Introduction to Harvesting Thermal Energy

Prof Douglas Paul

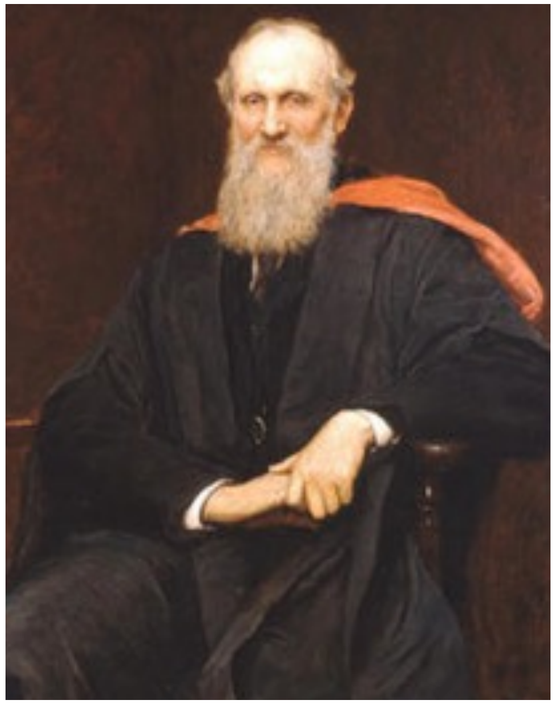
Director: James Watt Nanofabrication Centre
University of Glasgow
U.K.

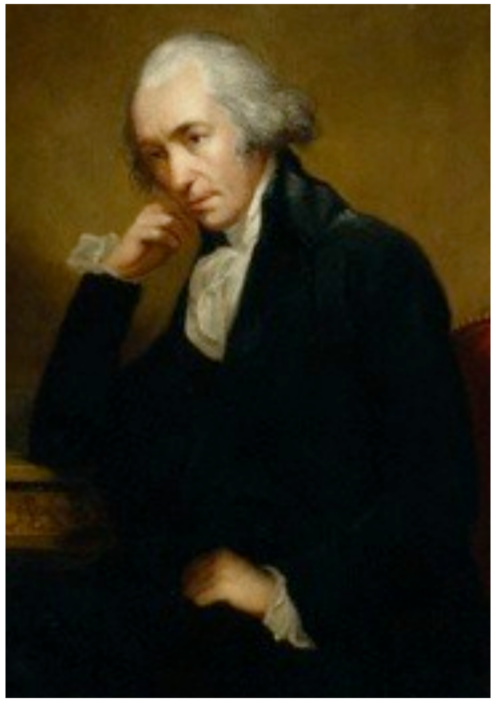
The University of Glasgow

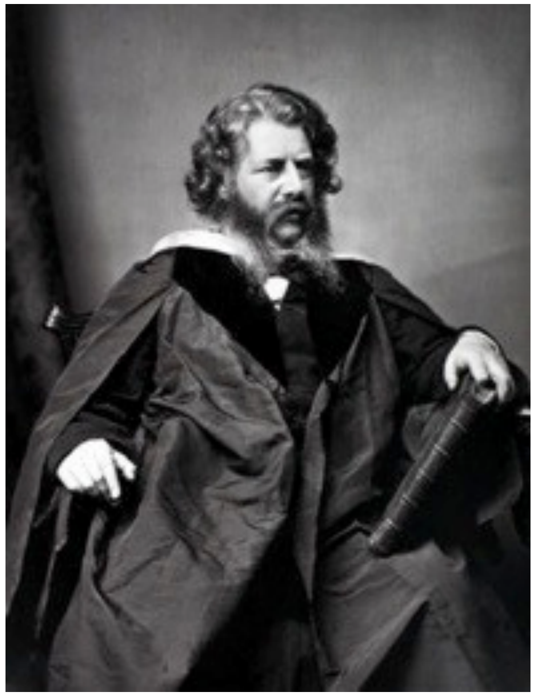
- Established in 1451
- 7 Nobel Laureates, 2 SI units, ultrasound, television, etc......
- 16,500 undergraduates, 5,000 graduates and 5,000 adult students
- £186M research income pa

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

Famous Glasgow Scholars

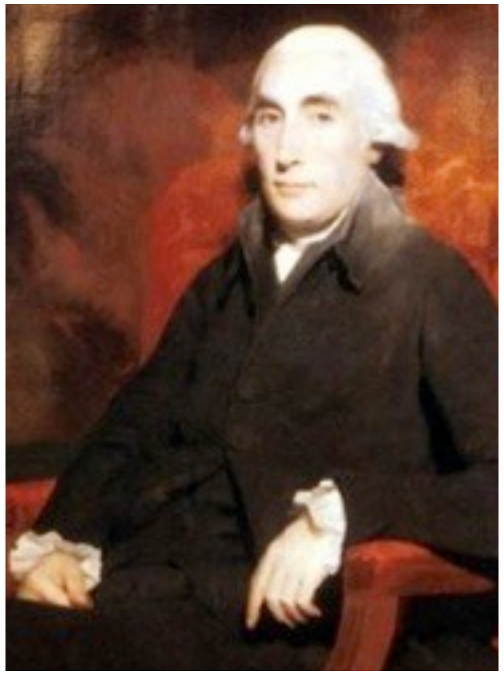

William Thomson (Lord Kelvin)


James Watt


William John Macquorn Rankine


Rev Robert Stirling


Rev John Kerr


Joseph Black


John Logie Baird

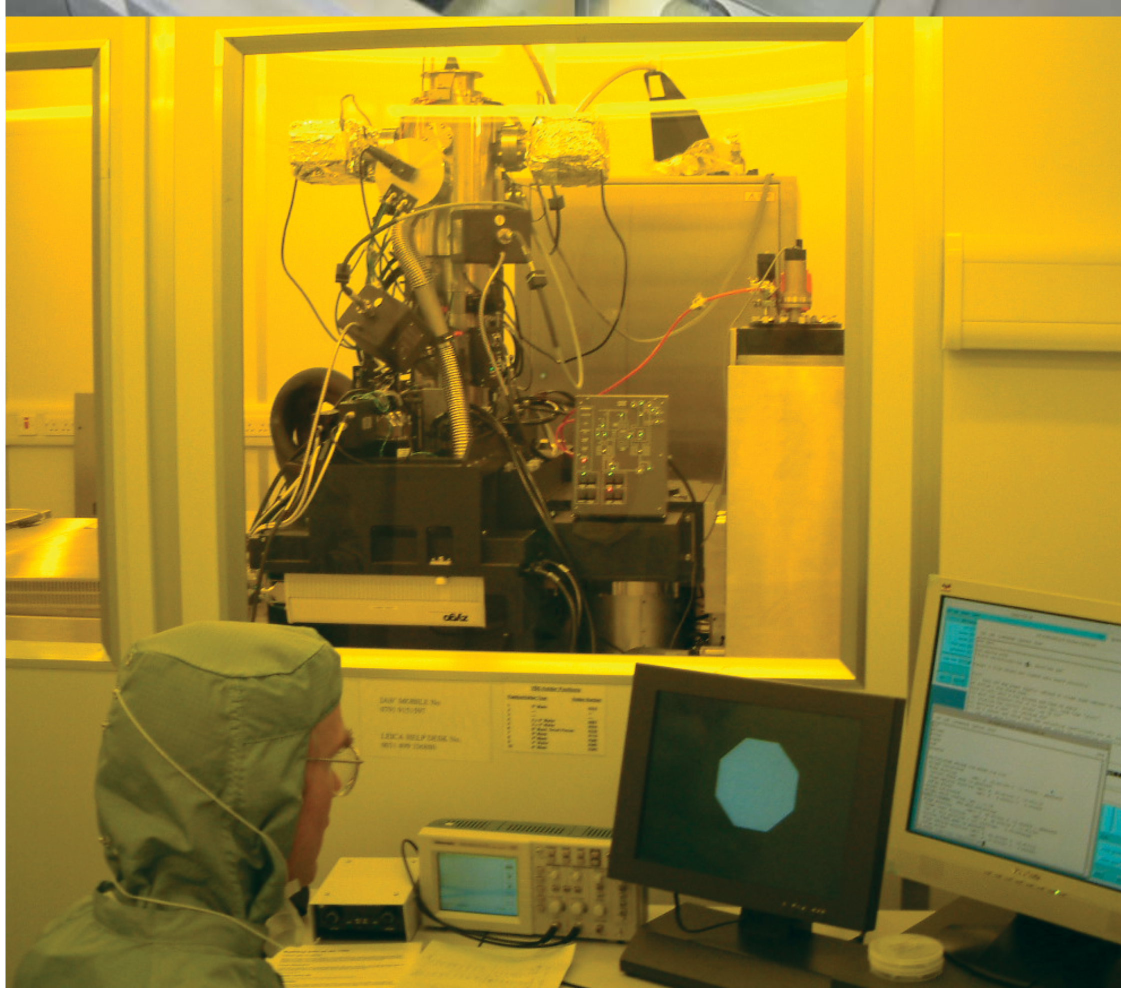

Adam Smith

James Watt's Laboratory

Many students and professors "with an interest in science" met in this "shop"

University of Glasgow

James Watt Nanofabrication Centre



University of Glasgow

James Watt Nanofabrication Centre @Glasgow

Vistec VB6

E-beam lithography

Süss MA6 optical lith

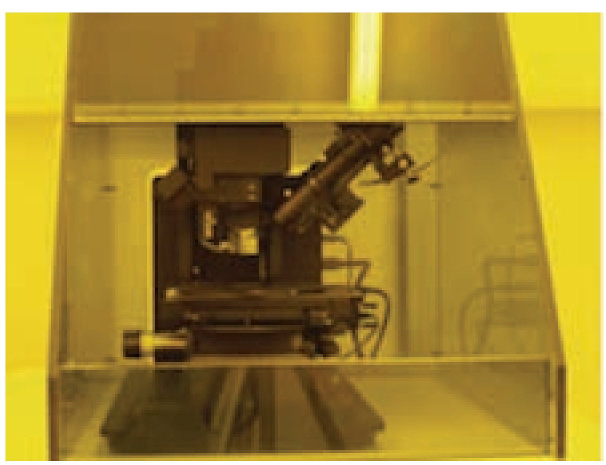
- 750m^2 cleanroom - pseudo-industrial operation
- 15 technicians + 4 PhD research technologists
- Processes include: III-V, Si/SiGe/Ge, magnetics, piezo, MMICs, photonics, metamaterials, MEMS, NEMS
- Part of EPSRC III-V National Facility & STFC Kelvin-Rutherford Facility
- Commercial access through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

8 RIE / 3 PECVD

6 Metal dep tools

4 SEMs: Hitachi S4700

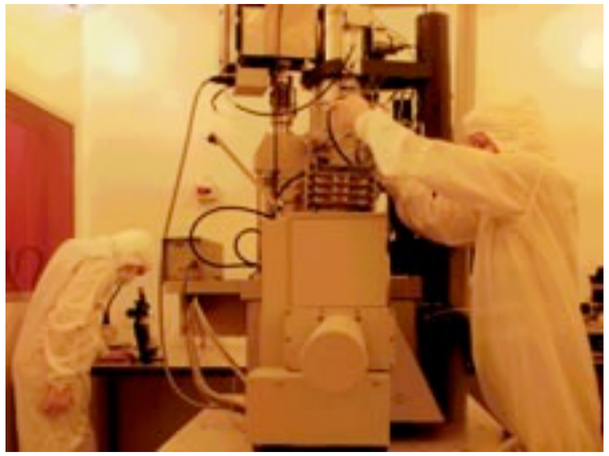
Veeco: AFMs



Electron Beam Lithography Capability

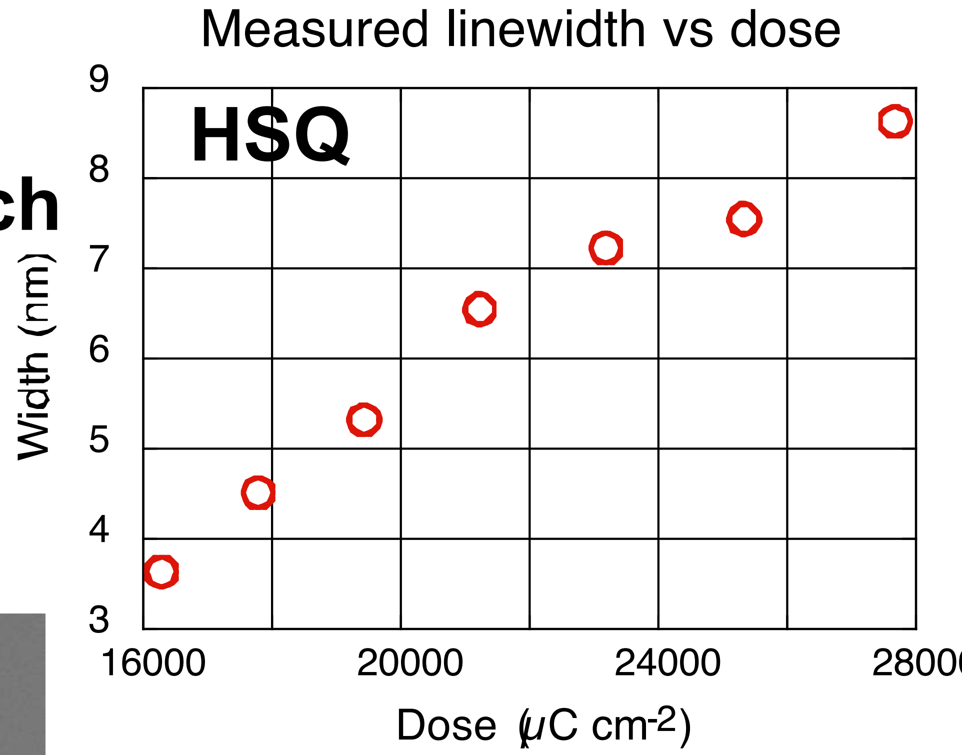
30 years experience of e-beam lithography

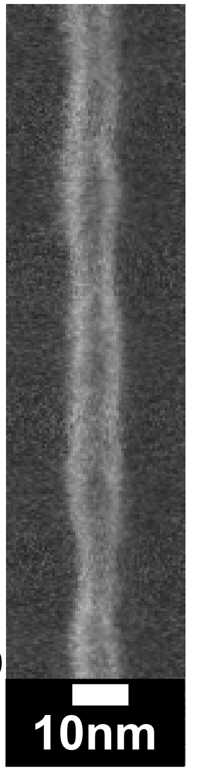
Vistec VB6

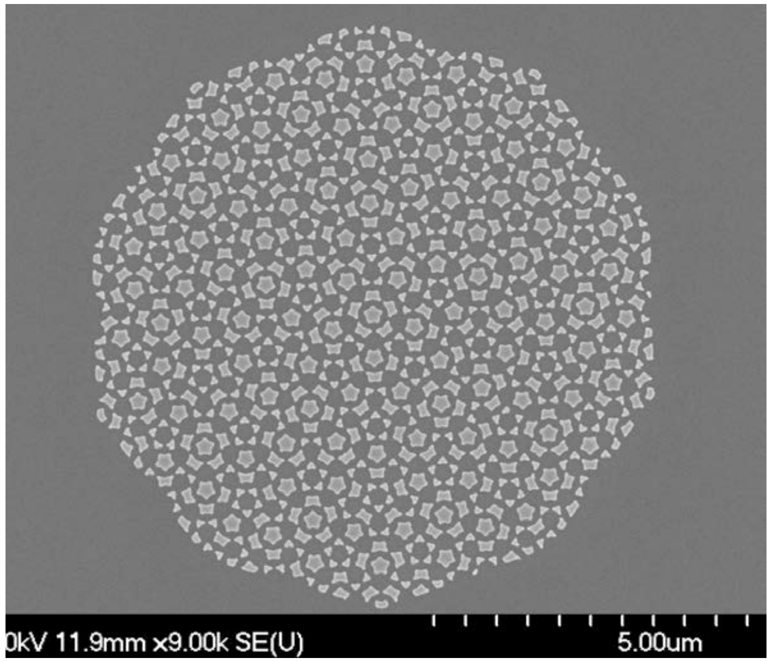


Vistec EBPG5

Sub-5 nm single-line lithography for research



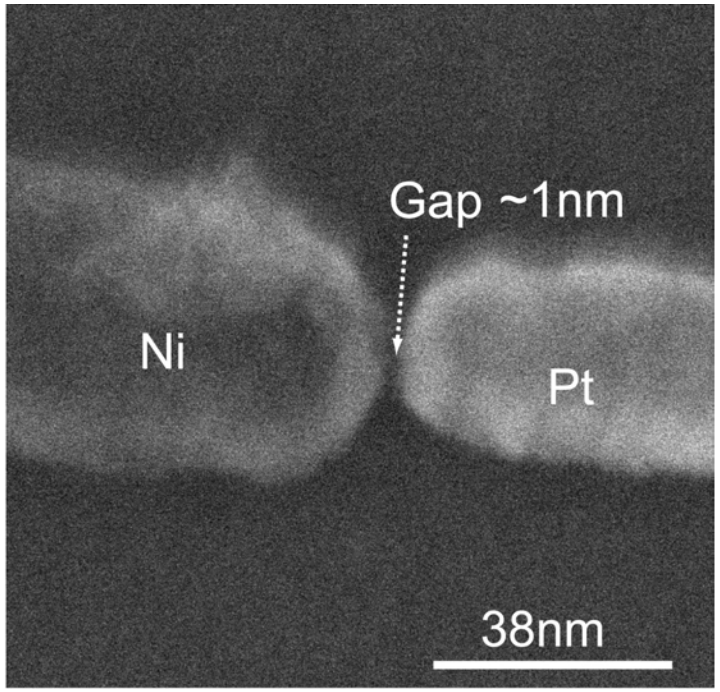




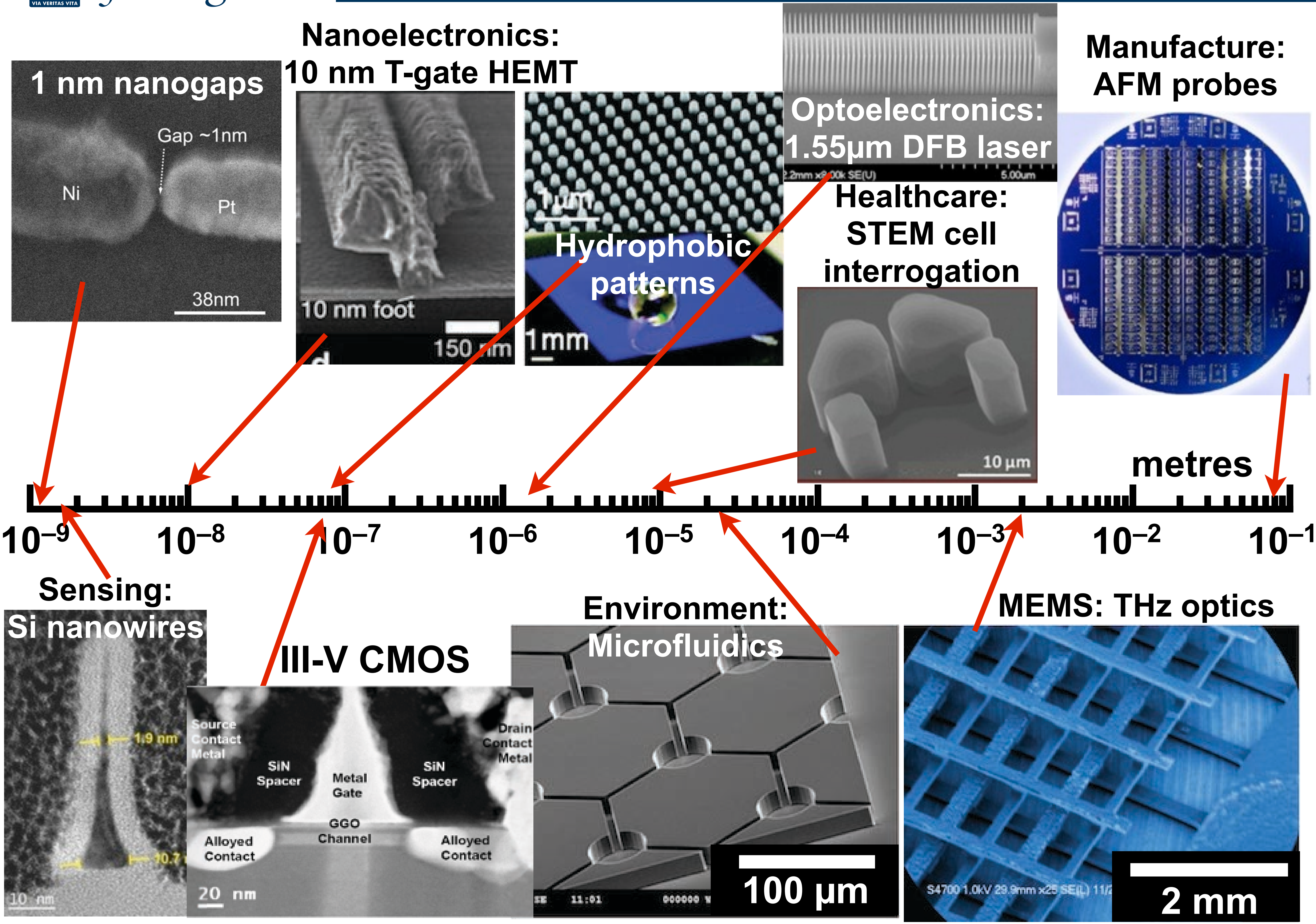
Penrose tile: layer-to-layer alignment 0.46 nm rms

Alignment allows 1 nm gaps between different layers:

