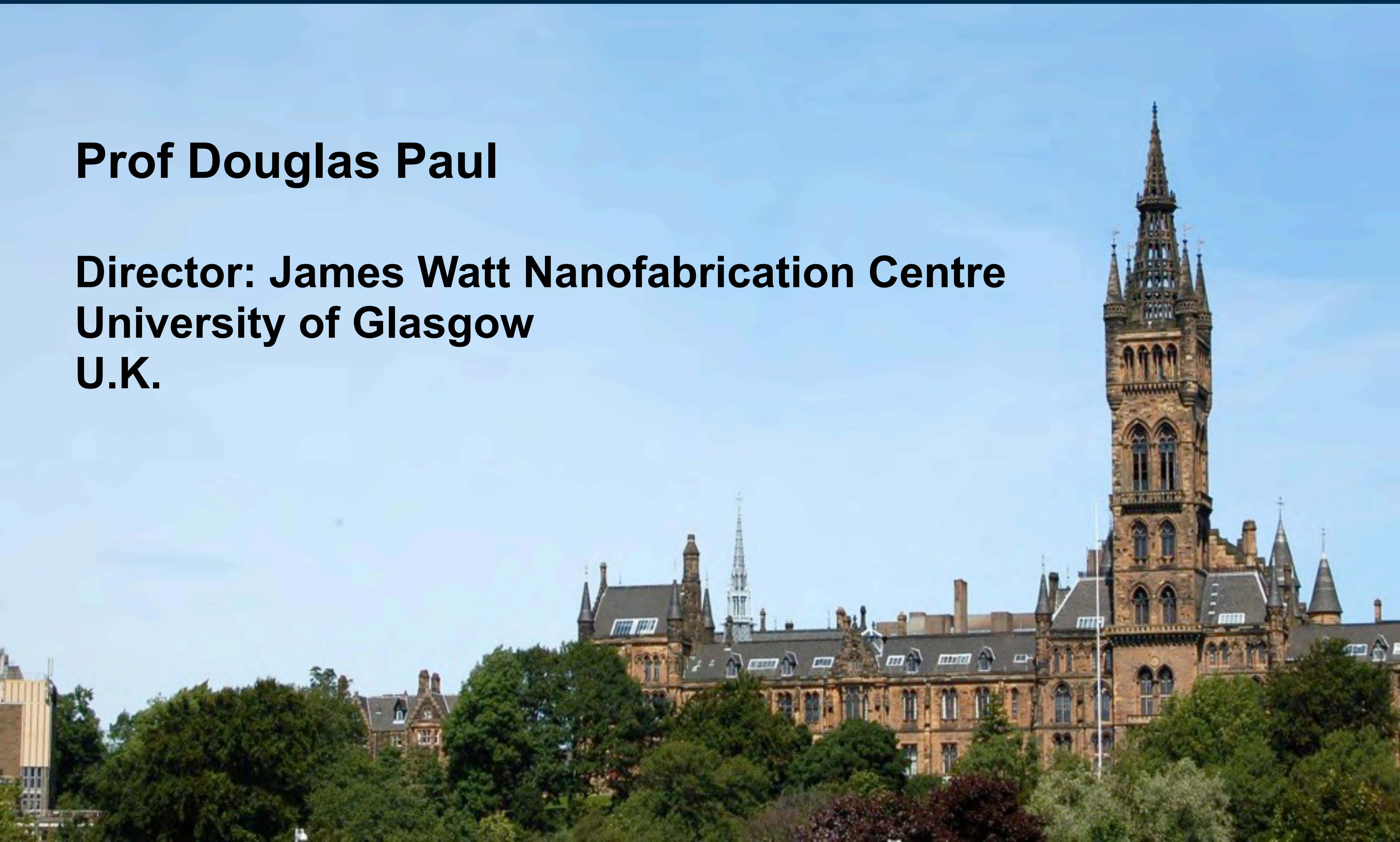


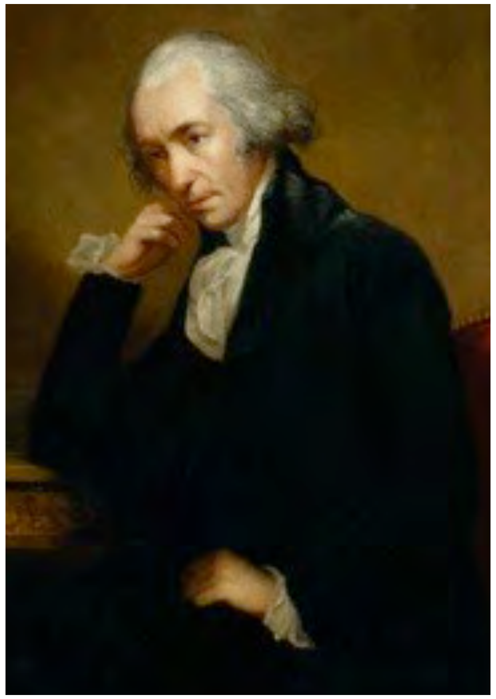
The University of Glasgow

- Established in 1451
- 7 Nobel Laureates, 2 SI units, ultrasound, television, etc......
- 16,500 undergraduates, 5,000 graduates and 5,000 adult students
- £186M research income pa

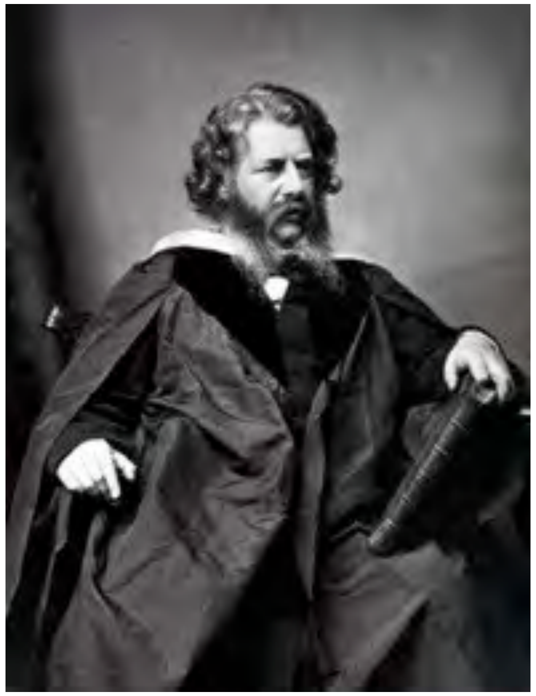
- 400 years in High Street
- Moved to Gilmorehill in 1870
- Neo-gothic buildings by Gilbert Scott

Famous Glasgow Scholars

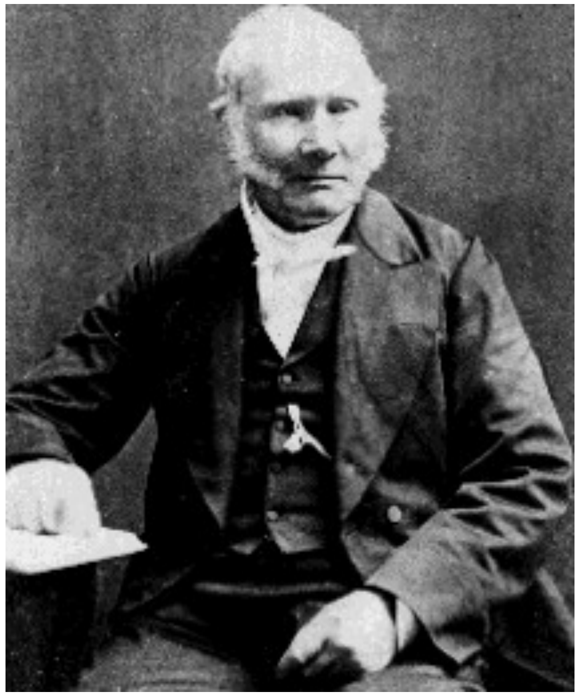
William Thomson (Lord Kelvin)



James Watt



William John Macquorn Rankine



Rev Robert Stirling

Rev John Kerr

Joseph Black

John Logie Baird

Adam Smith

James Watt Nanofabrication Centre @Glasgow

University of Glasgow

Vistec VB6

E-beam lithography

Süss MA6 optical lith

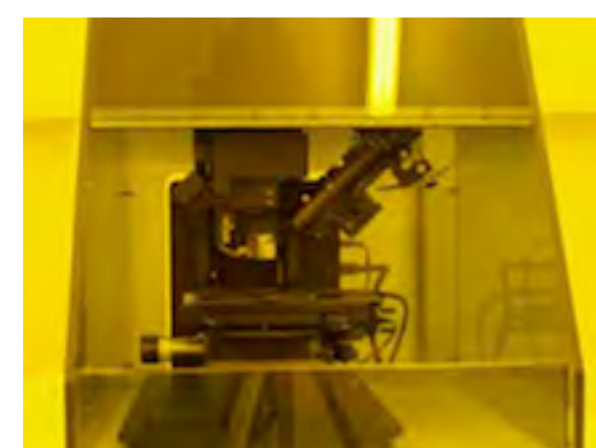
- 750m^2 (+150 m^2) cleanroom - pseudo-industrial operation
- 15 technicians + 4 PhD research technologists
- Processes include: MMICs, III-V, Si/SiGe/Ge, integrated photonics, metamaterials, MEMS (microfluidics)
- Part of EPSRC III-V National Facility & STFC Kelvin-Rutherford Facility
- Commercial access through Kelvin NanoTechnology
- http://www.jwnc.gla.ac.uk/

14 RIE / PECVD / ALD

6 Metal dep tools

4 SEMs: Hitachi S4700

Veeco: AFMs



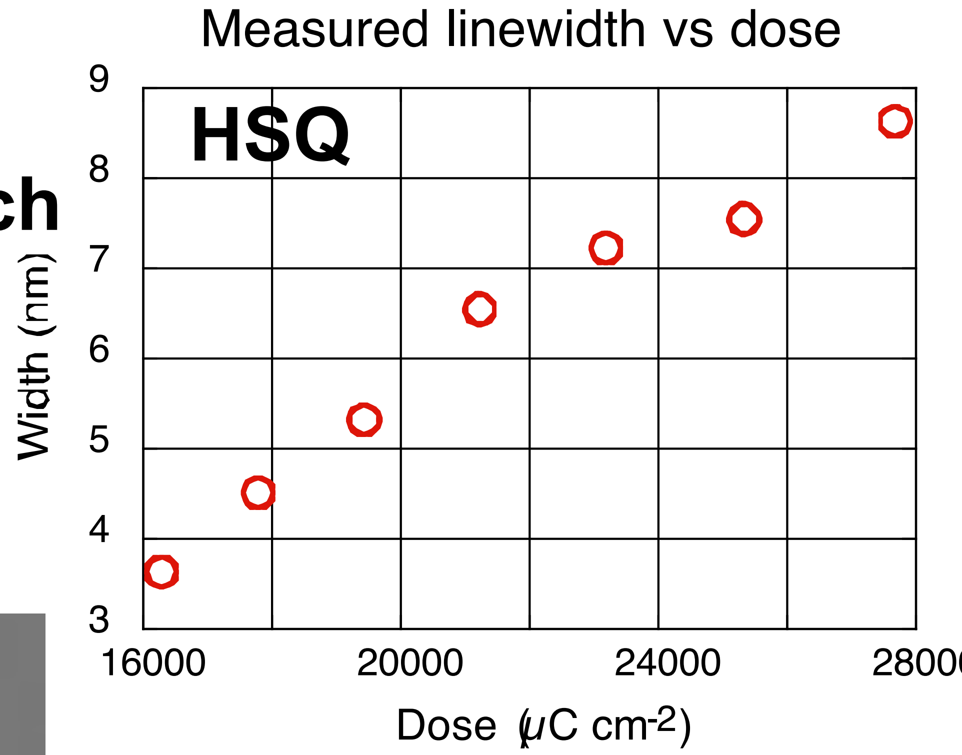
Electron Beam Lithography Capability

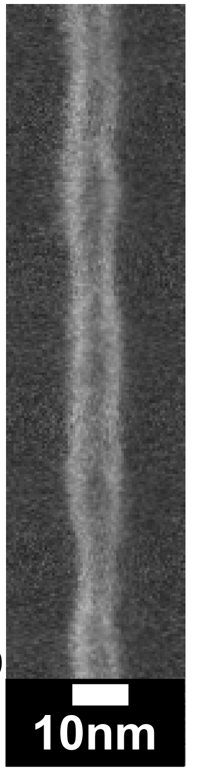
30 years experience of e-beam lithography

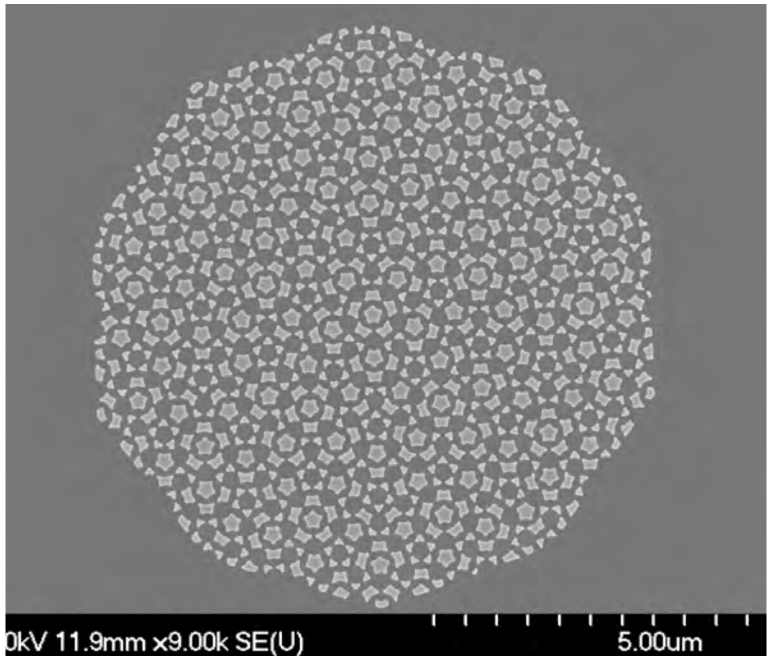
Vistec VB6

Vistec EBPG5

Sub-5 nm single-line lithography for research



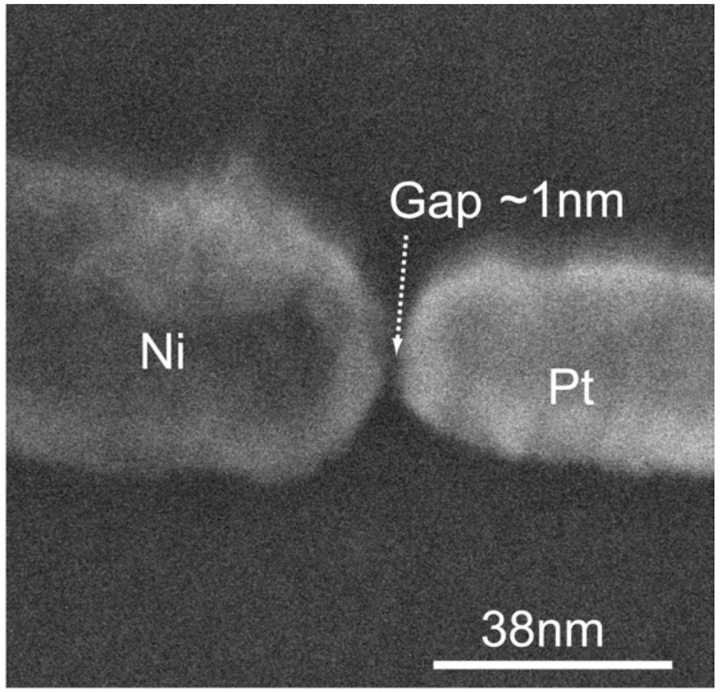




Penrose tile: layer-to-layer alignment 0.46 nm rms

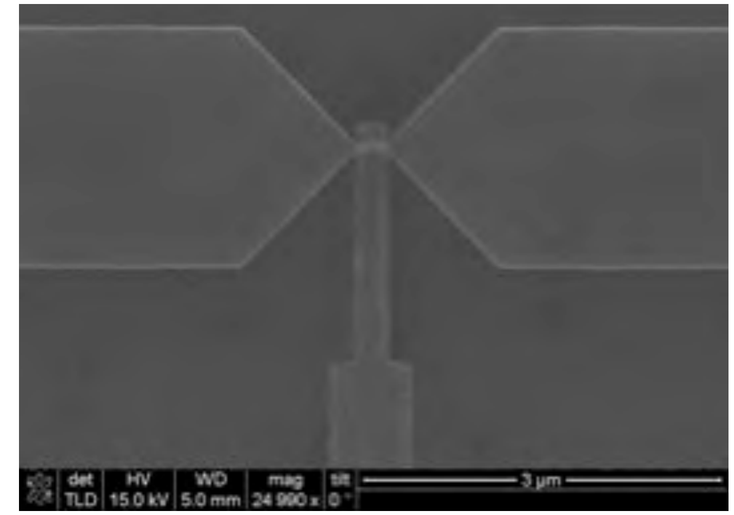
Alignment allows 1 nm gaps between different layers:

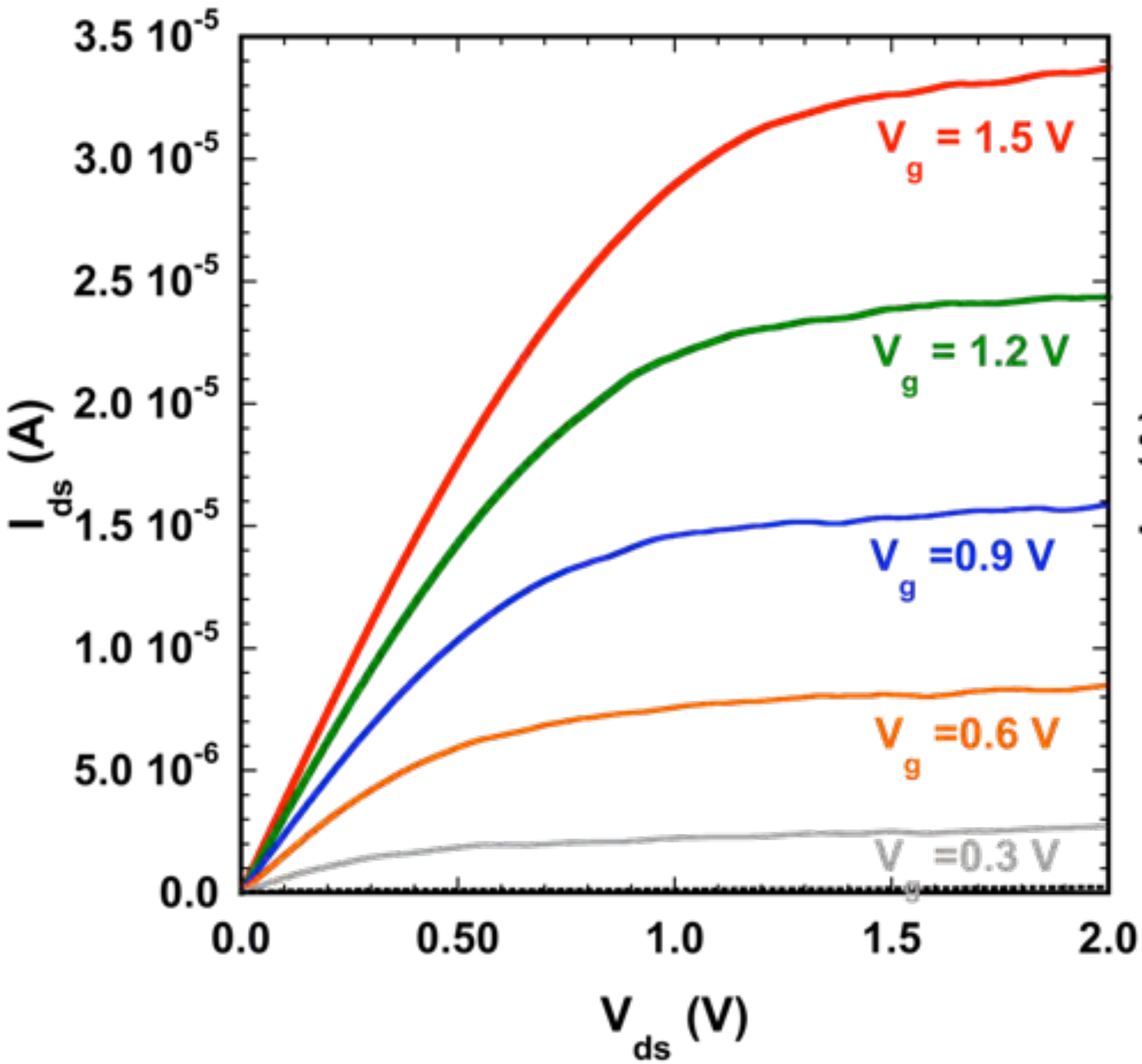
–> nanoscience: single molecule metrology