–> nanoscience: single molecule metrology



Micro and Nanotechnology from Glasgow

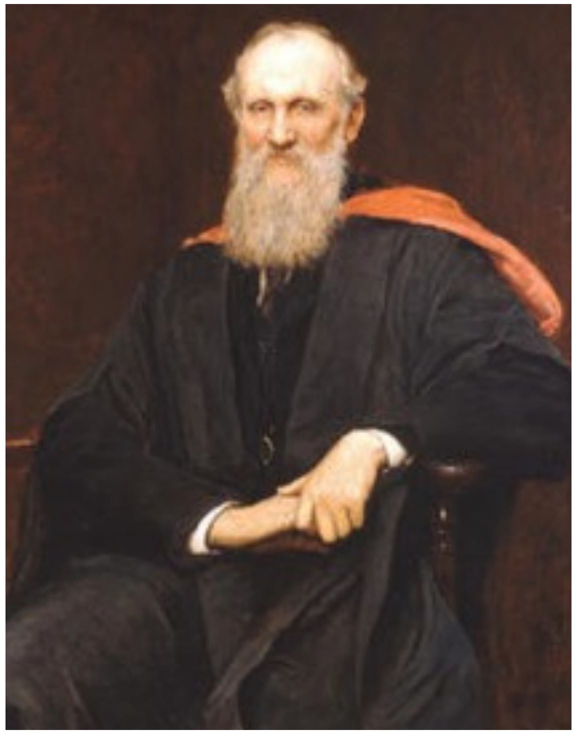


Thermoelectrics History

- History: Seebeck effect 1822

heat –> electric current

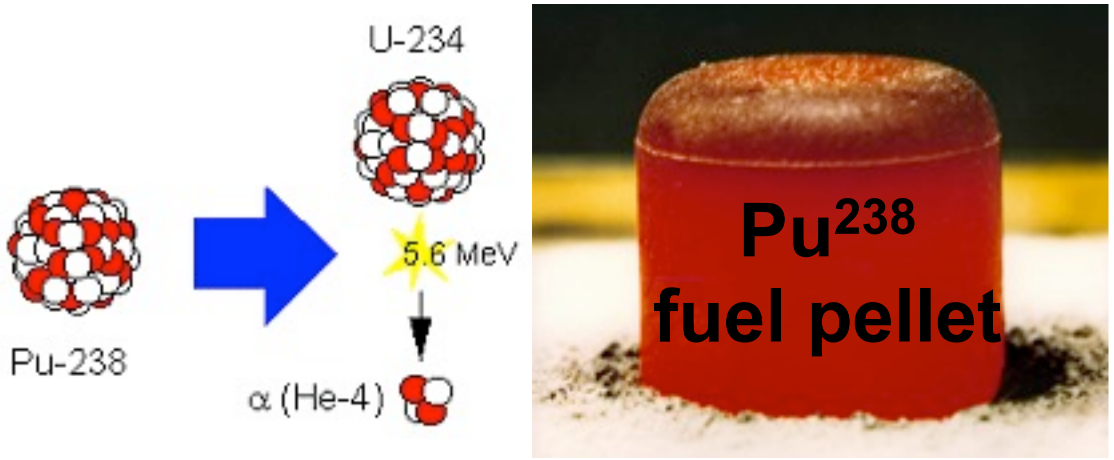
- Peltier (1834): current –> cooling

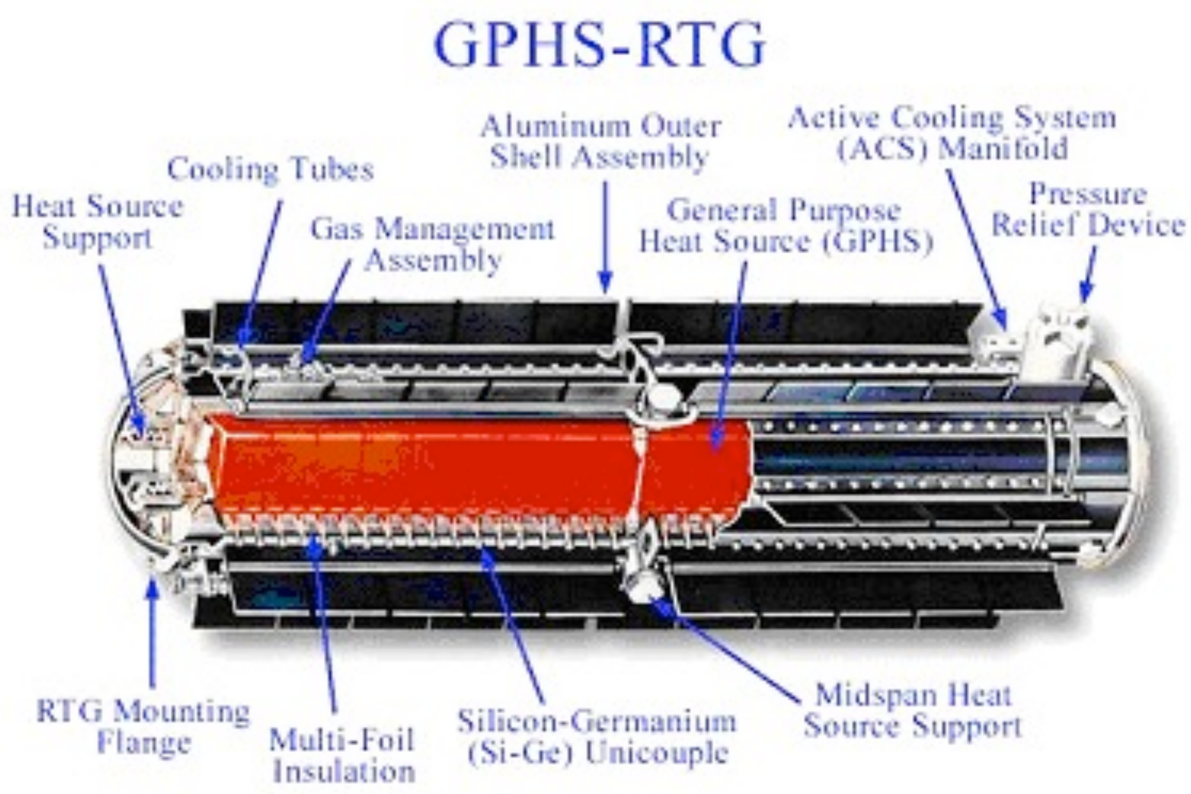


- Thomson effect: Thomson (Lord Kelvin) 1852

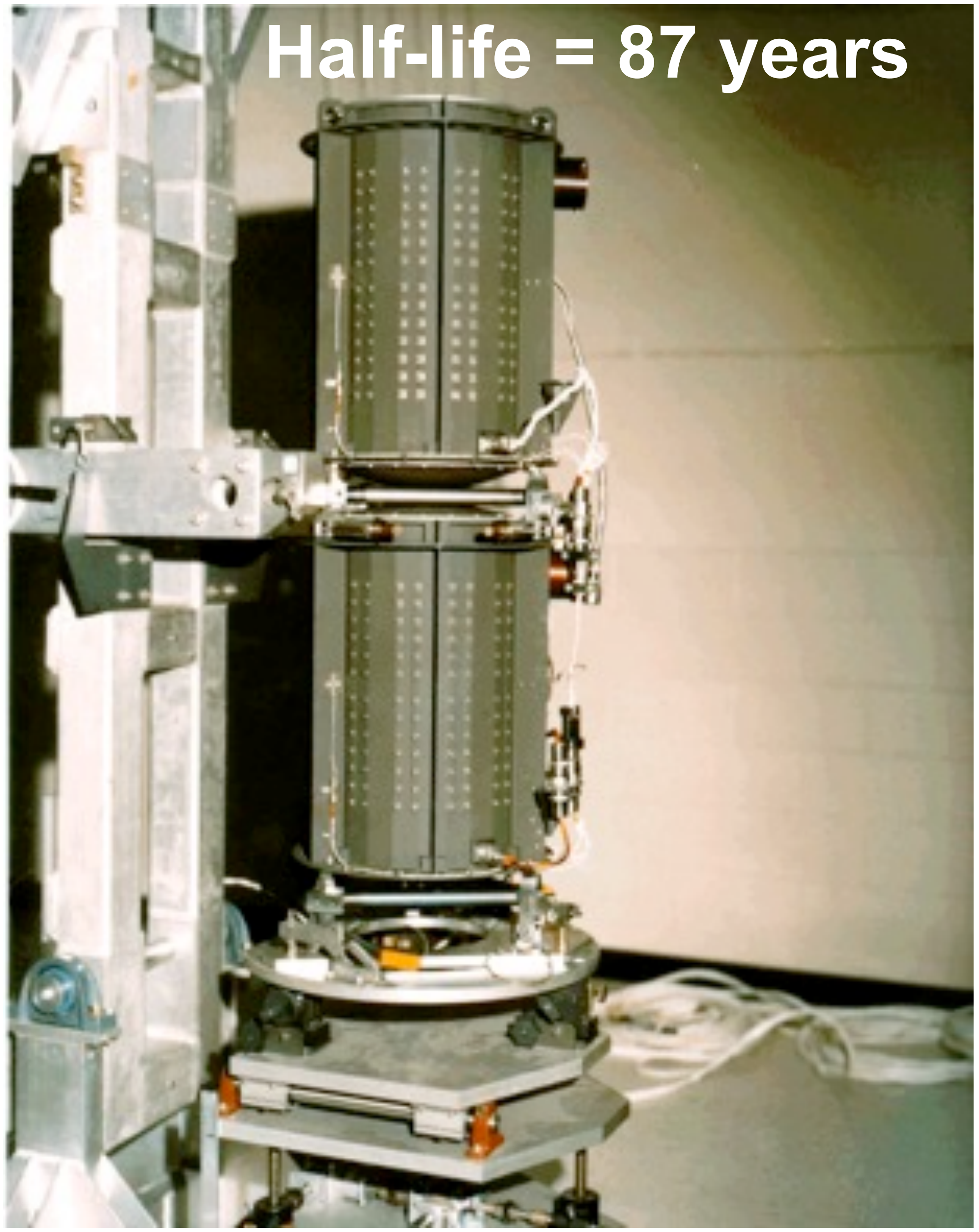
NASA Radioisotope Thermoelectric Generator

Radioisotope heater –> thermoelectric generator –> electricity





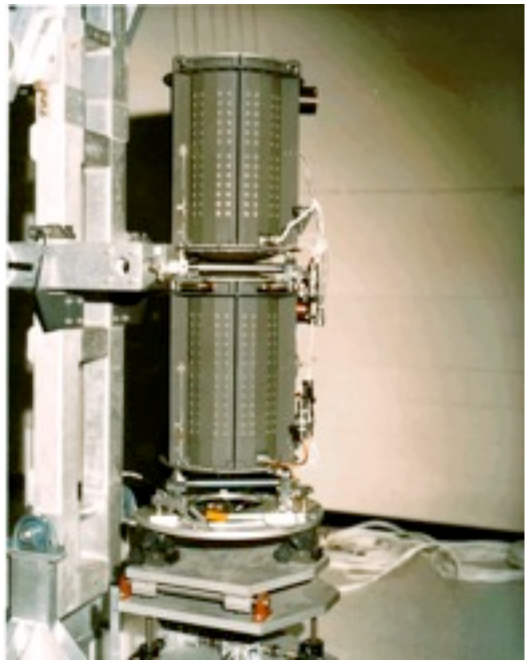
Voyager – Pu^{238}



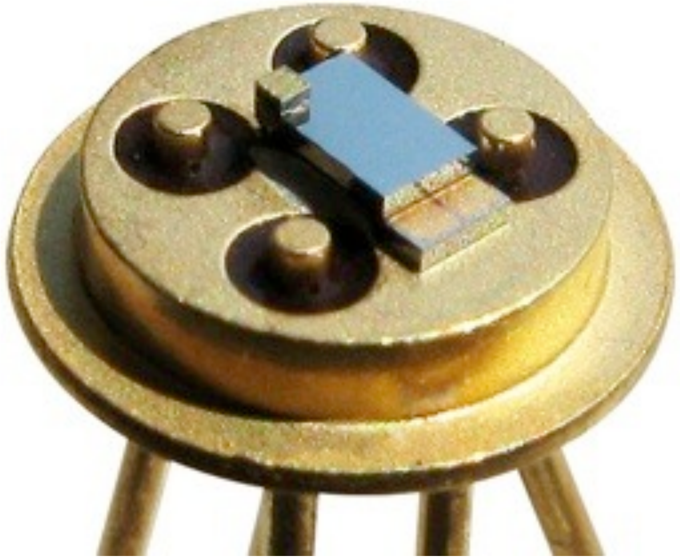
- **470 W @ 30 V on launch, after 35 years power =** $470 \times 2^{-\frac{35}{87}}$ **= 355 W**

Thermoelectric Applications

NASA Voyager I & II

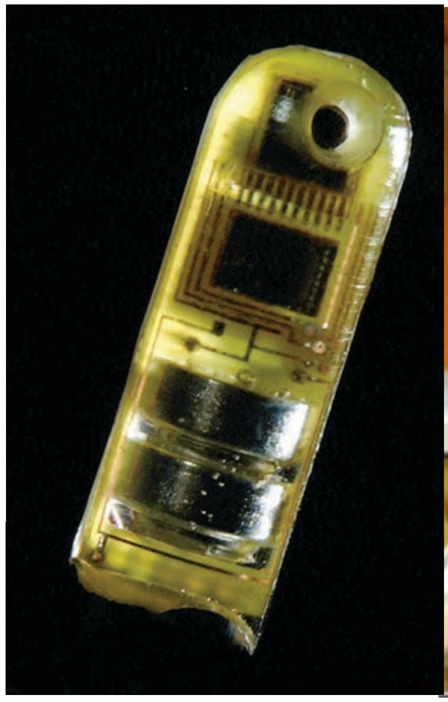


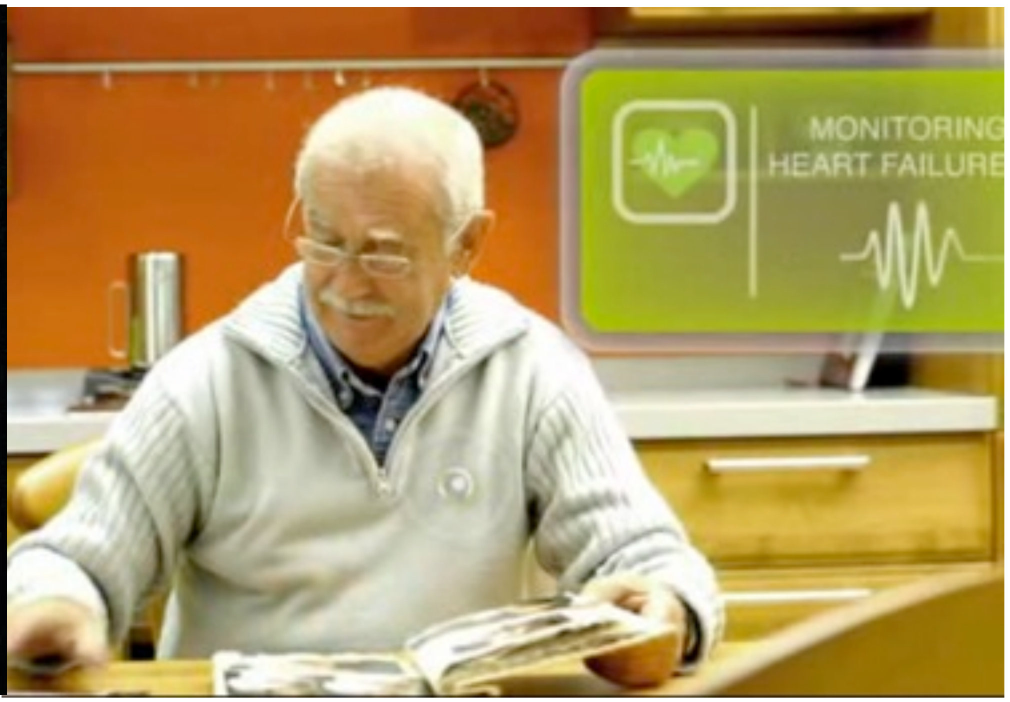
Peltier cooler: telecoms lasers



Cars: replace alternator

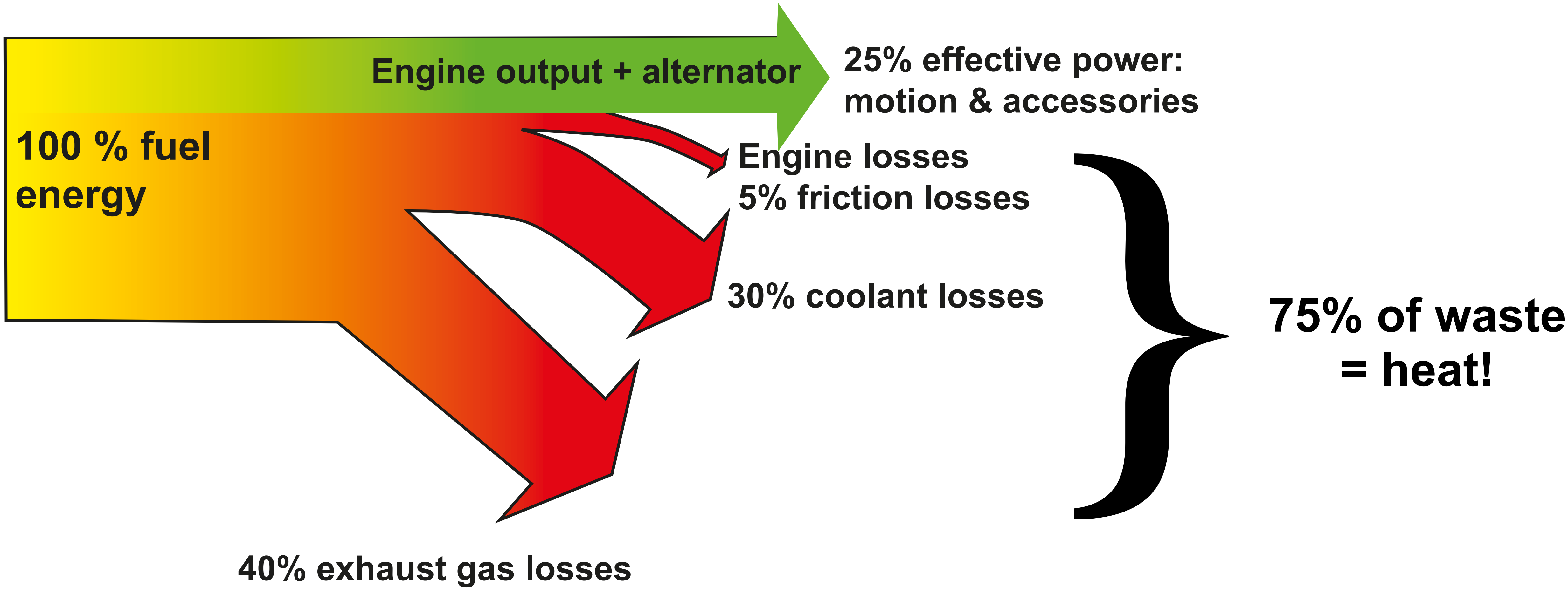
Temperature control for CO_2 sequestration





Powering autonomous sensors: ECG, blood pressure, etc.

Thermoelectric Energy Harvesting in Cars

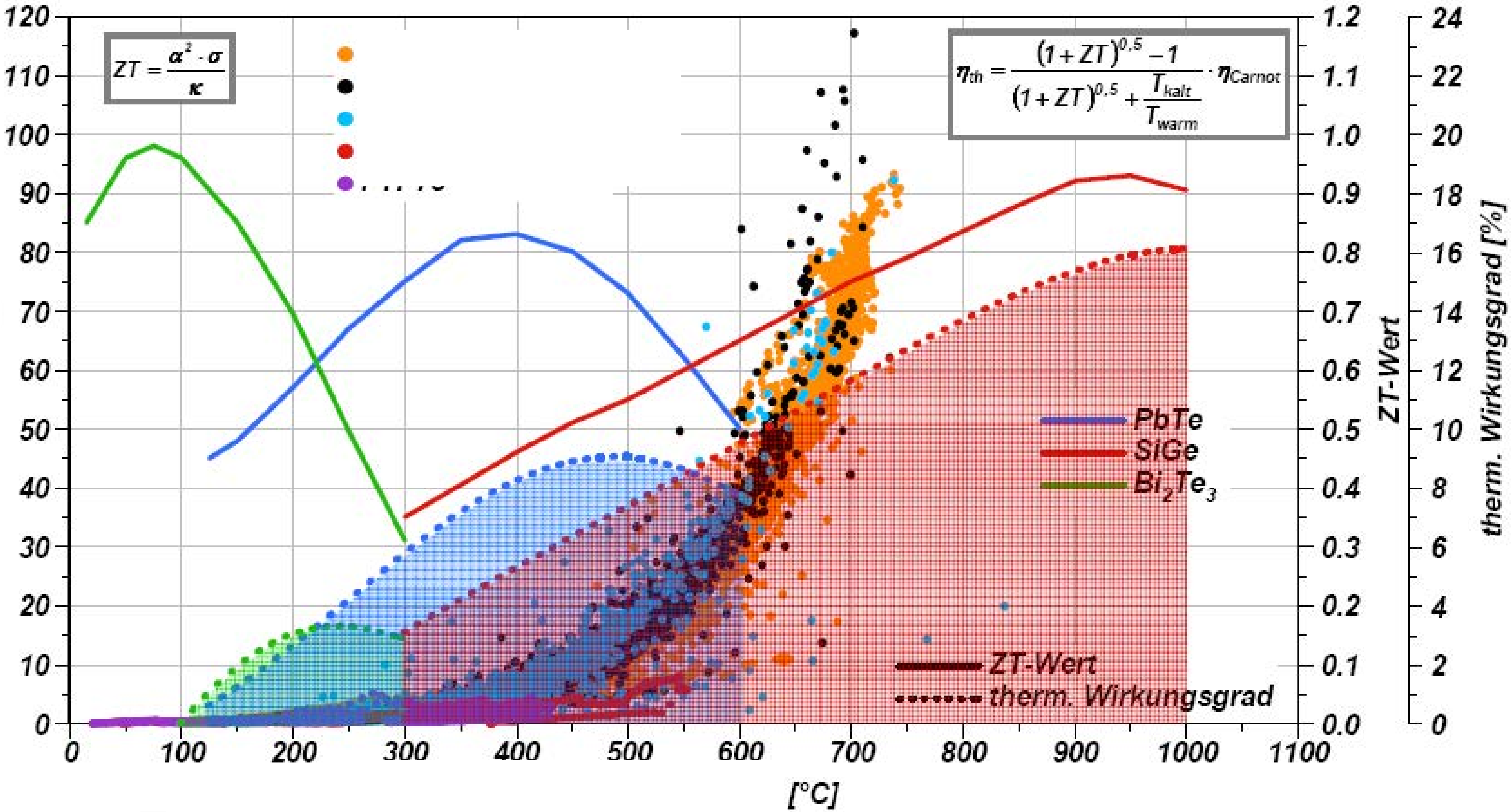


Fuel consumption $\propto$ $\eta_{powertrain}$ (kinetic energy + amenities energy)

Thermoelectrics in Cars:

- Use waste heat energy (75% of fuel!)
- Can reduce fuel consumption ≤ 5%
- Provide efficient local cooling

Heat from Car Exhaust



- PbTe the best present thermoelectrics for cars?

But

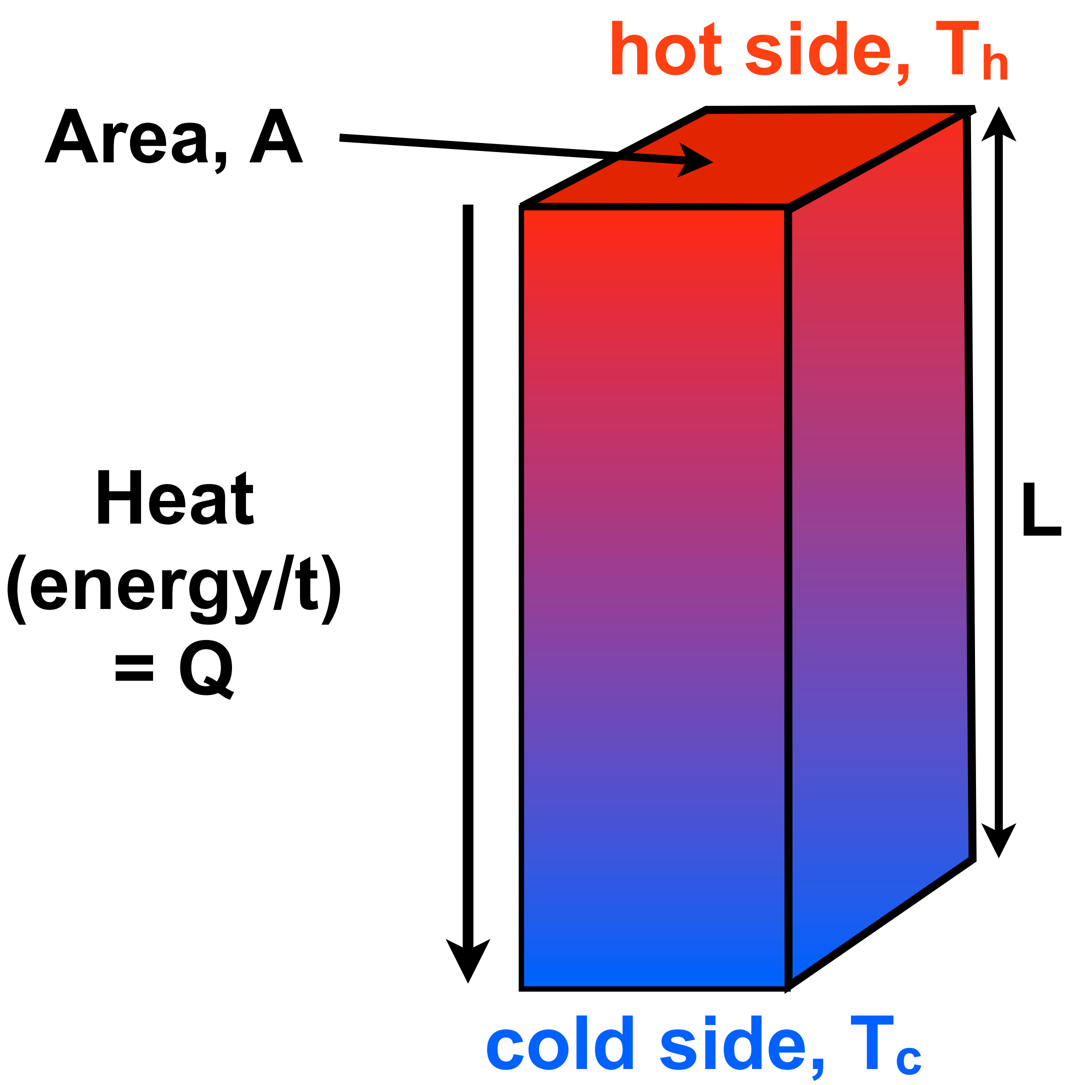
- Pb is toxic and banned, Te is unsustainable
- Cost per Watt is too expensive

BMW

Background Thermal Physics

Fourier thermal transport

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

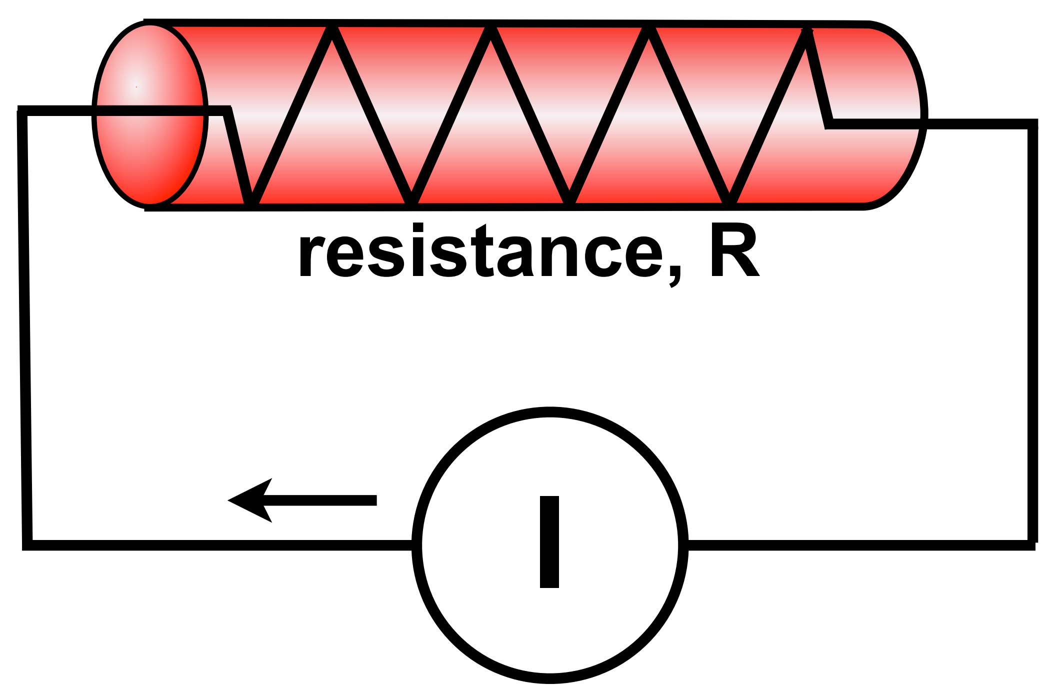


$$\mathbf{Q} = -\kappa \mathbf{A} \frac{\mathbf{T_c} - \mathbf{T_h}}{\mathbf{L}}$$

Joule heating

$$\mathbf{Q} = \mathbf{I}^2 \mathbf{R}$$

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



Background Physics

Fourier thermal transport

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

Joule heating

$$\mathbf{Q} = \mathbf{I}^2 \mathbf{R}$$

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

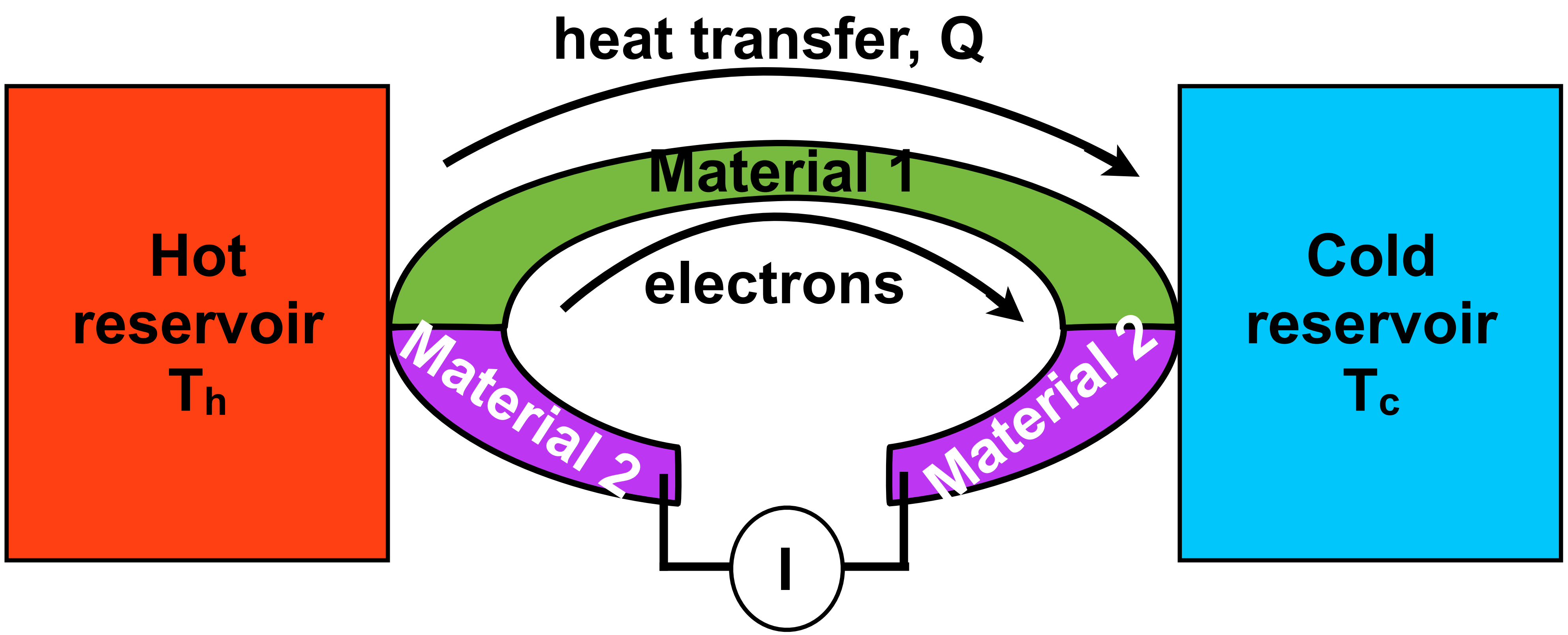
σ = electrical conductivity

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 heat energy carried by each electron per unit charge & time

The Peltier Coefficient

- Full derivation uses relaxation time approximation & Boltzmann equation

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

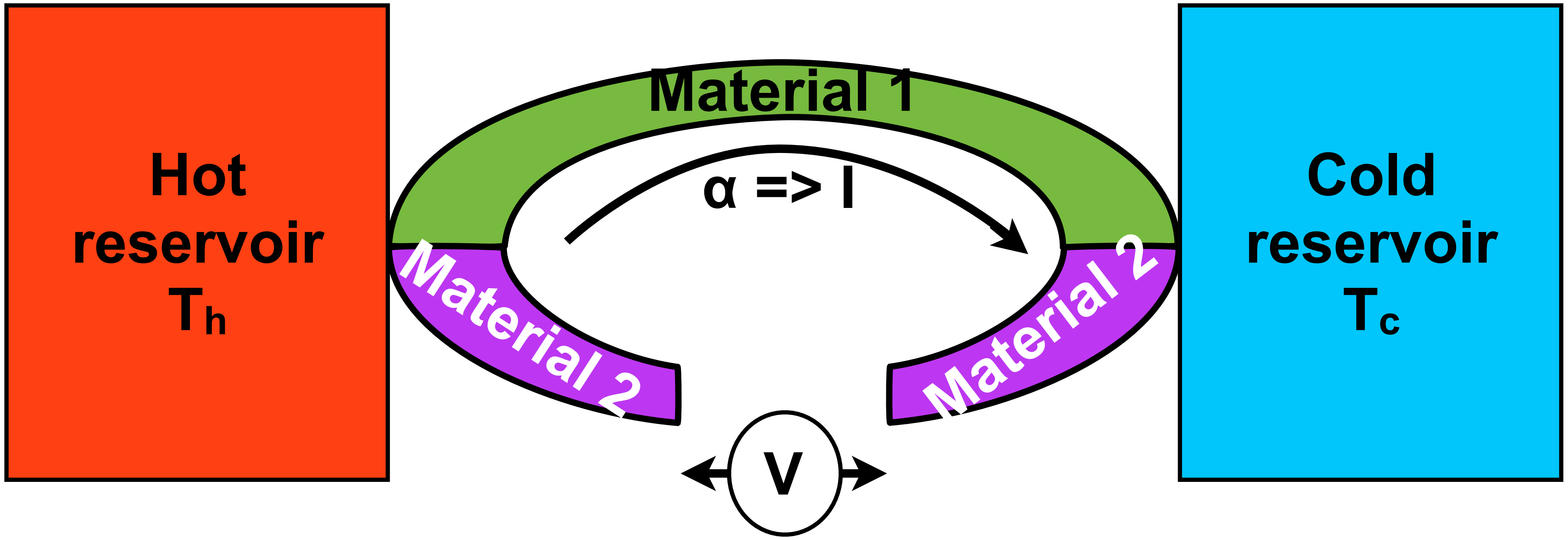
- $$\sigma = \int \sigma(E) dE = q \int g(E) \mu(E) f(E) [1 - f(E)] dE$$

- 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 electron

The Seebeck Coefficient

- **Full derivation uses relaxation time approximation, Boltzmann equation**

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

  τ = momentum relaxation time

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

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

For electrons in the conduction band, E_c of a semiconductor

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

see Mott and Jones (1974) and H. Fritzsche, Solid State Comm. 9, 1813 (1971)

The Seebeck Coefficient for Metals

- $$\mathbf{f(1-f) = -k_B T \frac{df}{dE}}$$

- **Expand $\mathbf{g(E)\mu(E)}$ in Taylor's series at E = E$_F$**

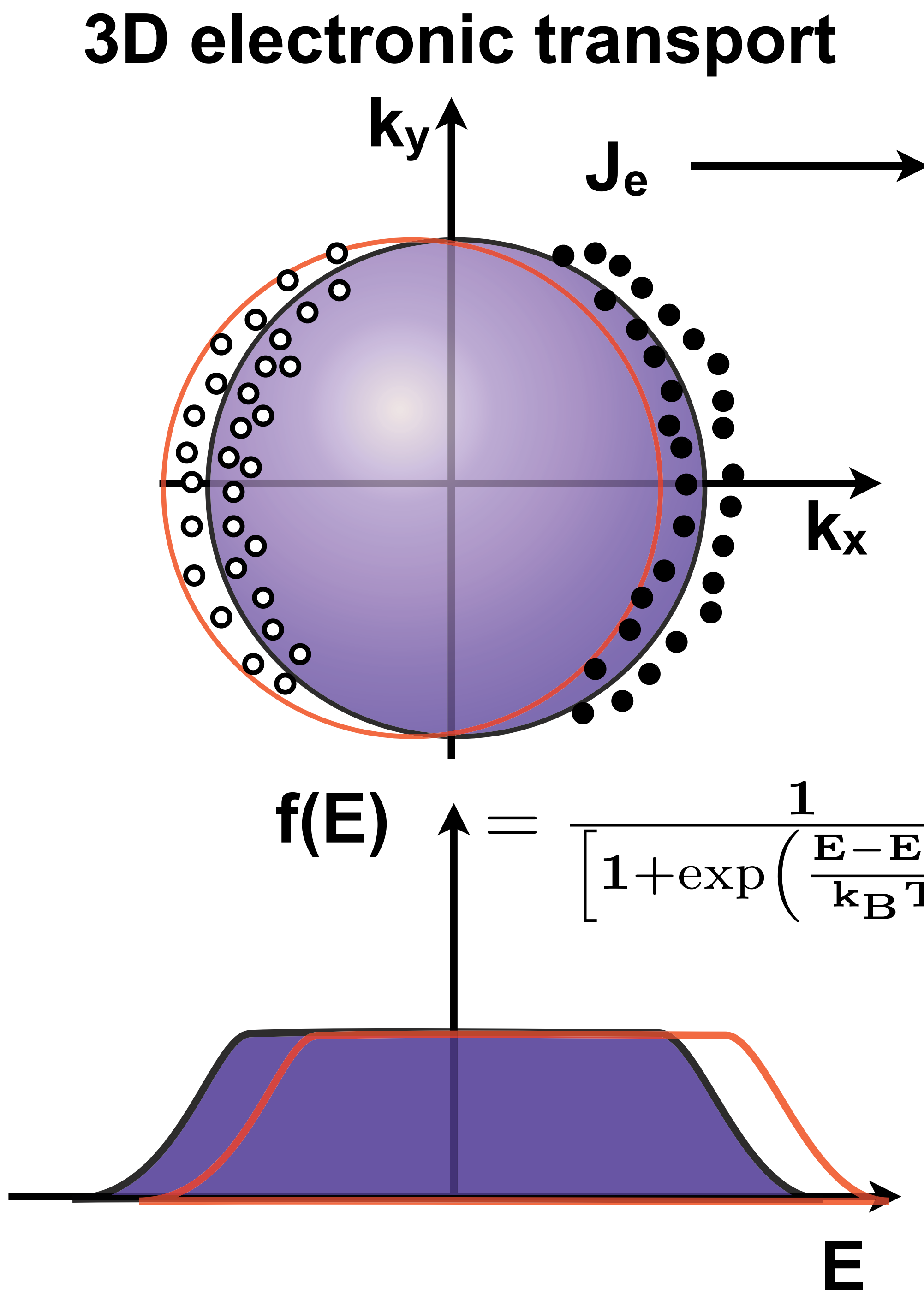
- $$\boxed{\alpha = -\frac{\pi^2}{3q} k_B^2 T \left[\frac{d\ln(\mu(E)g(E))}{dE}\right]_{E=E_F}}$$

  (Mott's formula for metals)

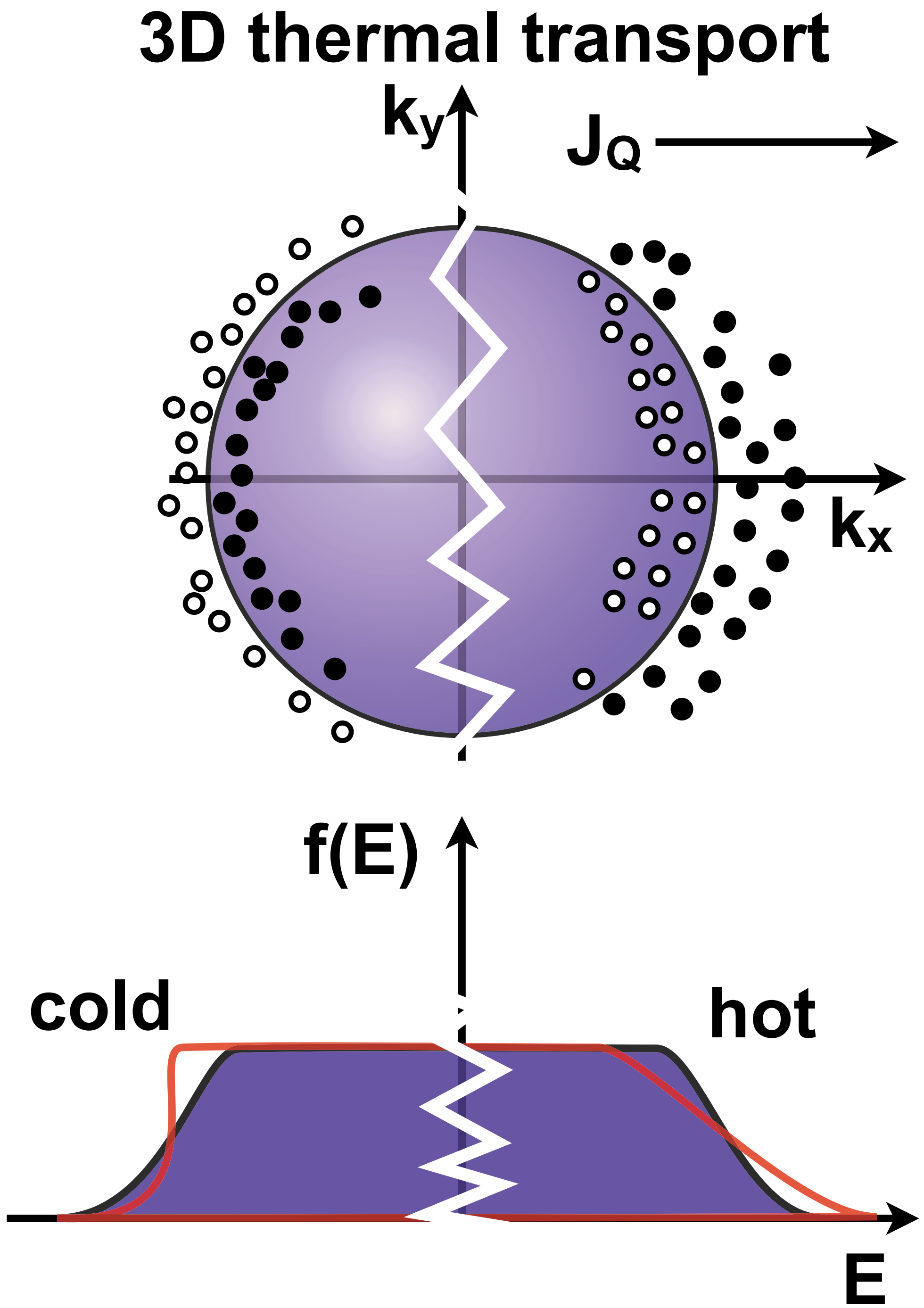
  M. Cutler & N.F. Mott, Phys. Rev. 181, 1336 (1969)

- **i.e. Seebeck coefficient depends on the asymmetry of the current contributions above and below E$_F$**

3D Electronic and Thermal Transport



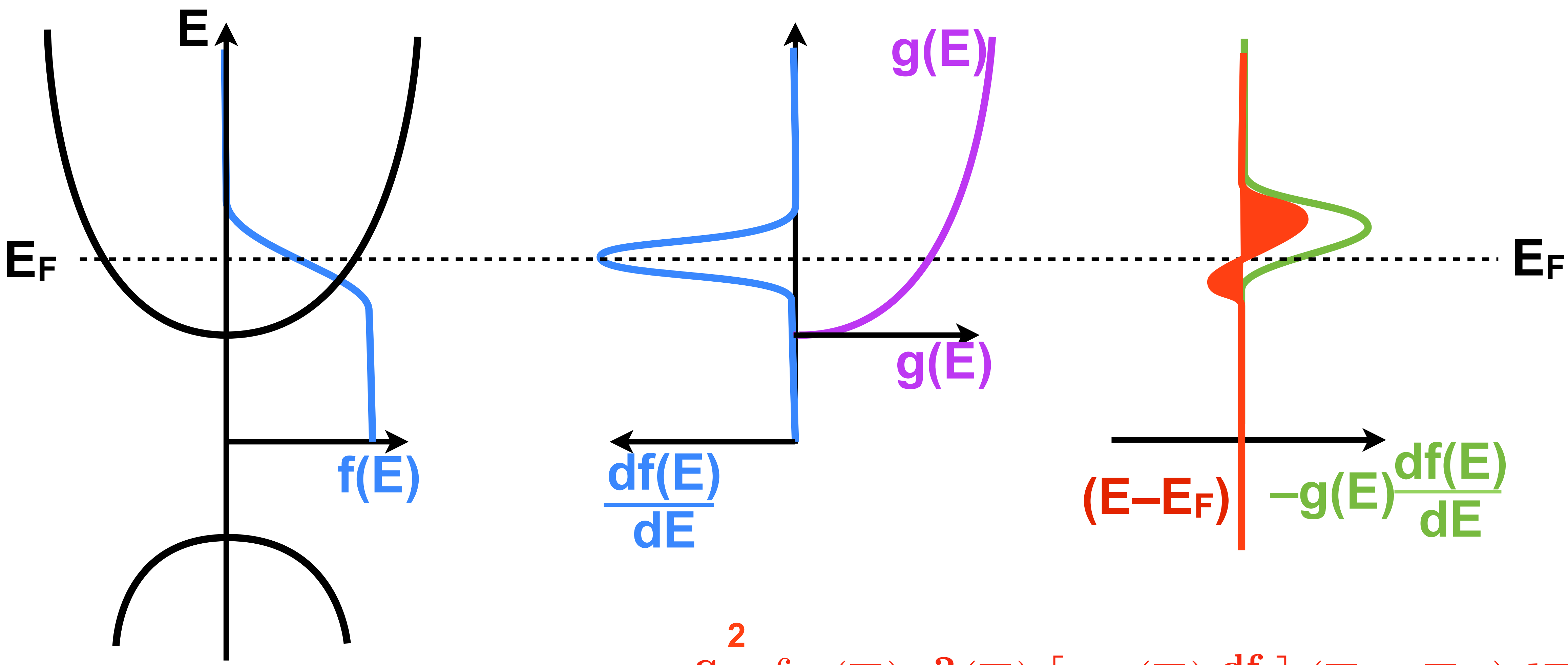
$$f(E) = \frac{1}{\left[1+\exp\left(\frac{E-E_F}{k_B T}\right)\right]}$$



The Physics of the Thermoelectric Effect

- **If we ignore energy dependent scattering (i.e. τ = τ(E)) then from J.M. Ziman**

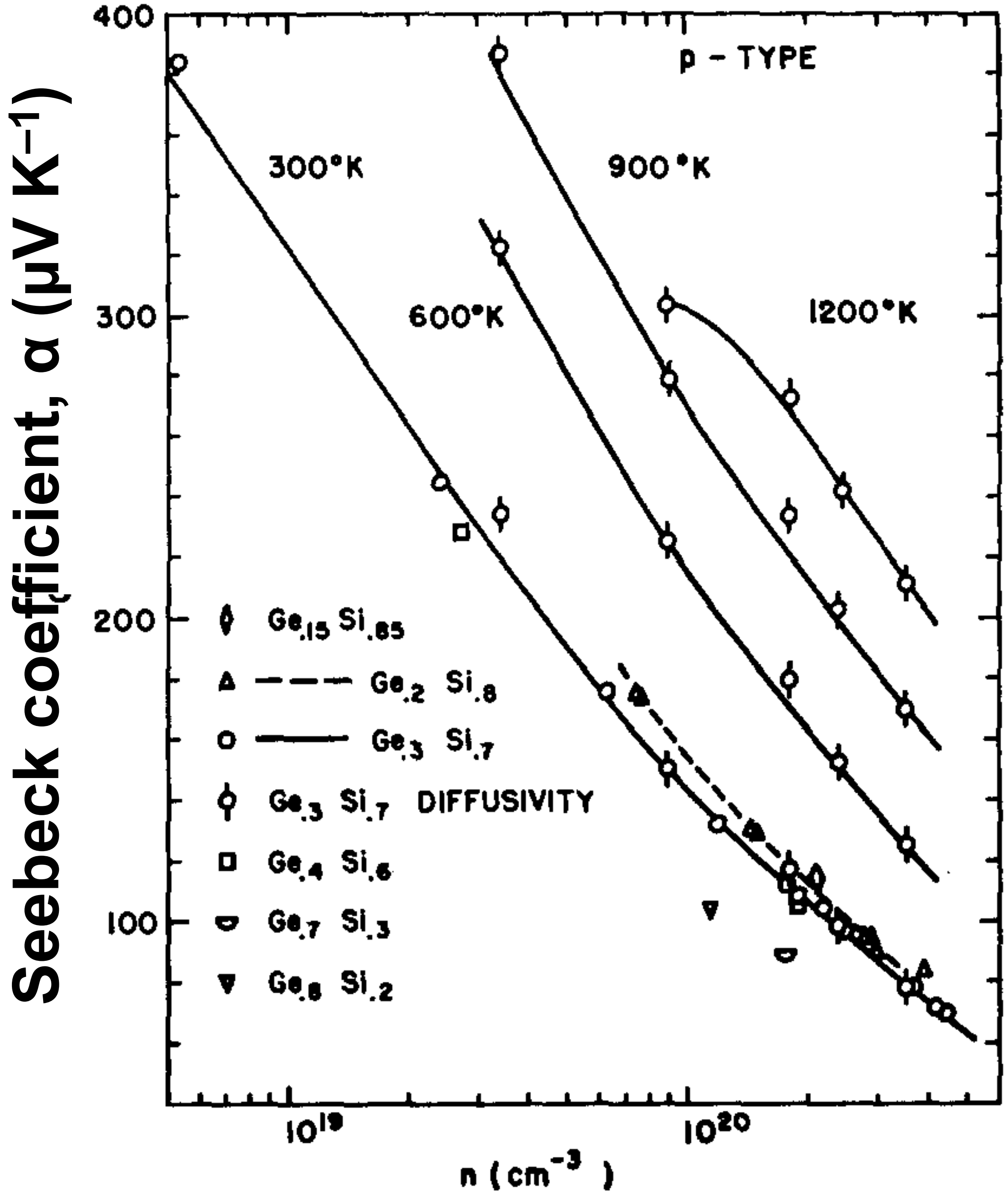
$$\sigma = \frac{q^2}{3}\int \tau(E)\nu^2(E)\left[-g(E)\frac{df}{dE}\right] dE$$



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

- **Thermoelectric power requires asymmetry in red area under curve**

Semiconductor Example: SiGe Alloys

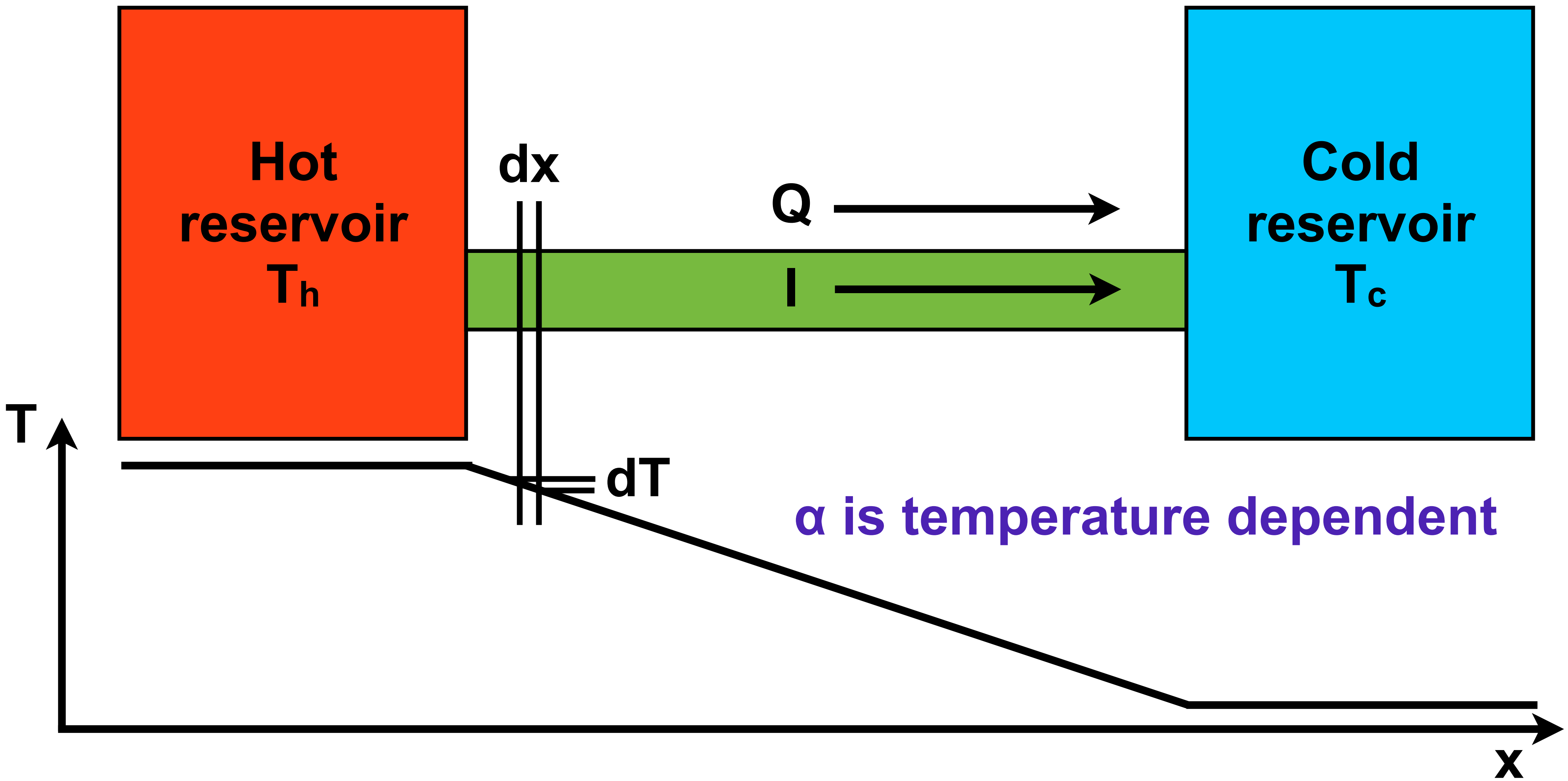


- Mott criteria ~ 2 x 10^{18} cm^{-3}
- Degenerately doped p-$Si_{0.7}Ge_{0.3}$
- α decreases for higher n
- For SiGe, α increases with T

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

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

The Thomson Effect



α is temperature dependent

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

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

units: V/K

The Kelvin Relationships

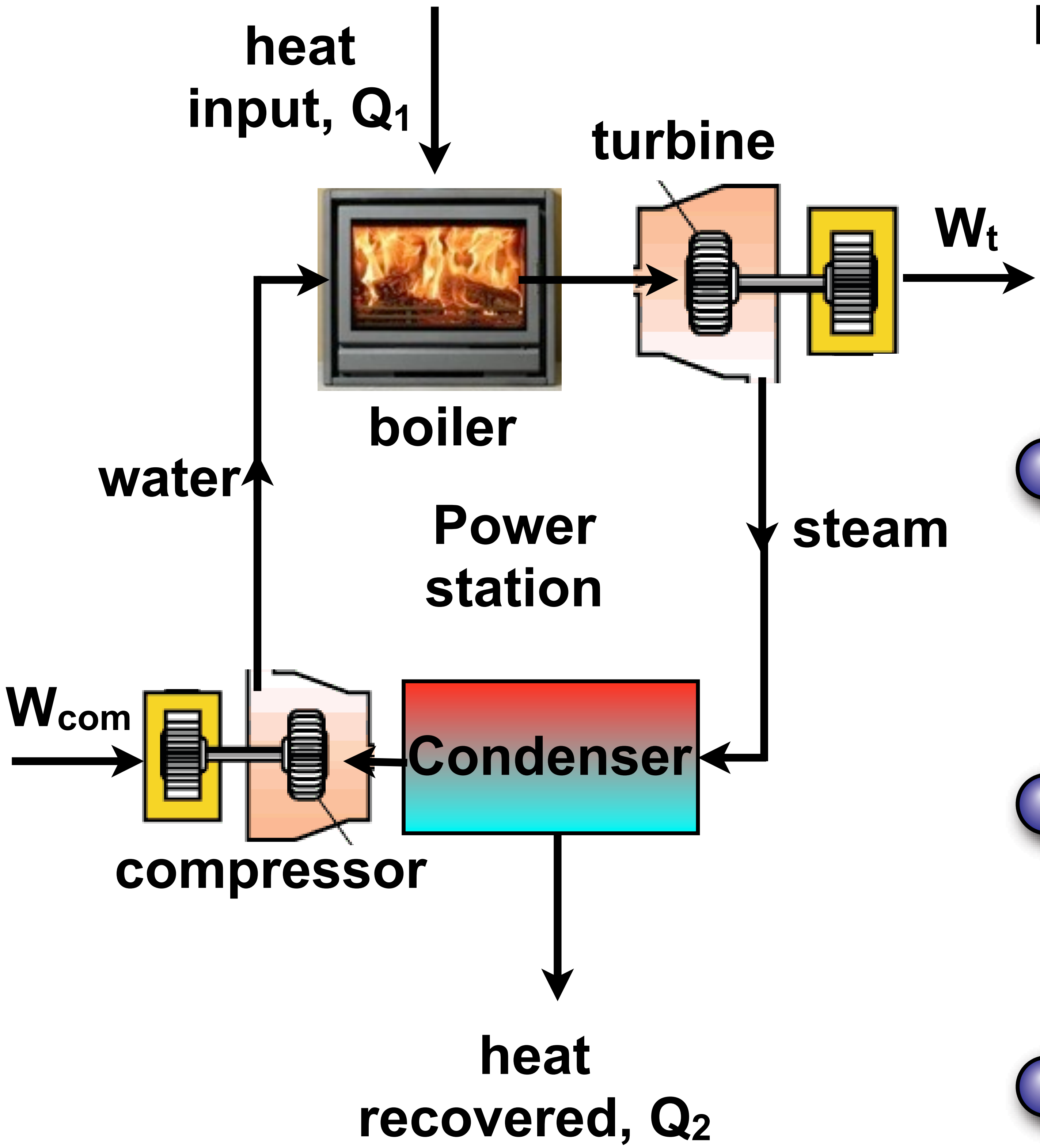
- Derived using irreversible thermodynamics