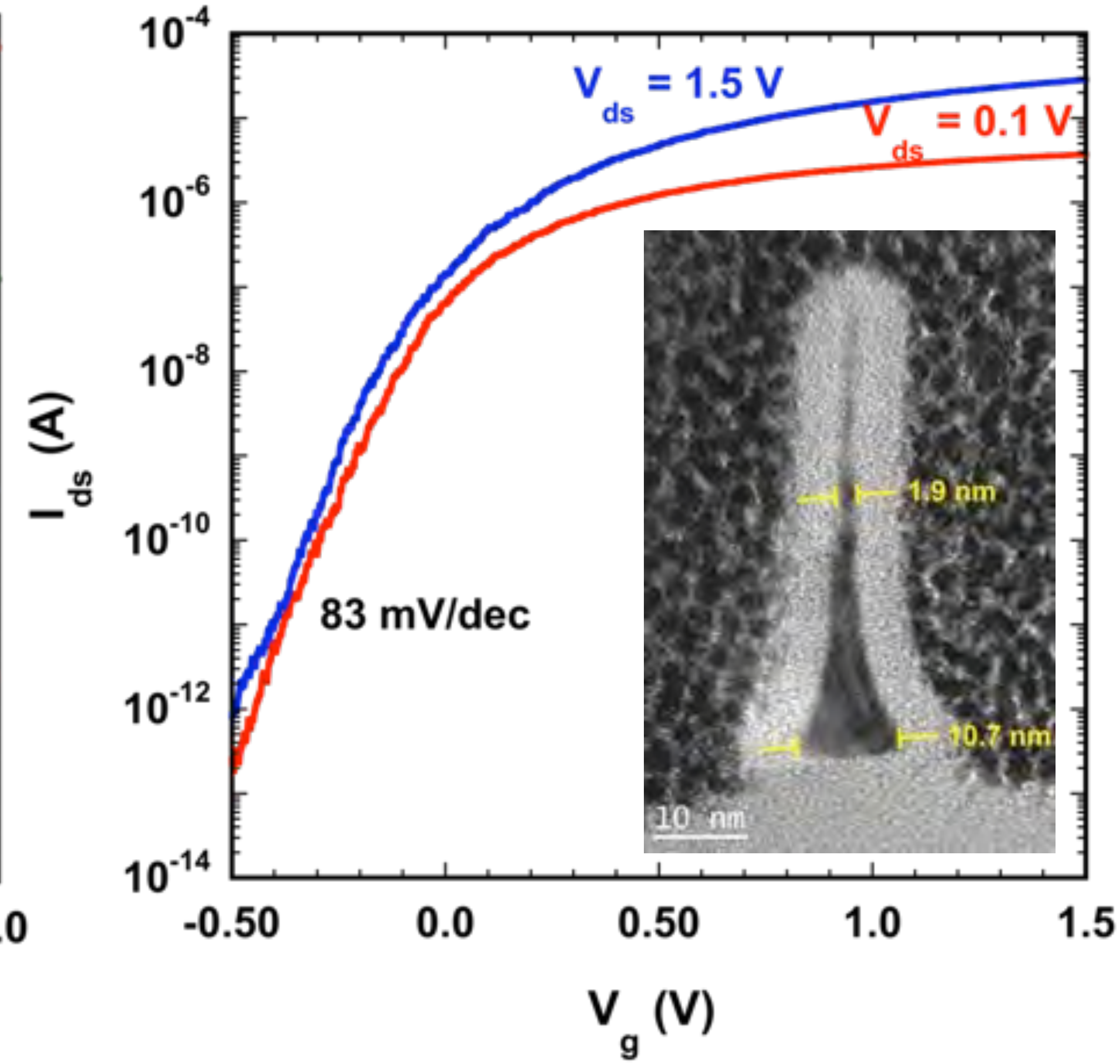


10 nm Width Si Nanowire FET

200 nm gate length
10 nm wide, 50 nm tall nanowire



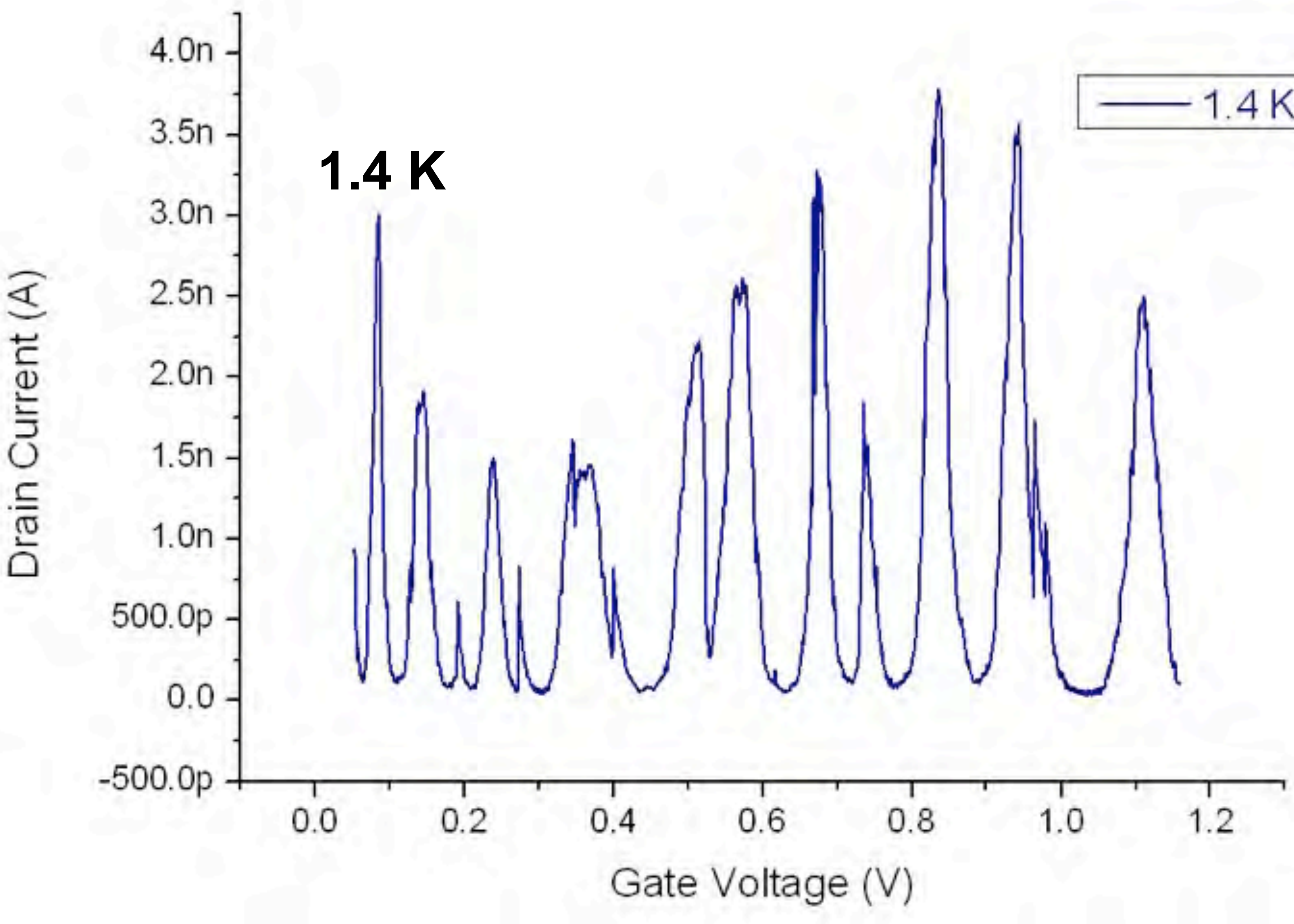


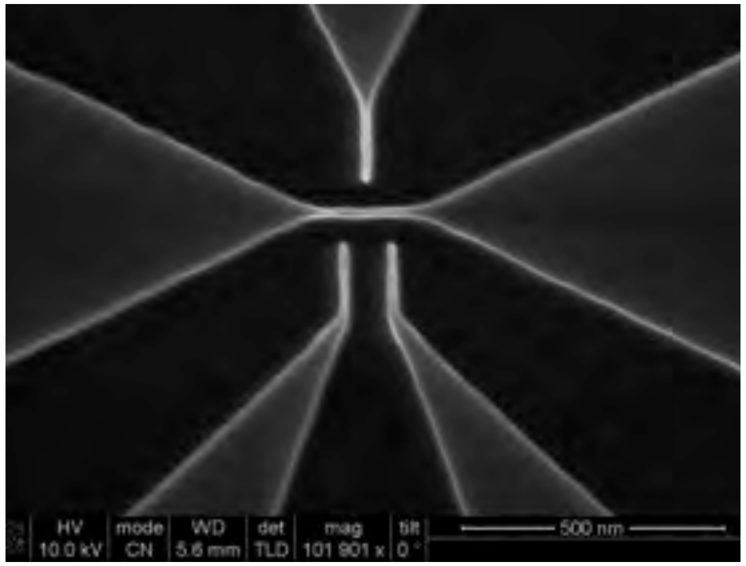


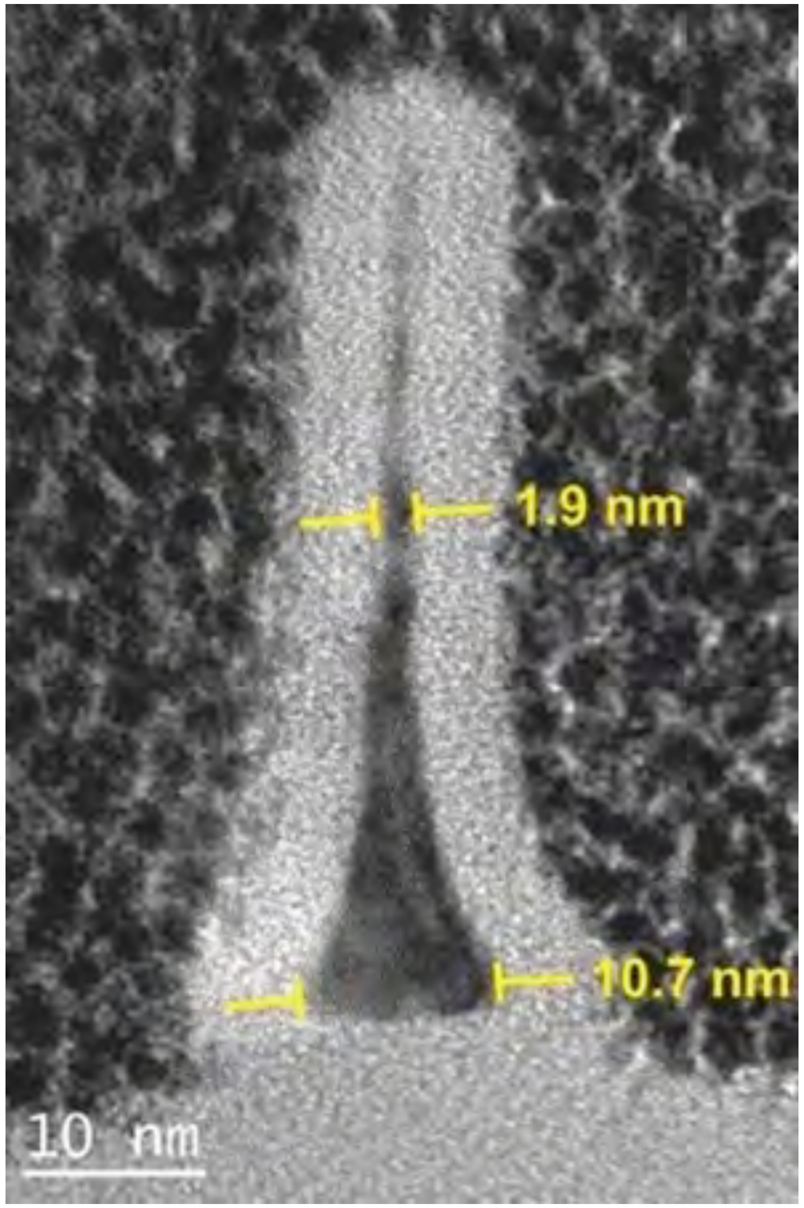
10 nm Wide Si Nanowire SET

- **Depletion mode nanowire**

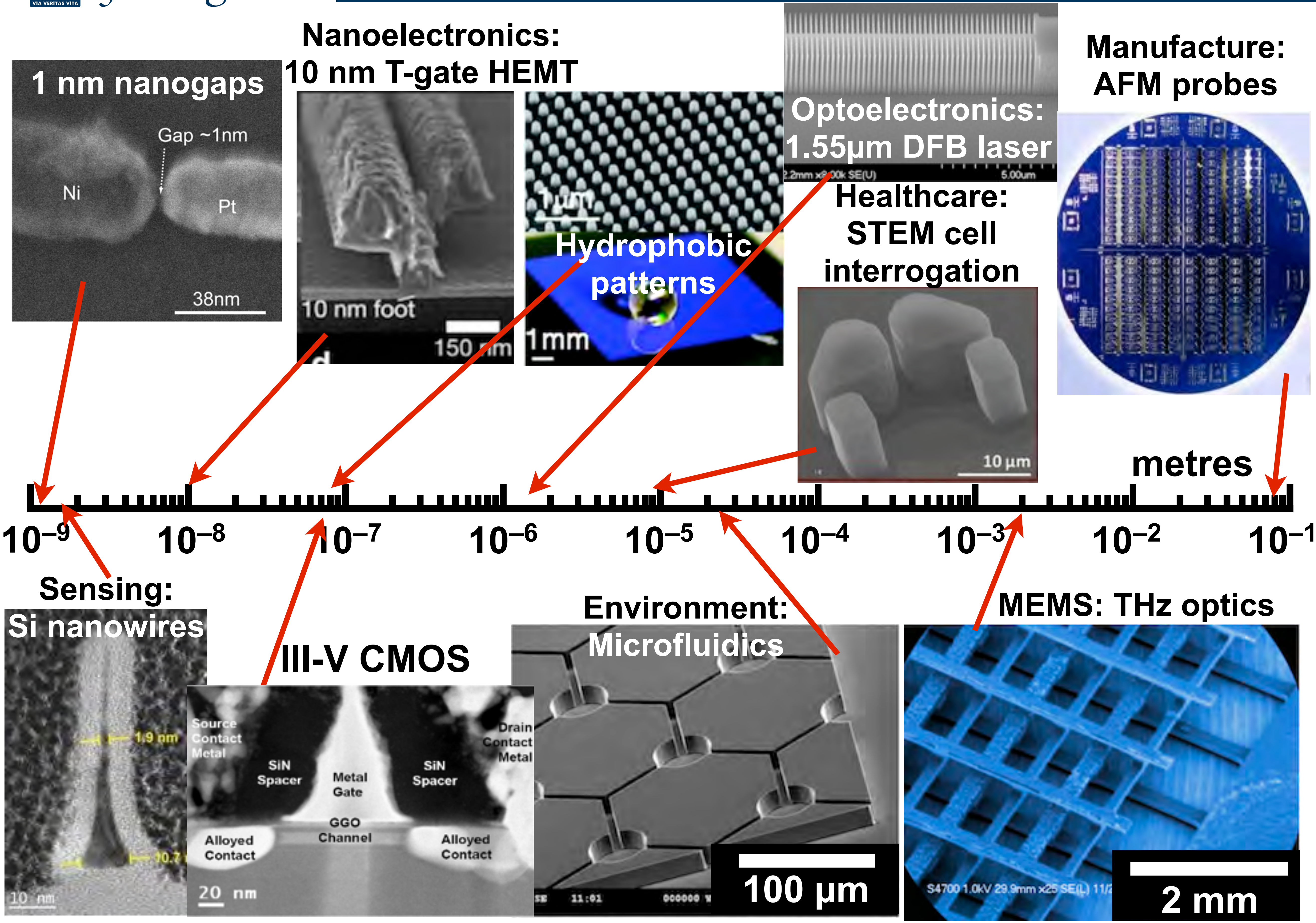
1.4 K







Micro and Nanotechnology from Glasgow



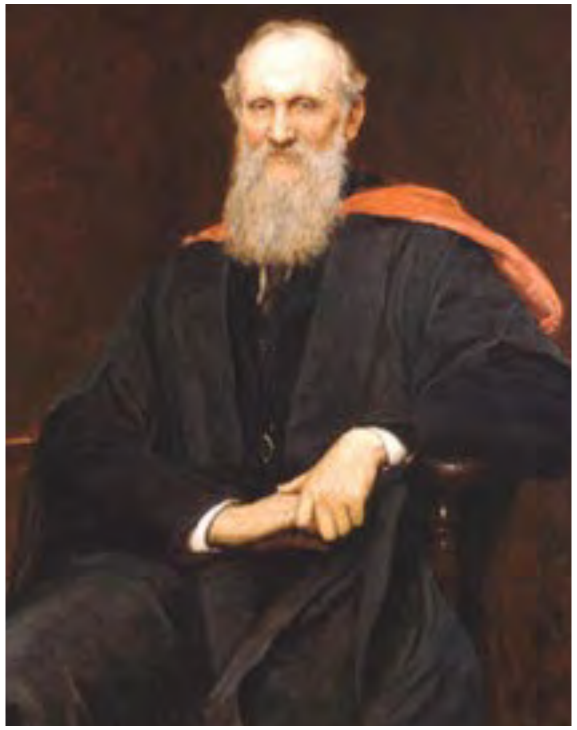
Thermoelectrics History

- History: Seebeck effect 1822

heat –> electric current

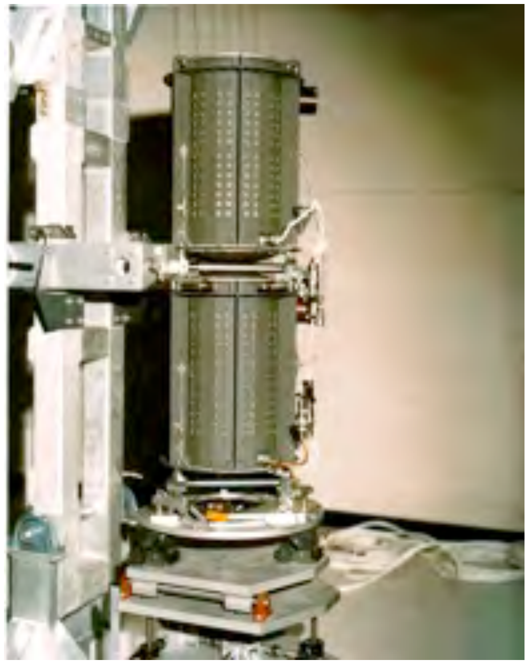
- Peltier (1834): current –> cooling

- Thomson effect: Thomson (Lord Kelvin) 1852

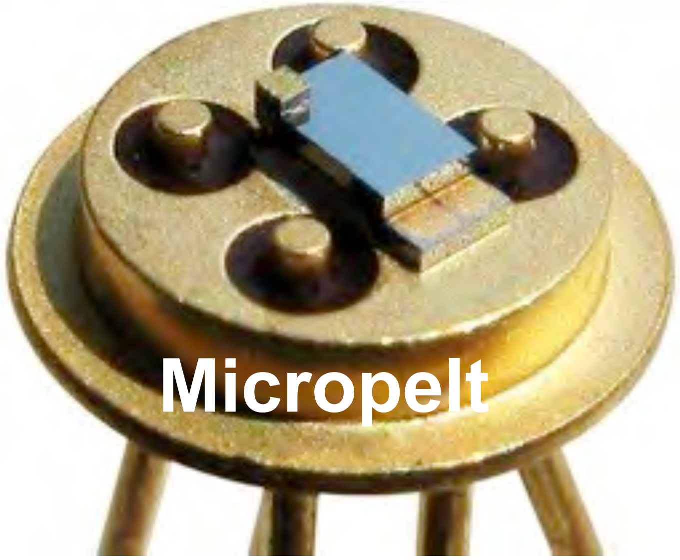


Thermoelectric Applications

NASA Voyager I & II



Peltier cooler: telecoms lasers



Cars: replace alternator

Temperature control for CO_2 sequestration

Buildings / industry temperature control – autonomous sensing

Energy Harvesting for Remote Sensing

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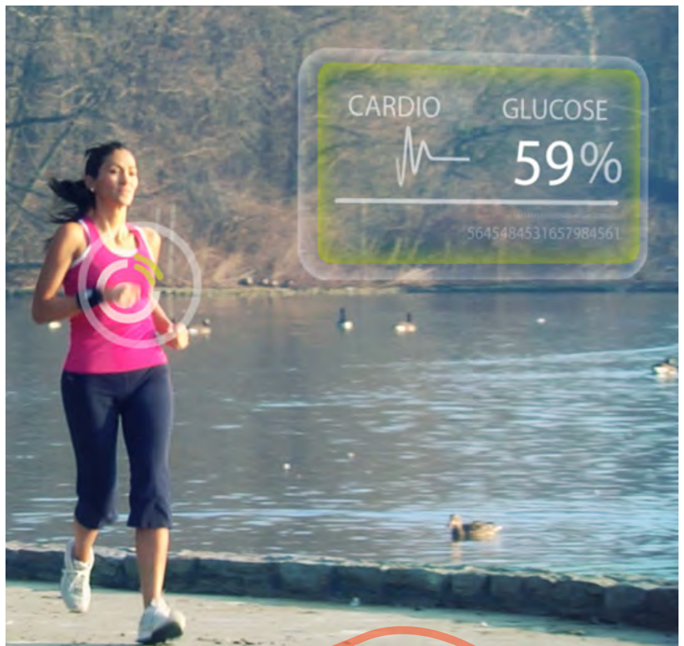
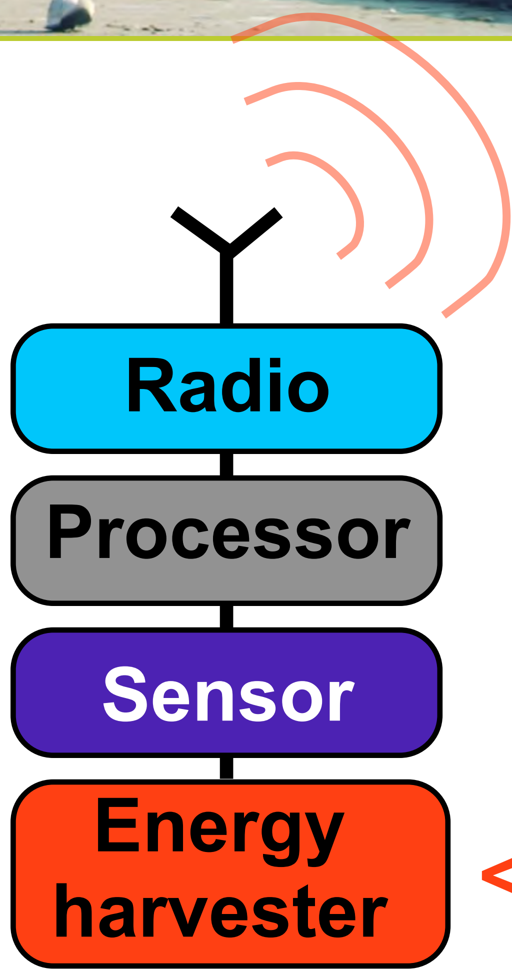
Sports performance sensors



Flood sensors

Weather monitoring

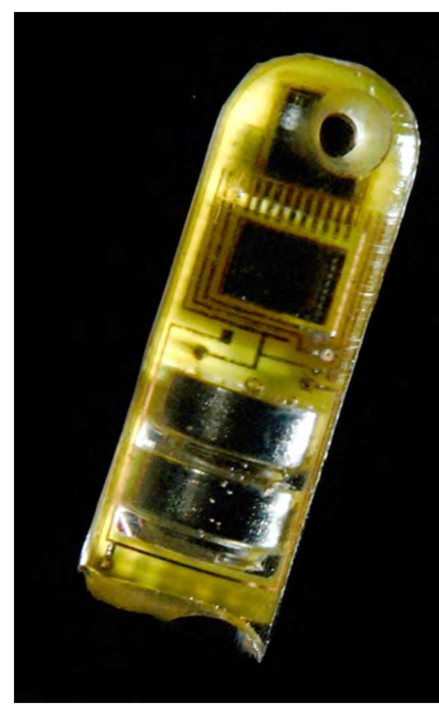


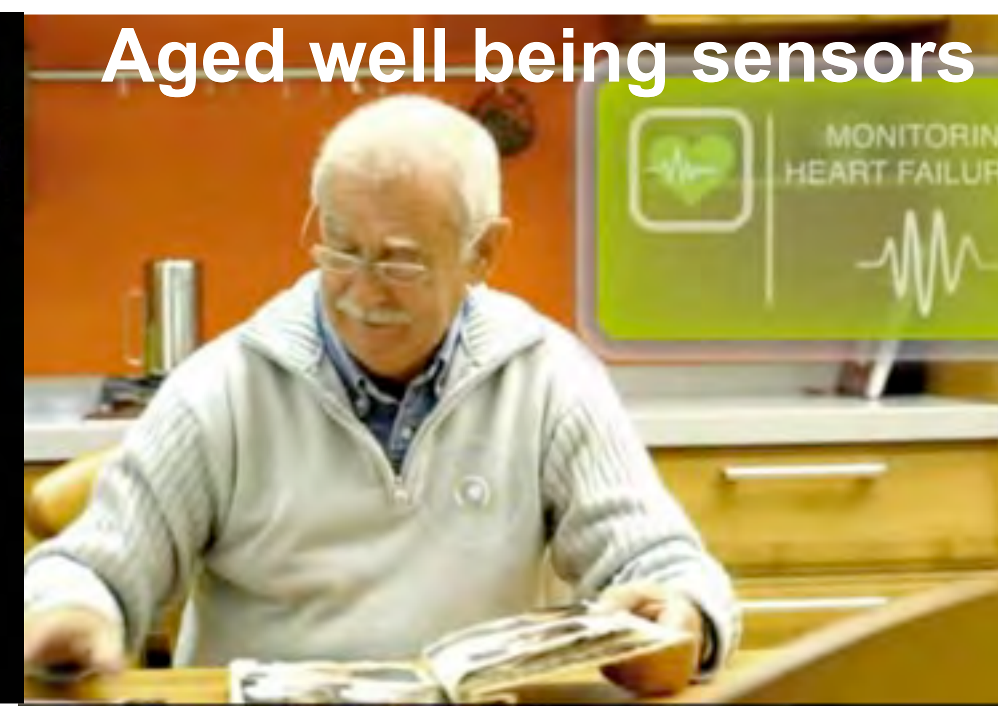
> 10 mW

> 100 µW

> 10 µW

< 100 µW/cm^2 !!!



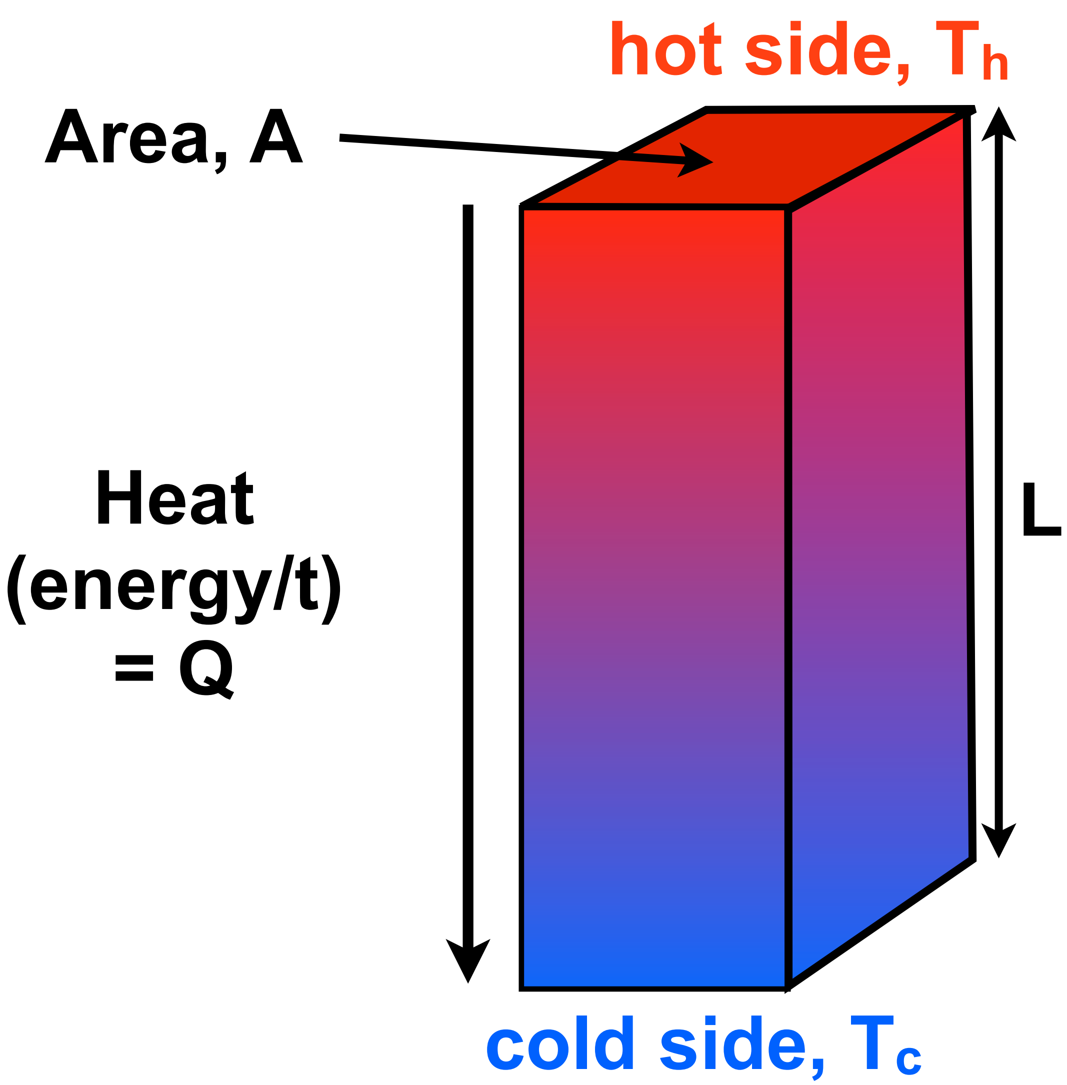


Battery free autonomous sensors: ECG, blood pressure, etc.

Background Thermal Physics

Fourier thermal transport

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

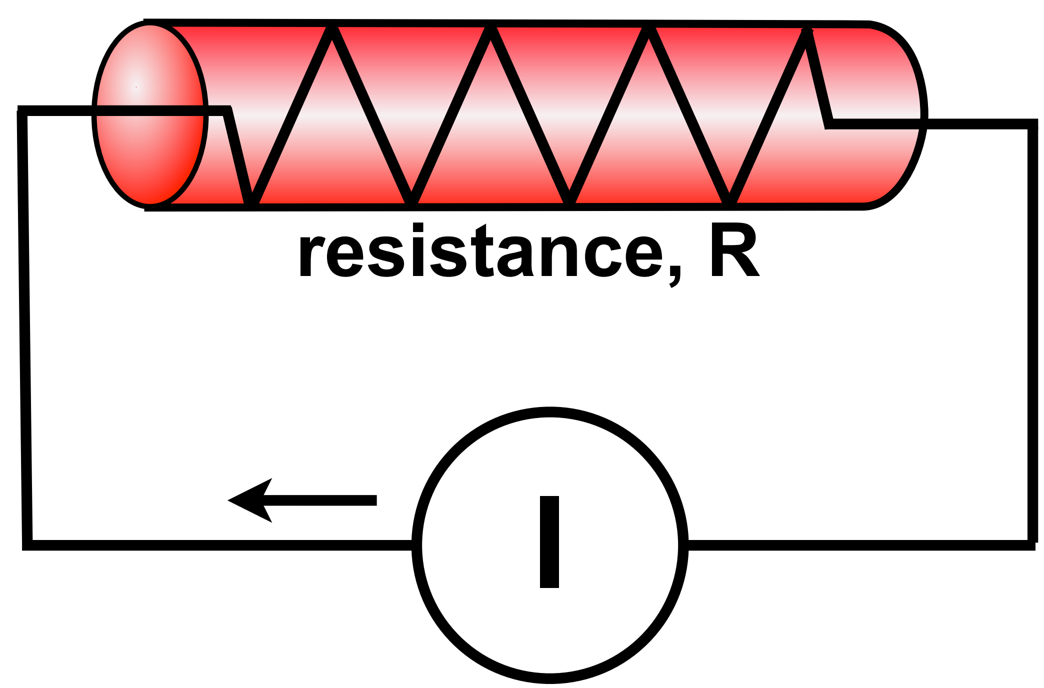


$$Q = -\kappa A \frac{T_c - T_h}{L}$$

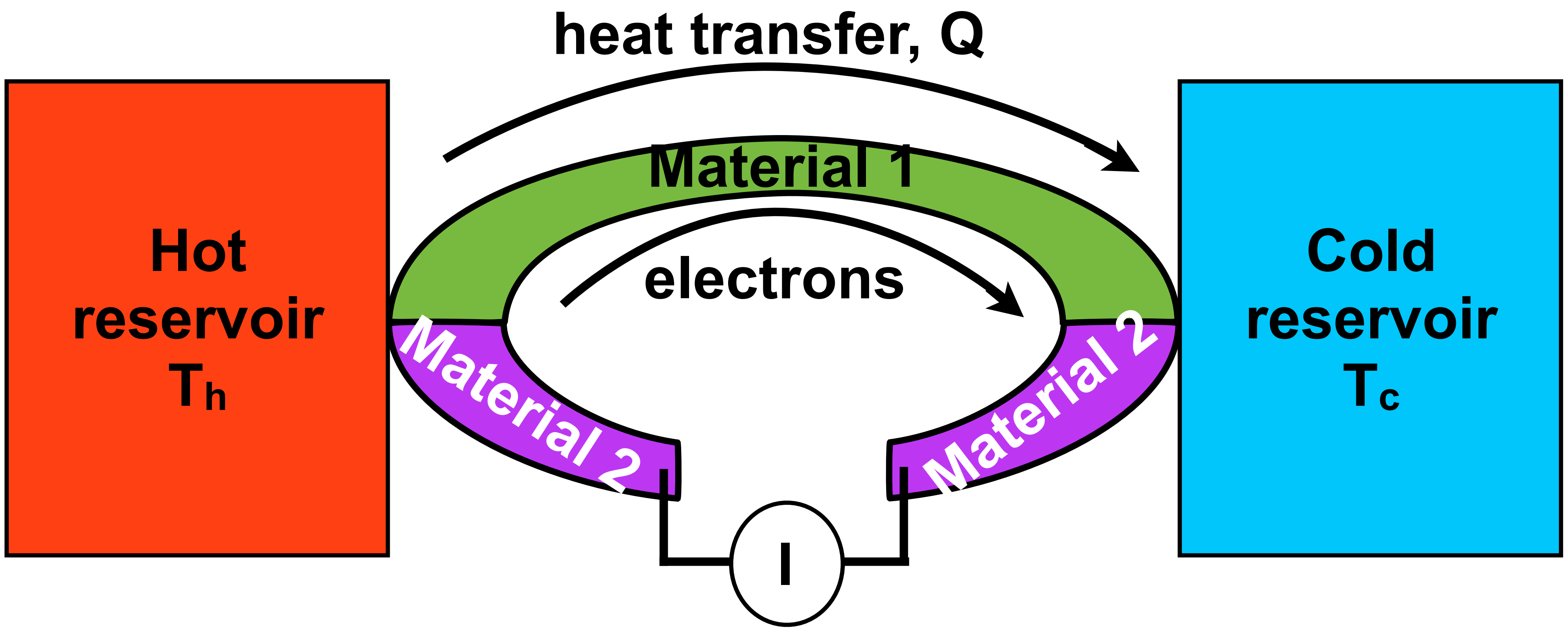
Joule heating

$$Q = I^2 R$$

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



The Peltier Effect

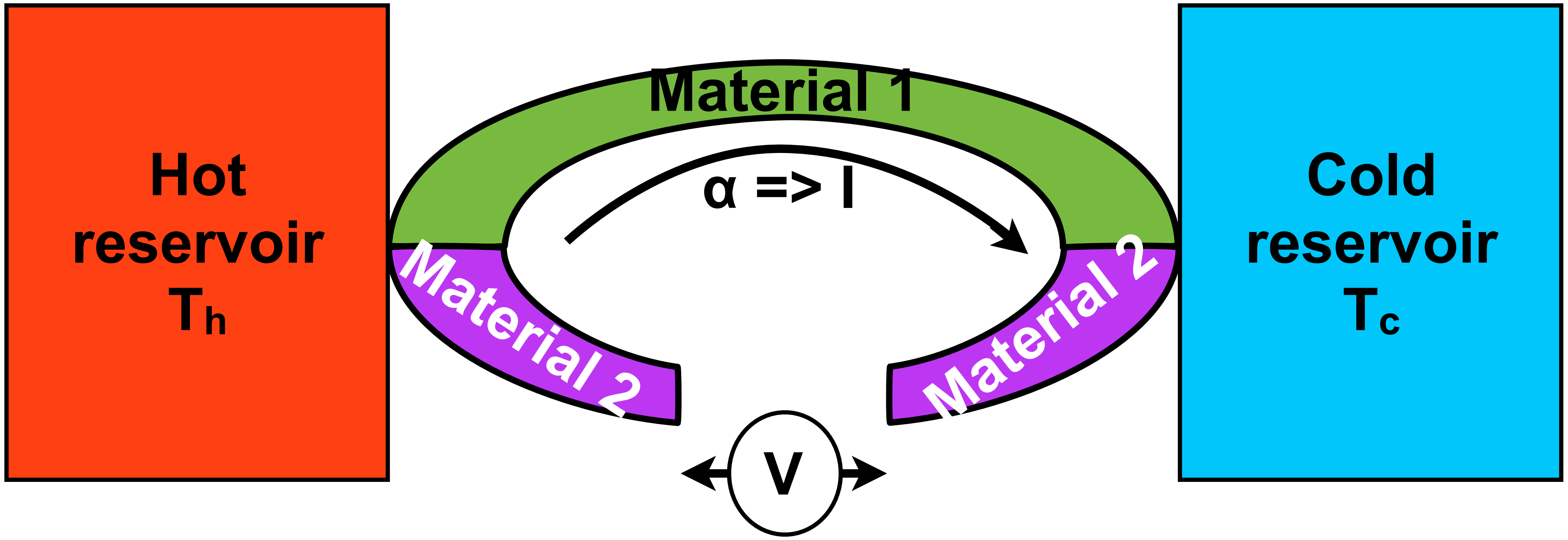


Peltier coefficient, $\Pi = \frac{Q}{I}$

units: W/A = V

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

The Seebeck Effect



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

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

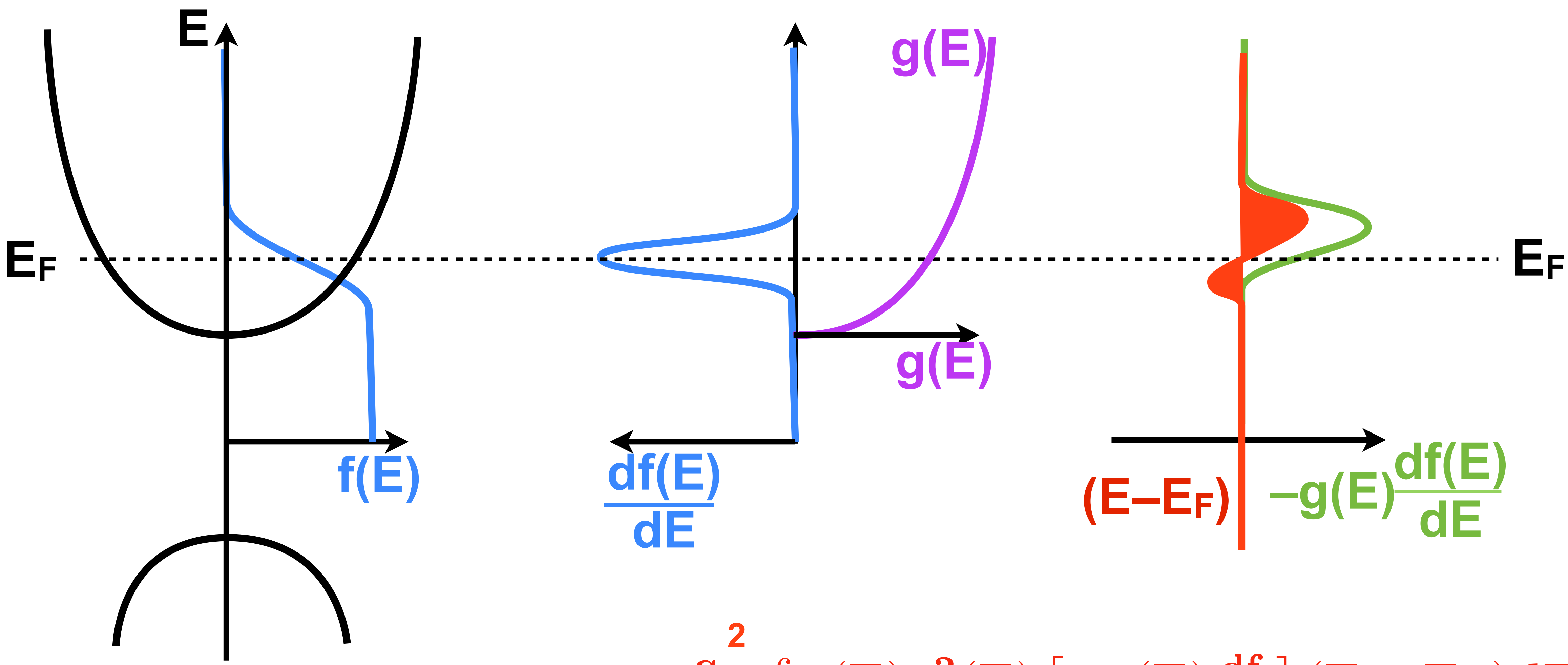
units: V/K

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

The Physics of the Thermoelectric Effect

- **If we ignore energy dependent scattering (i.e. τ = τ(E)) then from J.M. 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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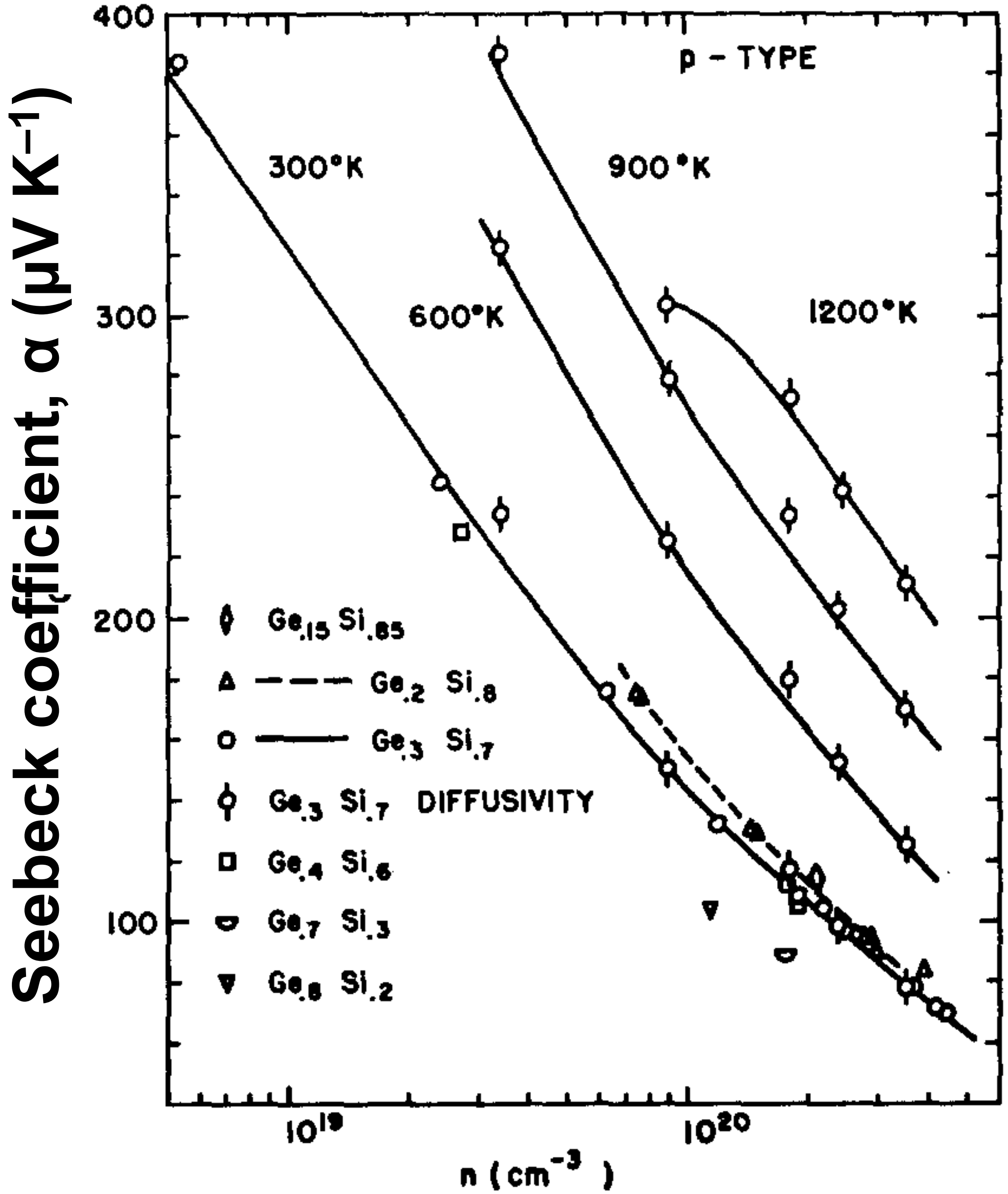
Semiconductor Example: SiGe Alloys

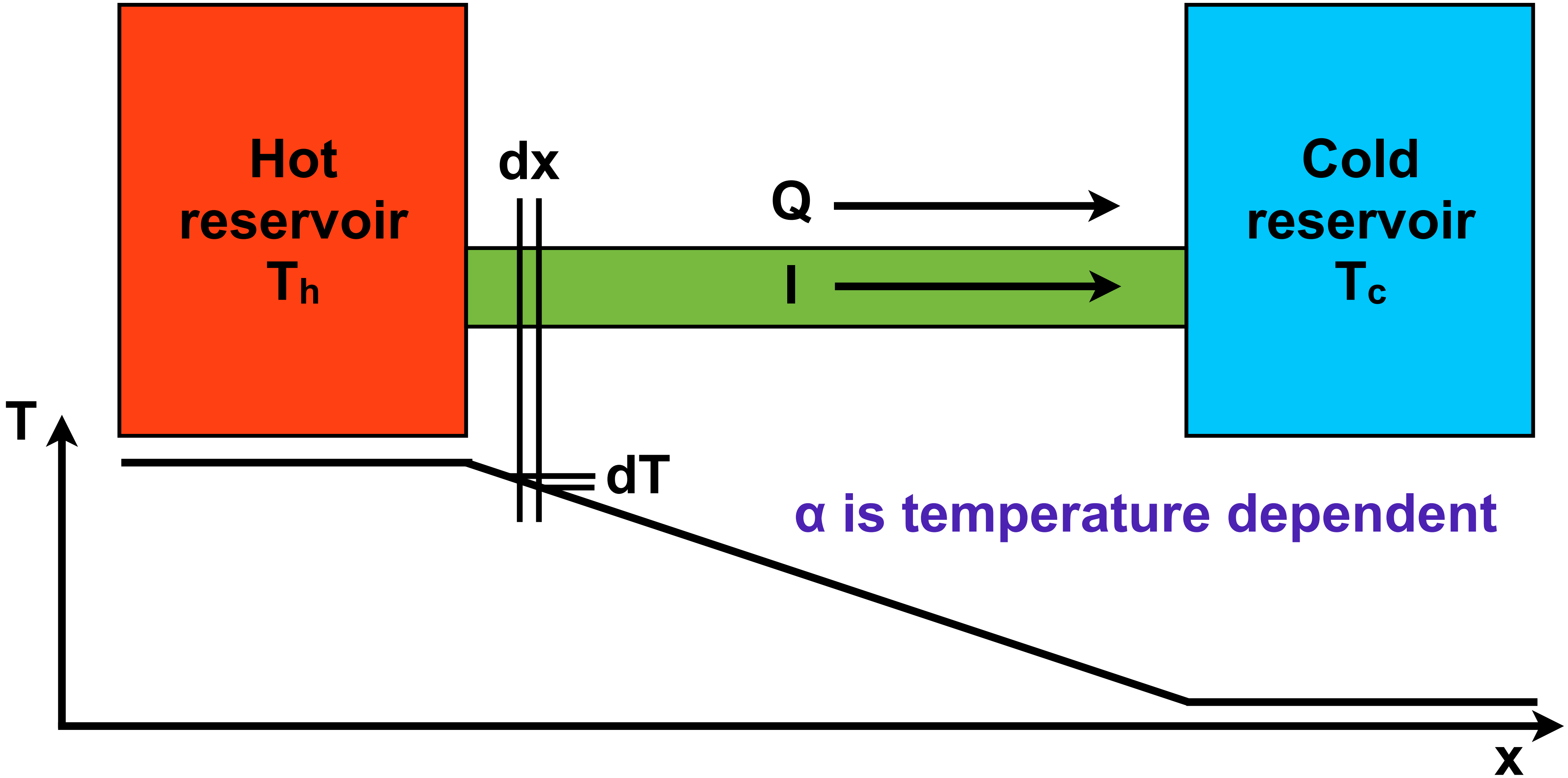


- Mott criteria ~ 2 x 10^{18} cm^{-3}
- Degenerately doped p-$Si_{0.7}Ge_{0.3}$
- α decreases for higher n
- For SiGe, α increases with T

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

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

The Thomson Effect



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

Thomson coefficient, β: $\mathrm{dQ} = \beta \mathrm{IdT}$

units: V/K

The Kelvin Relationships

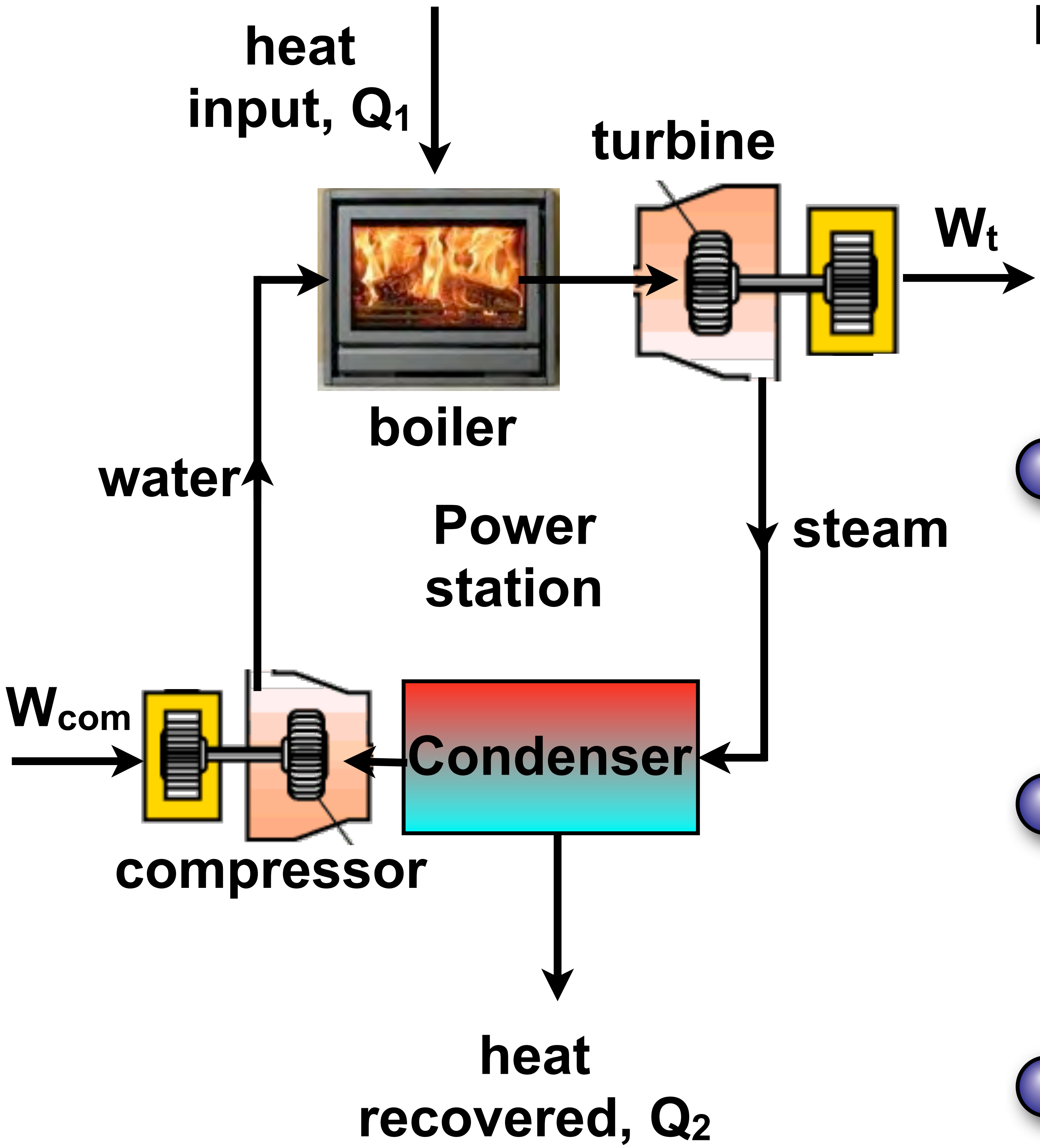
- Derived using irreversible thermodynamics

$$\Pi = \alpha \mathbf{T}$$

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

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

Carnot Efficiency for Thermal Engines



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

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

- 1st law thermodynamics
  $(Q_1 - Q_2) - (W_t - W_{com}) = 0$
- $\eta = \frac{Q_1 - Q_2}{Q_1}$
- $\eta = 1 - \frac{Q_2}{Q_1}$

Carnot Efficiency

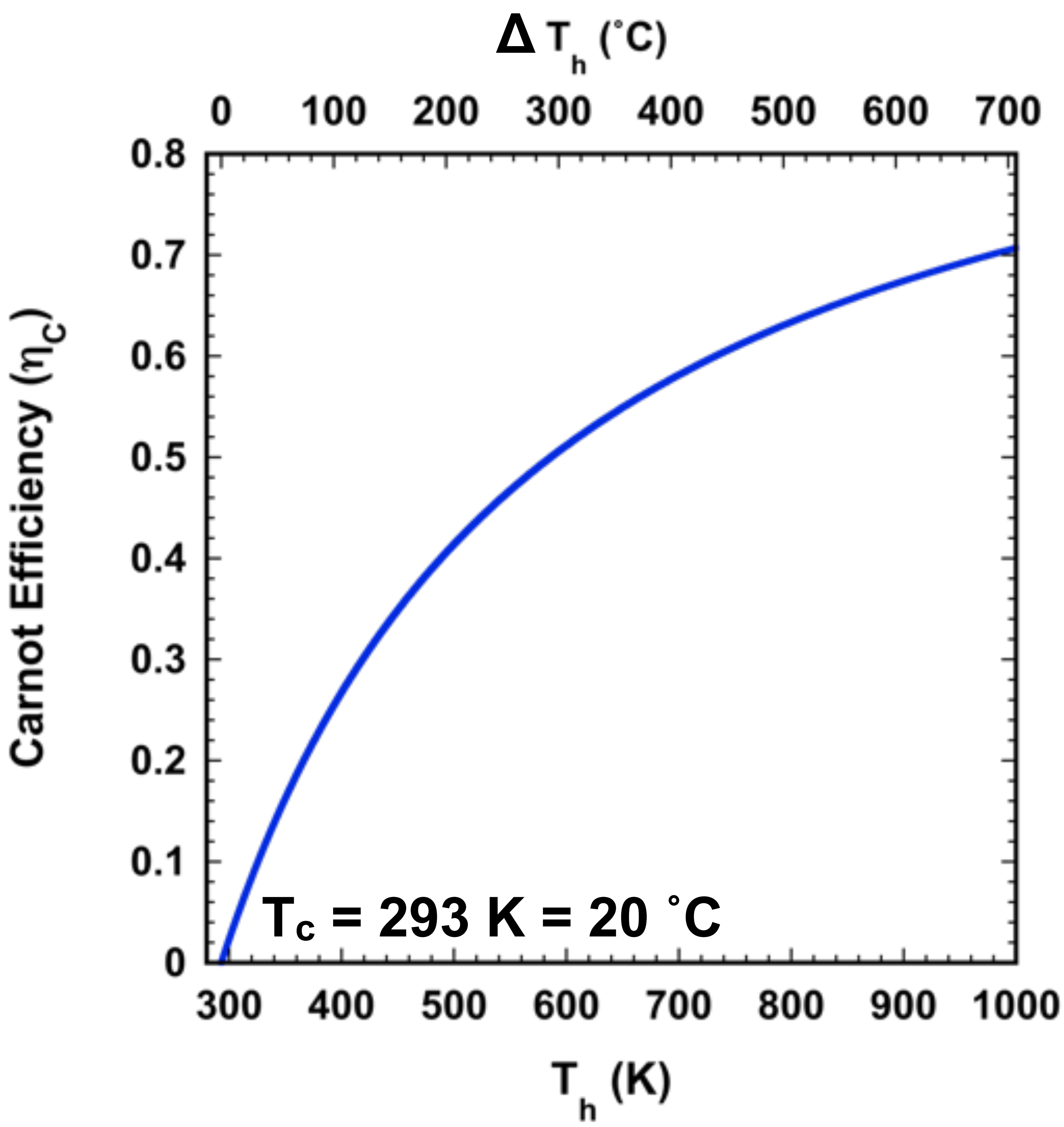
Efficiency =

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

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

Carnot: maximum η only depends on T_c and T_h

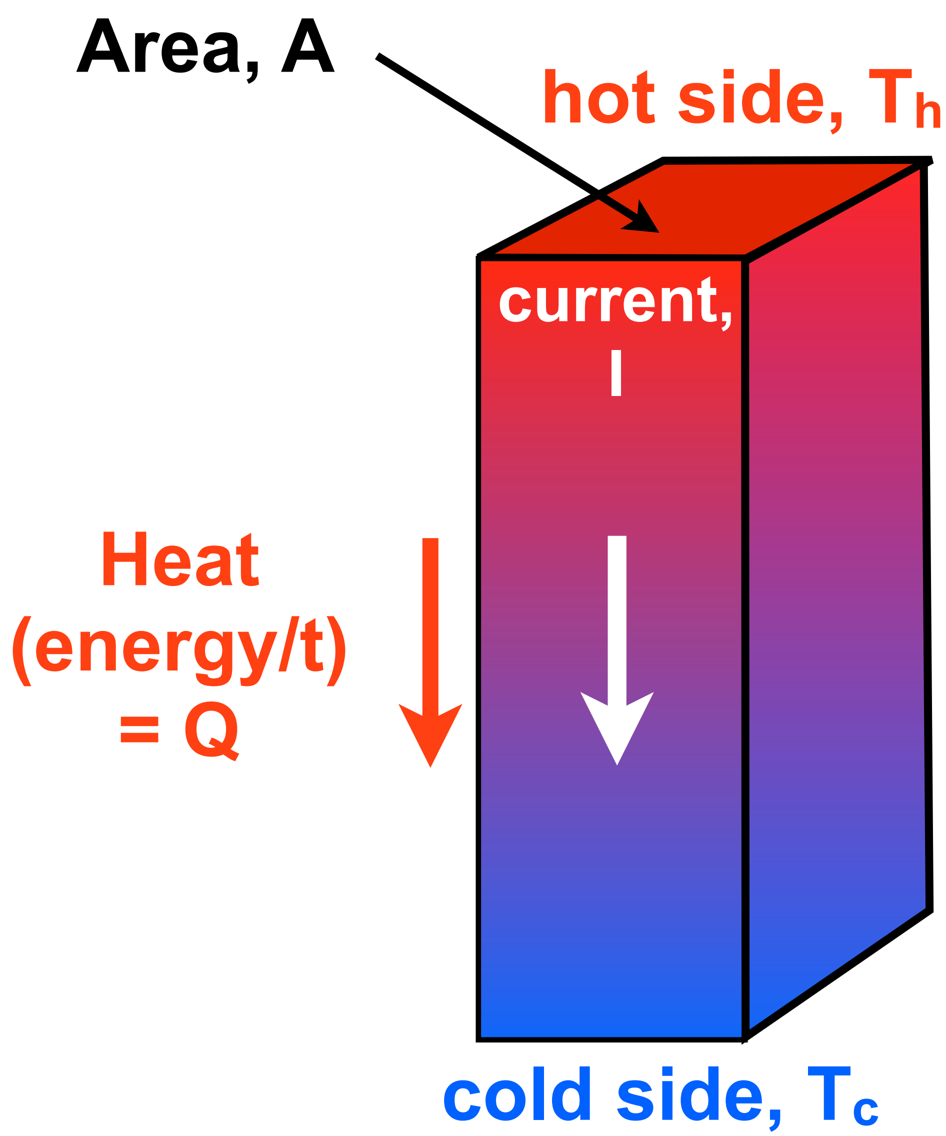
$$\eta_c = 1 - \frac{T_c}{T_h}$$



Higher temperatures give higher efficiencies

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)

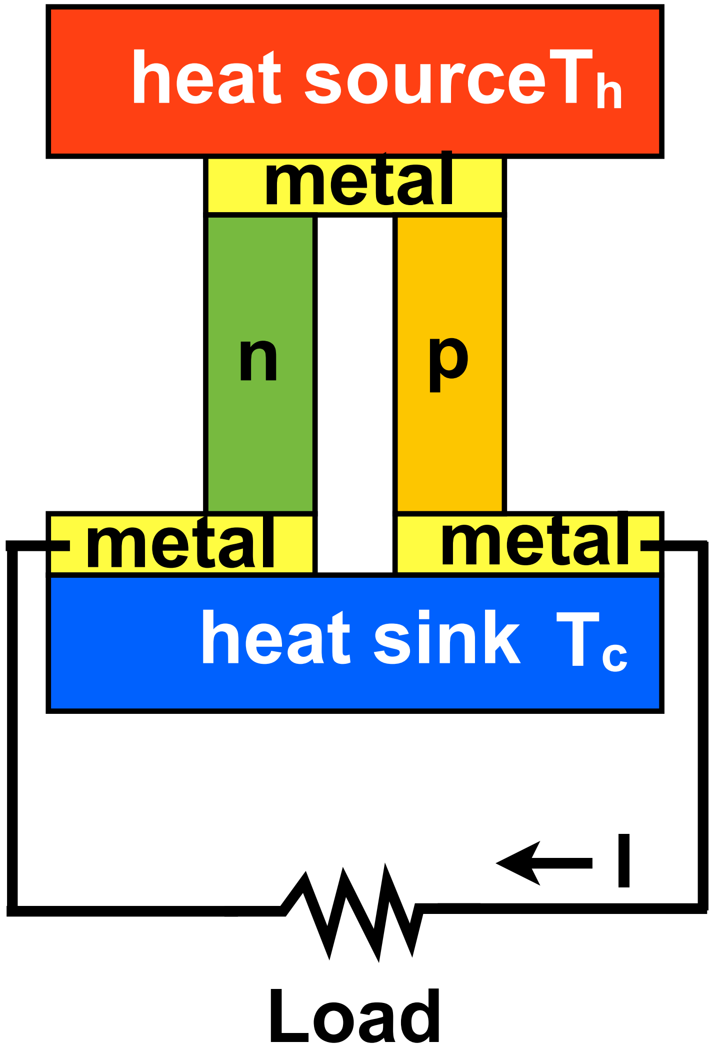
- $$\frac{Q}{A} = \Pi J - \kappa \nabla T$$