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

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

- 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

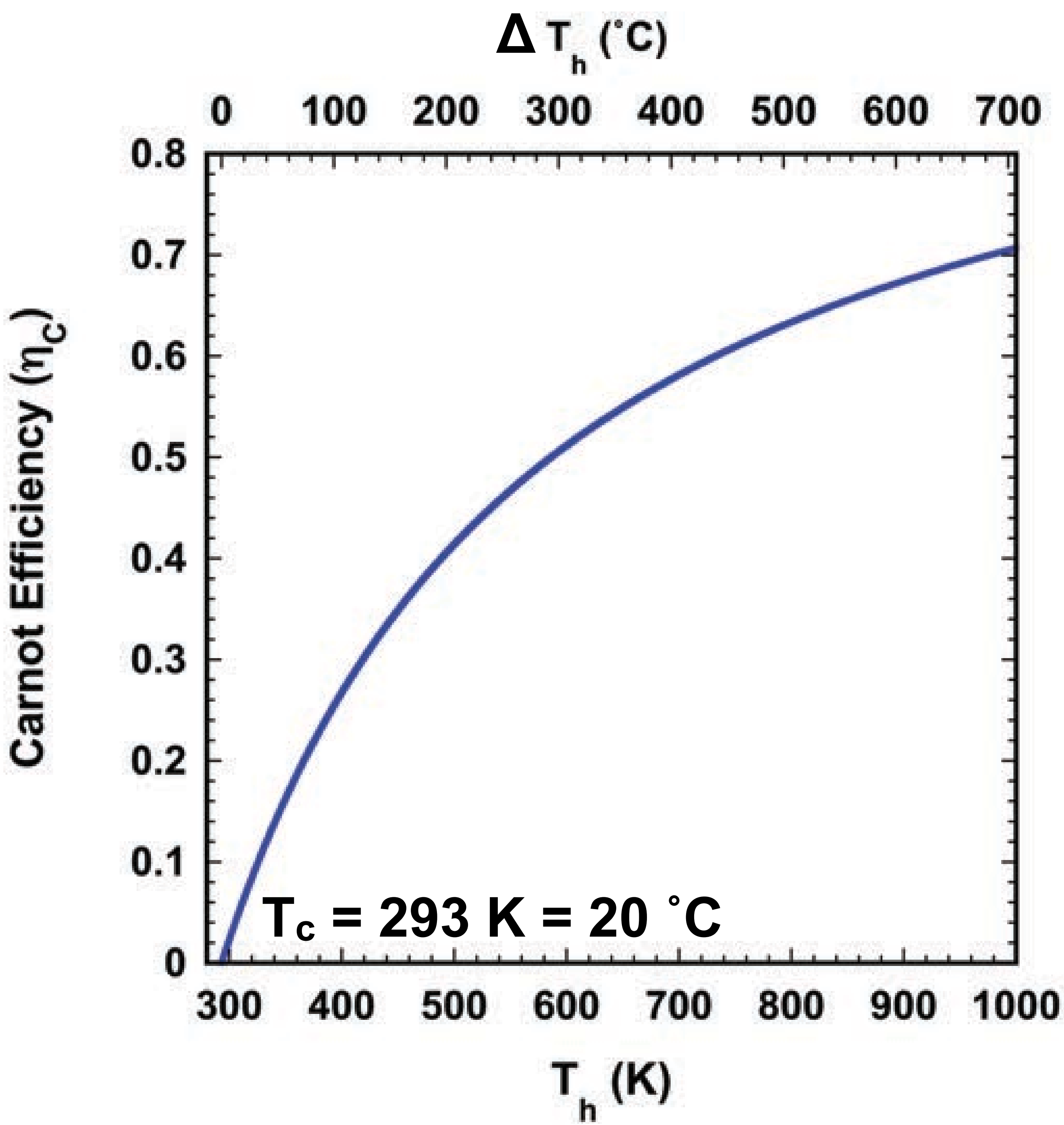
Efficiency =

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

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

Carnot: maximum η only depends on T_c and T_h

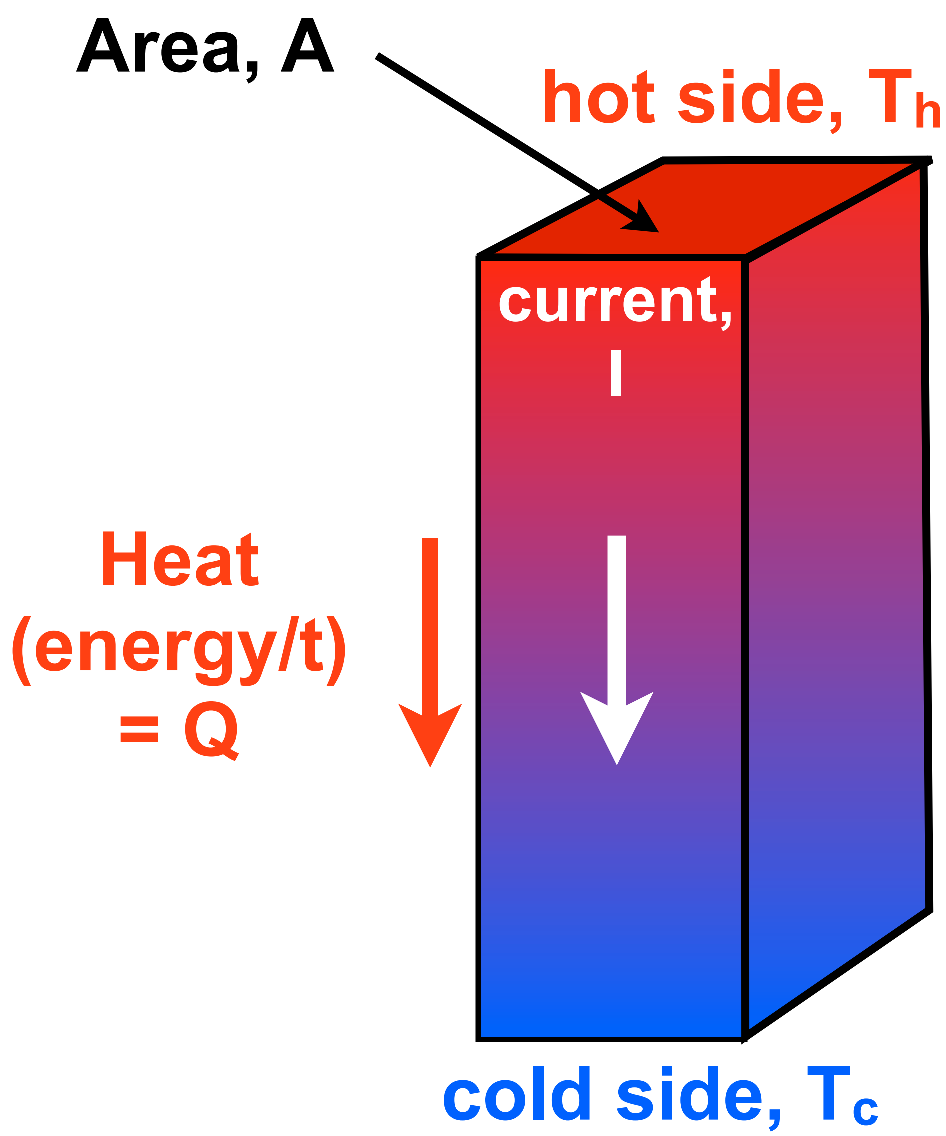
$$\boxed{\eta_c = 1 - \frac{T_c}{T_h}}$$



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 =

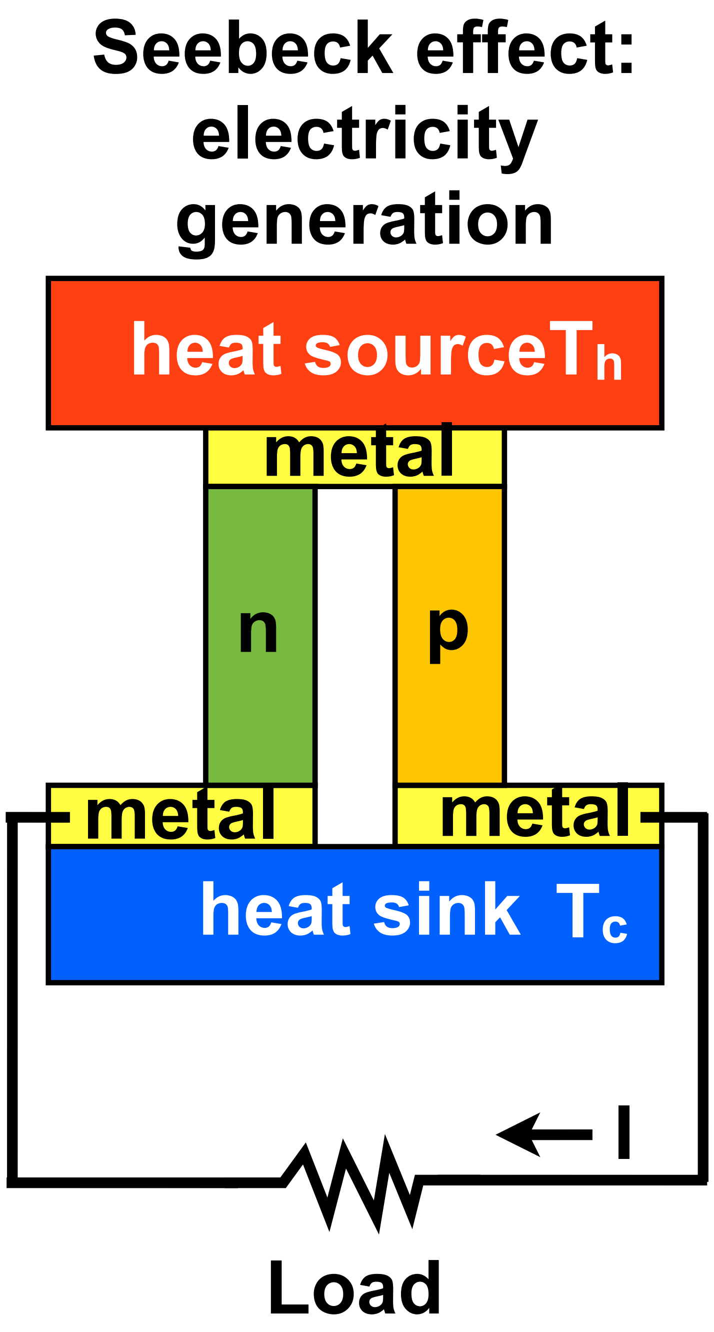
  (= Peltier + Fourier)

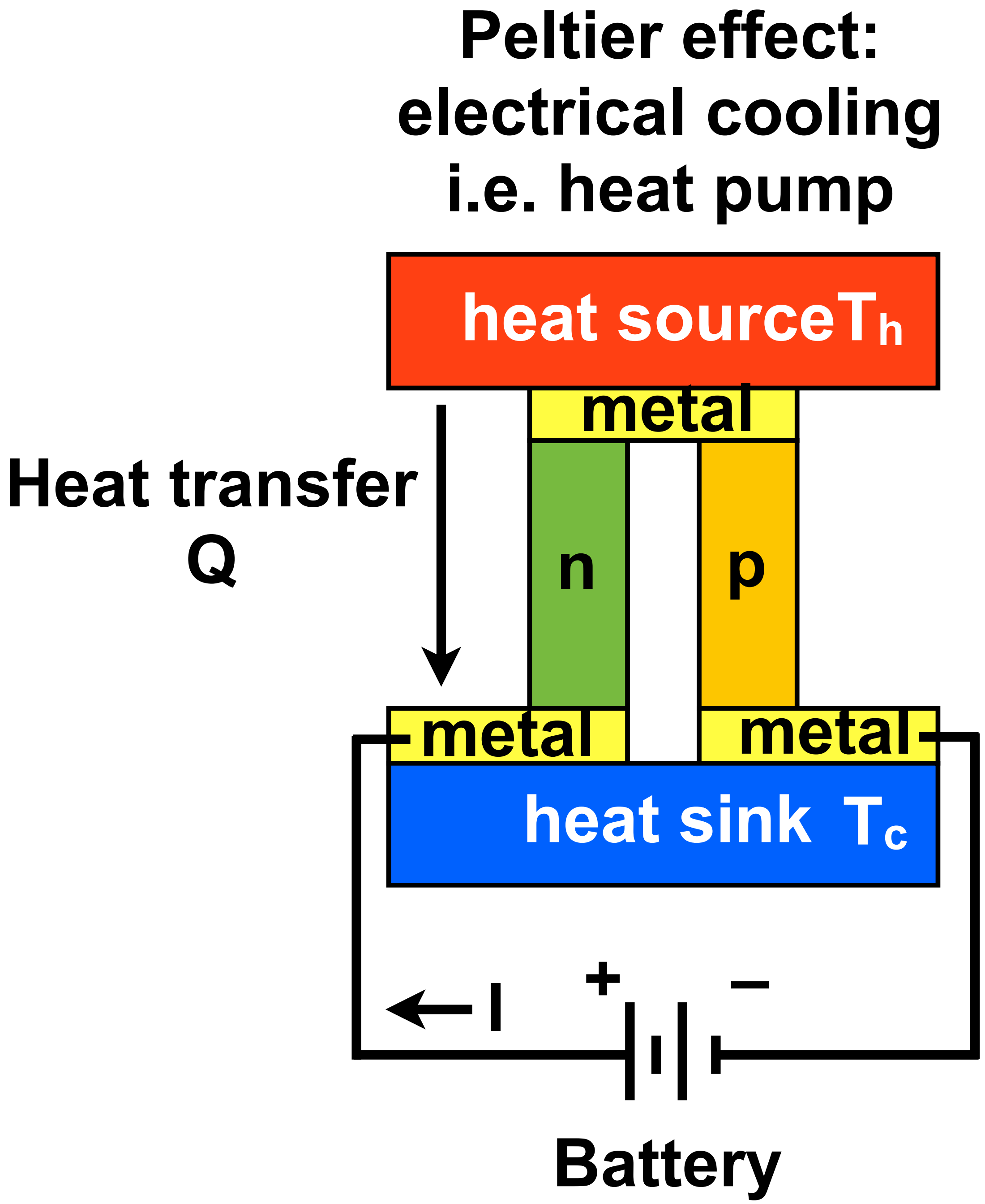
- $$\frac{\mathbf{Q}}{\mathbf{A}} = \mathbf{\Pi J} - \kappa \nabla \mathbf{T}$$

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

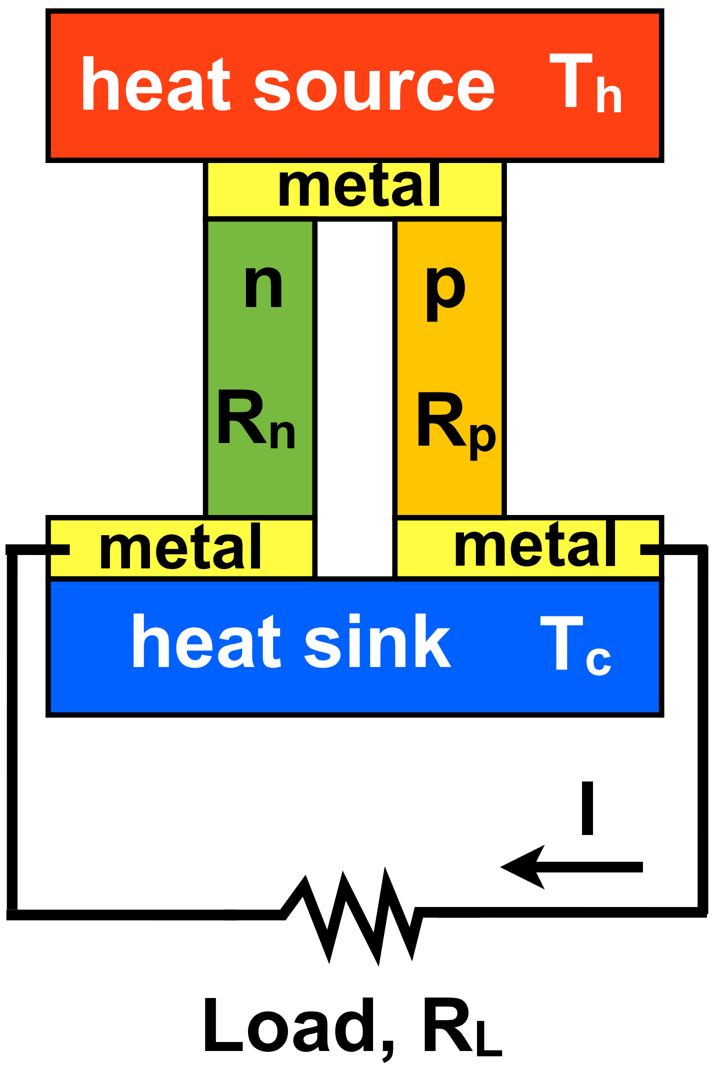
$$\boxed{\mathbf{Q} = \alpha \mathbf{IT} - \kappa \mathbf{A} \nabla \mathbf{T}}$$

Semiconductors and Thermoelectrics





Conversion Efficiency



$R = R_n + R_p$

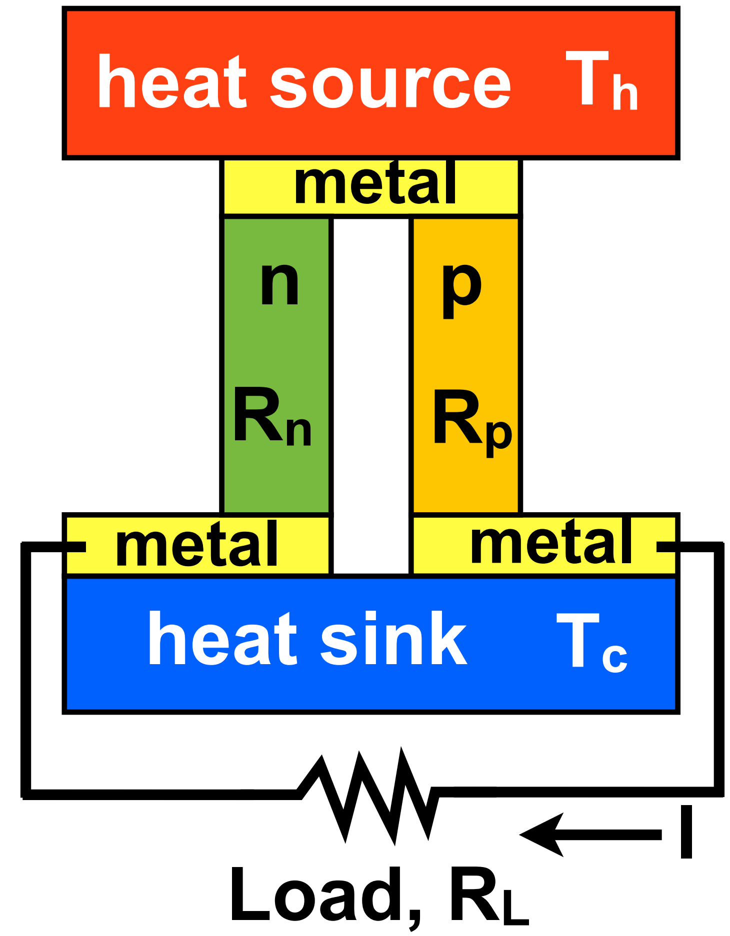
- $\eta = \dfrac{\text{power supplied to load}}{\text{heat absorbed at hot junction}}$
- Power to load (Joule heating) = I^2R_L
- Heat absorbed at hot junction = Peltier heat + heat withdrawn from hot junction
- Peltier heat $= \Pi I = \alpha I T_h$
- $I = \frac{\alpha(T_h - T_c)}{R + R_L}$ (Ohms Law)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

Thermoelectric Conversion Efficiency

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

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



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

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

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

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

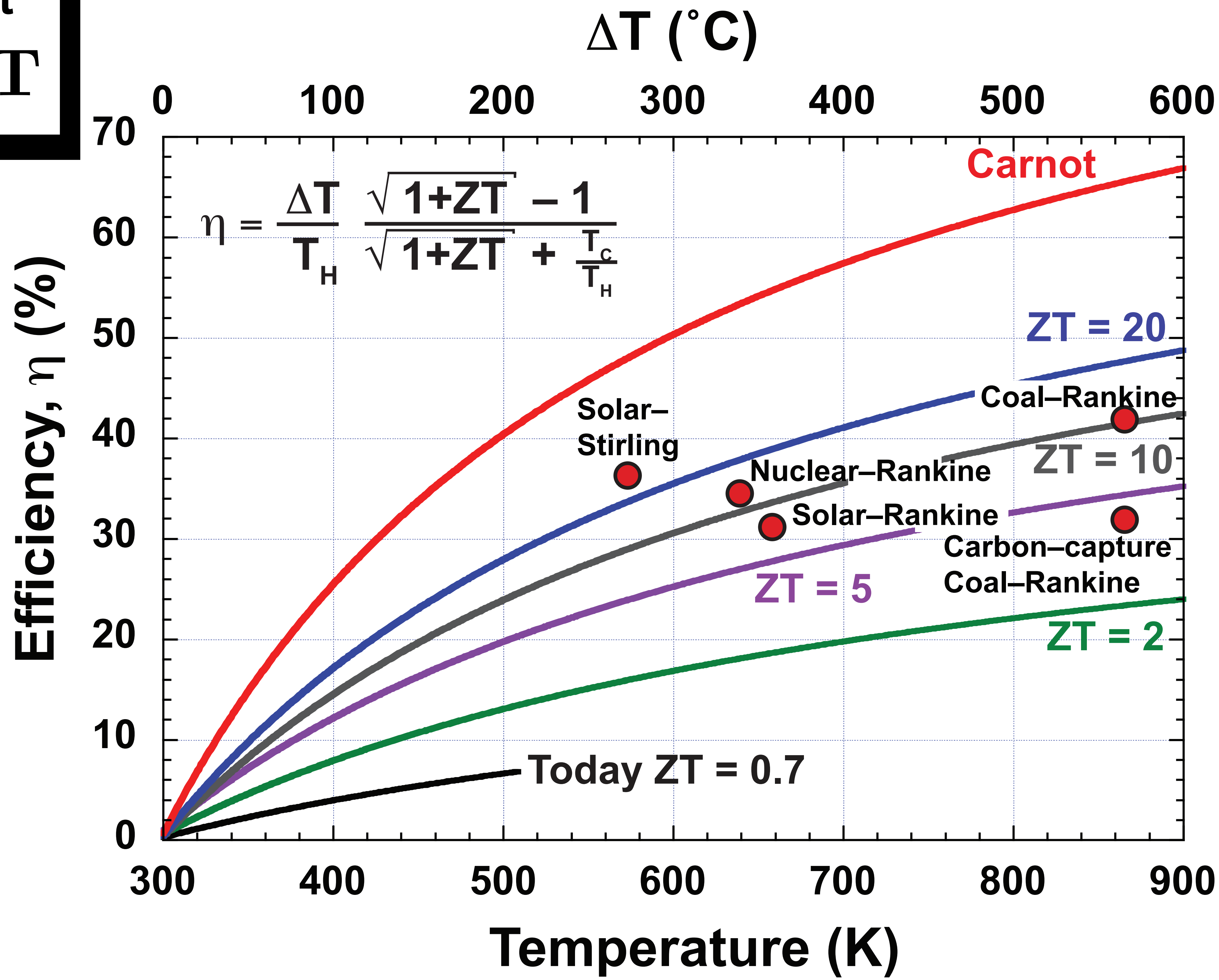
where $Z = \dfrac{\alpha^2}{R \kappa A} = \dfrac{\alpha^2 \sigma}{\kappa}$

= Carnot x Joule losses and irreversible processes

Thermodynamic Efficiency

Figure of merit

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

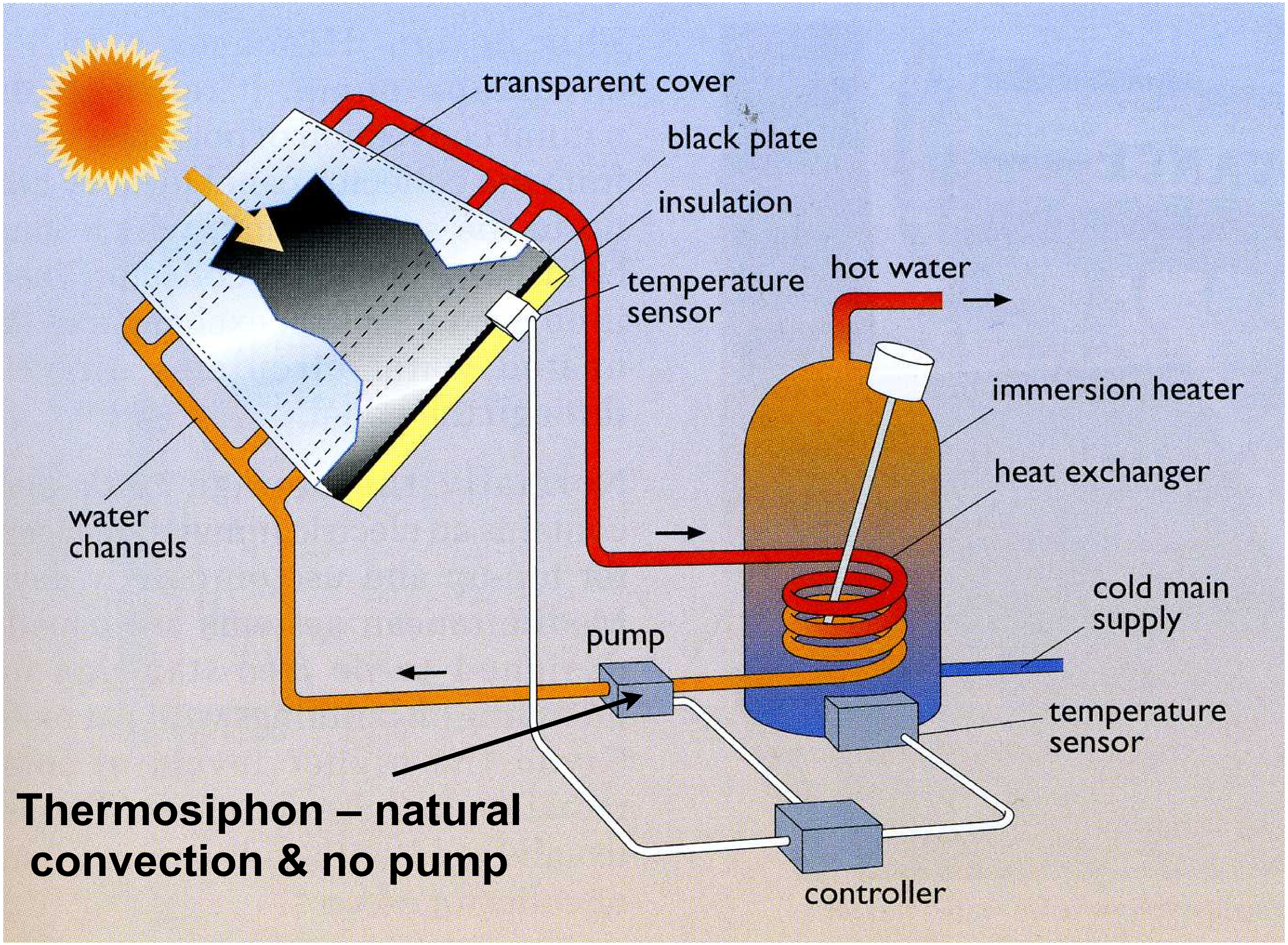


Energy Quality

Highest Quality
Electromagnetic
Mechanical (kinetic)
Photon (light)
Chemical
Heat (thermal)
Lowest Quality

- First proposed as availability by Kelvin in 1851 refined by Ohta
- Energy quality describes the ease (i.e. η) with which energy can be transformed
- A transition down the table will be more efficient than moving up the table
- Therefore solar heating is more efficient than photovoltaic electrical generation
- Expanded version from chemistry developed by Odum

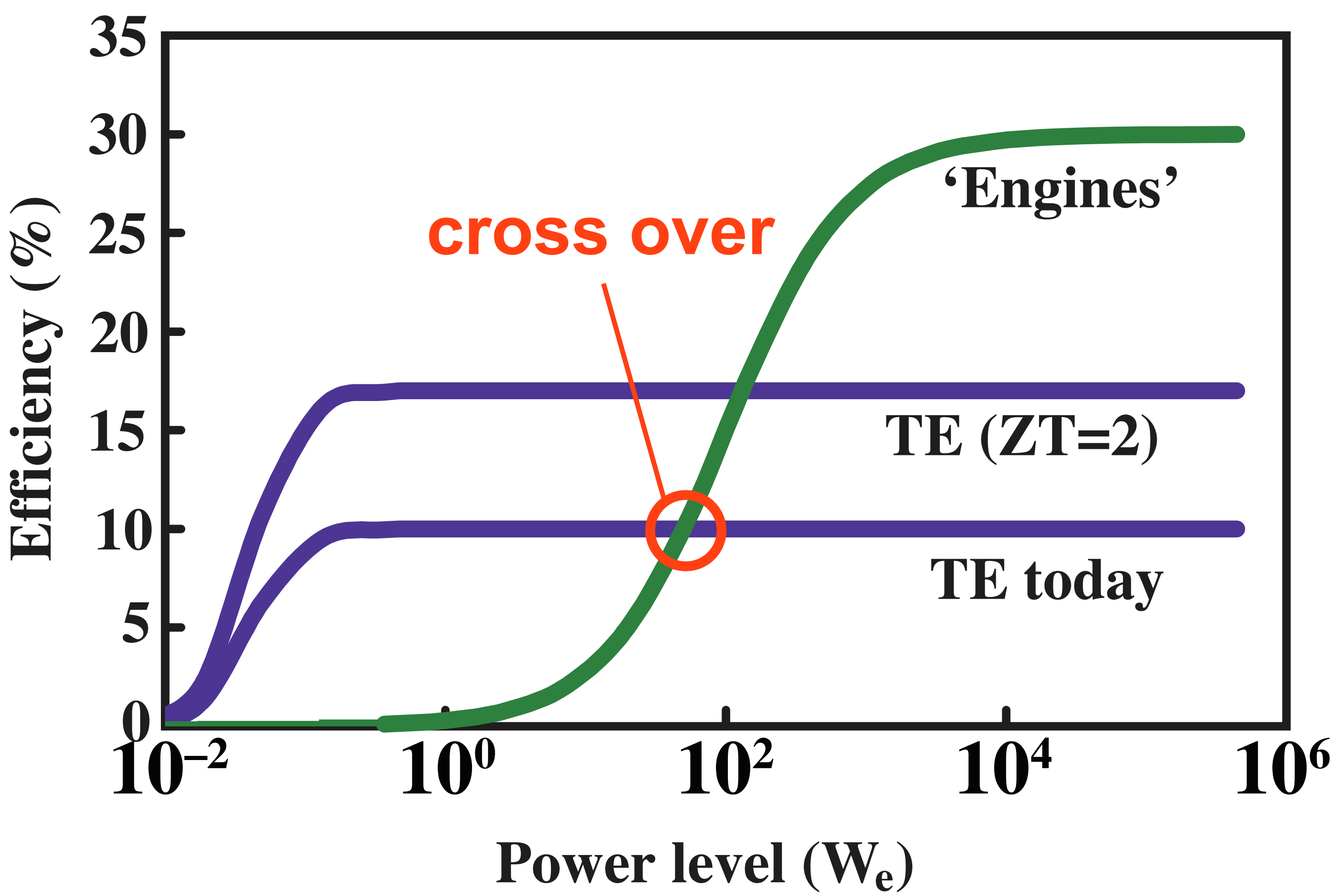
Solar Thermal Water Heating System



- **46% to 74% η for solar energy –> heat conversion are typical**

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**

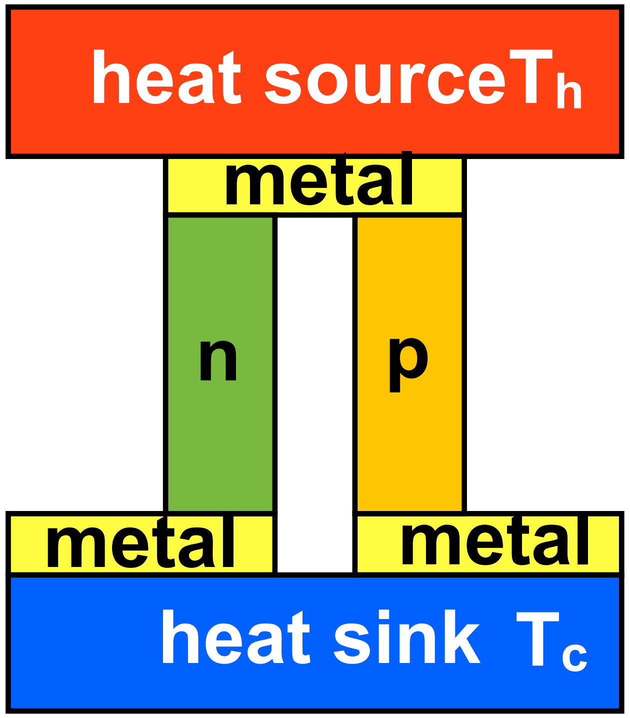
$$\text{Power} \propto \alpha^2\sigma$$

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

Thermal Conductivity of Bulk Materials

- Lattice and electron current can contribute to heat transfer

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

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

- For low carrier densities in semiconductors (non-degenerate)

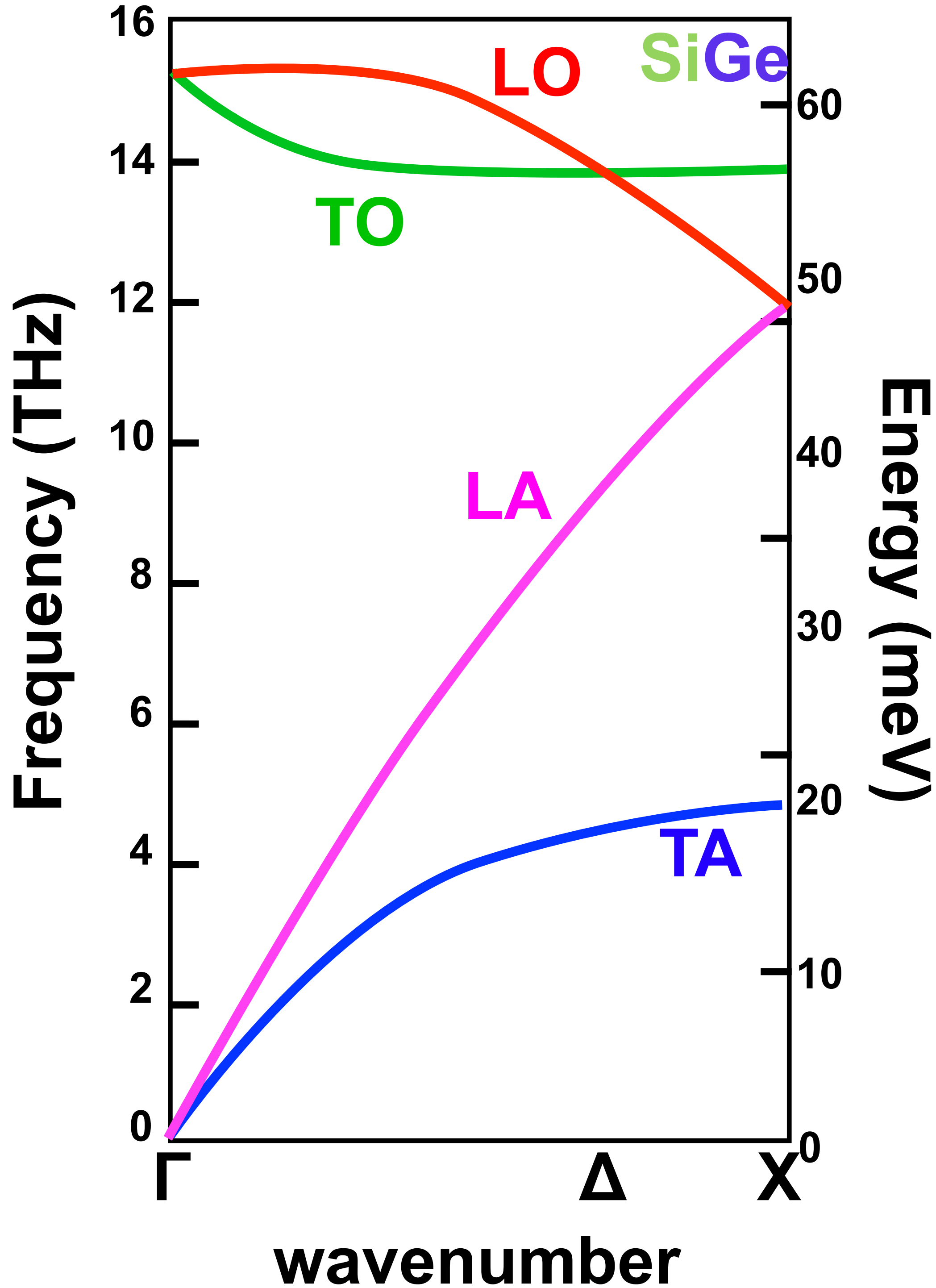
$$\kappa_{\mathbf{el}} \ll \kappa_{\mathbf{ph}}$$

- For high carrier densities in semiconductors (degenerate)

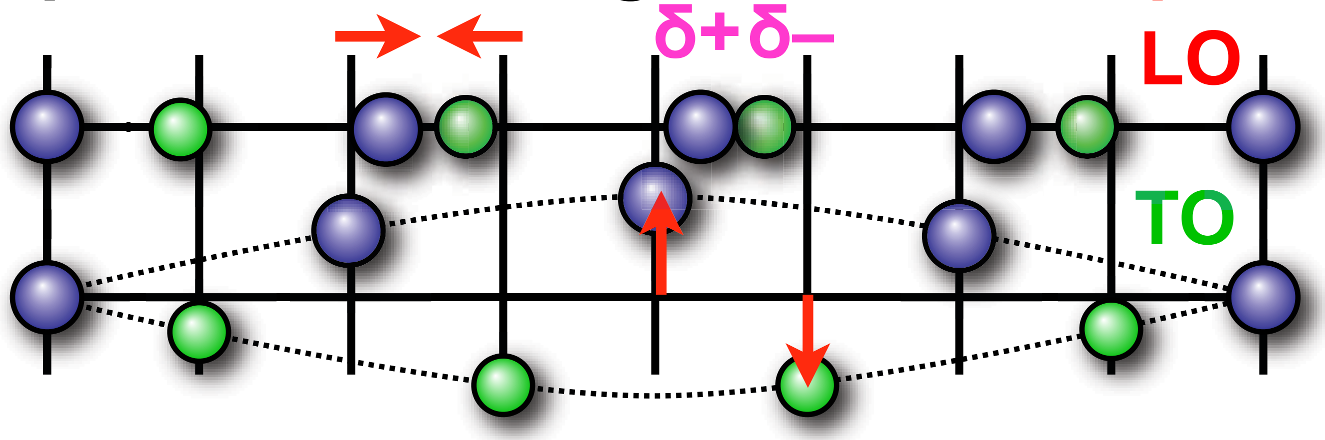
$$\kappa_{\mathbf{el}} \gg \kappa_{\mathbf{ph}}$$

- Good thermoelectric materials should ideally have $\kappa_{\mathbf{el}} \ll \kappa_{\mathbf{ph}}$
  i.e. electrical and thermal conductivities are largely decoupled

Phonons: Lattice Vibration Heat Transfer

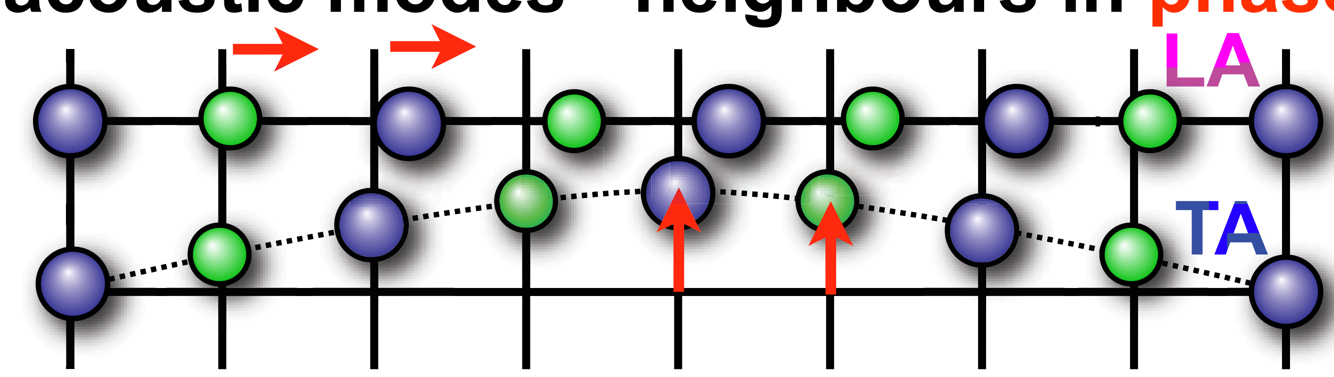


optic modes - neighbours in antiphase



NB acoustic phonons transmit most thermal energy

acoustic modes - neighbours in phase



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

Thermal Conductivity

Lattice contribution:

$$\kappa_{\mathbf{ph}} = \frac{\mathbf{k_B}}{\mathbf{2\pi^2}} \left(\frac{\mathbf{k_B}}{\hbar}\right)^{\mathbf{3}} \mathbf{T^3} \int_{\mathbf{0}}^{\frac{\theta_{\mathbf{D}}}{\mathbf{T}}} \frac{\tau_{\mathbf{c}}(\mathbf{x})\mathbf{x}^{\mathbf{4}}\mathbf{e}^{\mathbf{x}}}{\upsilon(\mathbf{x})(\mathbf{e}^{\mathbf{x}}-\mathbf{1})^{\mathbf{2}}}\mathbf{dx}$$

θ_D = Debye temperature (640 K for Si)

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

τ_c = combined phonon scattering time

$\upsilon(\mathbf{x})$ = velocity

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

Electron (hole) contribution:

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

τ(E) = total electron momentum relaxation time

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

Wiedemann-Franz Law

- **Empirical law from experimental observation that $\frac{\kappa}{\sigma \mathbf{T}}$ = 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}

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

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

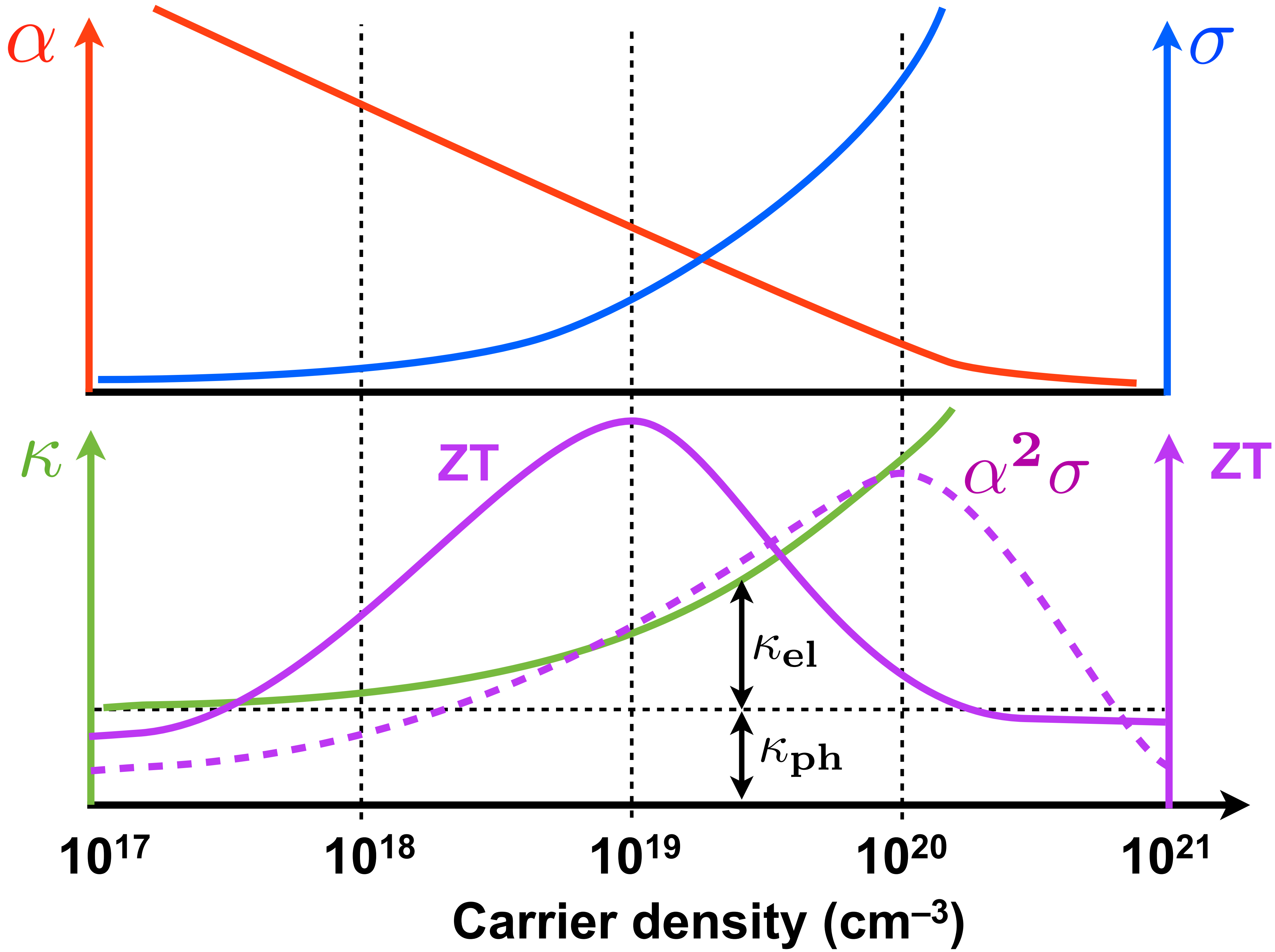
$$\boxed{\mathbf{ZT} = \frac{\mathbf{3}}{\pi^{\mathbf{2}}} \left(\frac{\mathbf{q}\alpha}{\mathbf{k_B}} \right)^{\mathbf{2}} = 4.09 \times 10^{7}\ \alpha^{\mathbf{2}}}$$

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

Exceptions:

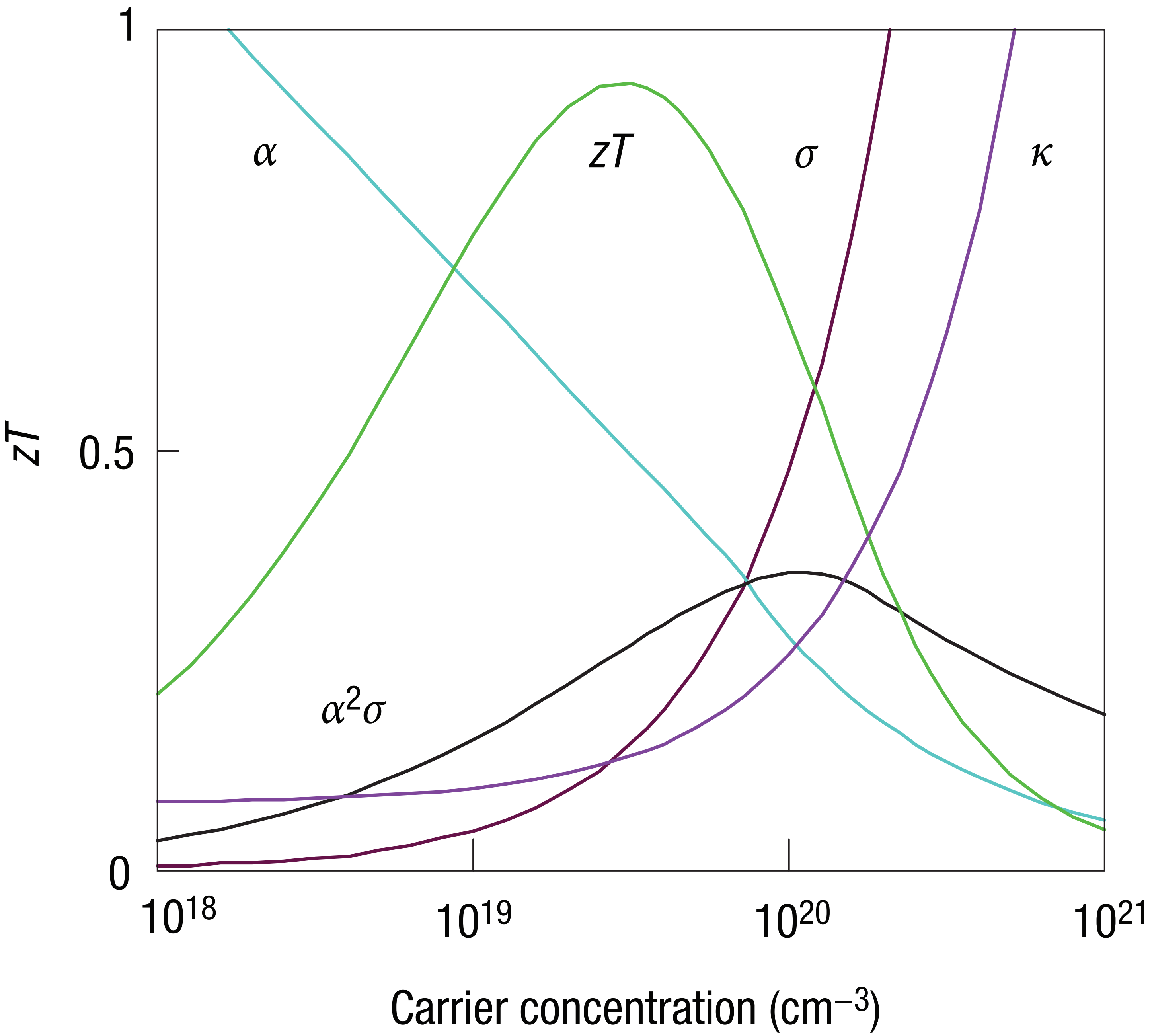
- most exceptions systems with $\kappa_{\mathrm{el}} \ll \kappa_{\mathrm{ph}}$
- some pure metals at low temperatures
- alloys where small κ_{el} results in significant κ_{ph} contribution
- certain low dimensional structures where κ_{ph} can dominate

Thermoelectric vs Doping of Semiconductors



- **Electrical and thermal conductivities are not independent**
- **Wiedemann Franz rule: electrical conductivity $\propto$ thermal conductivity at high doping**

Bi_2Te_3 ZT Optimisation Through Doping

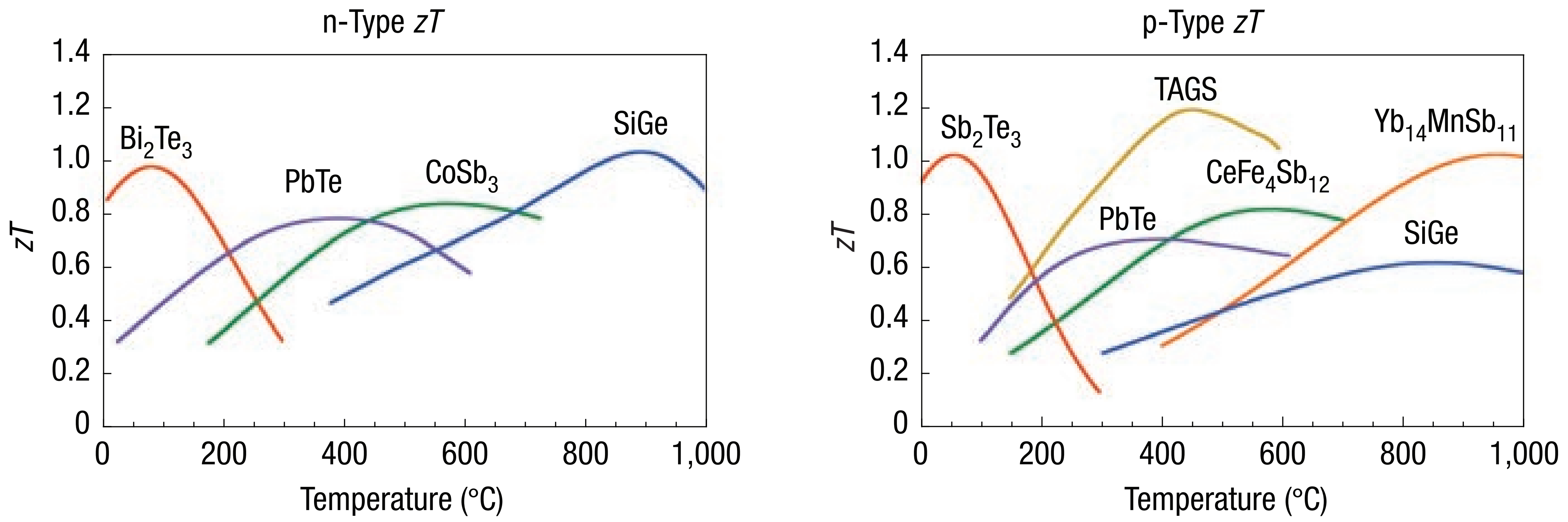


- **Maximum ZT requires compromises with α, σ & κ**
- **Limited by Wiedemann-Franz Law**
- **Maximum ZT ~ 1 at ~100 ˚C**

- **Bulk 3D materials are limited to ZT ≤ ~1 below 100 ˚C**

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

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 7th 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