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

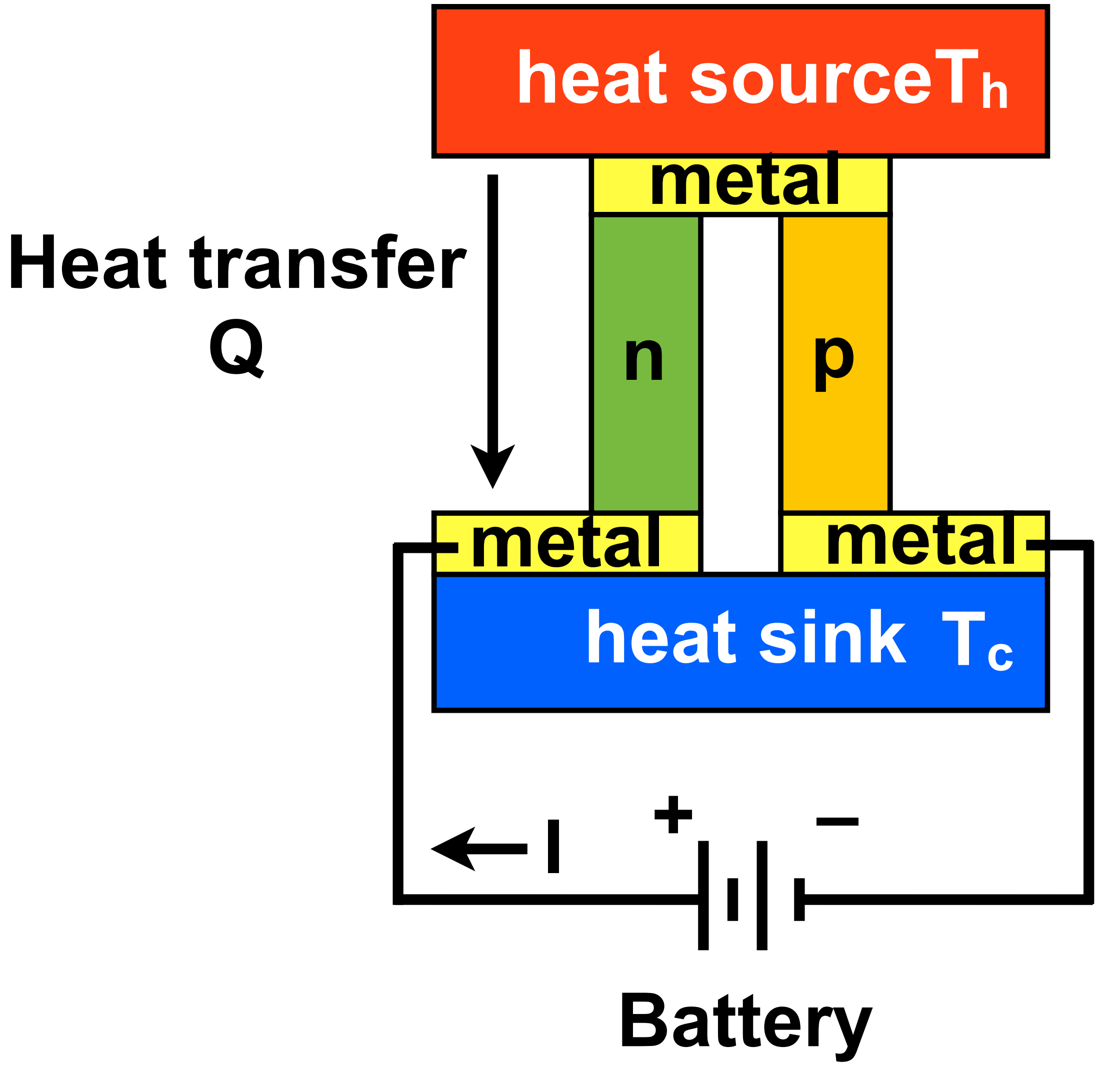
$$Q = \alpha I T - \kappa A \nabla T$$

Semiconductors and Thermoelectrics

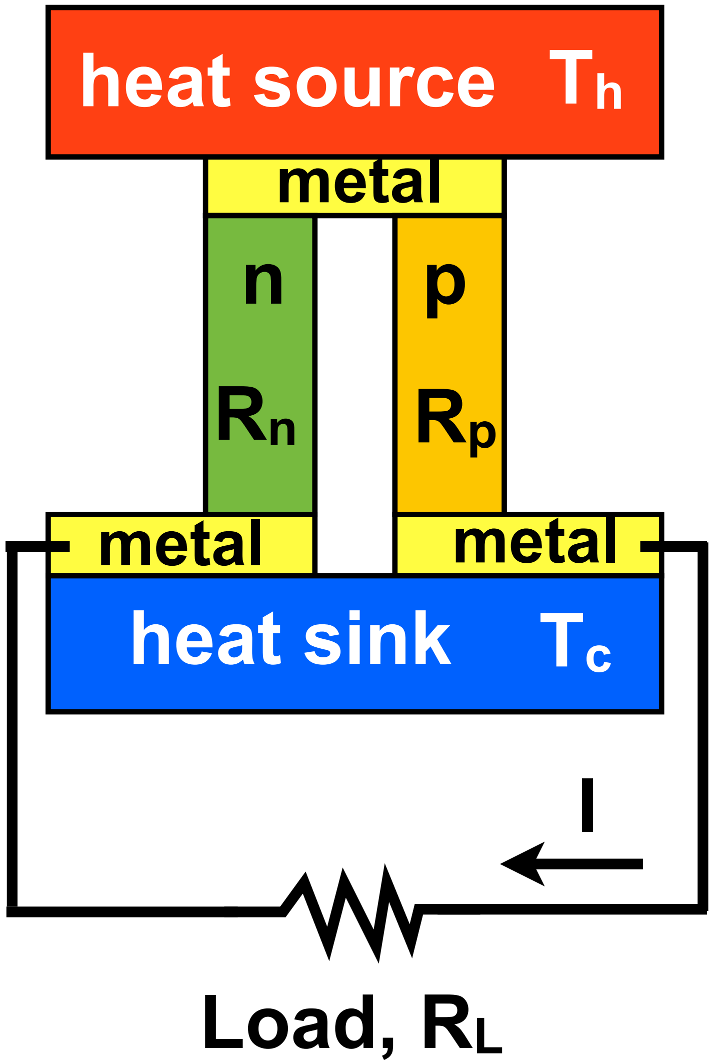
Seebeck effect: electricity generation



Peltier effect: electrical cooling i.e. heat pump



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 $= \Pi I = \alpha I T_h$
- $I = \frac{\alpha(T_h - T_c)}{R + R_L}$ (Ohms Law)
- Heat withdrawn from hot junction $= \kappa A\left(T_h - T_c\right) - \frac{1}{2}I^2R$

NB half Joule heat returned to hot junction

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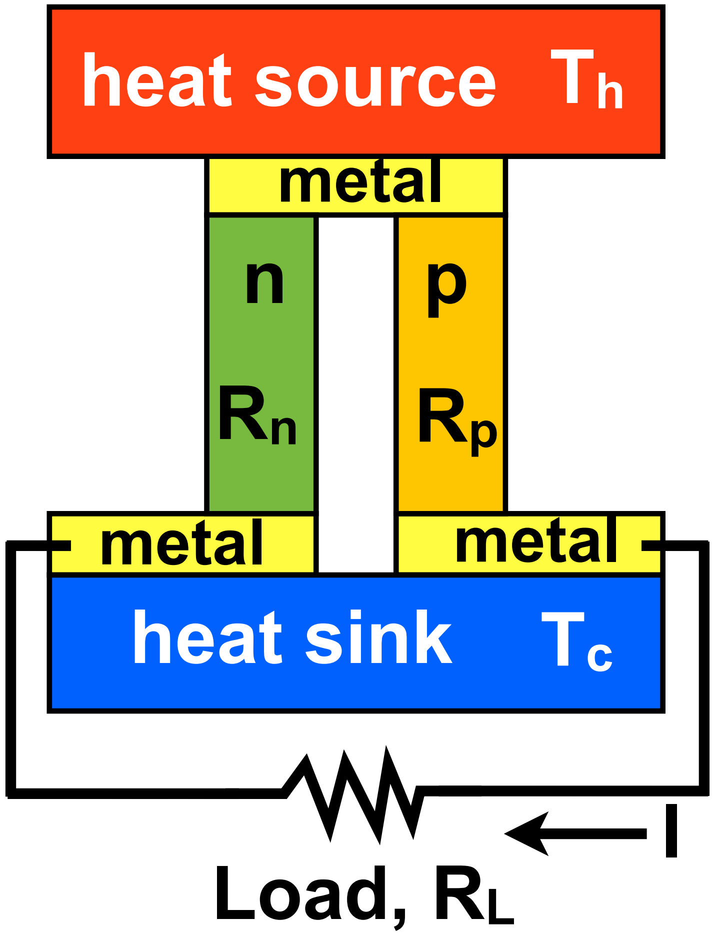
Thermoelectric Conversion Efficiency

- $\eta = \dfrac{\text{power supplied to load}}{\text{heat absorbed at hot junction}}$

  $= \dfrac{\text{power supplied to load}}{\text{Peltier + heat withdrawn}}$



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

- For maximum value $\dfrac{d\eta}{d(\frac{R_L}{R})} = 0$

$$T = \tfrac{1}{2}(T_h + T_c)$$

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

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

= Carnot x Joule losses and irreversible processes

Thermodynamic Efficiency

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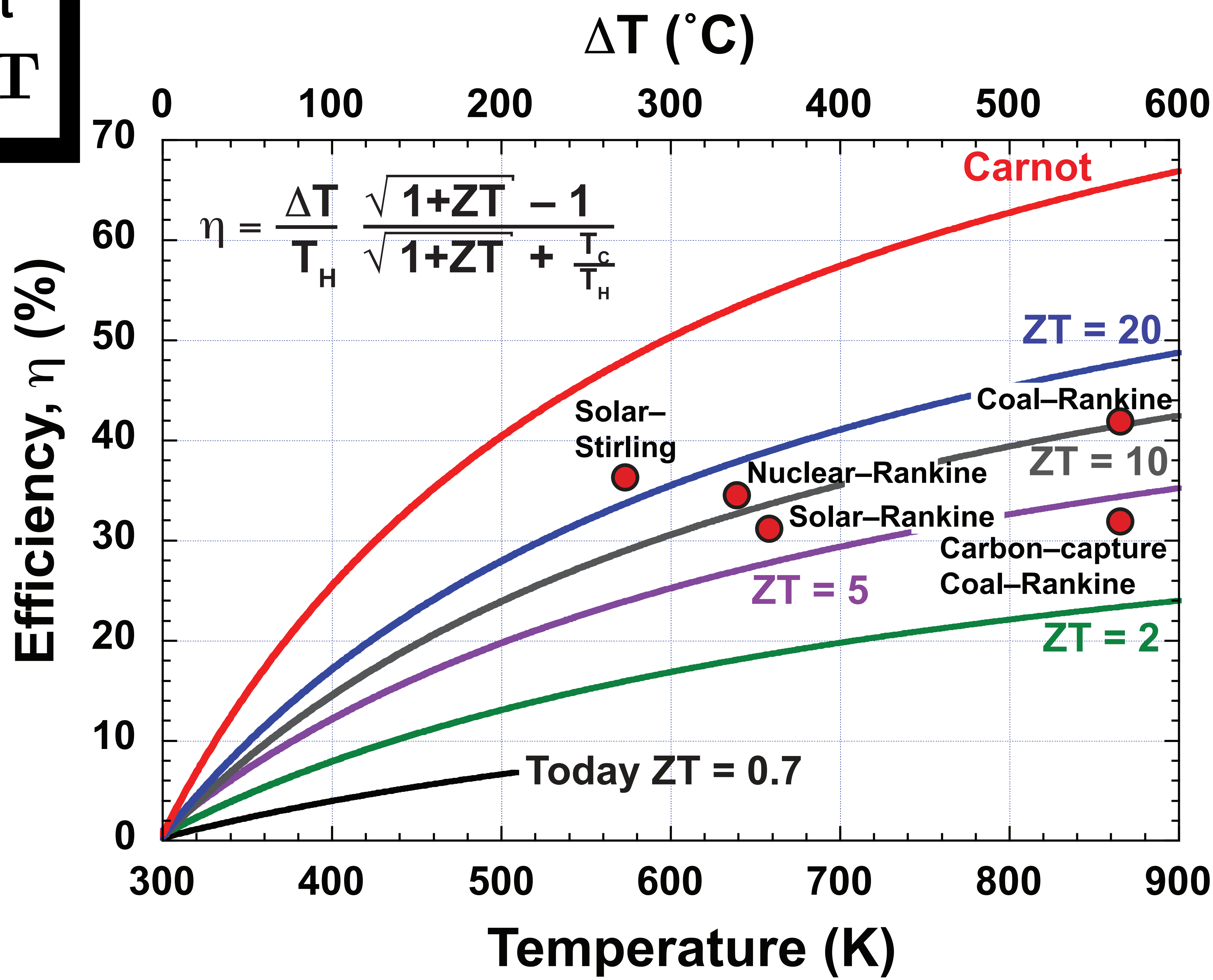
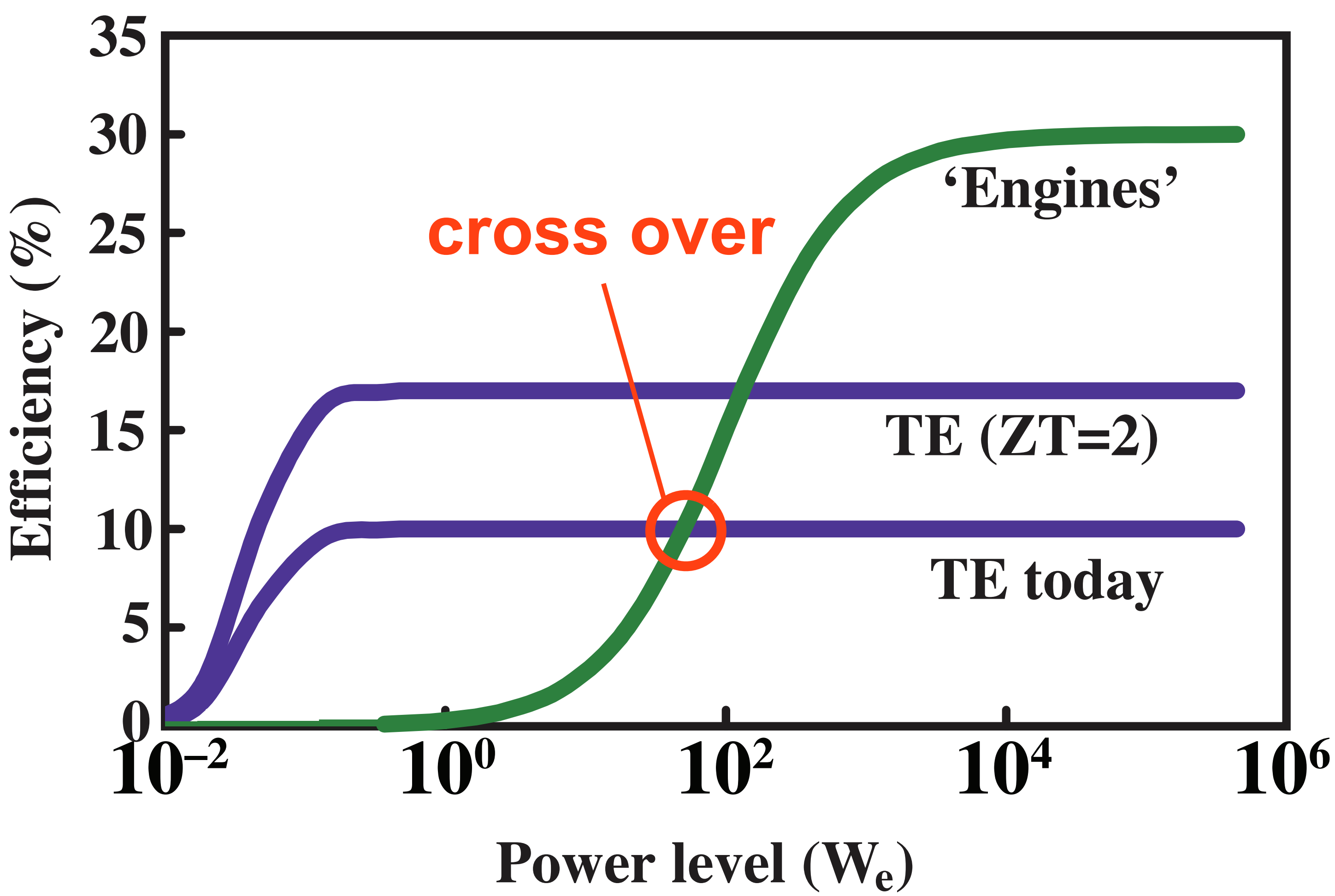
Figure of merit

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



Power Generation From Macro to Micro

Illustrative schematic diagram



At large scale, thermodynamic engines more efficient than TE

ZT average for both n and p over all temperature range

Diagram assumes high ΔT

- **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)

Application Reality Check

- NASA with finite Pu fuel for RTG requires high efficiency
- Automotive requires high power (heat is abundant)
- Industrial sensing requires high power (heat is abundant)
- Autonomous sensing requires high power (heat is abundant)
- As heat is abundant the issue is how to maximise power output NOT efficiency for most applications

$$\text{Power} \propto \alpha^2\sigma$$

Maximum Temperature Drop

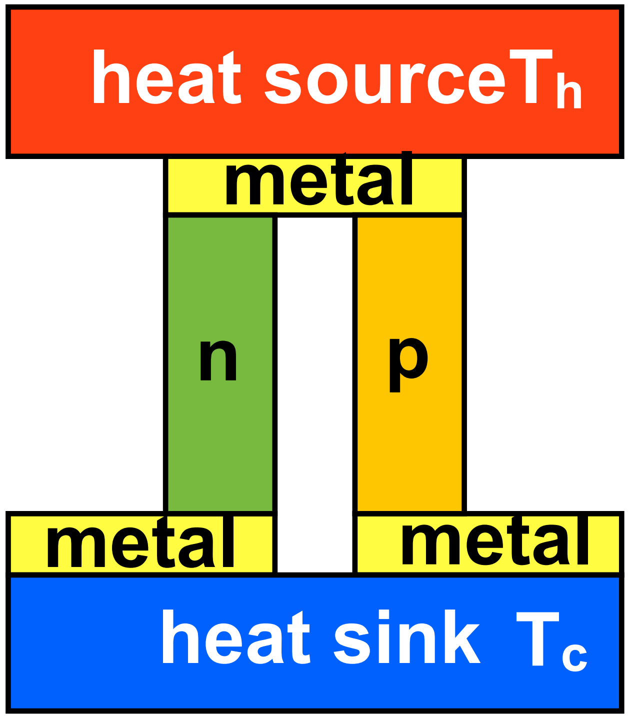
- As the system has thermal conductivity κ a maximum ΔT can be sustained across a module limited by heat transport

- $$\Delta T_{max} = \frac{1}{2} Z T_c^2$$

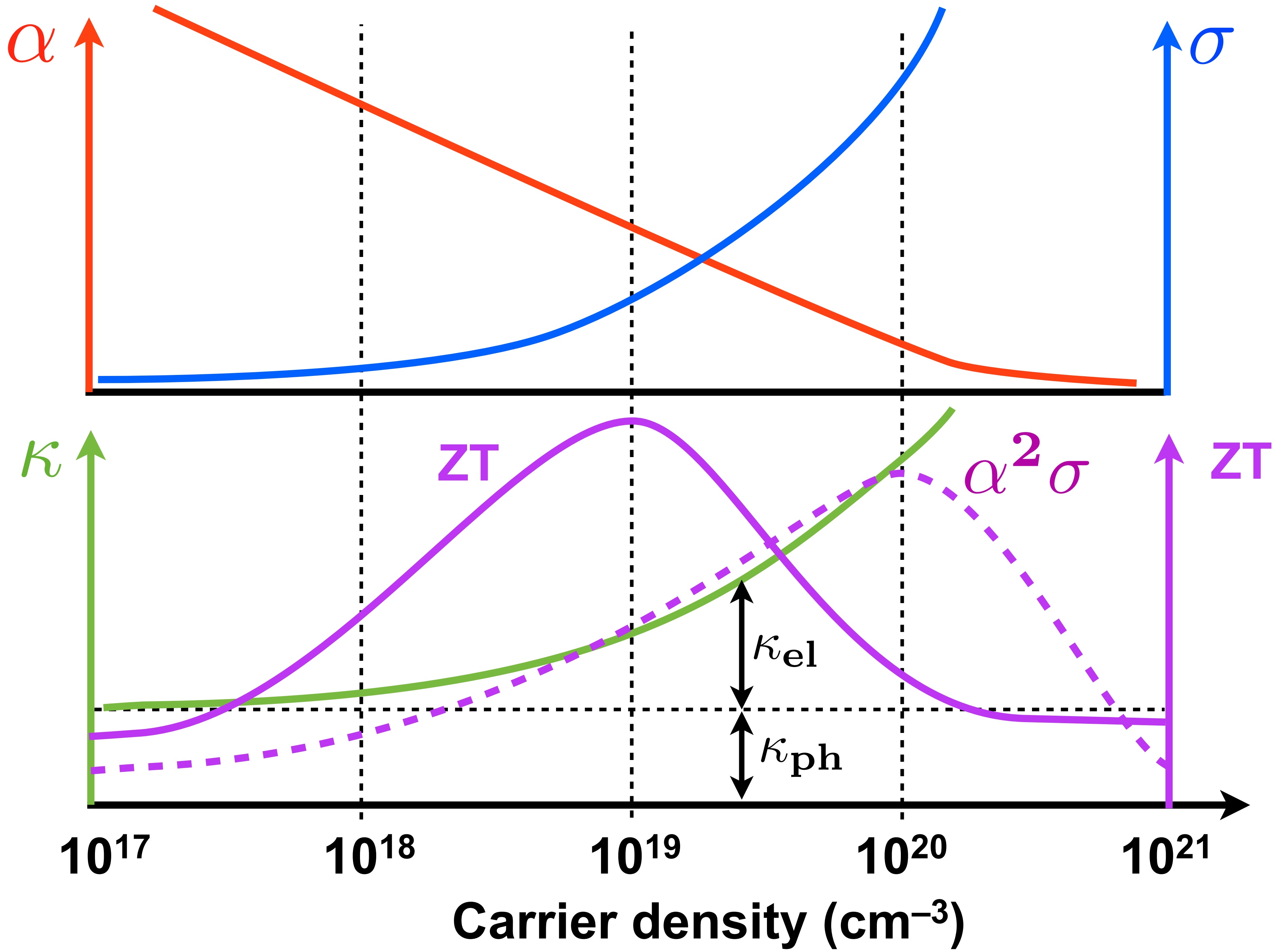
- The efficiency cannot be increased indefinitely by increasing T_h

- The thermal conductivity also limits maximum ΔT in Peltier coolers

- Higher ΔT_{max} requires better Z materials

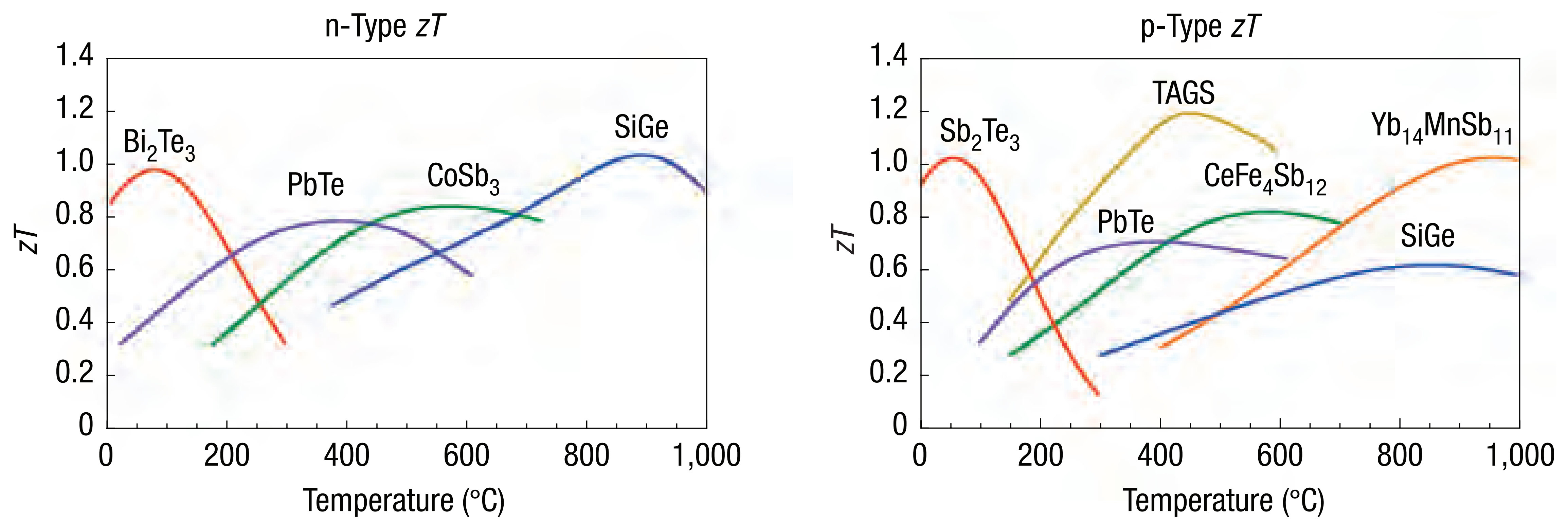


Thermoelectric vs Doping of Semiconductors



- Electrical and thermal conductivities are not independent
- Wiedemann Franz rule: electrical conductivity ∝ thermal conductivity at high doping

Bulk Thermoelectric Materials Performance



***Nature Materials* 7, 105 (2008)**

- **Bulk n-Bi_2Te_3 and p-Sb_2Te_3 used in most commercial thermoelectrics & Peltier coolers**
- **But tellurium is 9th rarest element on earth !!!**
- **Bulk $Si_{1-x}Ge_x$ (x~0.2 to 0.3) used for high temperature satellite applications**

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

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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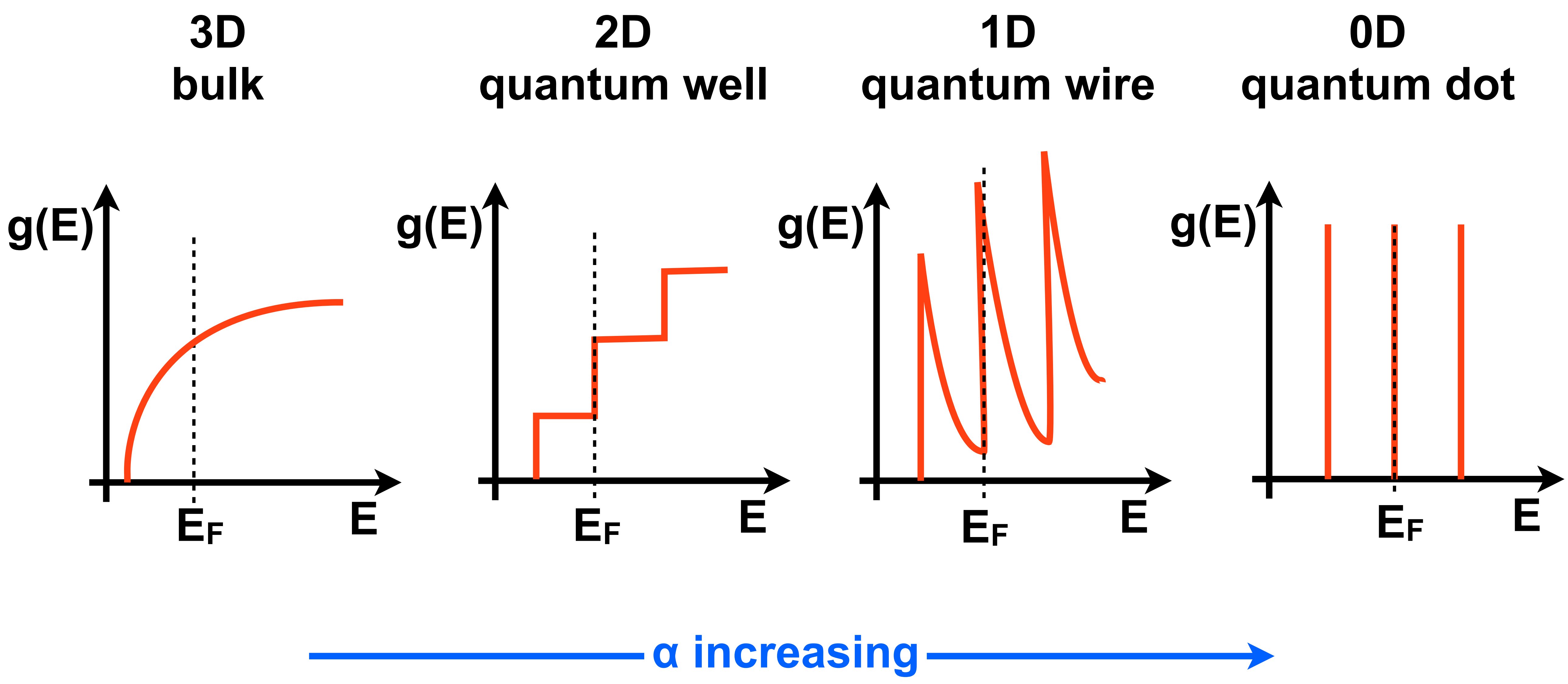
Seebeck Enhancement at Low Dimensions