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

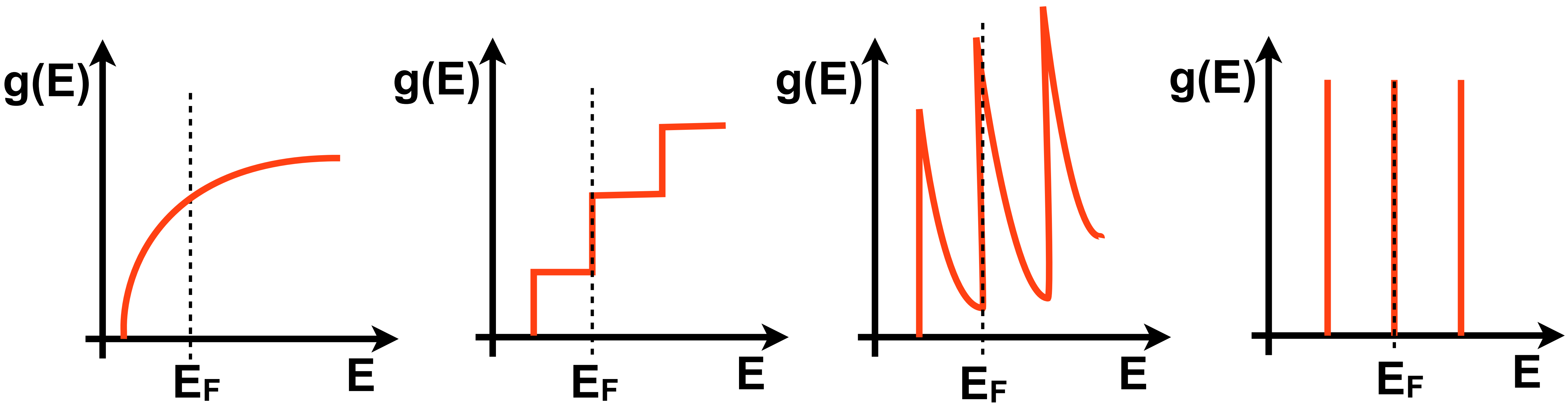
Y.I. Ravich et al., Phys. Stat. Sol. (b) 43, 453 (1971)

Seebeck Enhancement at Low Dimensions

- **Increase α through enhanced DOS:**

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

3D	2D	1D	0D
bulk	quantum well	quantum wire	quantum dot



α increasing

Length Scales: Mean Free Paths

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

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

3D phonon mean free path $\boxed{\Lambda_\mathbf{ph} = \frac{3\kappa_\mathbf{ph}}{\mathbf{C_v}\langle\mathbf{v_t}\rangle\rho}}$

- C_v = specific heat capacity
- $\langle v_t \rangle$ = average phonon velocity
- ρ = density of phonons

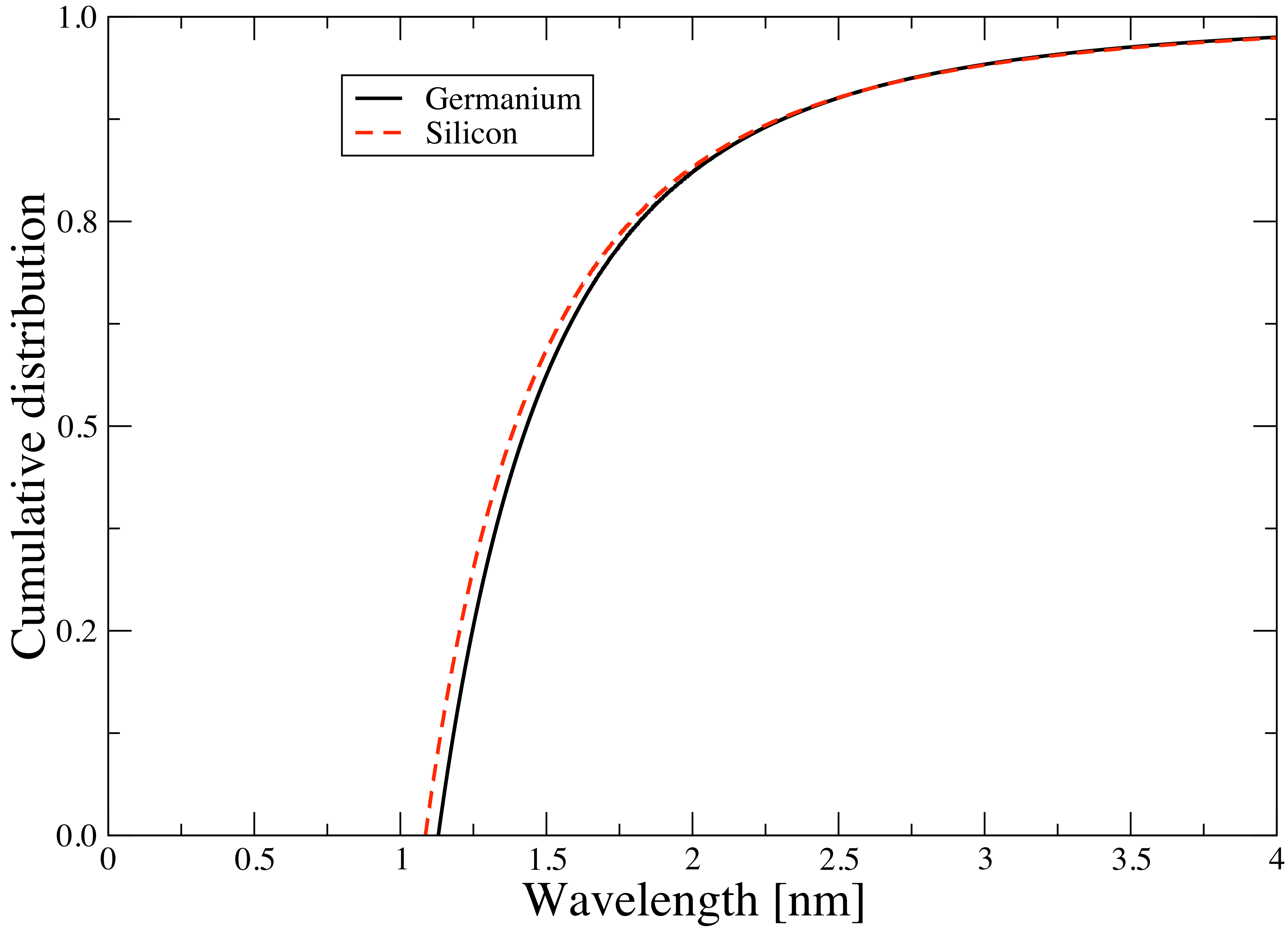
- A structure may be 2D or 3D for electrons but 1 D for phonons (or vice versa!)

Phonon Mean Free Paths

Material	Model	Specific Heat ($\times 10^6$ $Jm^{-3}K^{-1}$)	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:

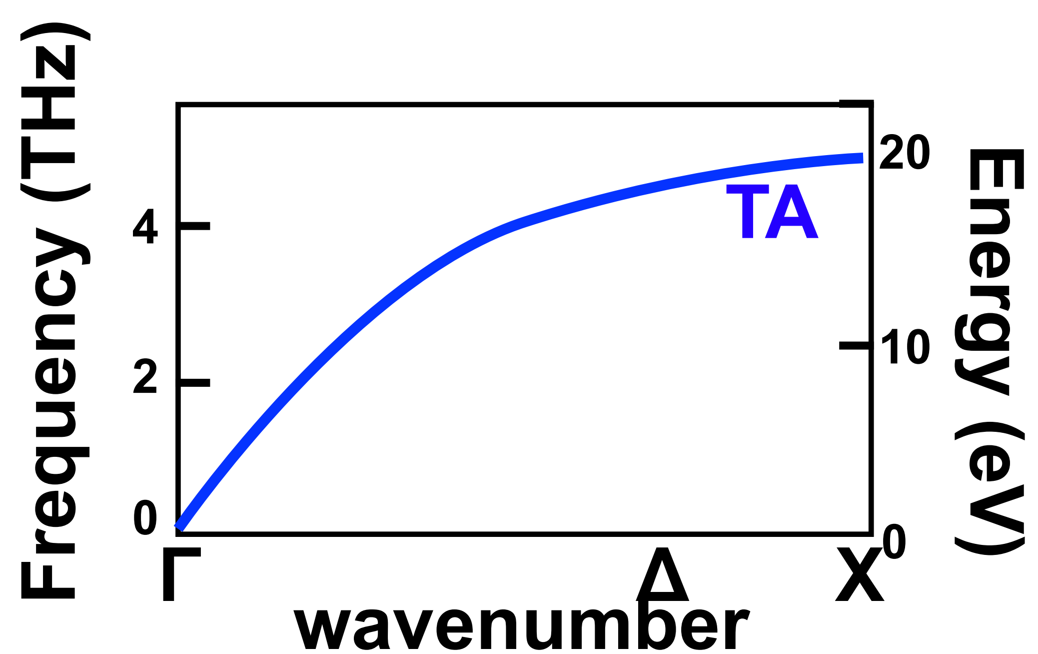
- Require structures below the phonon mean free path (10s nm)

Phonon Bandgaps:

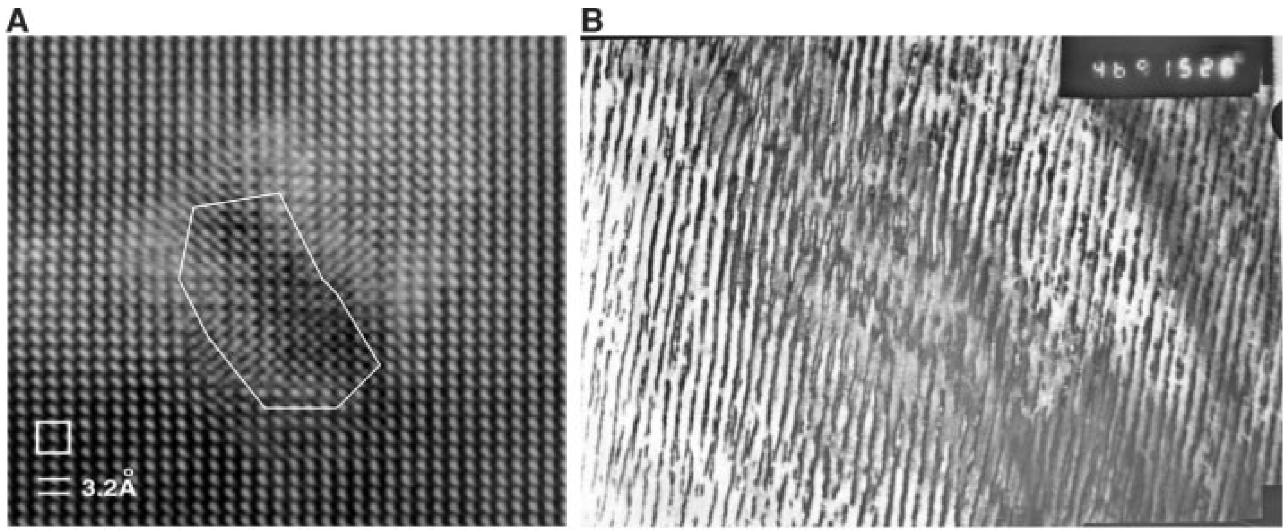
- Change the acoustic phonon dispersion –> stationary phonons or bandgaps

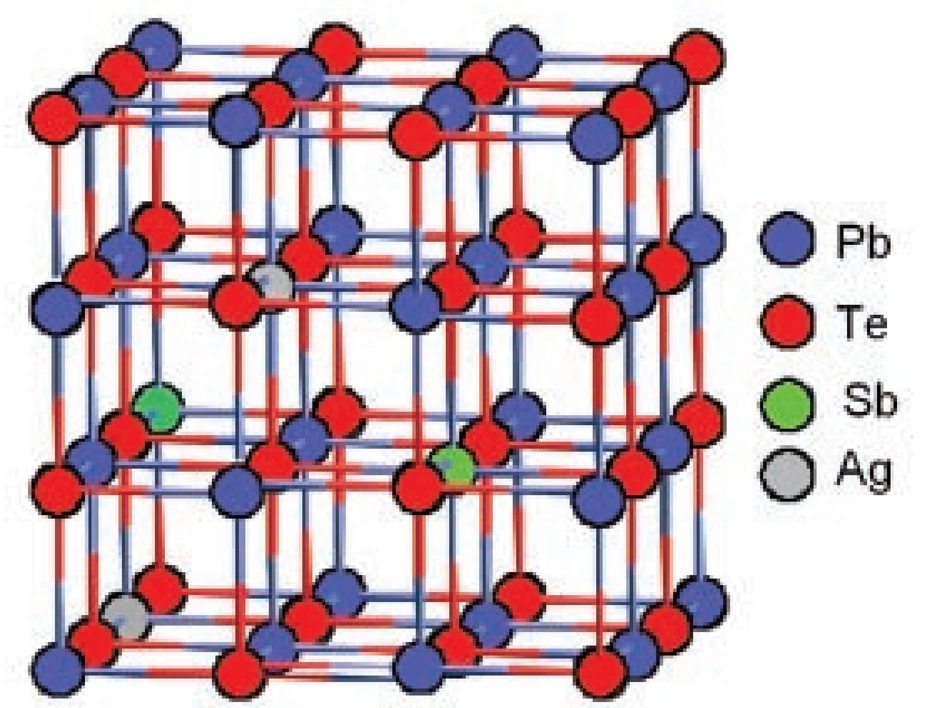
- Require structures with features at the phonon wavelength (< 5 nm)

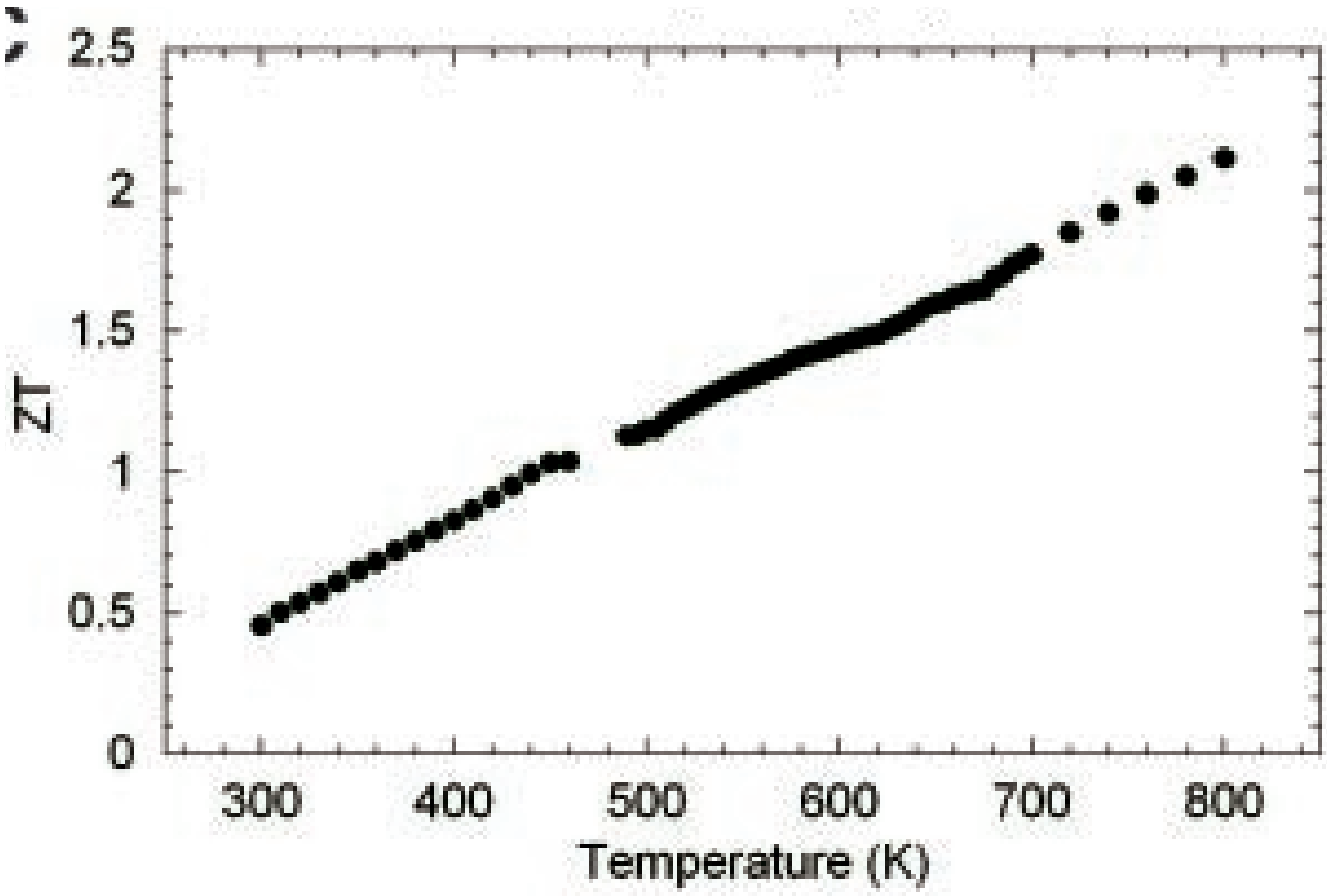
- Phonon group velocity $\propto \frac{dE}{dk_q}$



$AgPb_{18}SbTe_{20}$ – Nanoparticle Scattering?



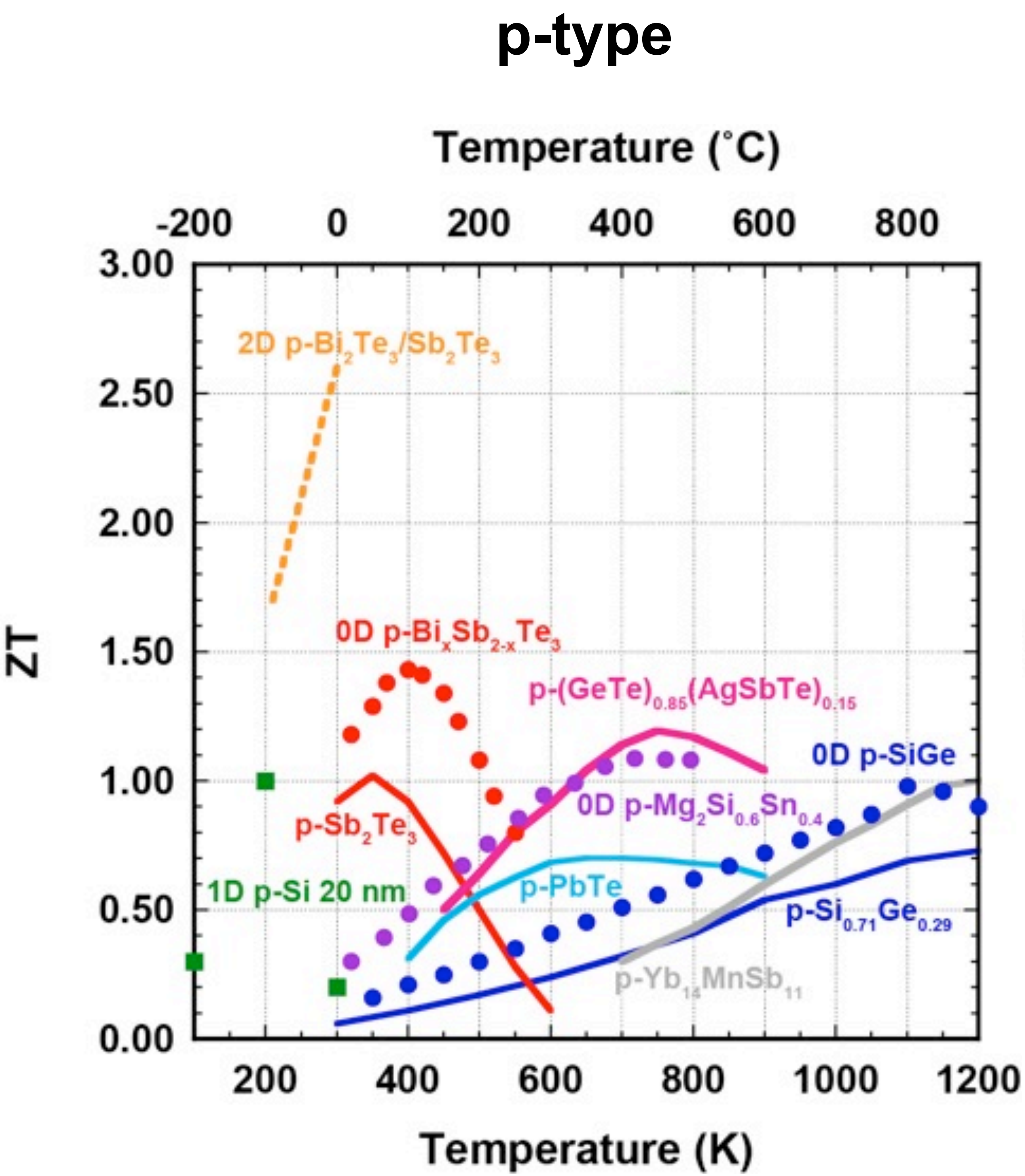


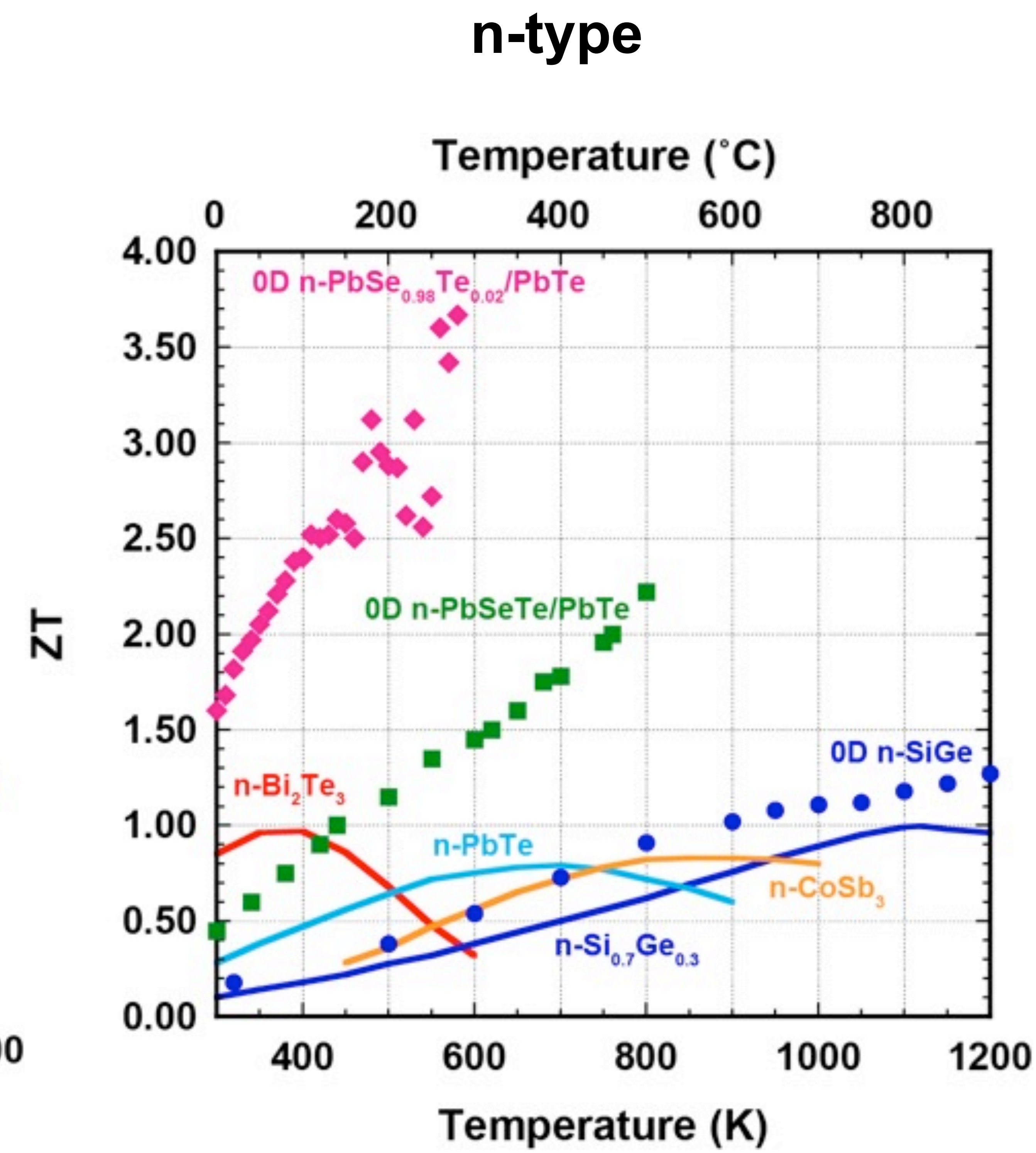


α = –335 μVK^{-1}
σ = 30,000 S/m
κ = 1.1 $Wm^{-1}K^{-1}$
at 700 K

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

ZT versus Temperature

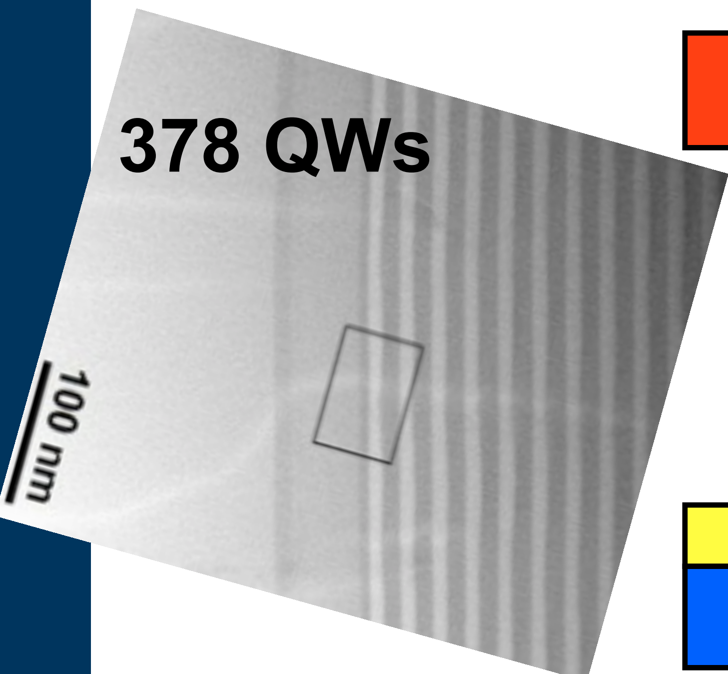




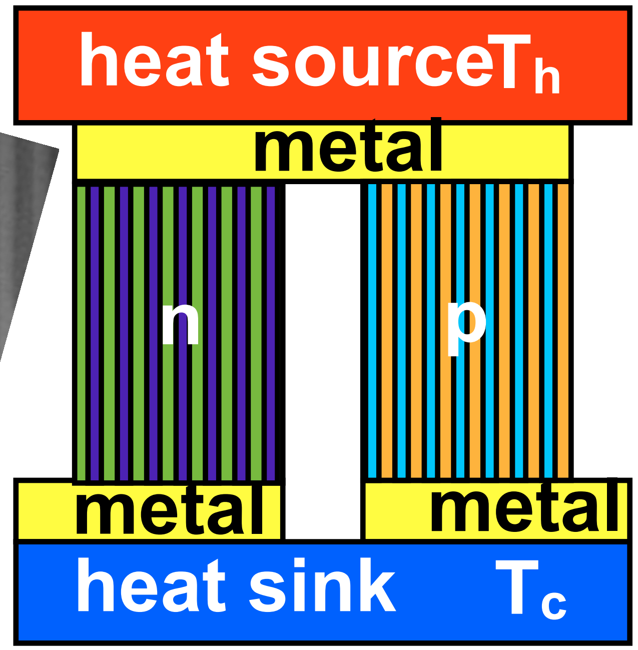
- Nanostructures can improve Seebeck coefficient and/or decrease thermal conductivity

University of Glasgow

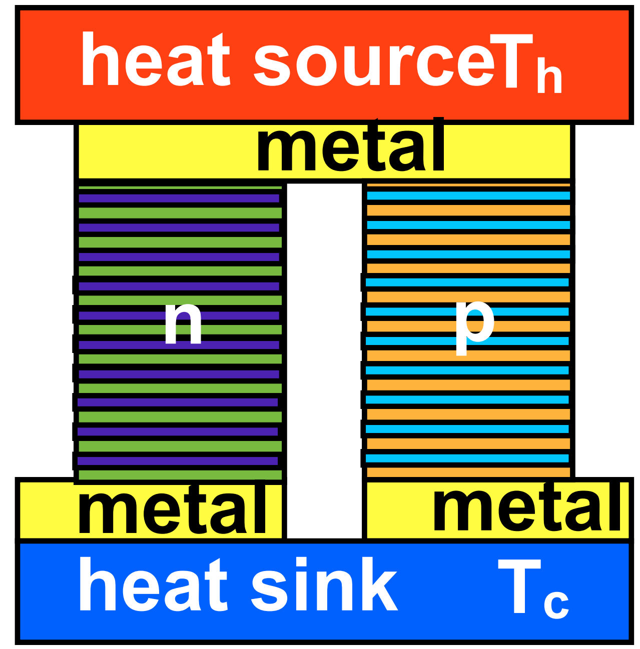
Thermoelectric Low Dimensional Structures

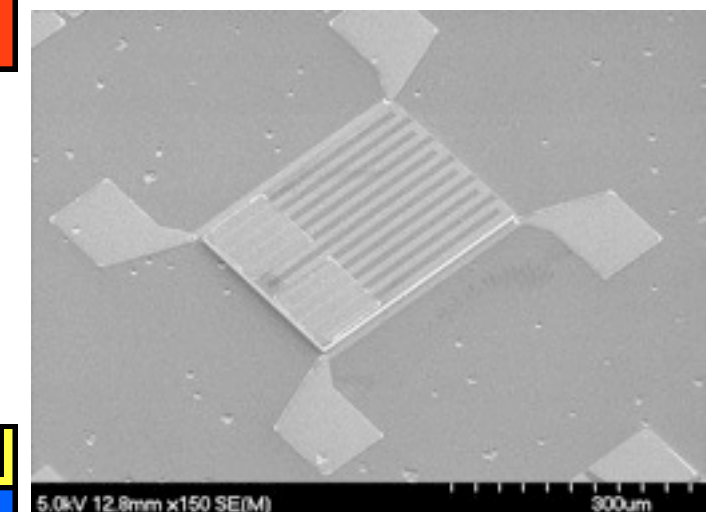


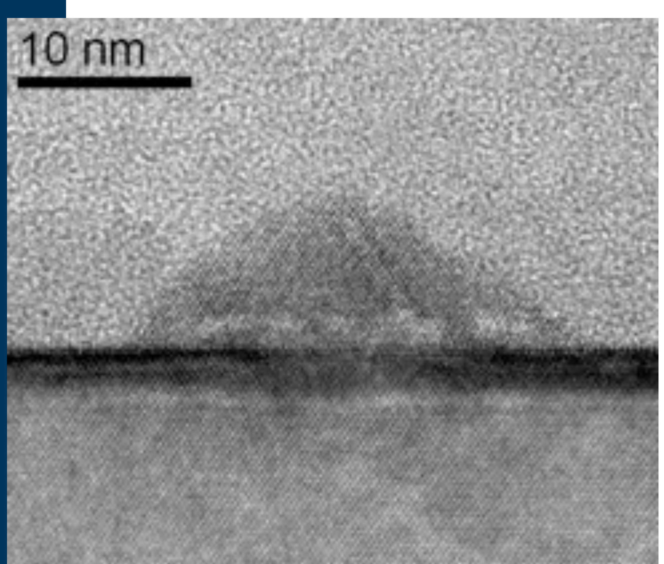
Lateral superlattice



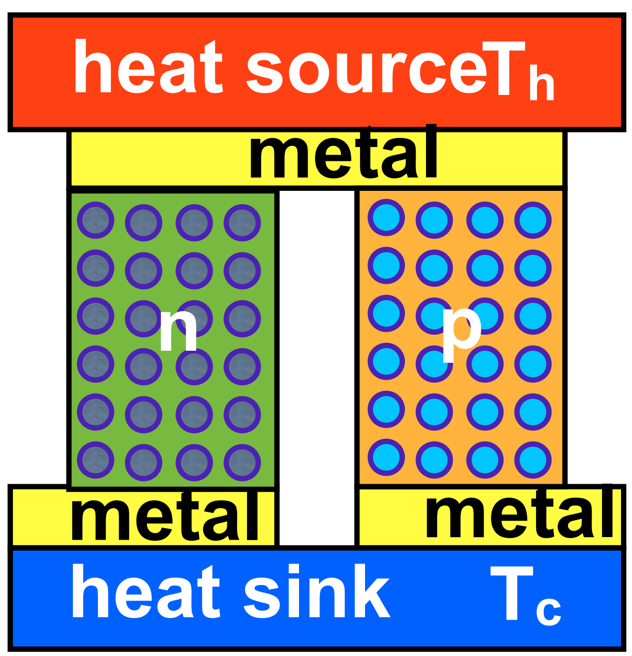
Vertical superlattice



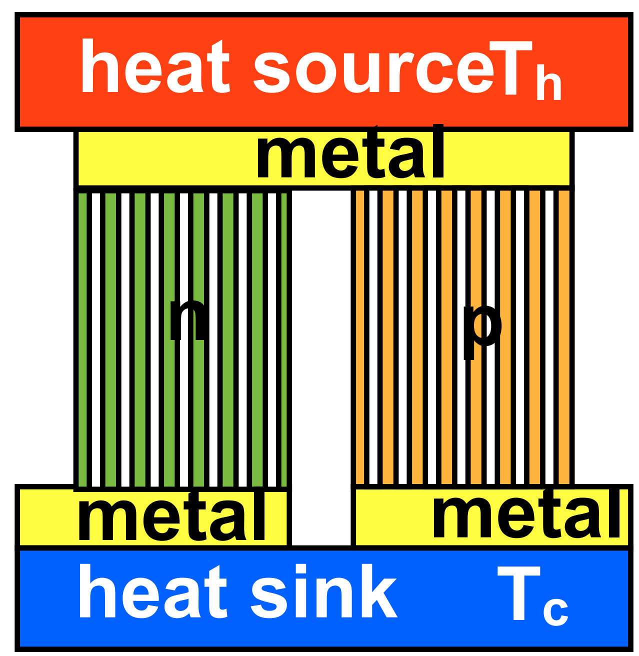


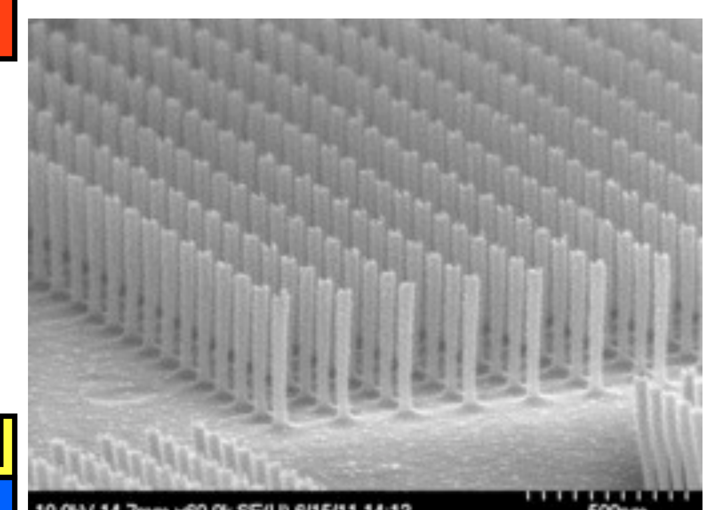


Quantum Dots

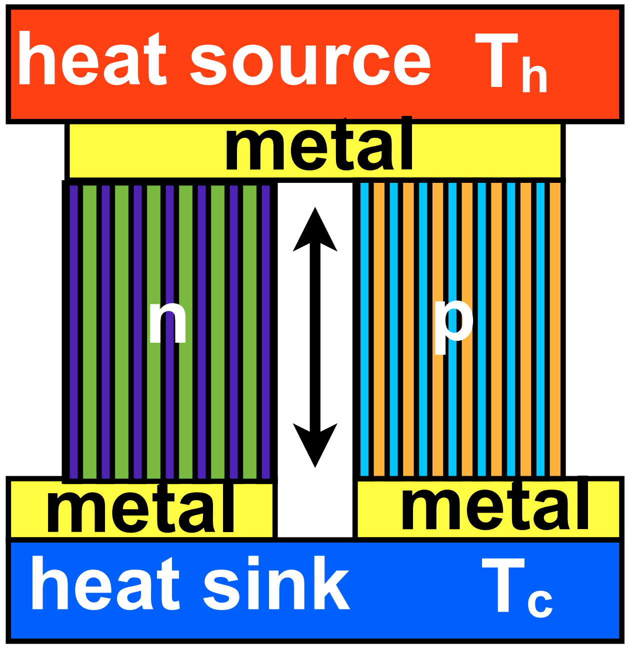


Nanowires





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} from phonon scattering at heterointerfaces
- Disadvantage: higher κ_{el} with higher σ (but layered structure can reduce this effect)
- Overall Z and ZT should increase

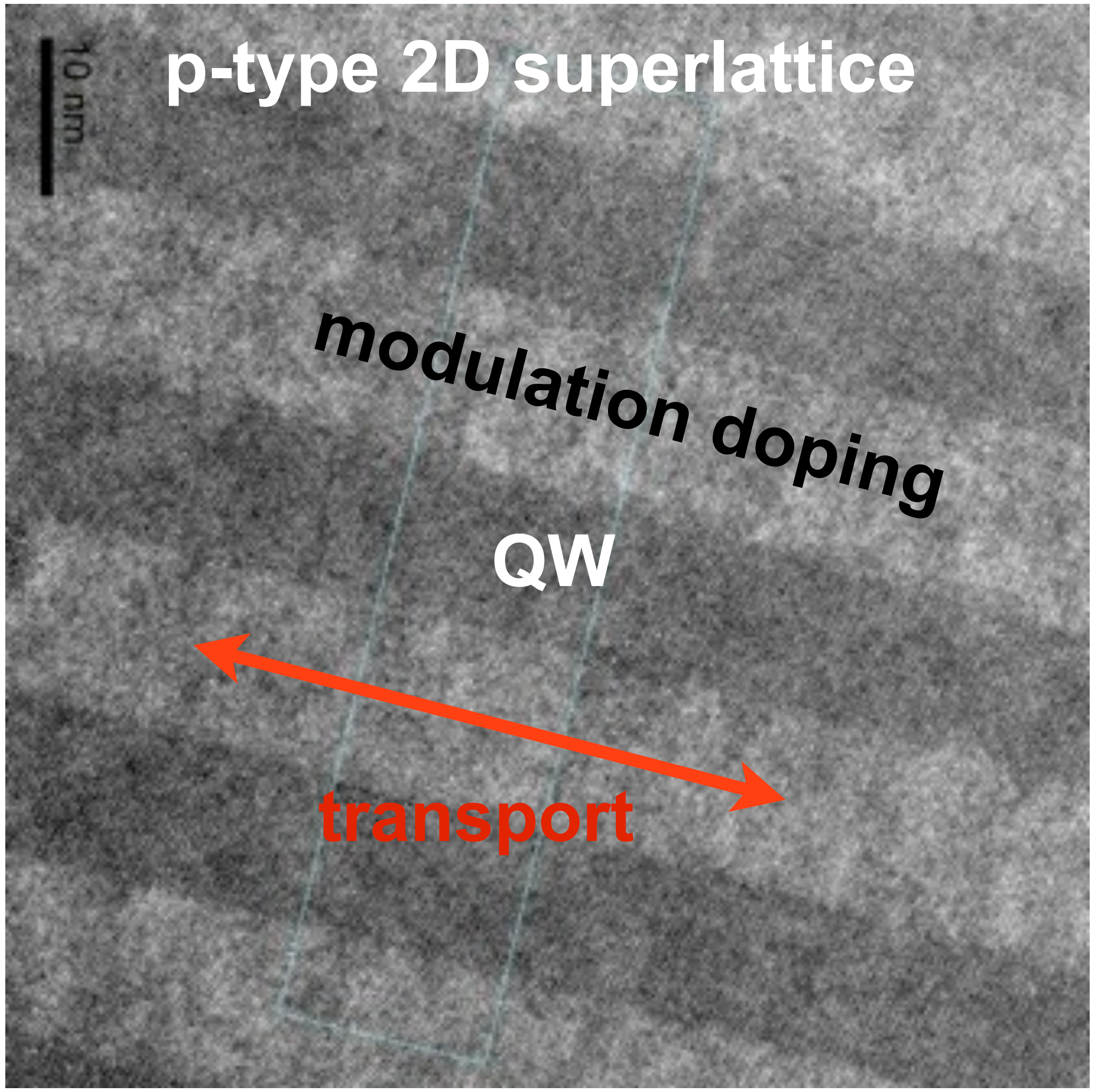
Figure of merit

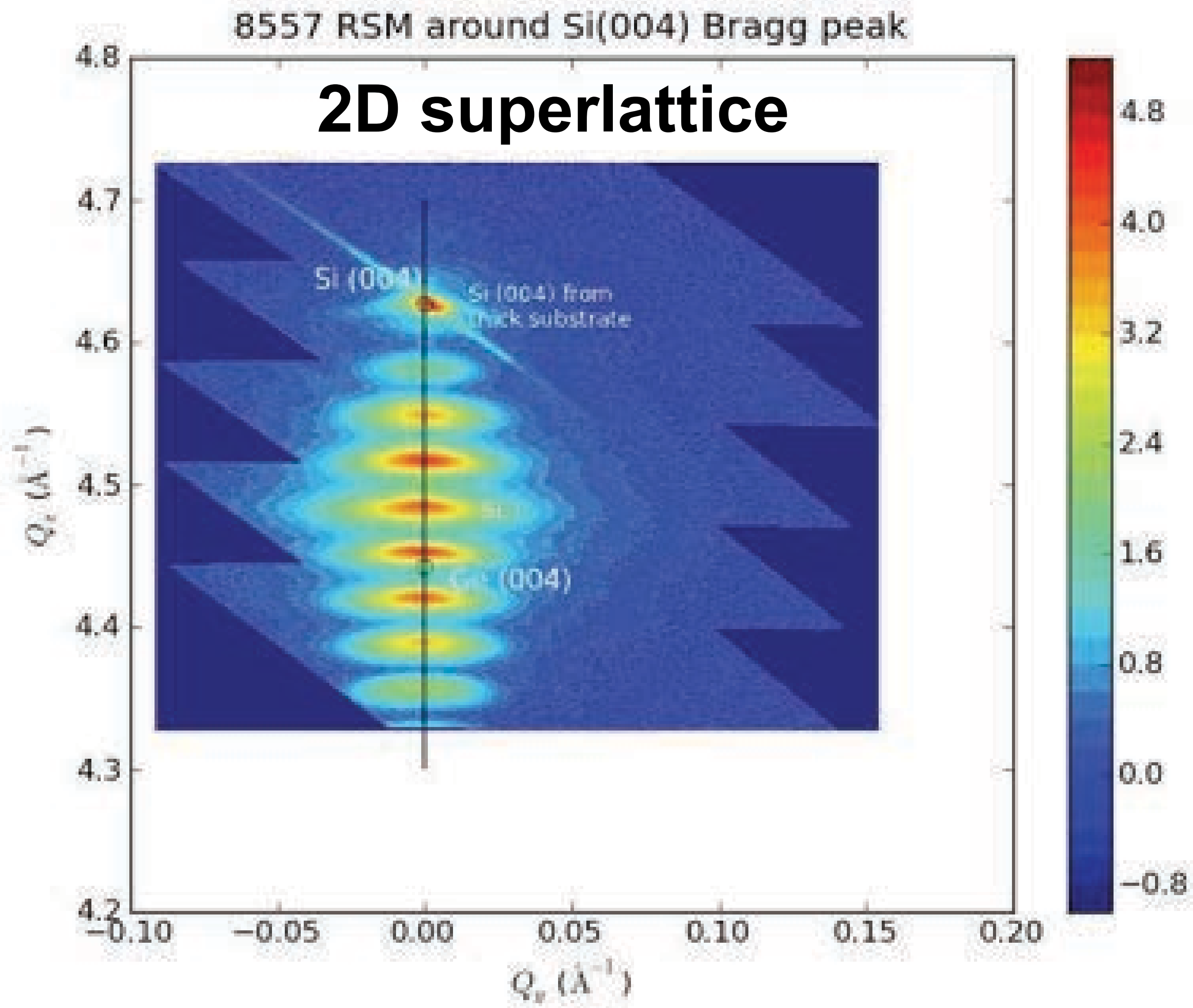
$$\mathrm{ZT} = \frac{\alpha^2 \sigma}{\kappa} \mathrm{T}$$

TE Whall and EHC Parker, 1987

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

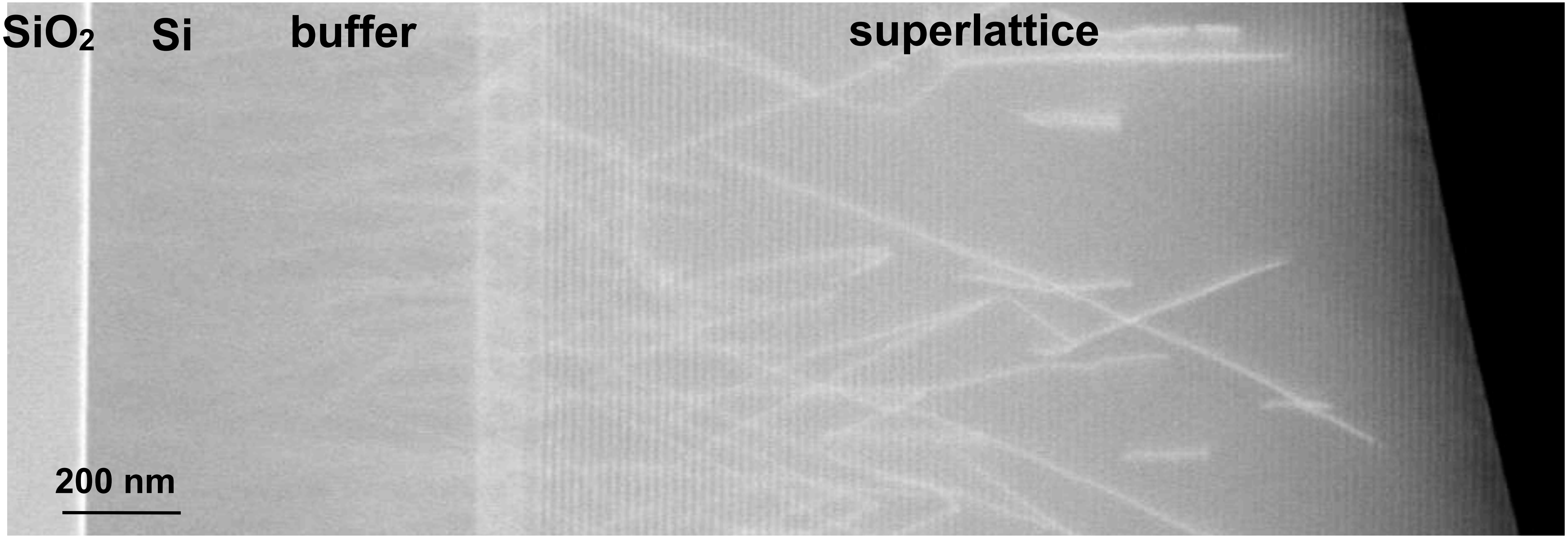
Modulation Doped Si/SiGe





- **TEM & XRD characterisation of 2D modulation-doped QW superlattice designs**
- **Threading dislocation densities from 5x10^{8} to 3x10^{9} cm^{-2}**

TEM-characterisation



DF STEM:
sample 8569 B6

- Threading dislocations penetrating from the buffer to the superlattice
- Intermediate layer not able to stop the dislocations to cross the interface from buffer to SL –> new design
- Threading dislocation density ~3×10^{9} cm^{-2}

The Uncertainty in Measuring ZT

- Many materials with ZT > 1.5 reported
  but few confirmed by others (!)

- No modules demonstrated with such high efficiencies

- Due to: measurement uncertainty & complexity
  of fabricating devices

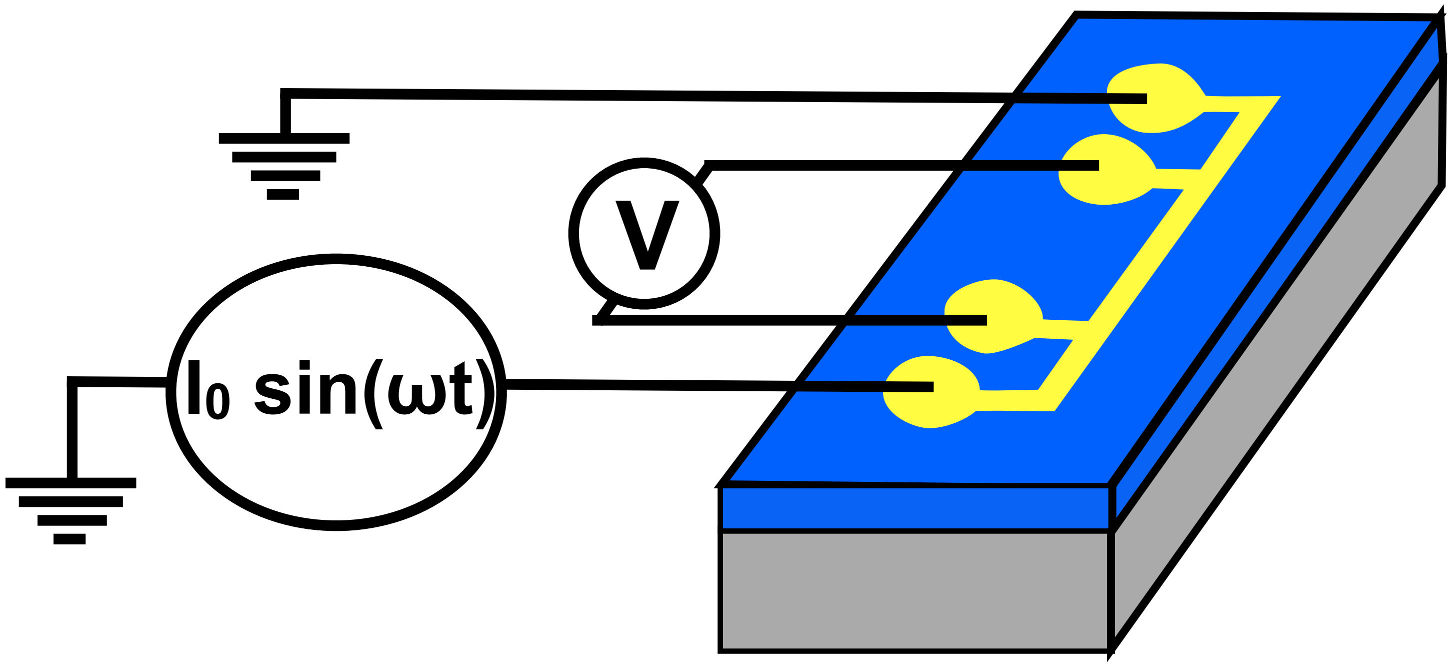
- $$\frac{\mathbf{\Delta(ZT)}}{\mathbf{ZT}} = \mathbf{2}\frac{\mathbf{\Delta}\alpha}{\alpha} + \frac{\mathbf{\Delta}\sigma}{\sigma} + \frac{\mathbf{\Delta}\kappa}{\kappa} + \frac{\mathbf{\Delta T}}{\mathbf{T}}$$