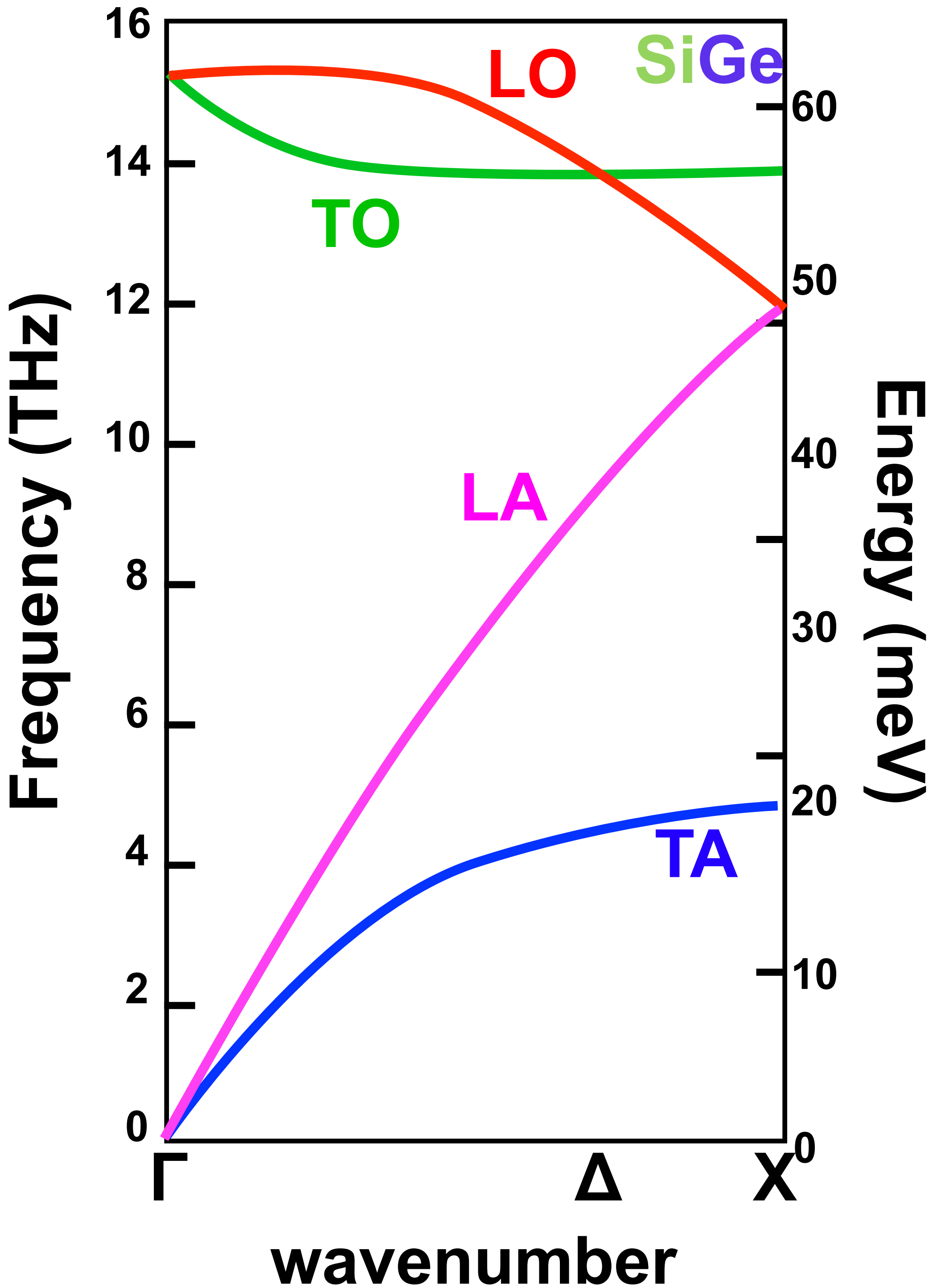
- **Increase α through enhanced DOS:**

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

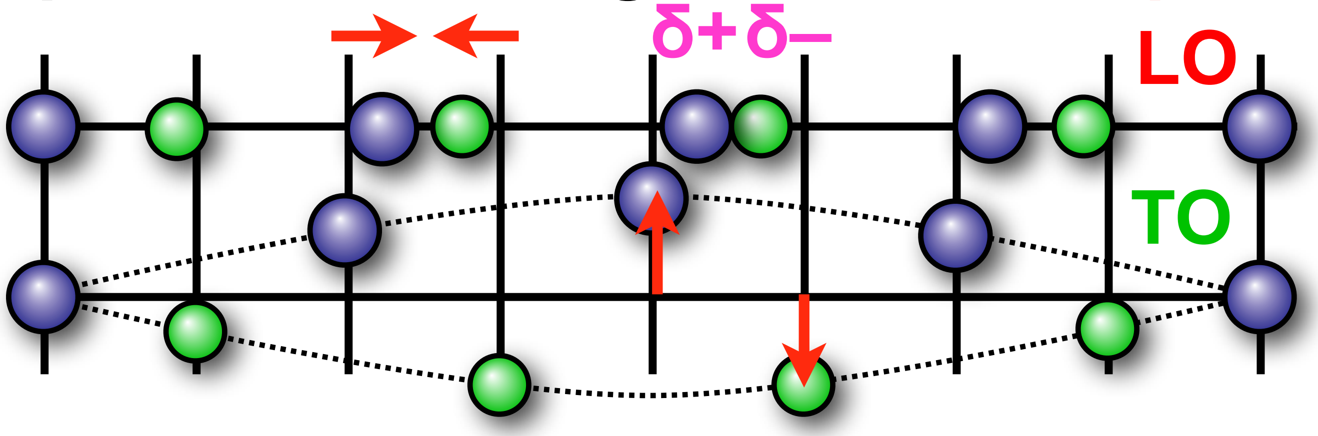


M. Cutler & N.F. Mott, Phys. Rev. 181, 1336 (1969)

Phonons: Lattice Vibration Heat Transfer

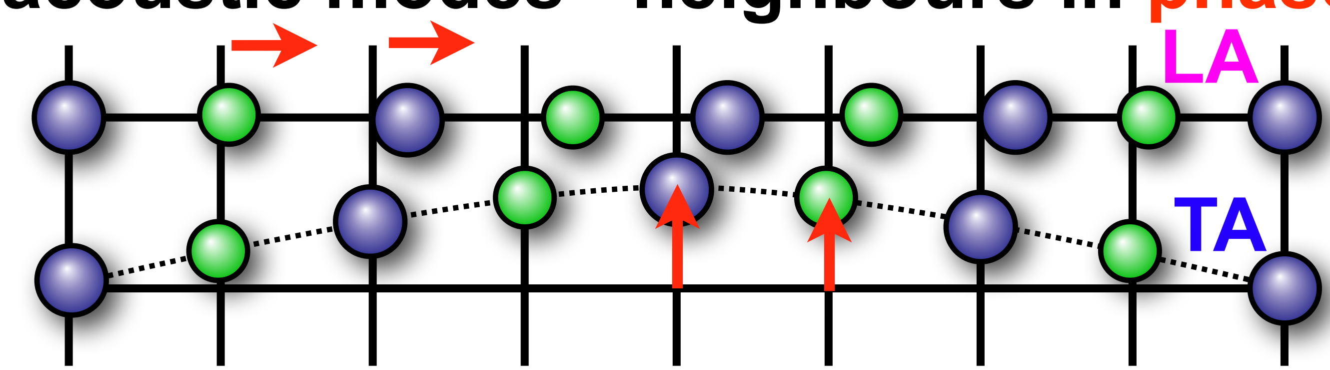


optic modes - neighbours in antiphase



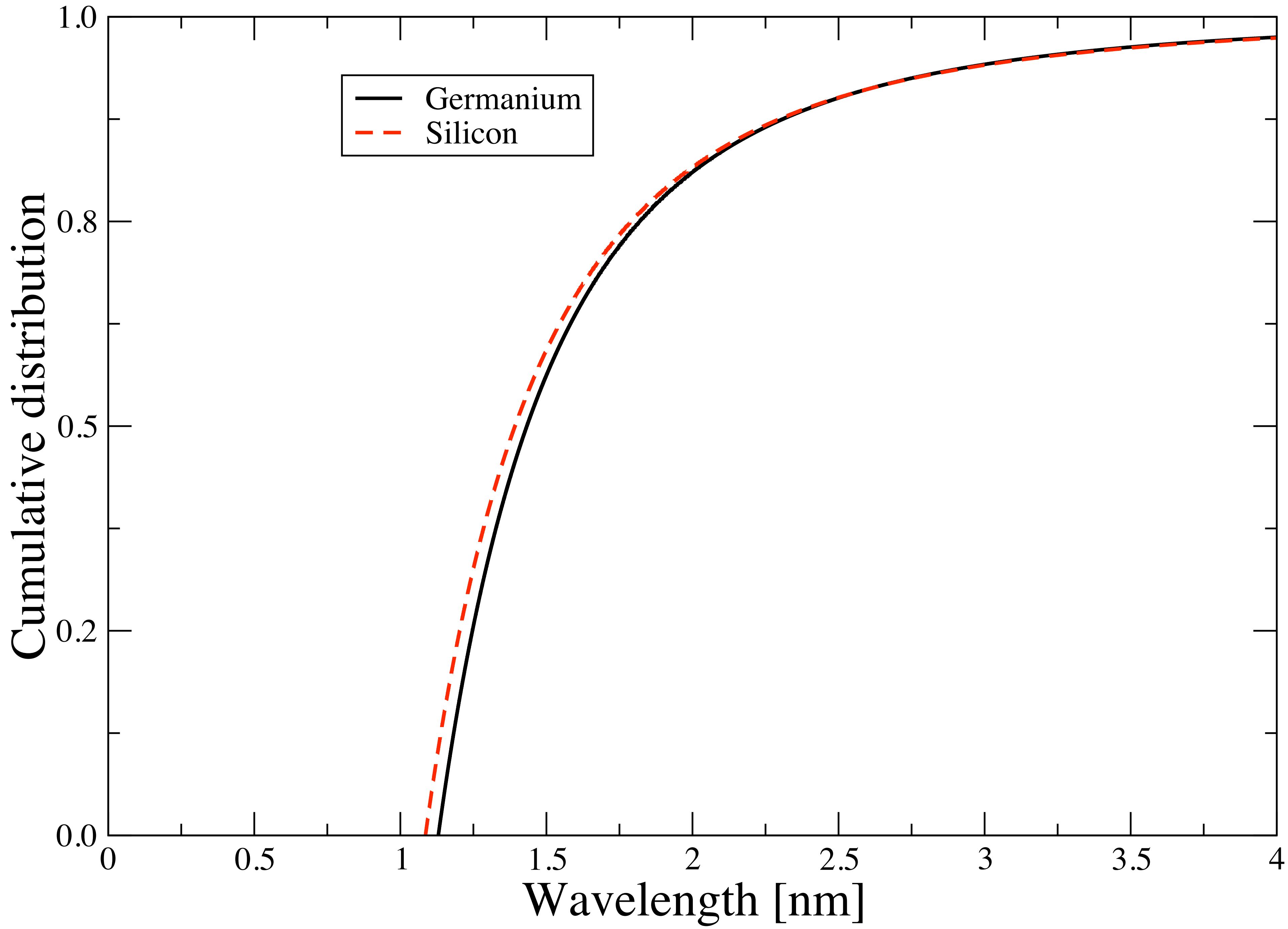
NB acoustic phonons transmit most thermal energy

acoustic modes - neighbours in phase



- The majority of heat in solids is transported by acoustic phonons

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:

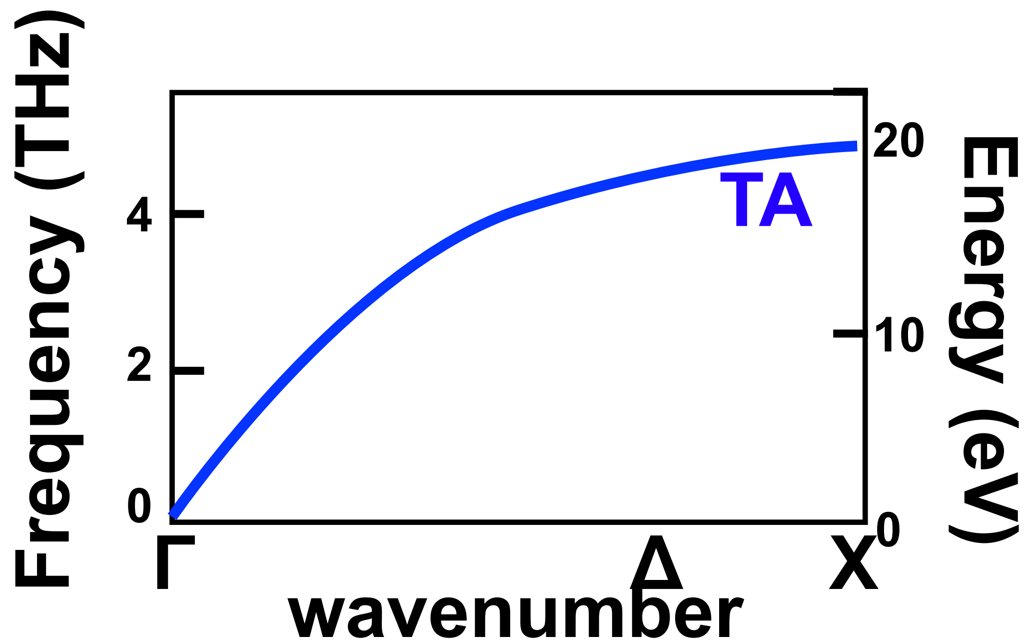
- Require structures below the phonon mean free path (10s nm)

Phonon Bandgaps:

- Change the acoustic phonon dispersion –> stationary phonons or bandgaps

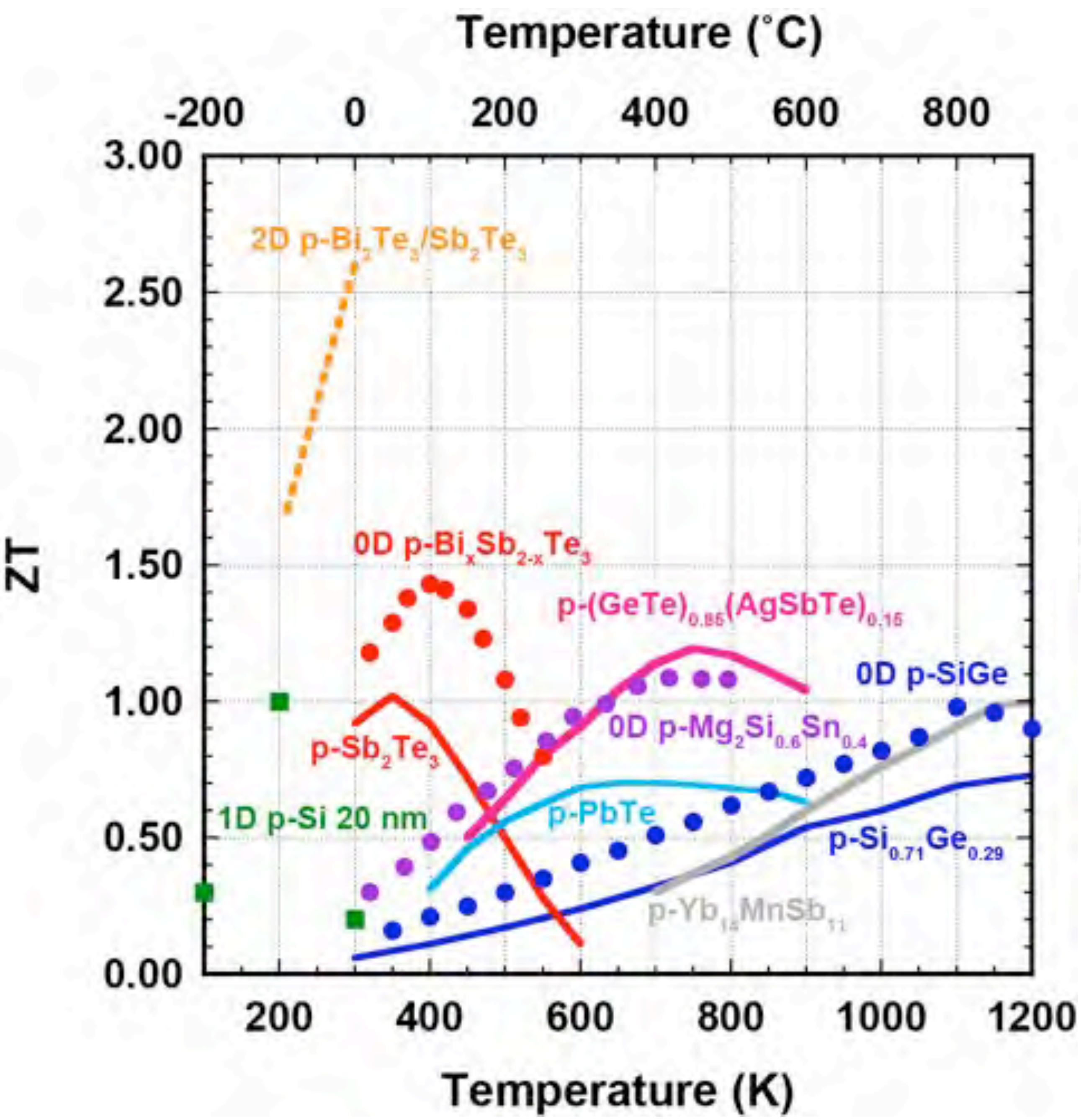
- Require structures with features at the phonon wavelength (< 5 nm)

- Phonon group velocity $\propto \frac{dE}{dk_q}$

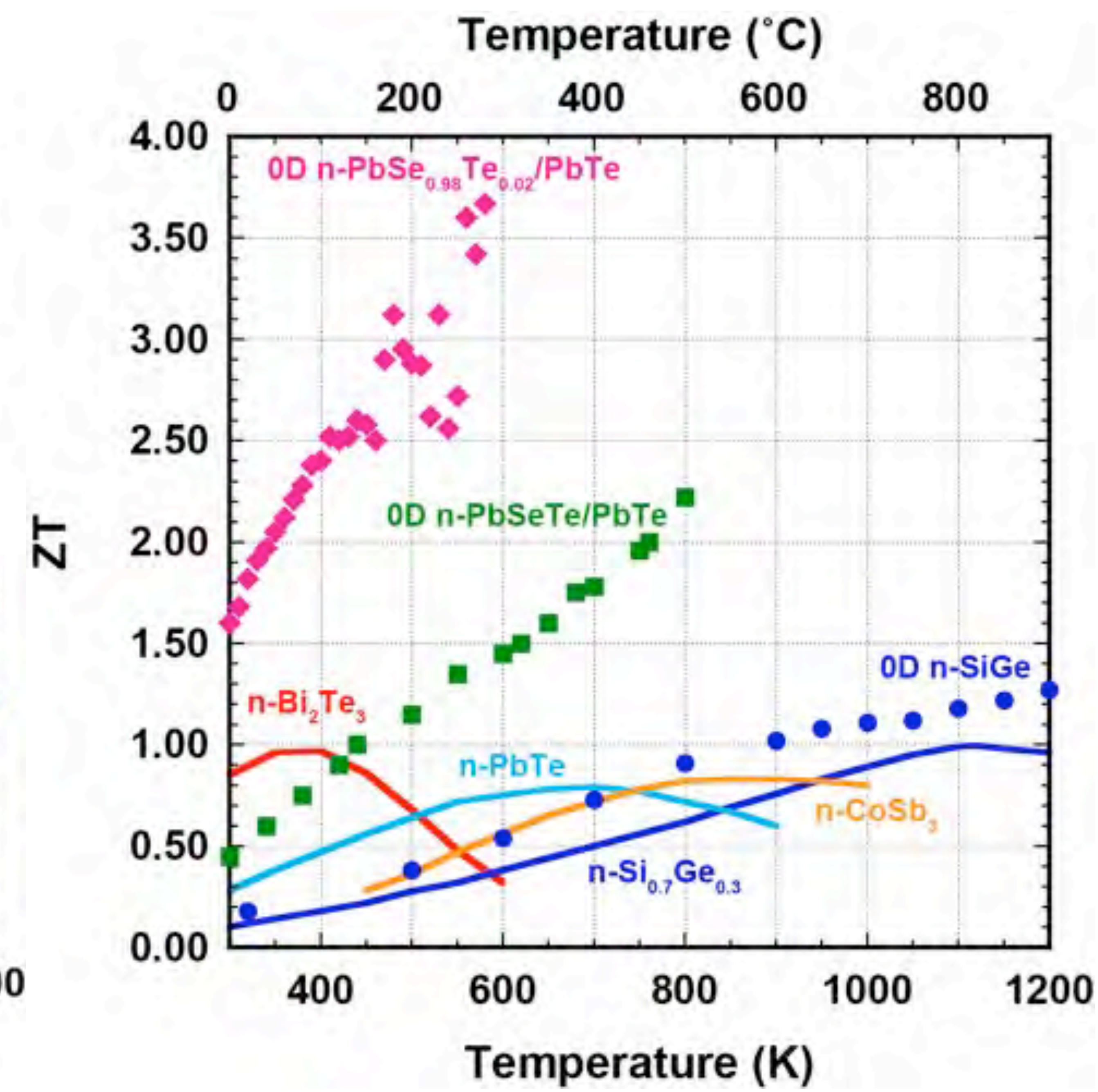


ZT versus Temperature

p-type

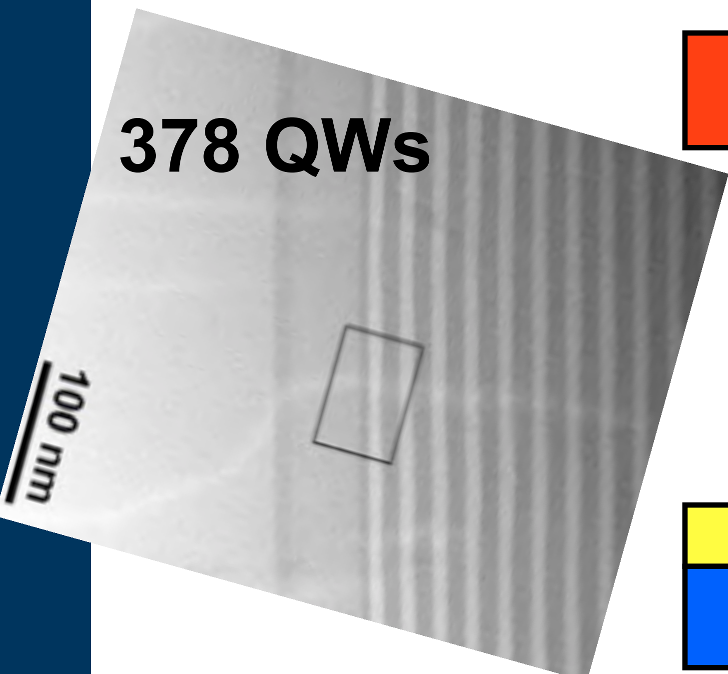


n-type

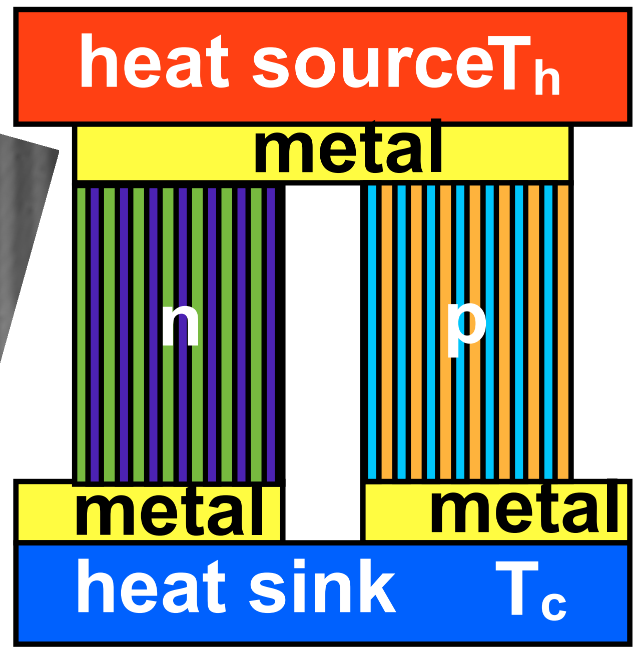


- **Nanostructures can improve Seebeck coefficient and/or decrease thermal conductivity**

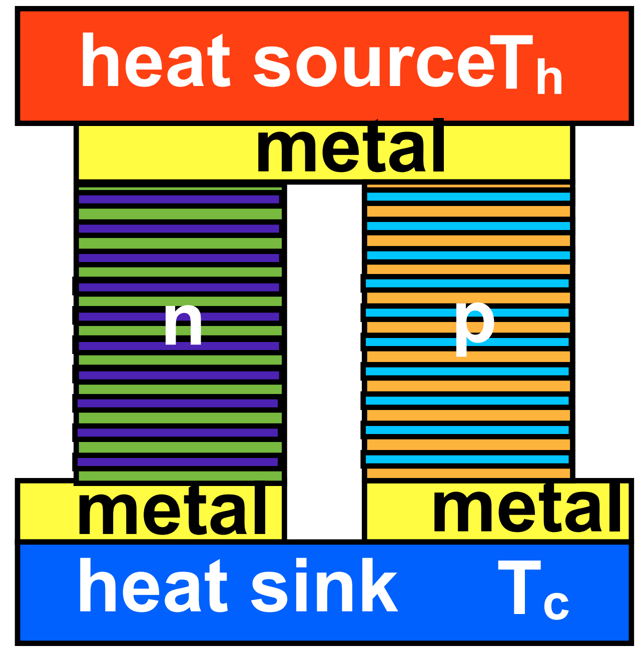
Thermoelectric Low Dimensional Structures

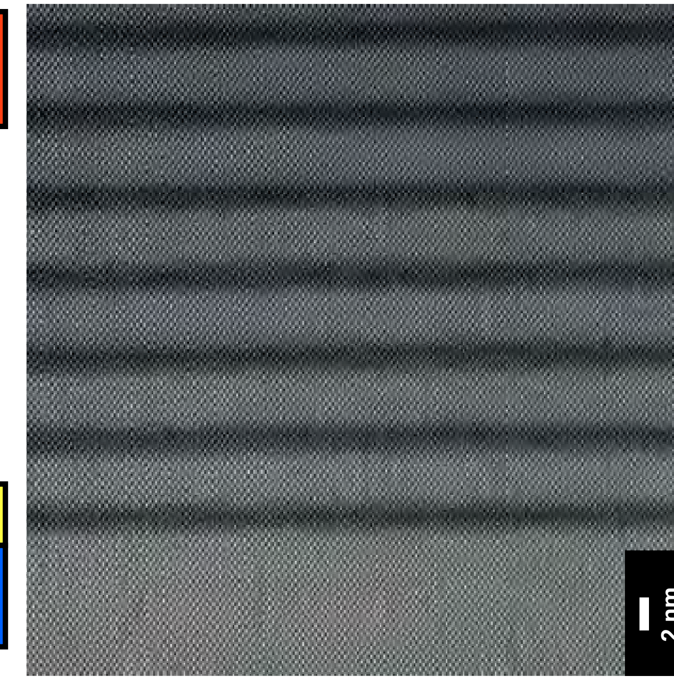


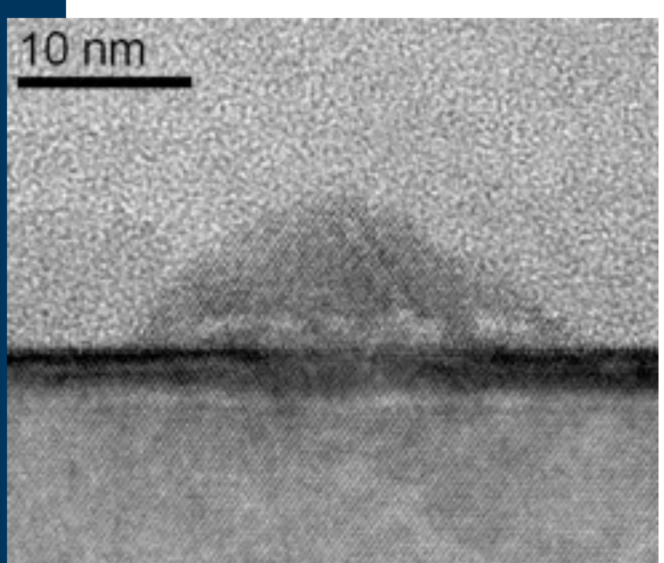
Lateral superlattice



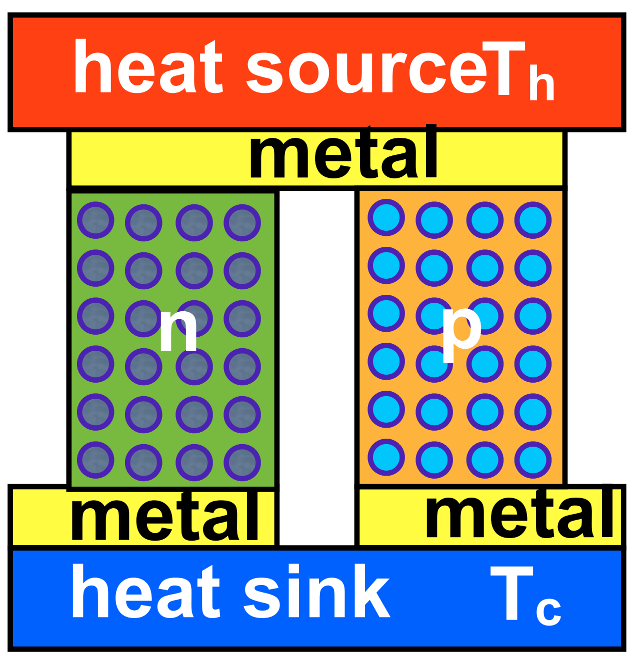
Vertical superlattice



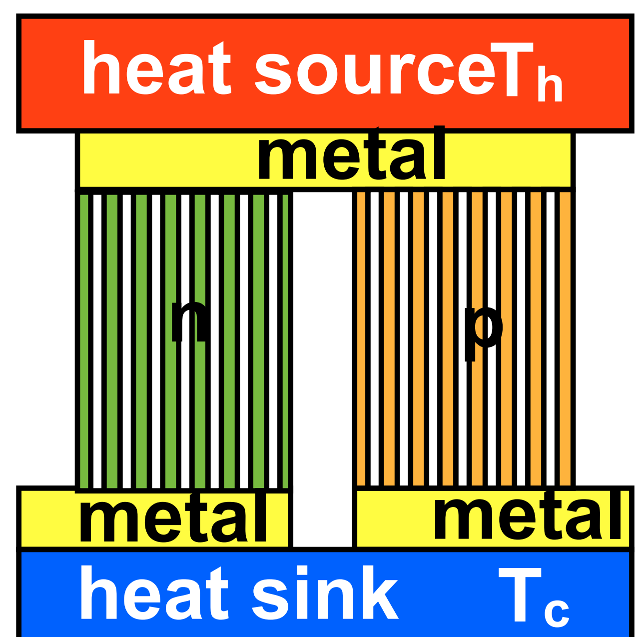


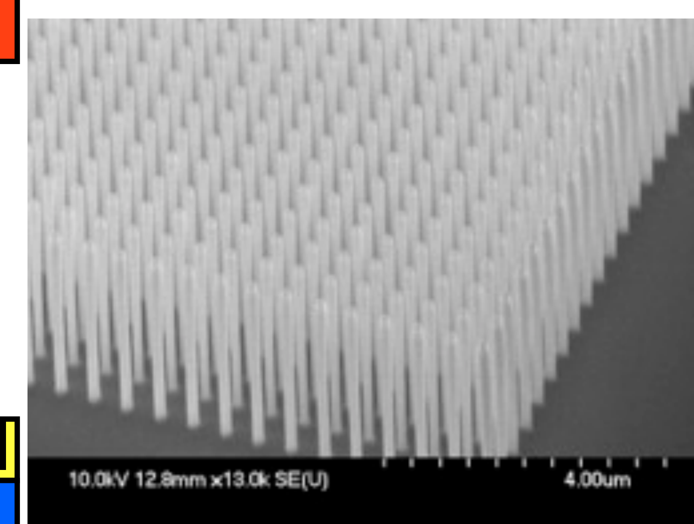


Quantum Dots



Nanowires





Vertical (Cross-plane) Superlattice TEs

University of Glasgow

- Use of transport perpendicular to superlattice quantum wells
- Higher α from the higher density of states
- Lower electron conductivity from tunnelling
- Lower κ_{ph} from phonon scattering at heterointerfaces
- Able to engineer lower κ_{ph} with phononic bandgaps
- Overall Z and ZT should increase

Vertical superlattice

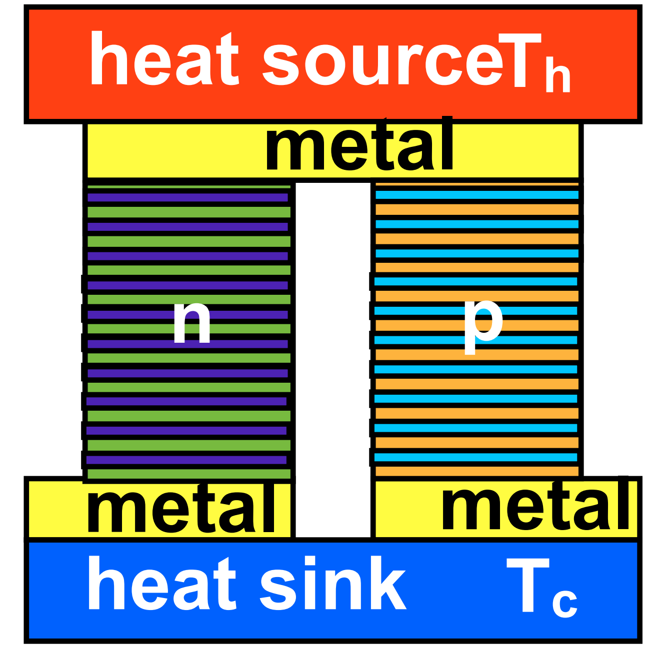
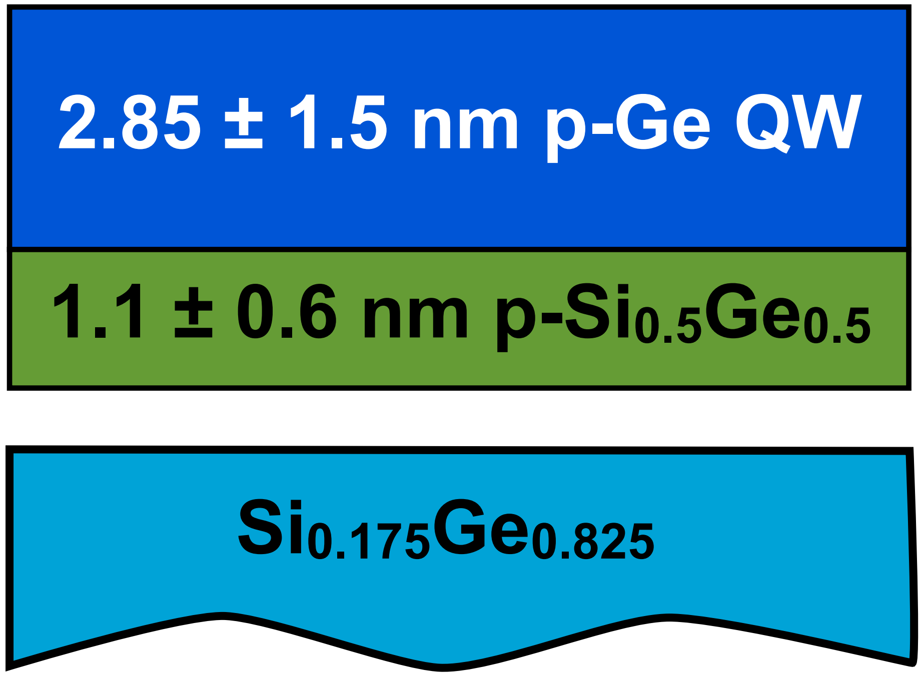


Figure of merit

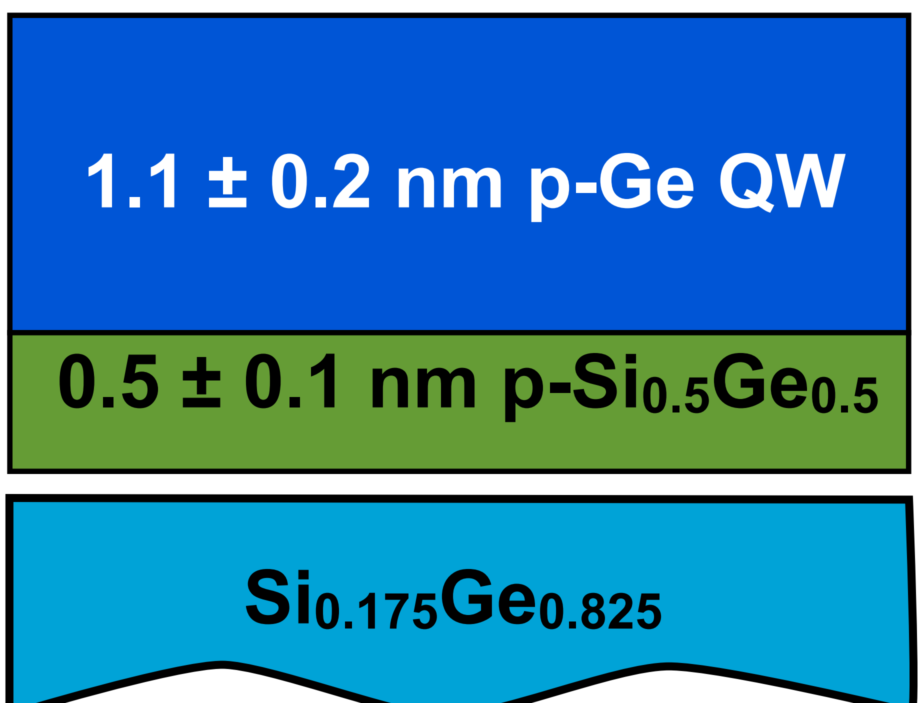
$$\mathrm{ZT} = \frac{\alpha^2 \sigma}{\kappa} \mathrm{T}$$

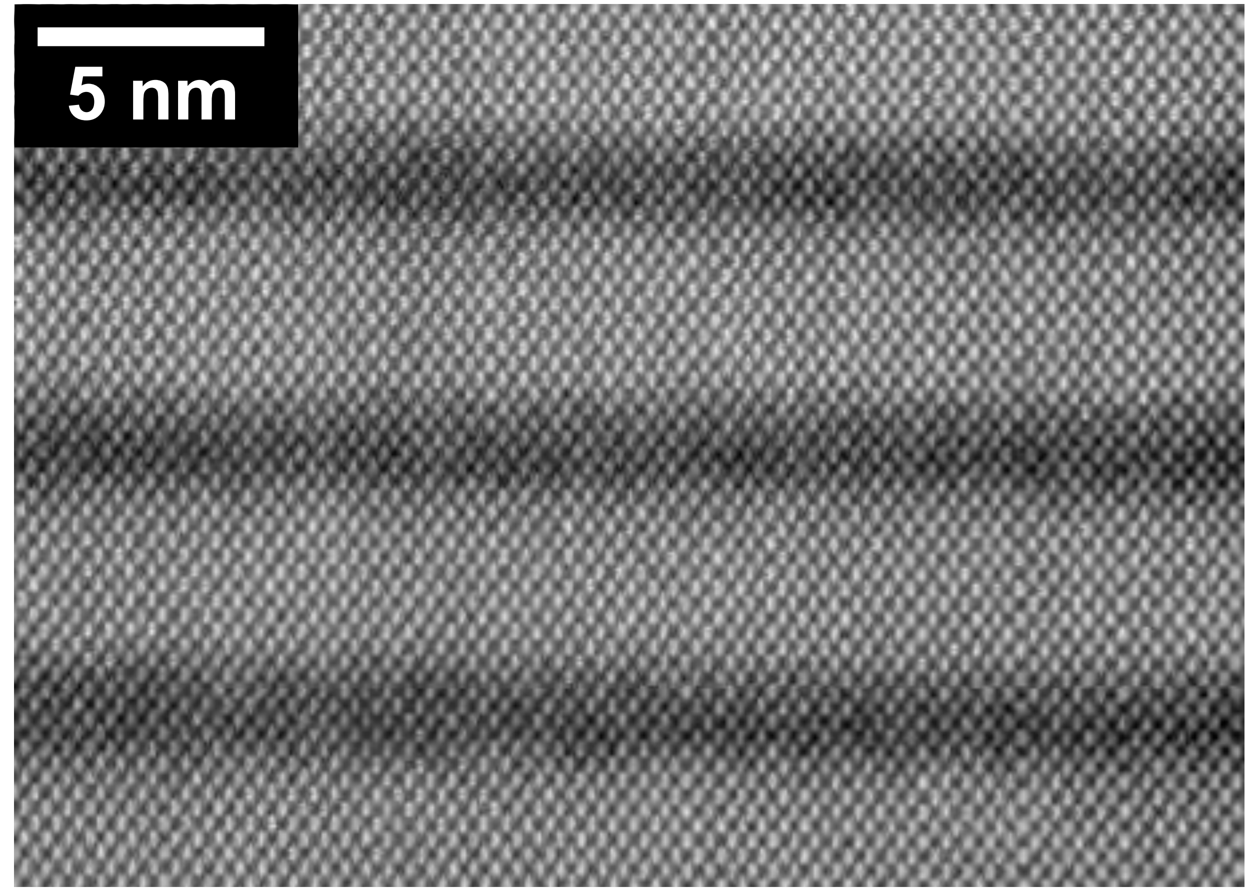
p-type Wafer Designs

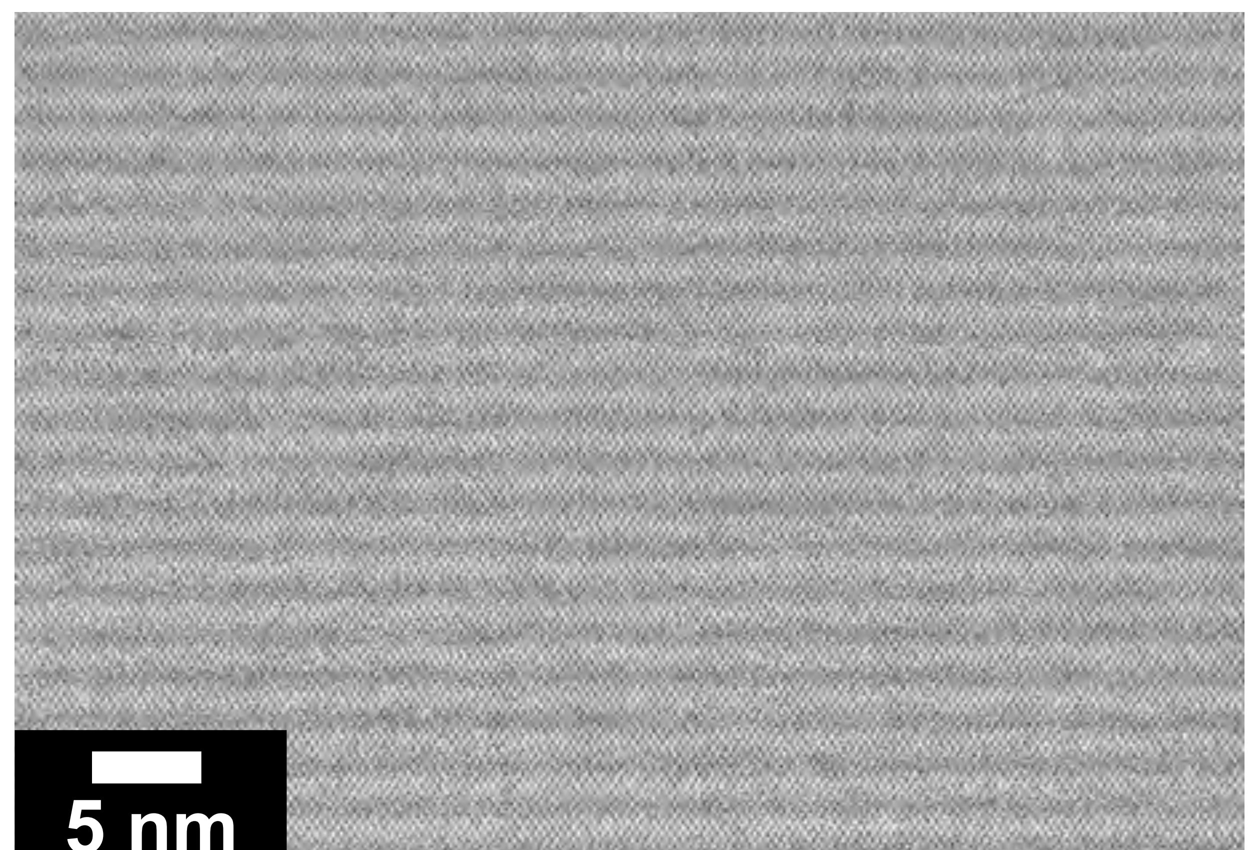
SL1 to SL4: 922 x



SL5: 2338 x

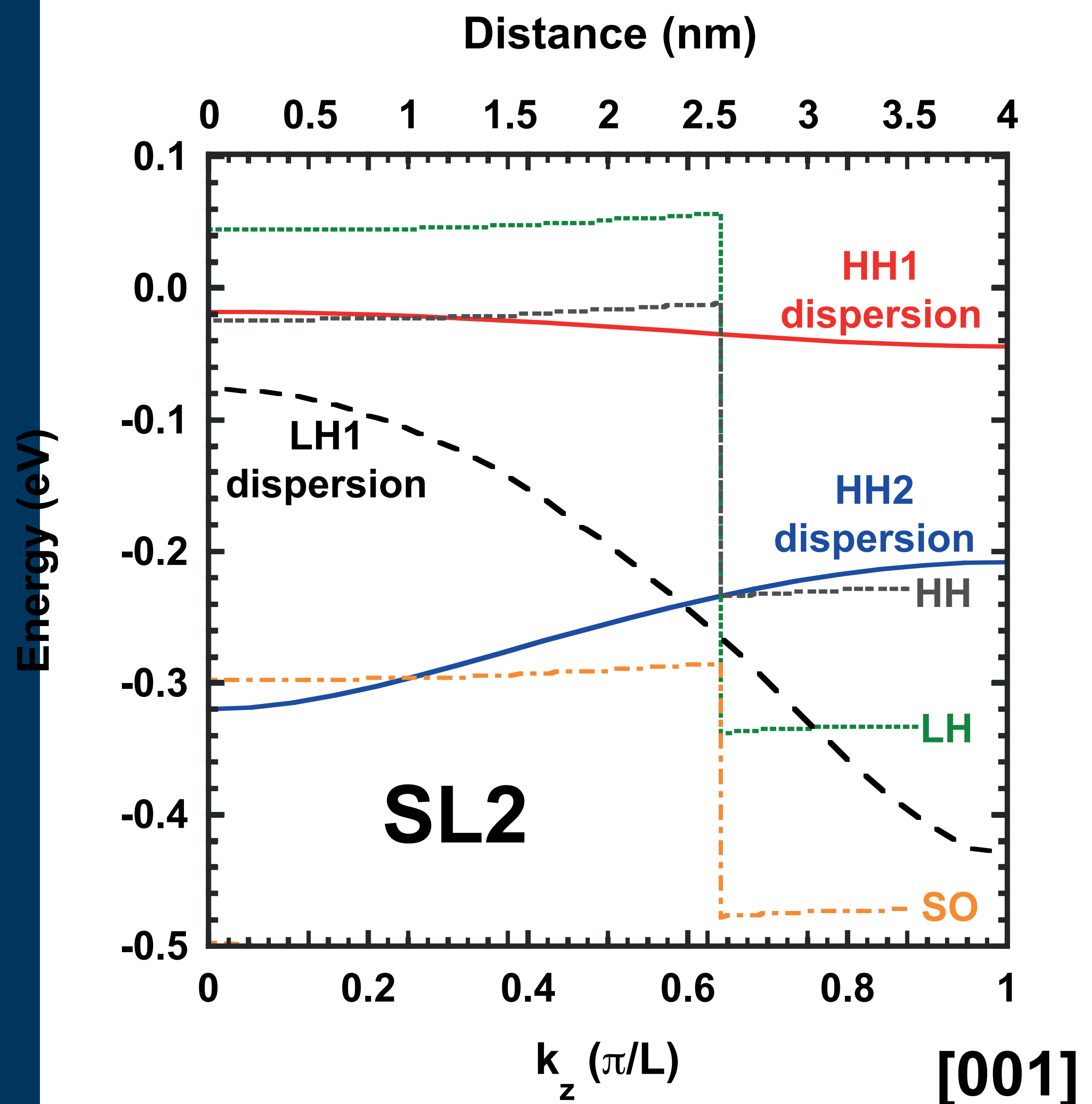




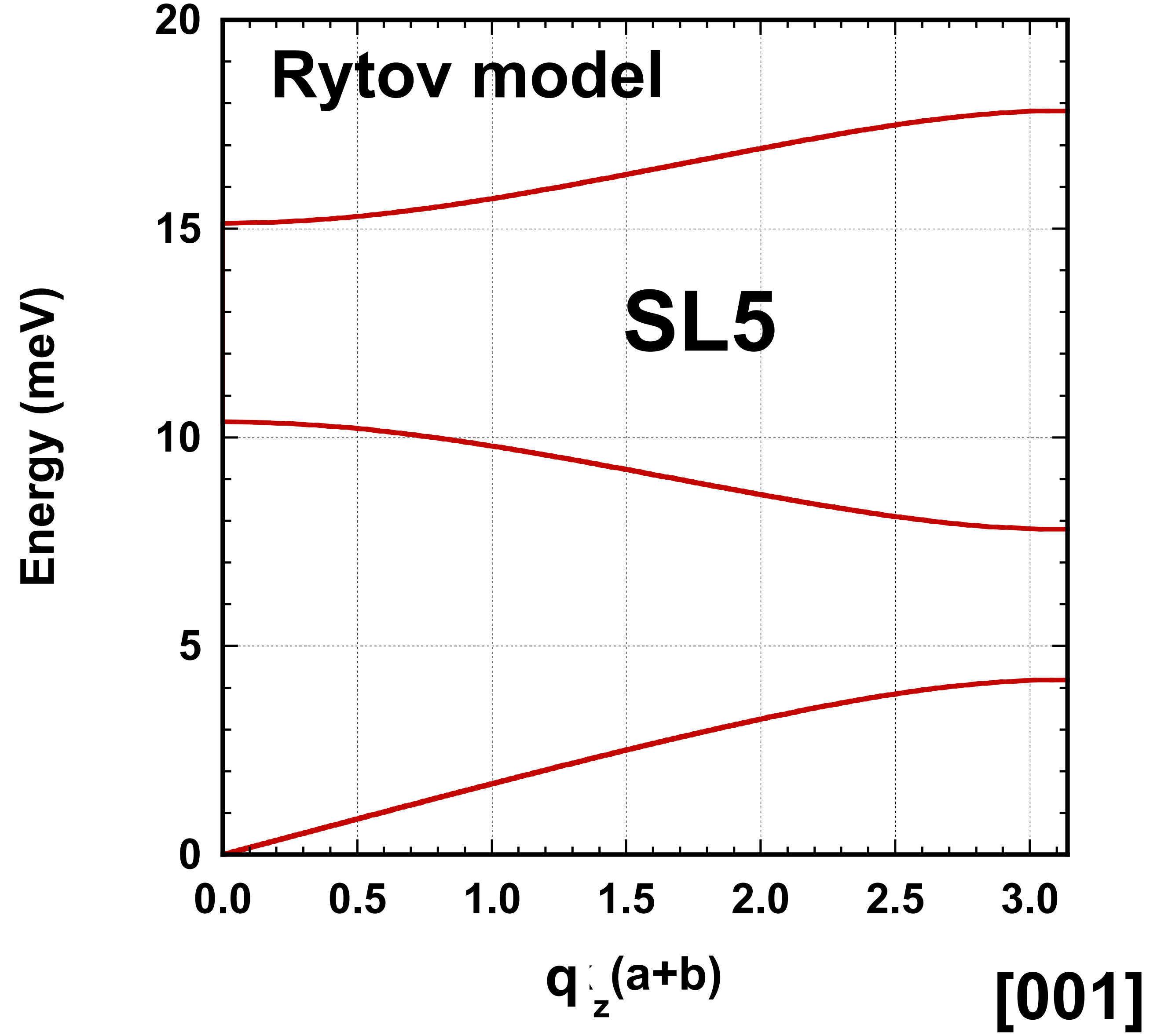


Electron and Phonon Dispersion

Holes (Electronic Dispersion)

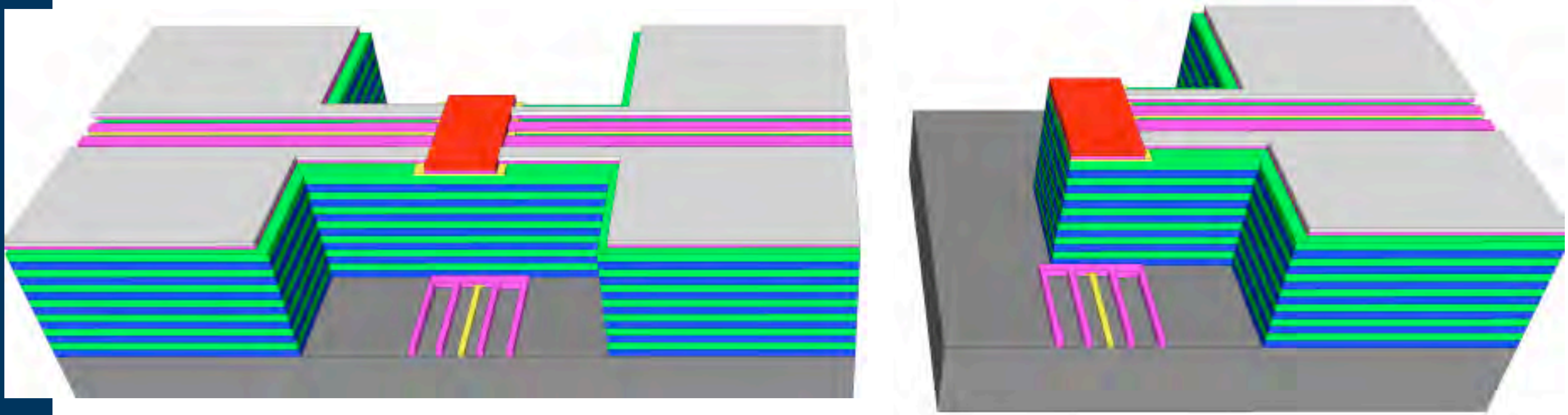


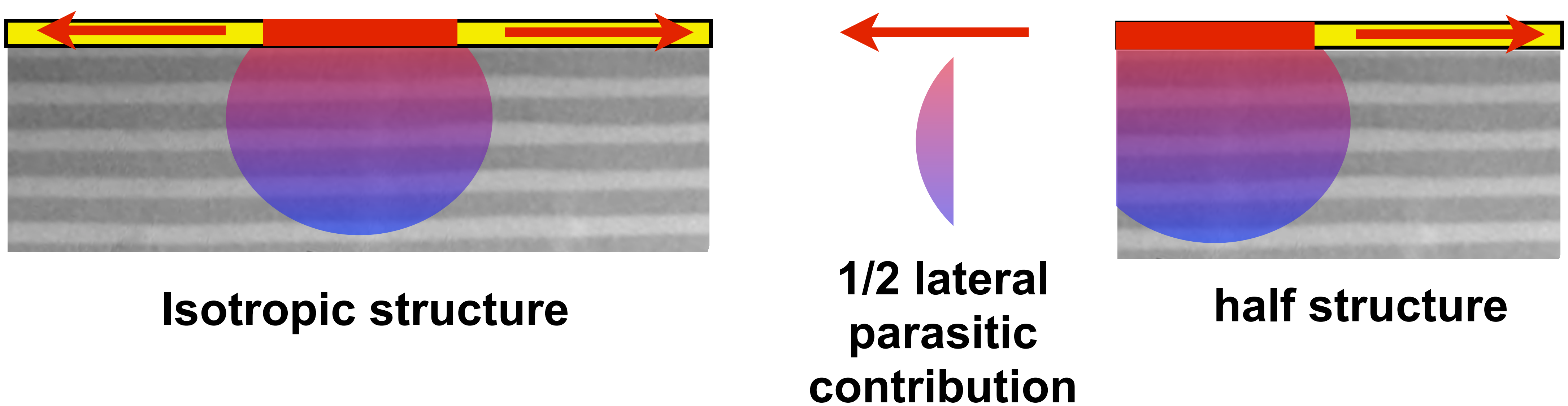
Phonon Dispersion



S.V. Rytov, Sov. Phys. Acoustics 2, 67 (1956)

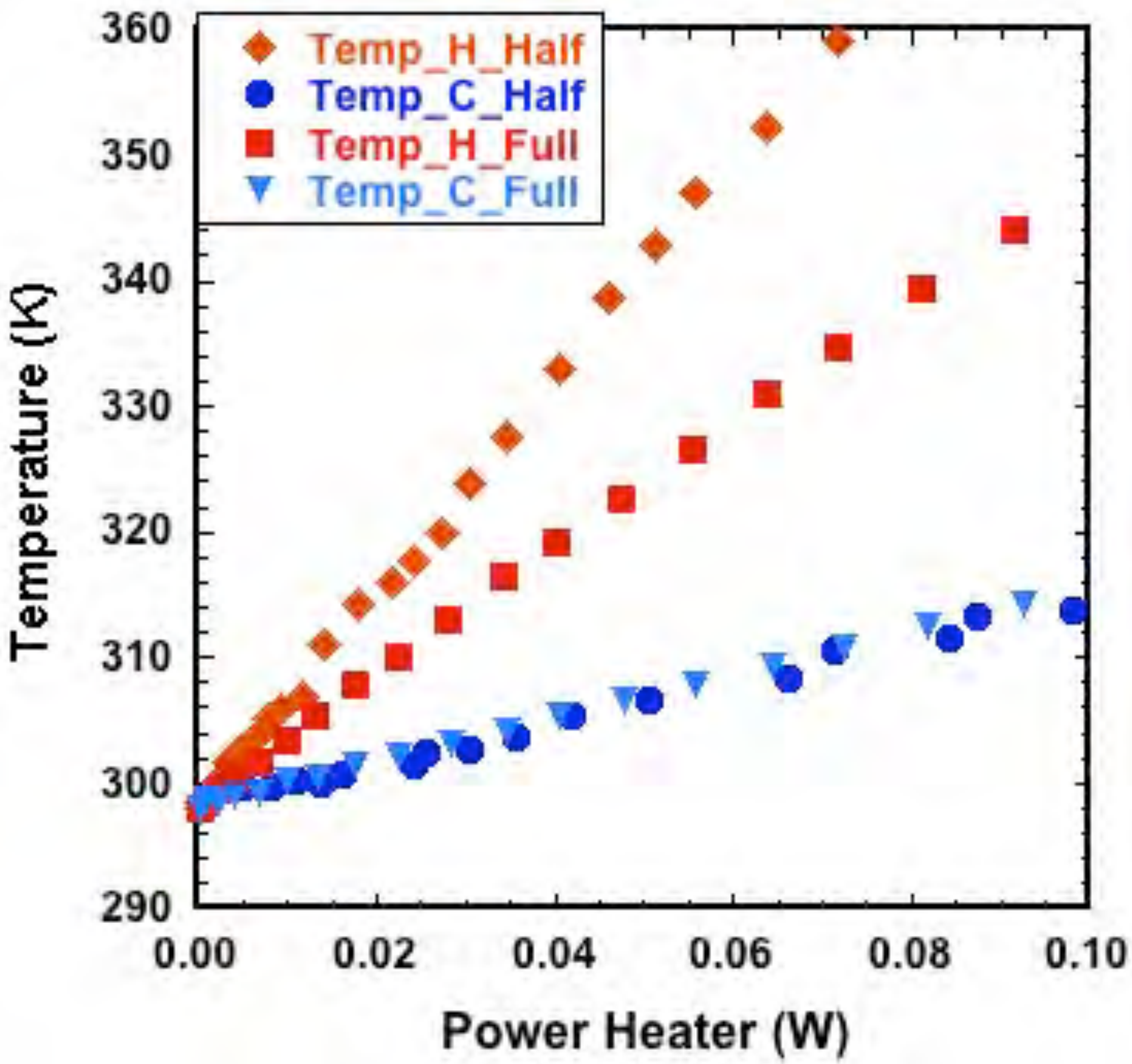
Thermal Parasitic Removal

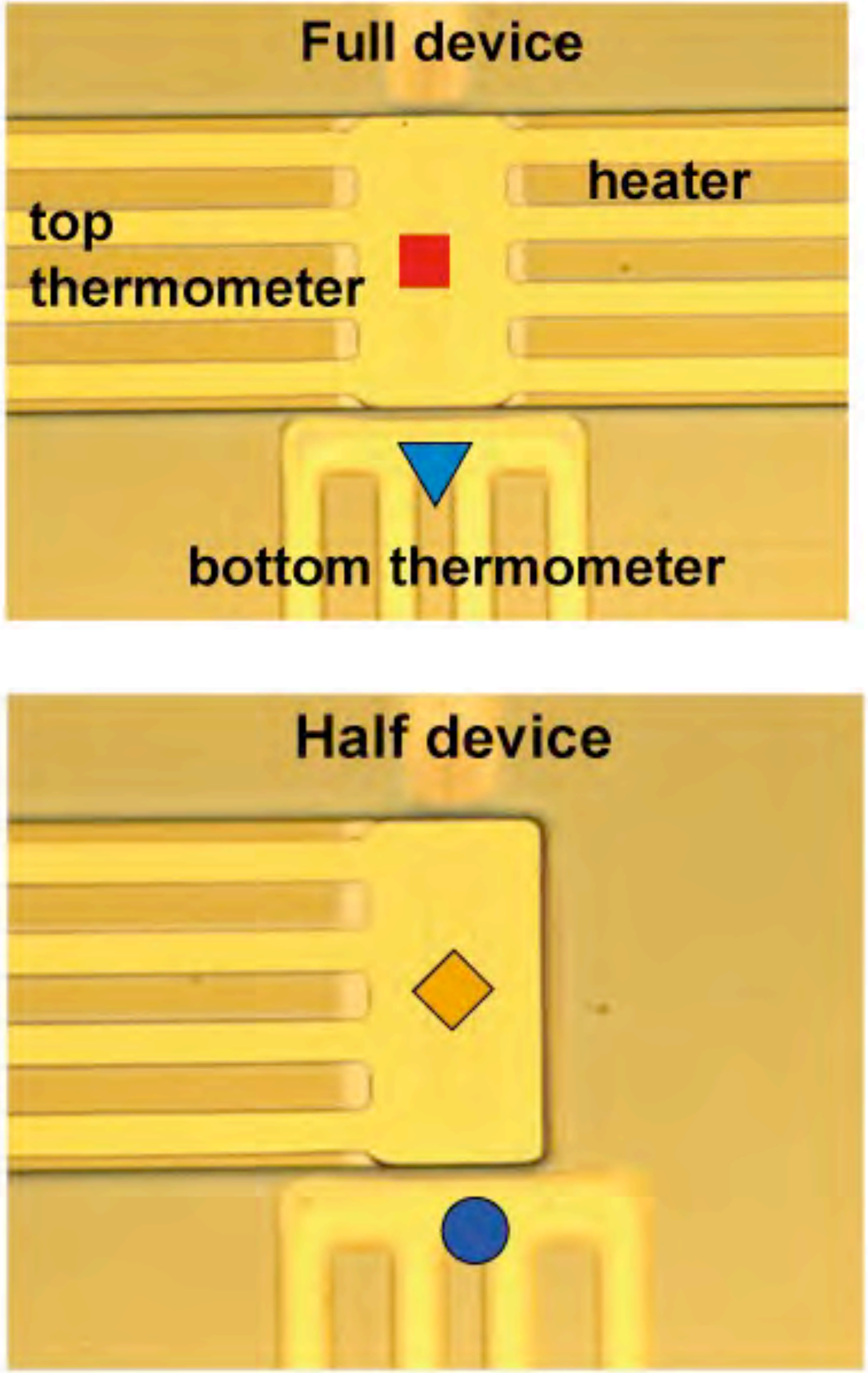




- Half structure allows parasitics to be measured and removed for more accurate heat flux determination

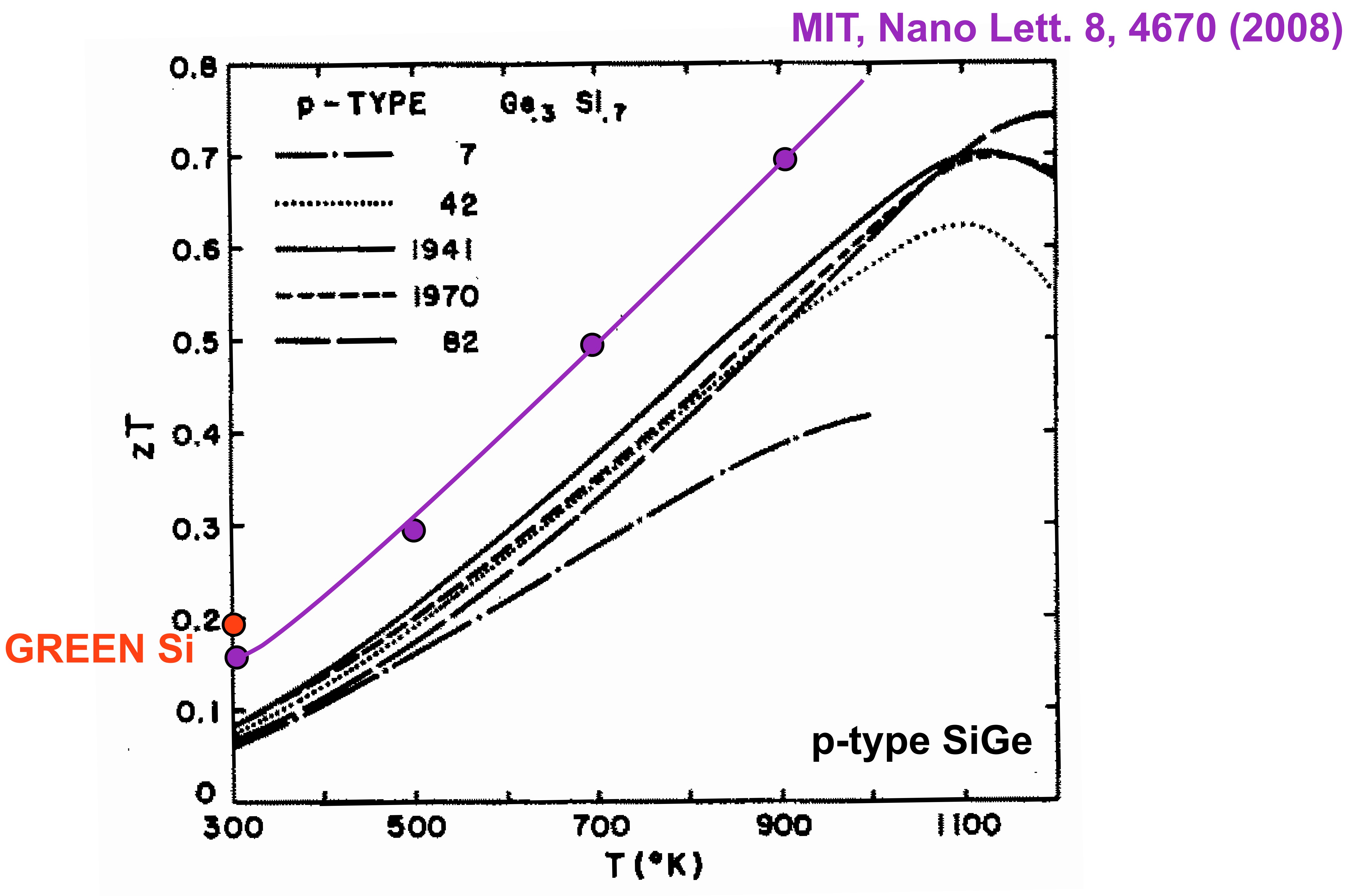
Thermal Measurements





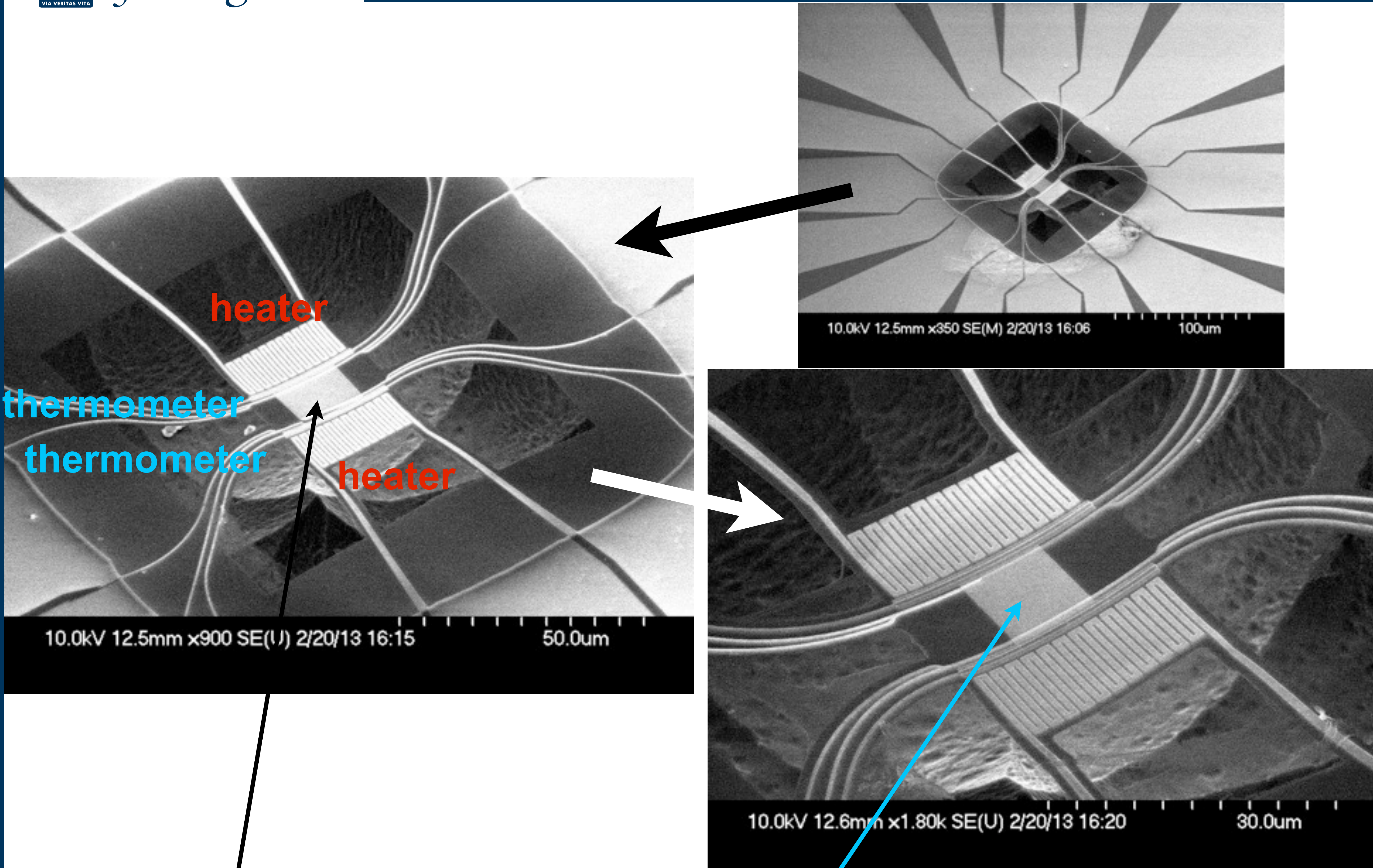
- Measured 41% of heat in vertical transport

Bulk SiGe ZT Comparisons



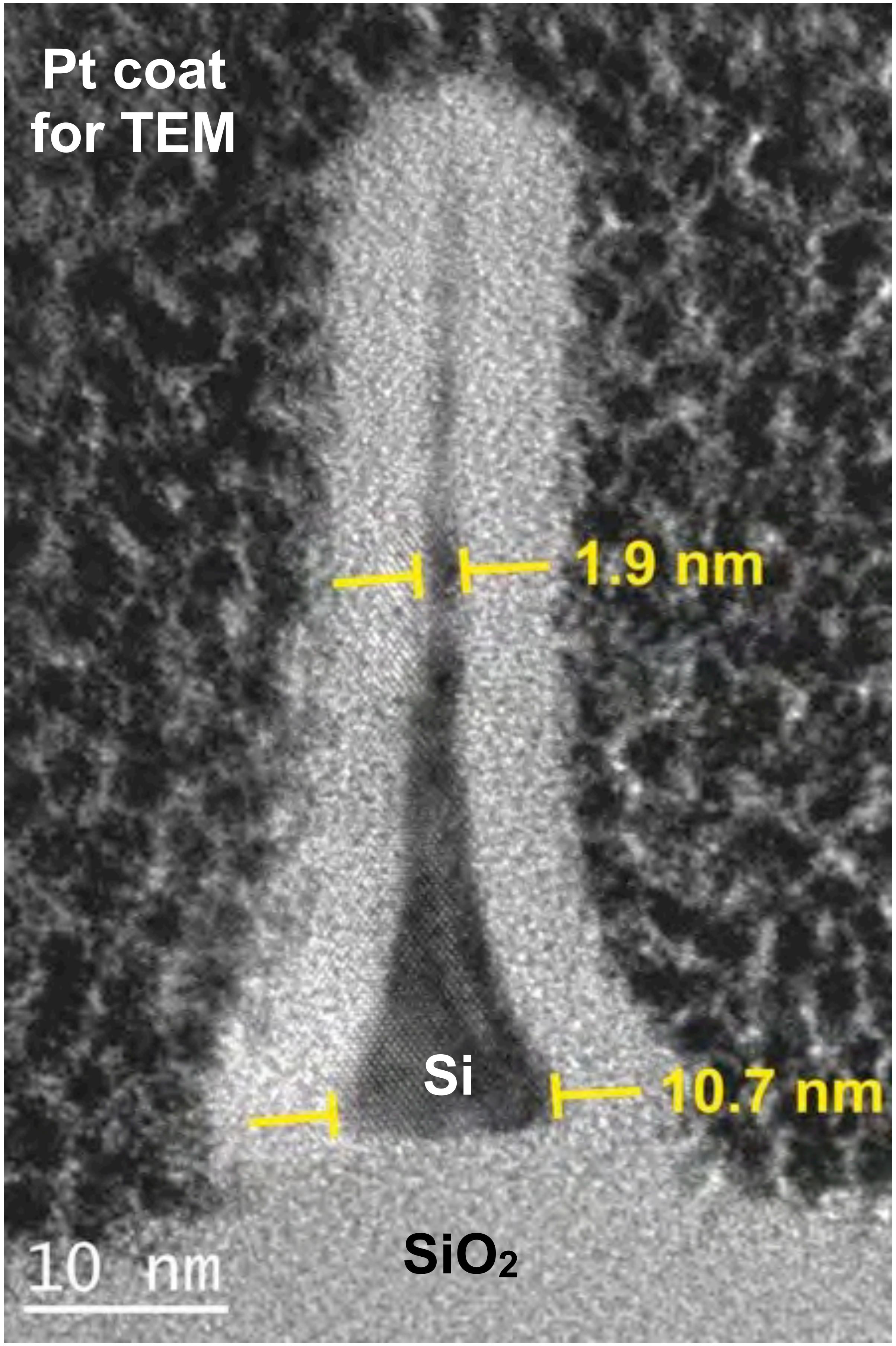
J.P. Dismukes et al., J. Appl. Phys. 35, 2899 (1964)

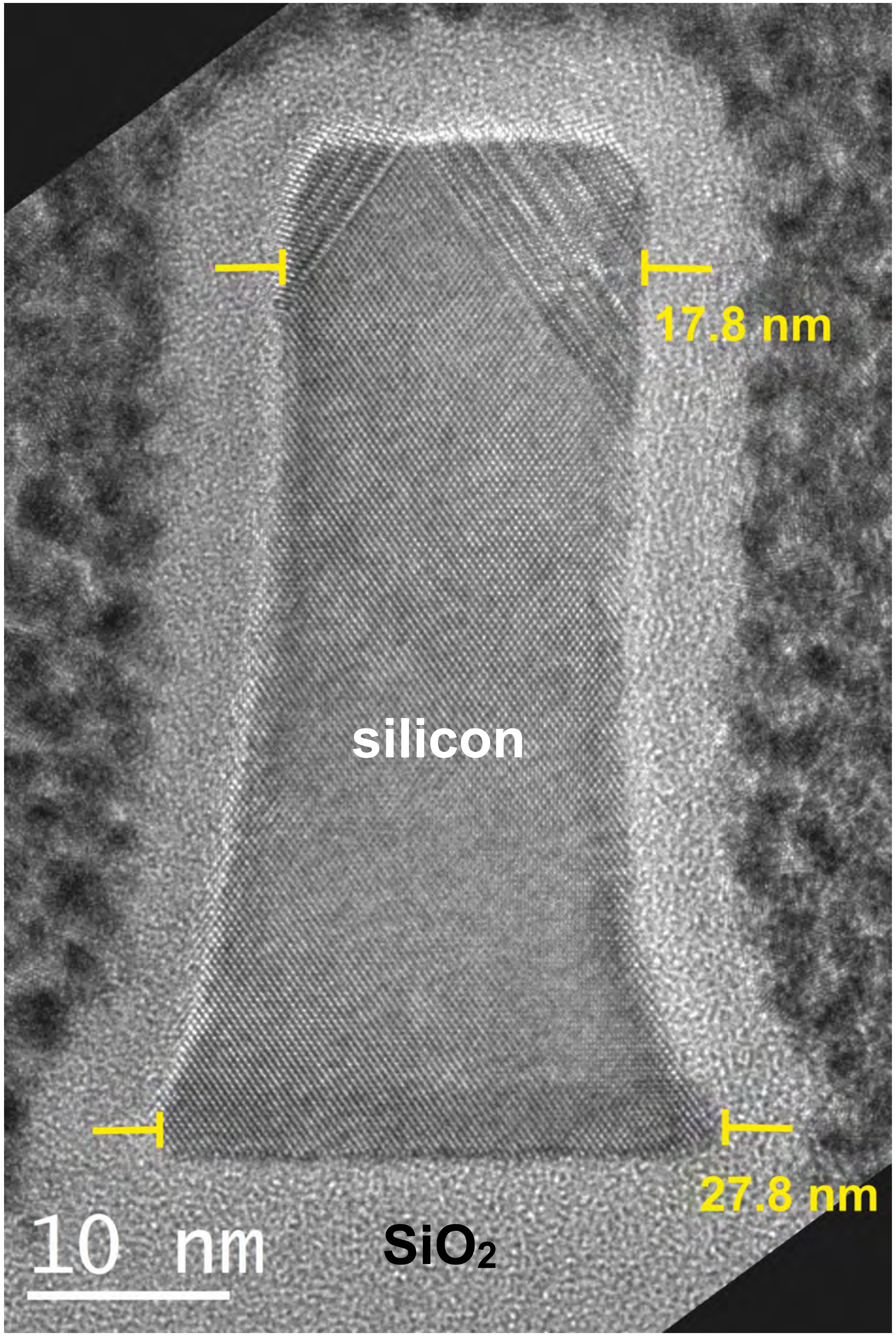
Nanowire Fabrication on Suspended Hall Bar



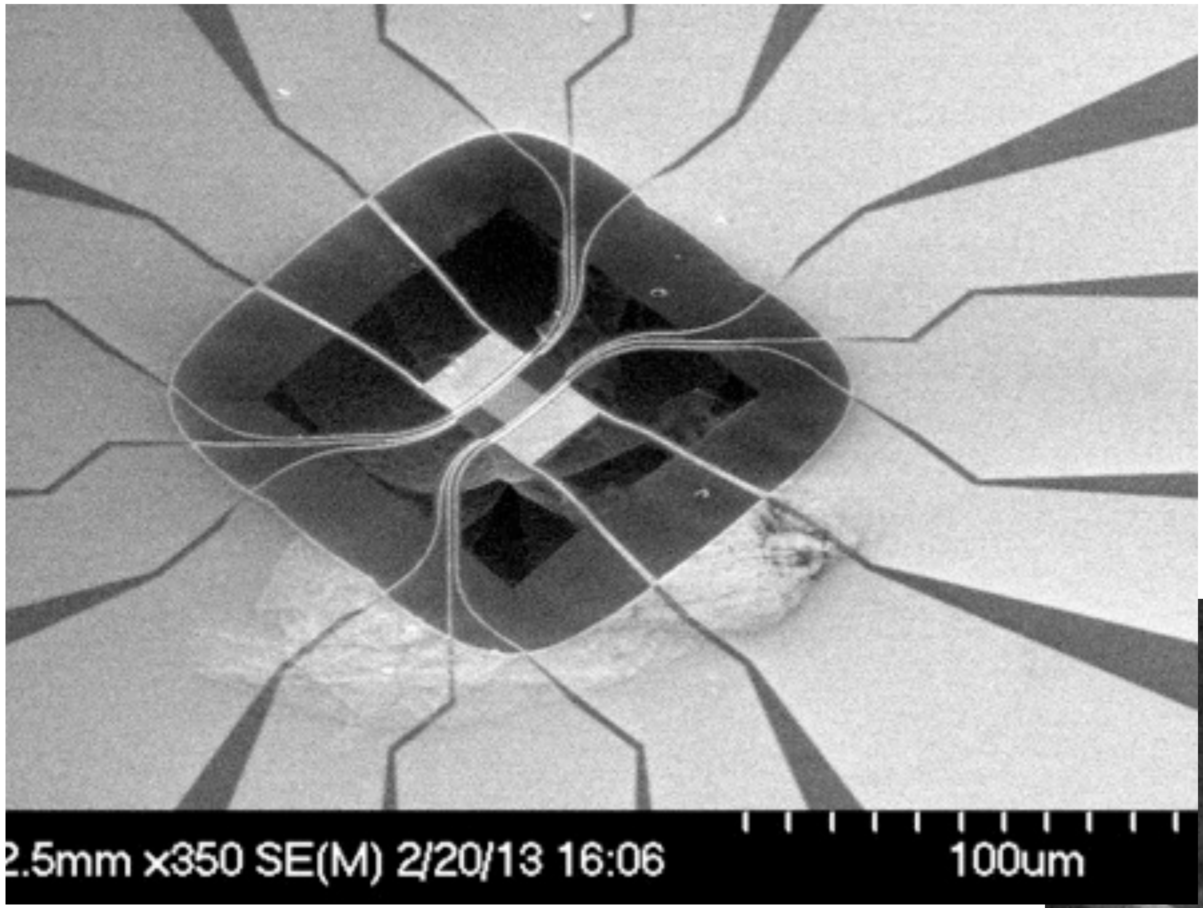
- **100 x 45 nm wide Si nanowires with integrated heaters, thermometers and electrical probes**

Si Nanowires: How many atoms wide?





45 nm Wide n-Silicon Nanowires

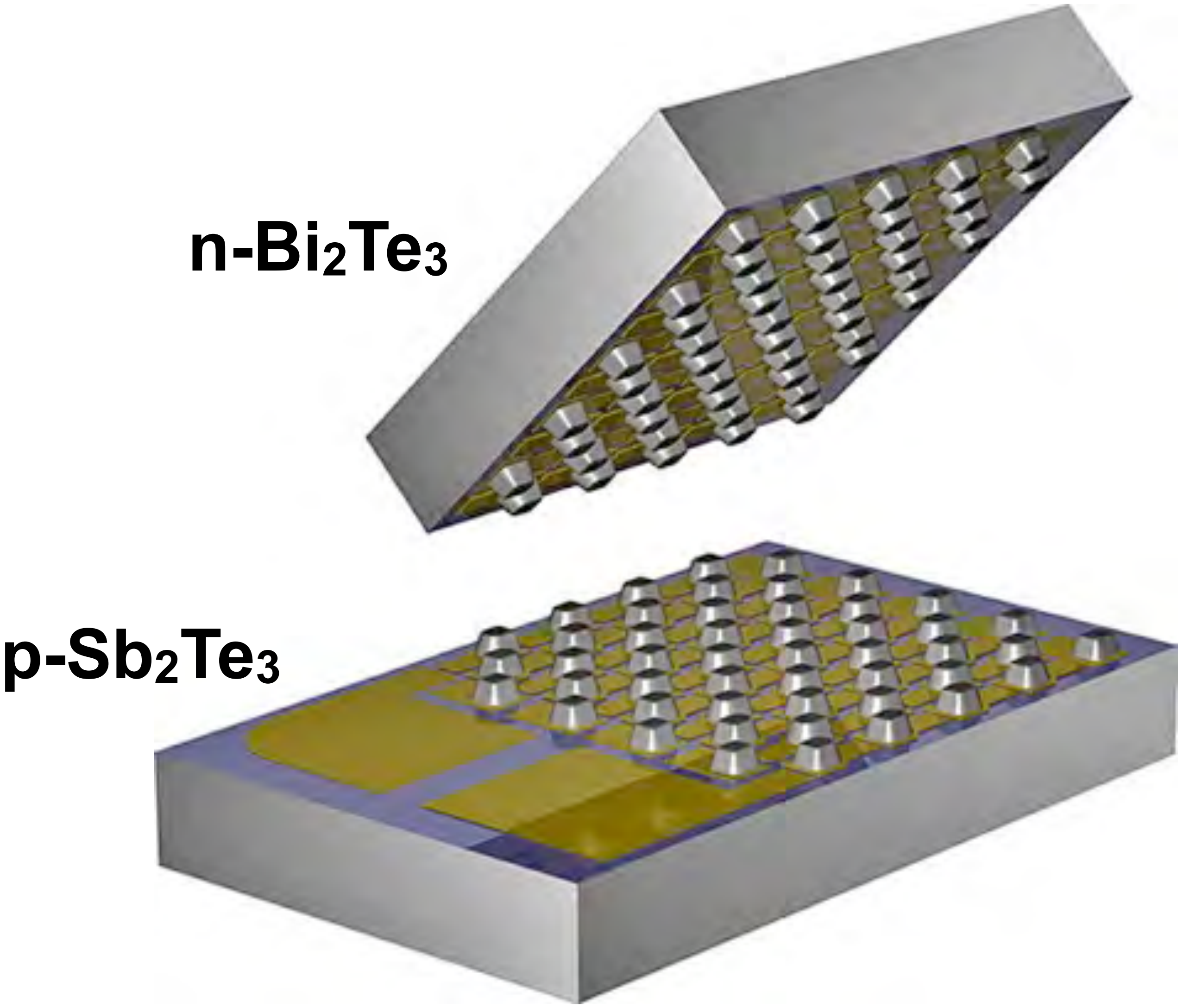


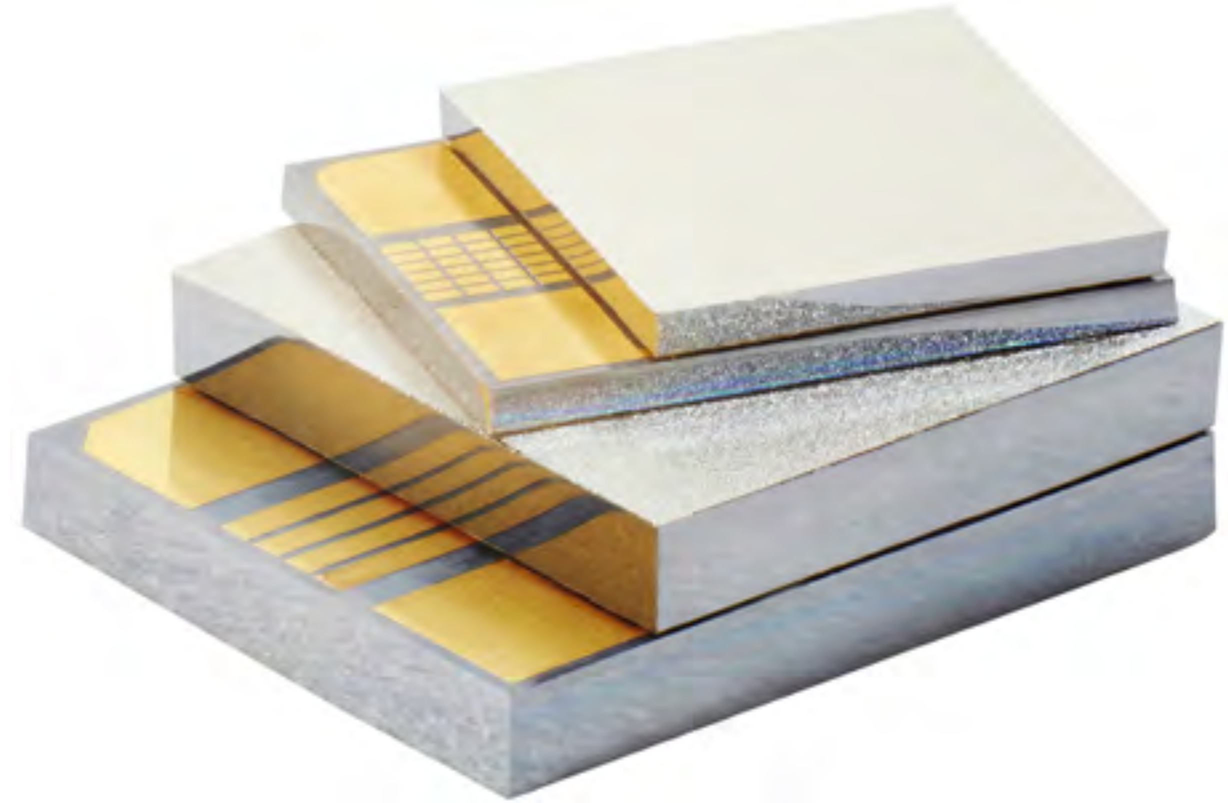
@ 300 K:

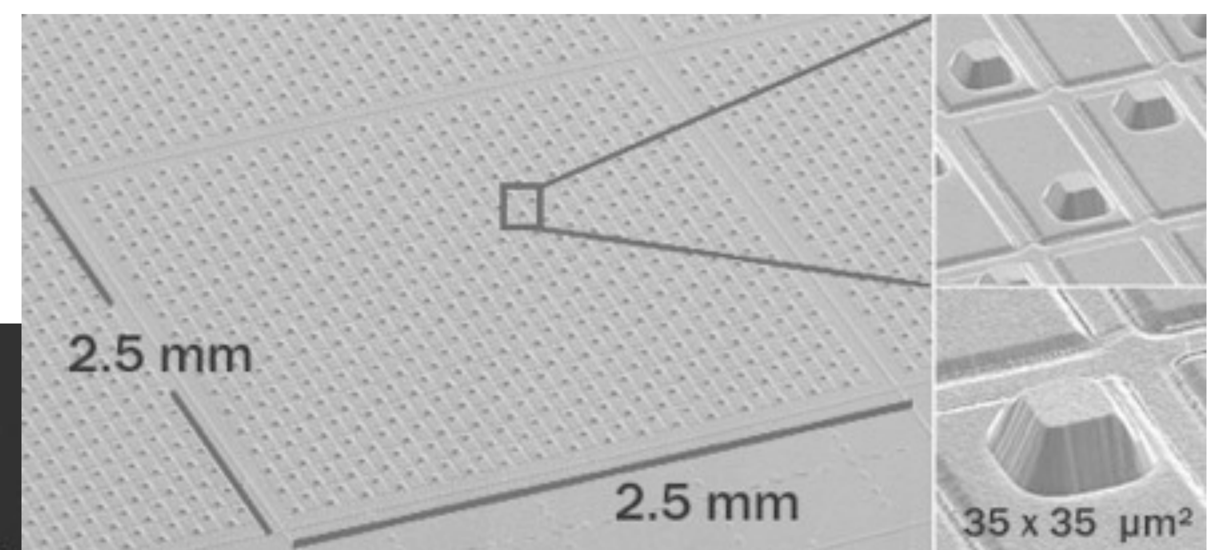
- σ = 20,300 S/m
  4 terminal
- κ = 7.78 W/mK
- α = –271 μV/K
- ZT = 0.057

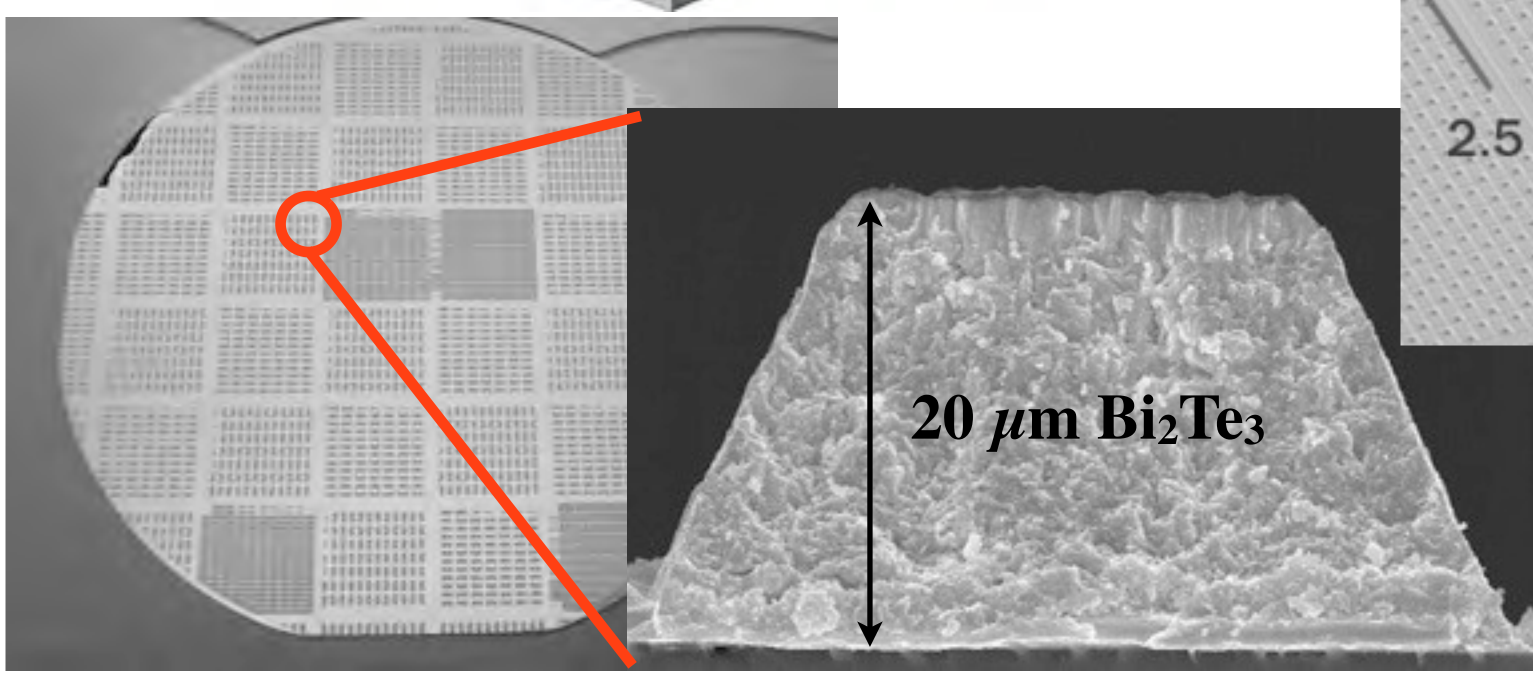
- ZT enhanced by x117
- $\alpha^2\sigma$ = 1.49 mW $m^{-1}K^{-2}$
- What enhancements with SiGe ?

Micropelt Microfabrication of BiTe Alloys



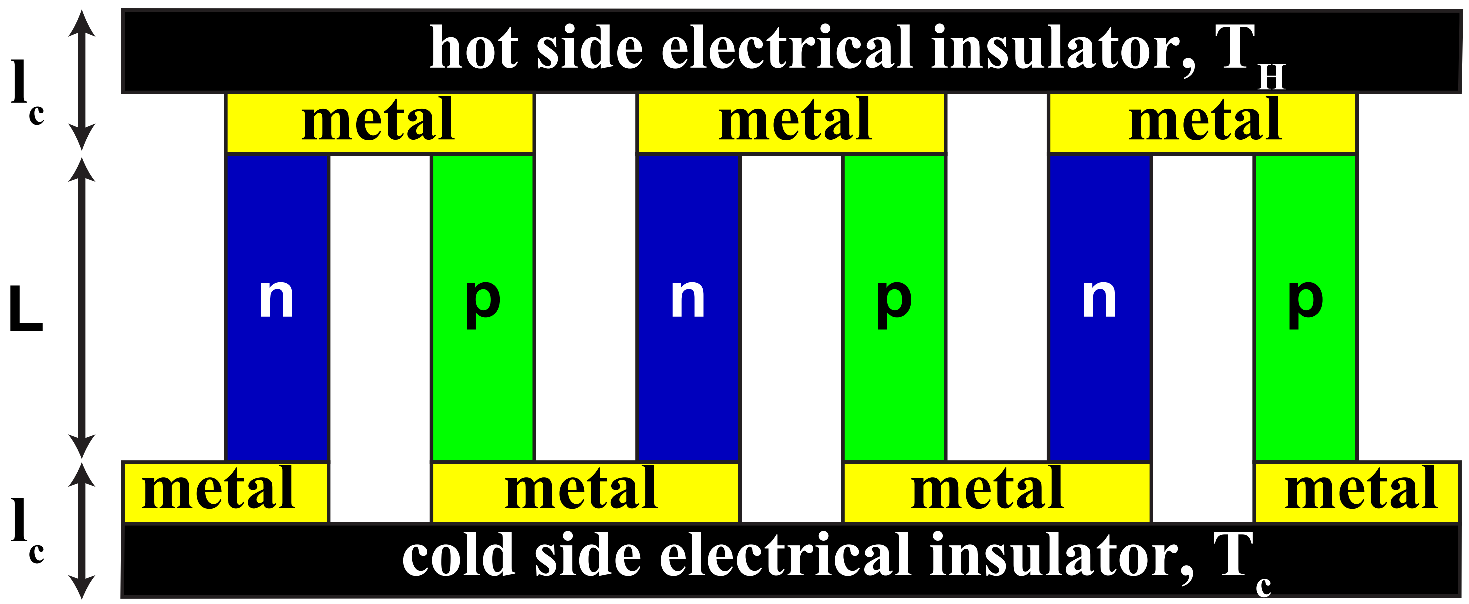






http://www.micropelt.com/

System Design: Power Output



A = module leg area

L = module leg length

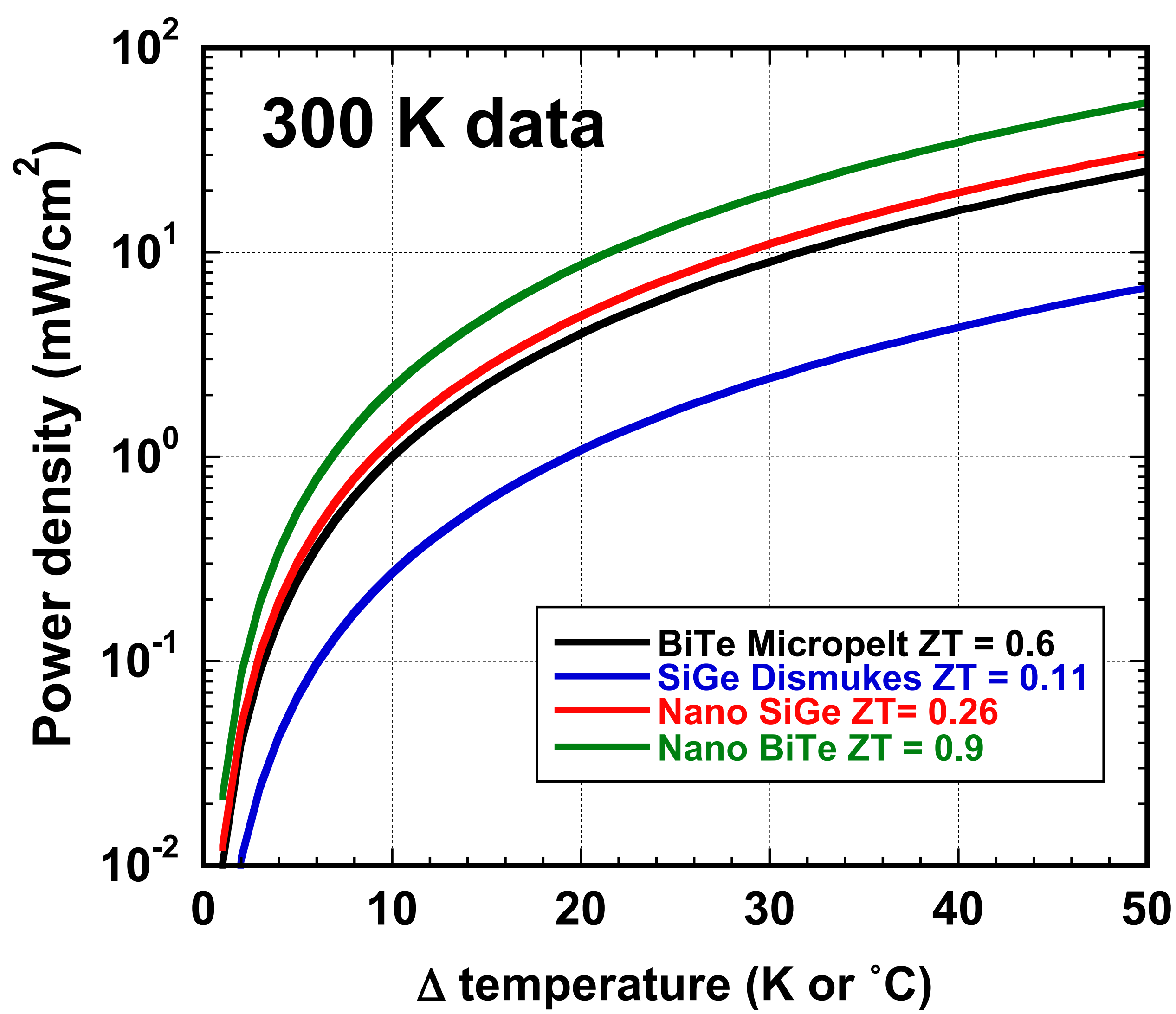
N = number of modules

κ_c = thermal contact conductivity

ρ_c = electrical contact resistivity

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

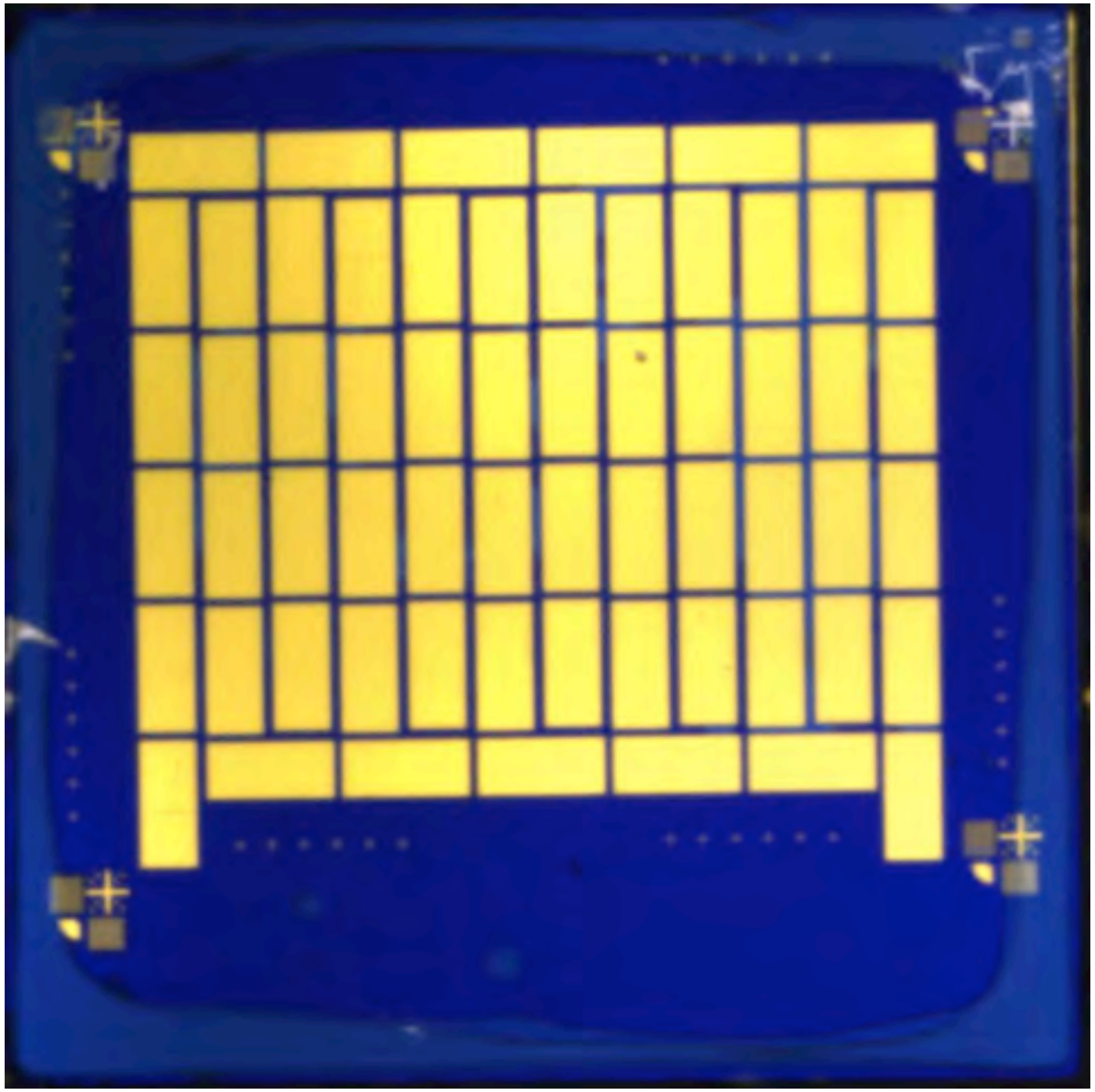
D.M. Rowe & M. Gao, IEE Proc. Sci. Meas. Technol. 143, 351 (1996)



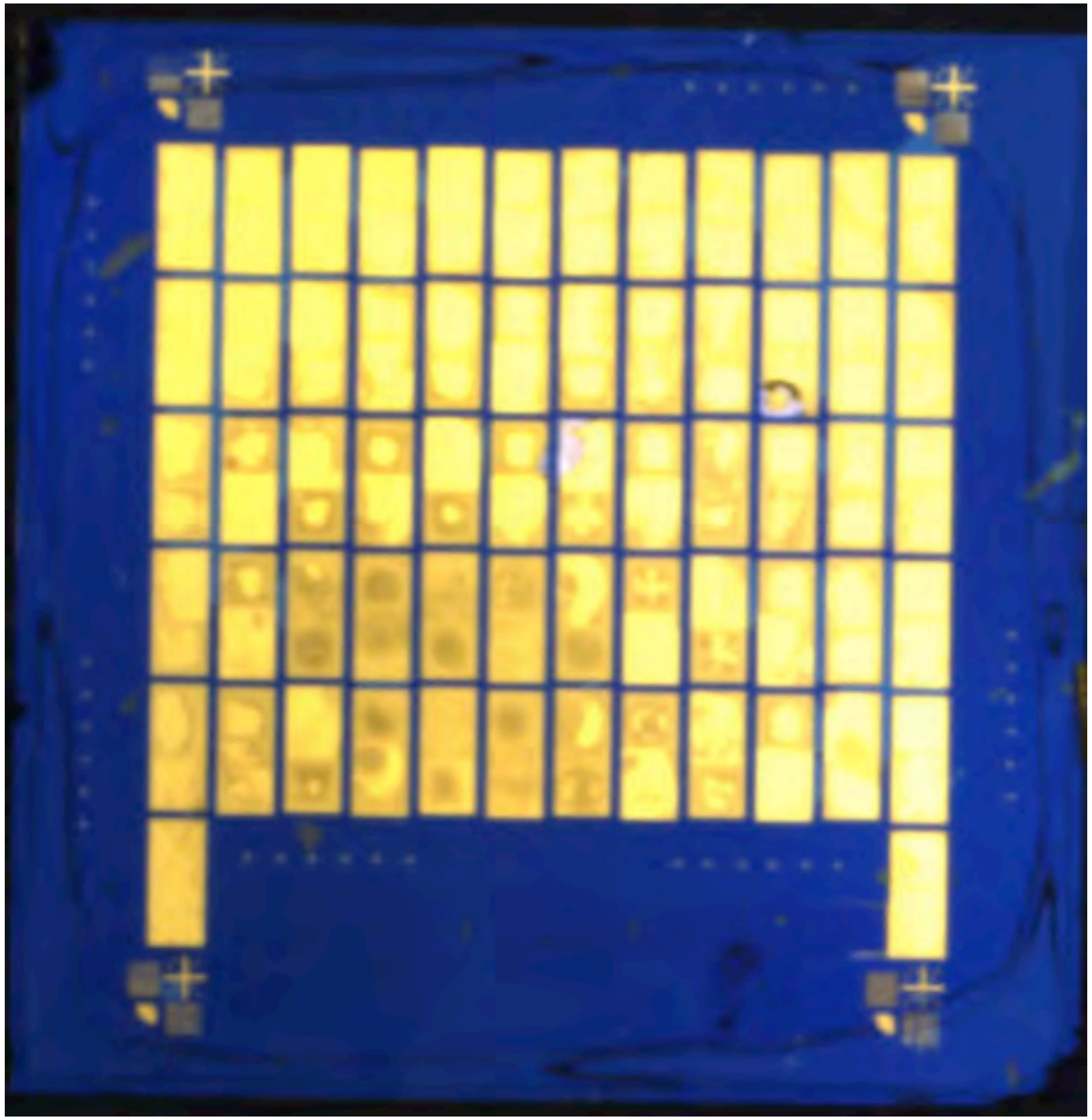
- System: power in BiTe alloys limited by Ohmic contacts
- ρ_c (Bi_2Te_3) ≅ 1 x 10^{-7} Ω-cm^2
- ρ_c ($Si_{1-x}Ge_x$) = 1.2 x 10^{-8} Ω-cm^2

122 Leg Modules

n-type



p-type



- Process tested and works well
- SOI growths now in progress for final modules

Thermoelectric References

- 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)

- D.J. Paul, "*Thermoelectric Energy Harvesting*" Intech Open Access from "ICT - Energy - Concepts Towards Zero - Power Information & Communication Technology " (2014) - DOI: 10.5772/57347

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