  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%

3ω Thermal Conductivity Measurements



$I \sim \omega$

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

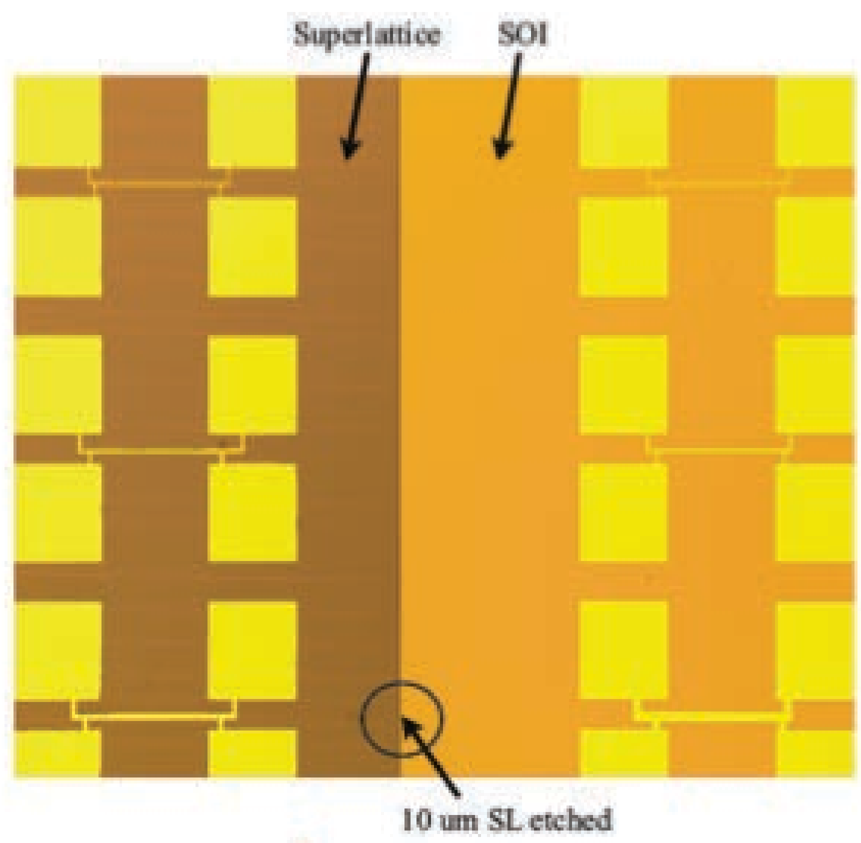
$R \sim T \sim 2\omega$

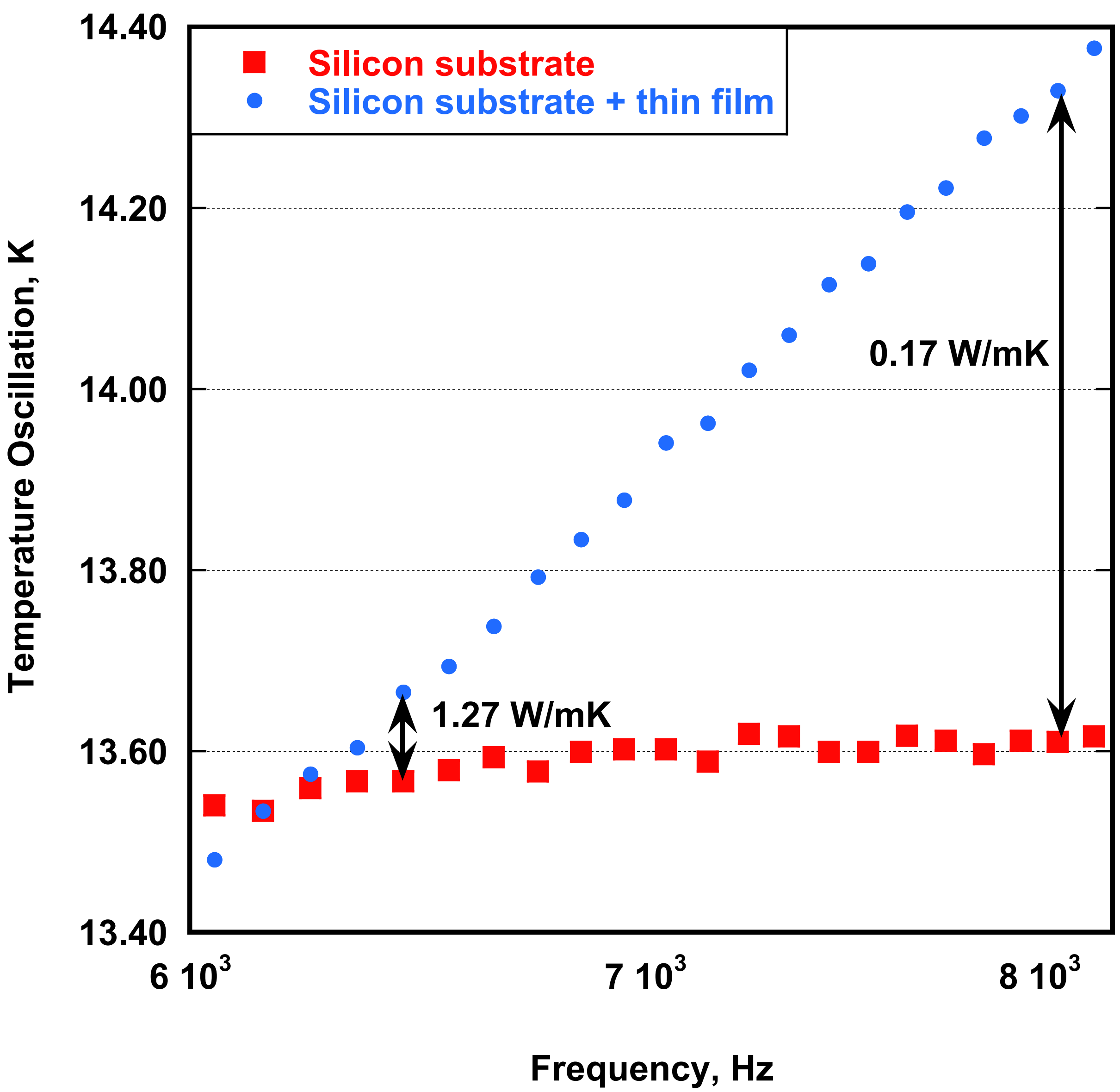
$V = IR \sim 3\omega$

- 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
- $$\mathbf{V = IR = I_0 e^{i\omega t}\left[R_0 + \frac{\delta R}{\delta T}\Delta T\right]}$$

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

Differential 3 Omega

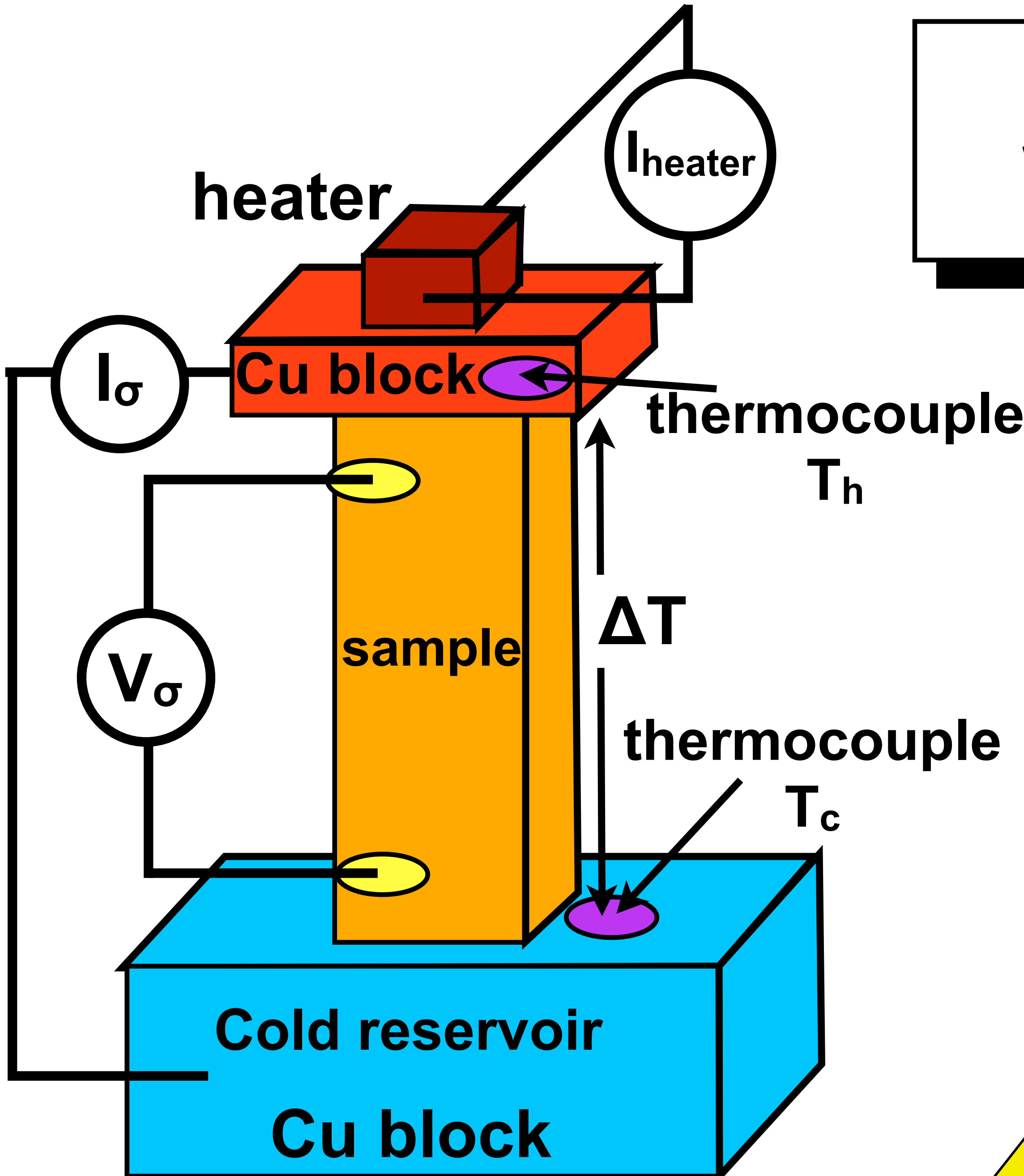


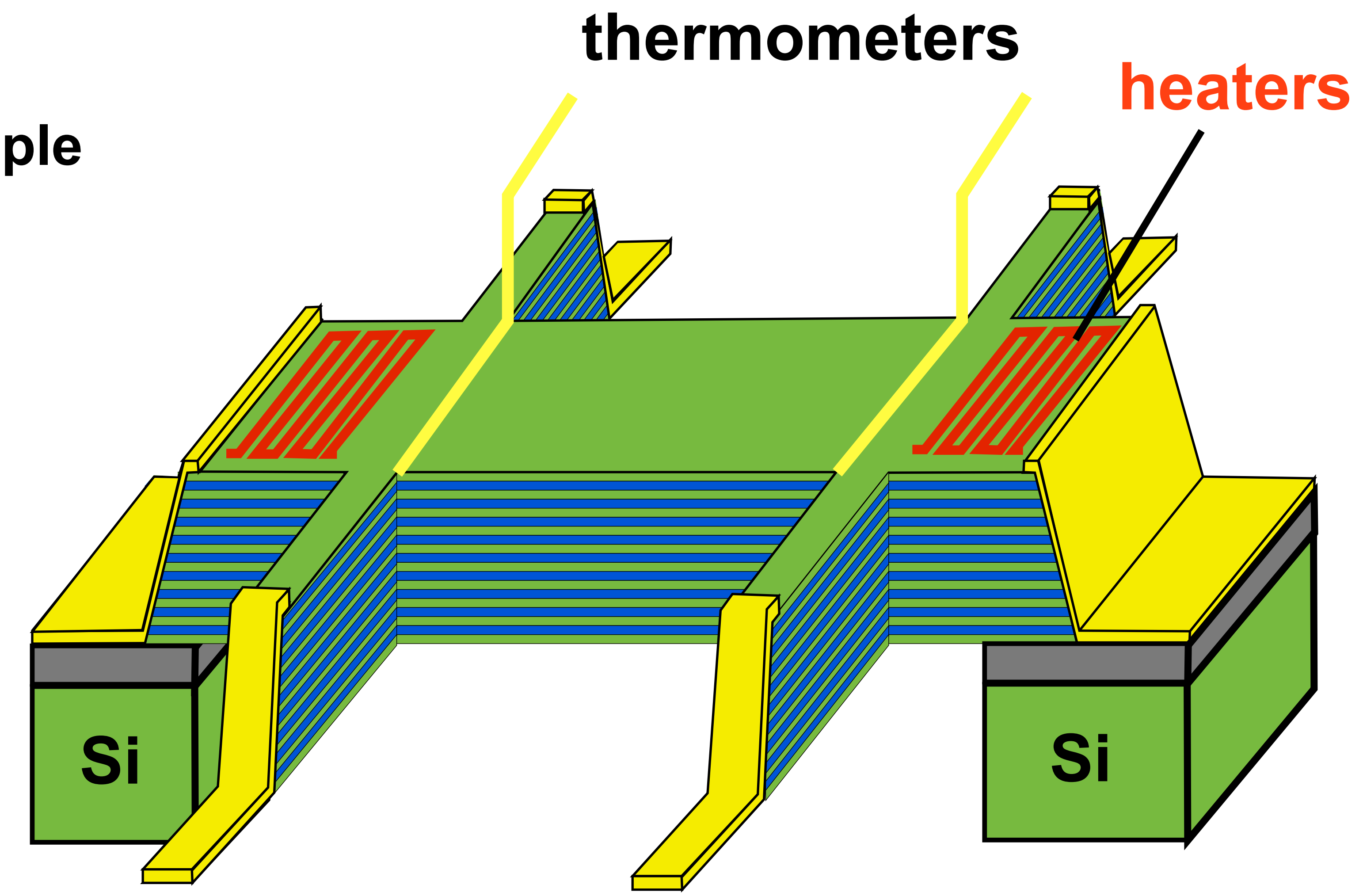


- α = 280 µV/K
- σ = 79,000 S/m
- κ = 0.17 W/mK
- => ZT = 10.9 !!
- BUT is the 3ω technique valid for superlattices?
- NO: lines should be parallel

Measuring Seebeck and Thermal Conductivity

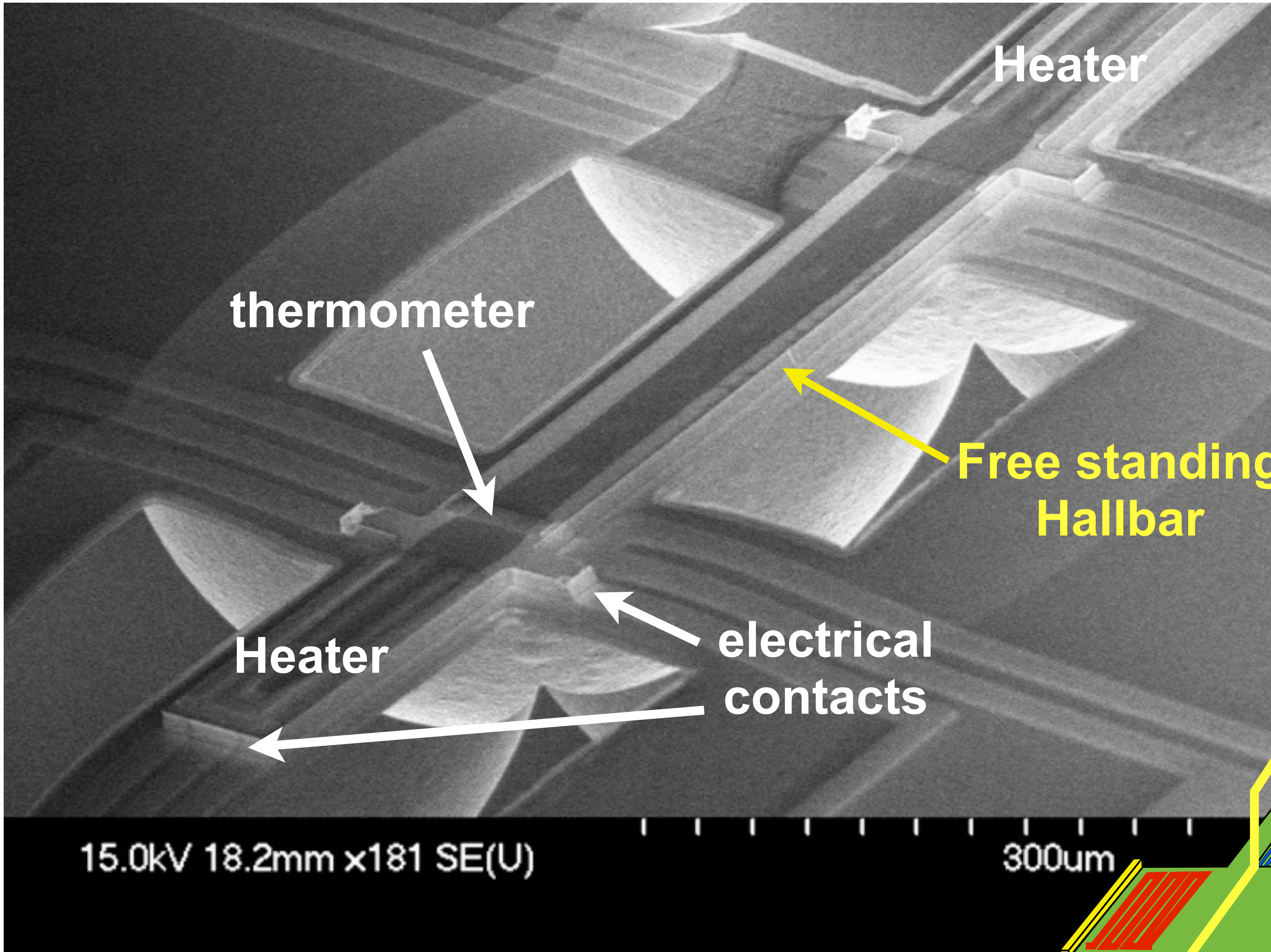
Seebeck coefficient, $\alpha = \frac{dV}{dT}$

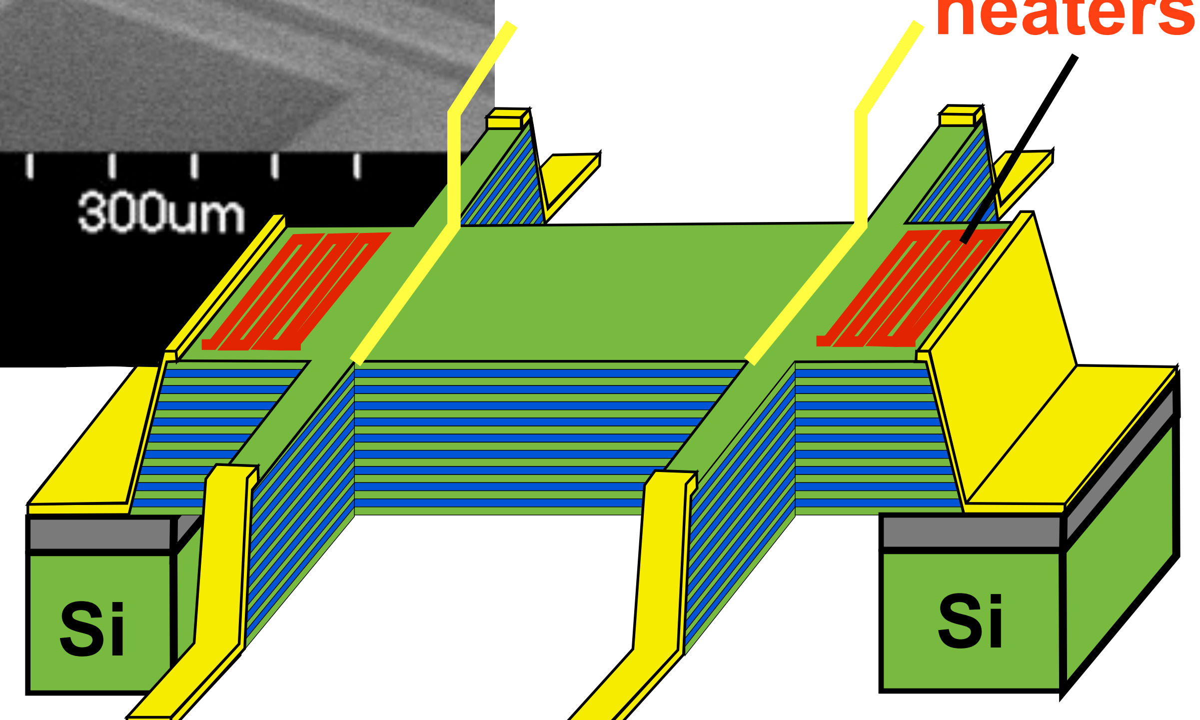




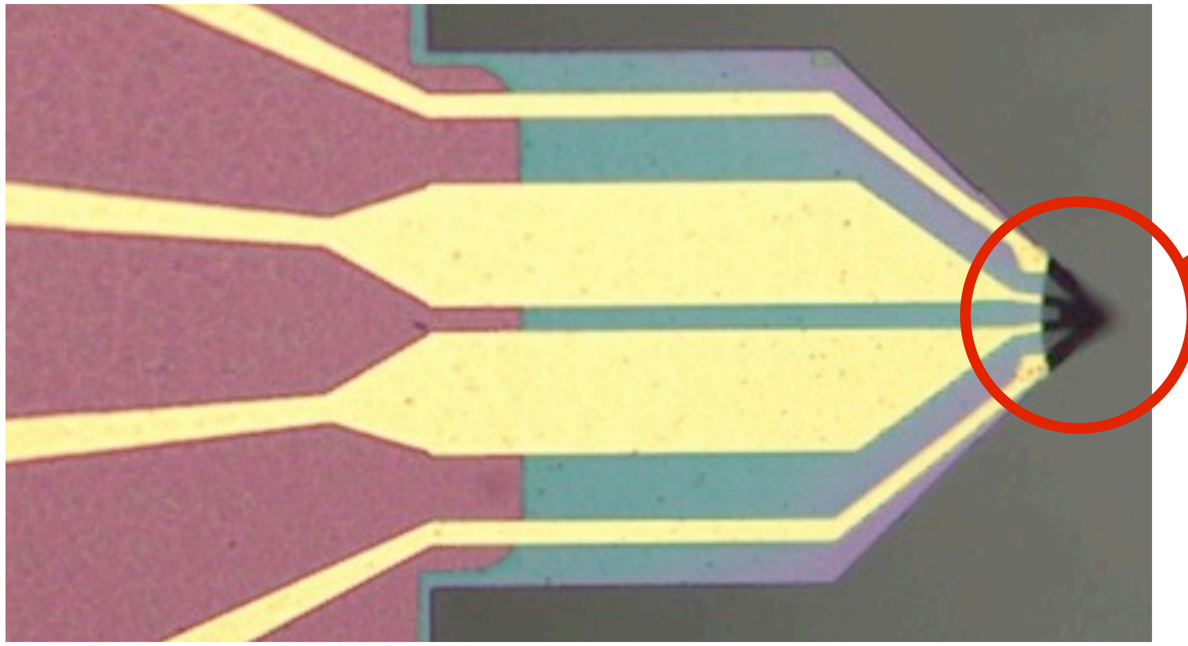
$$Q = -\kappa A \frac{T_c - T_h}{L}$$

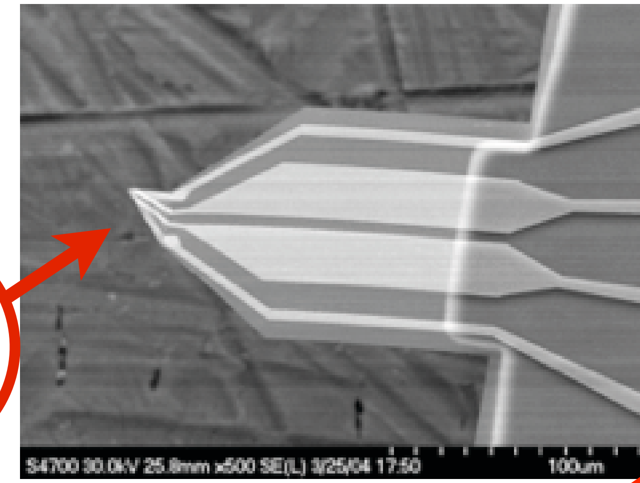
Free Standing Hallbars

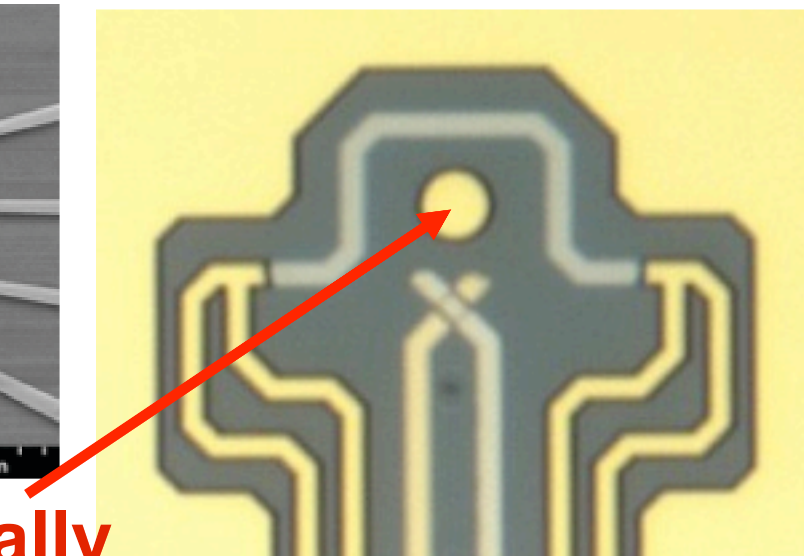




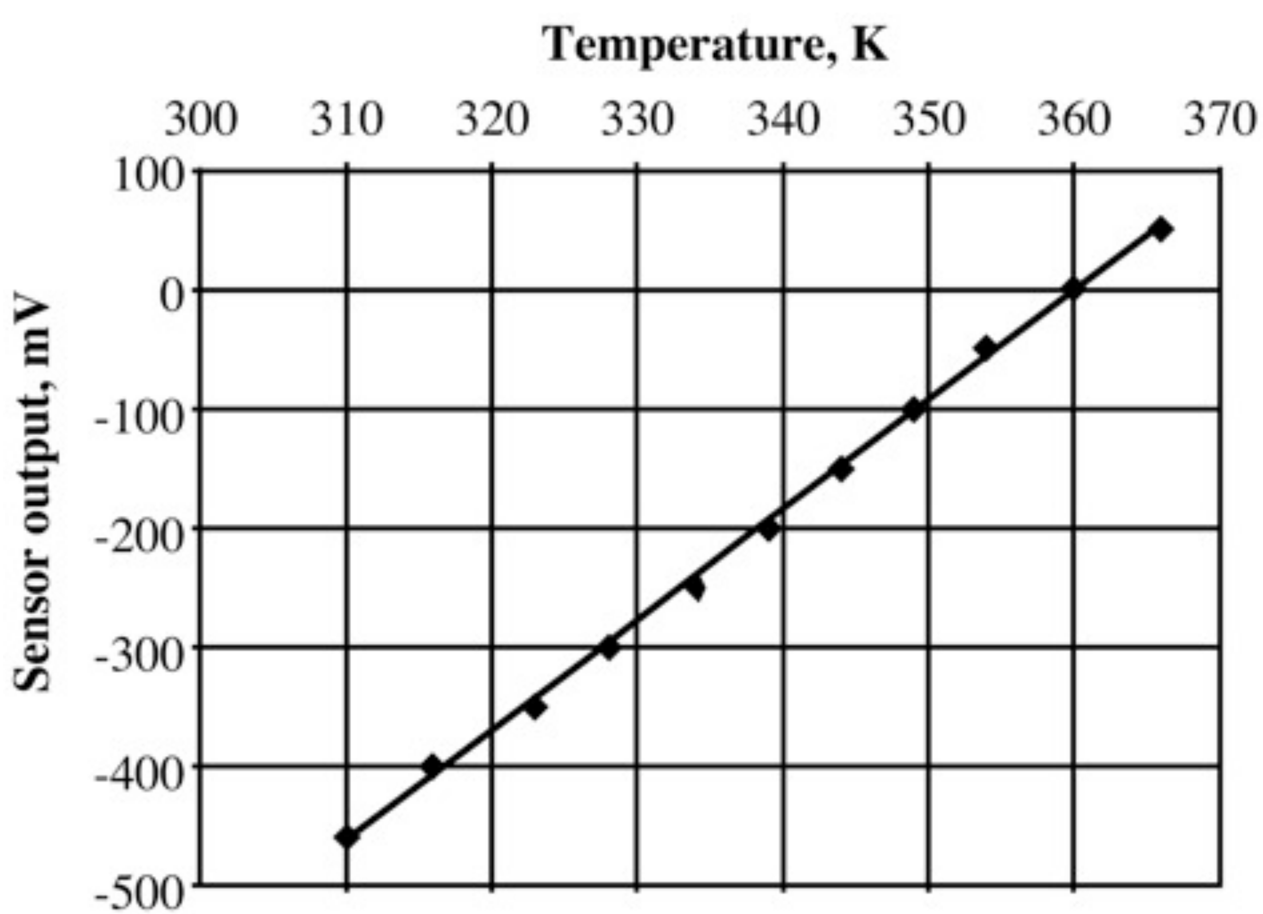
Scanning Thermal Microscopy

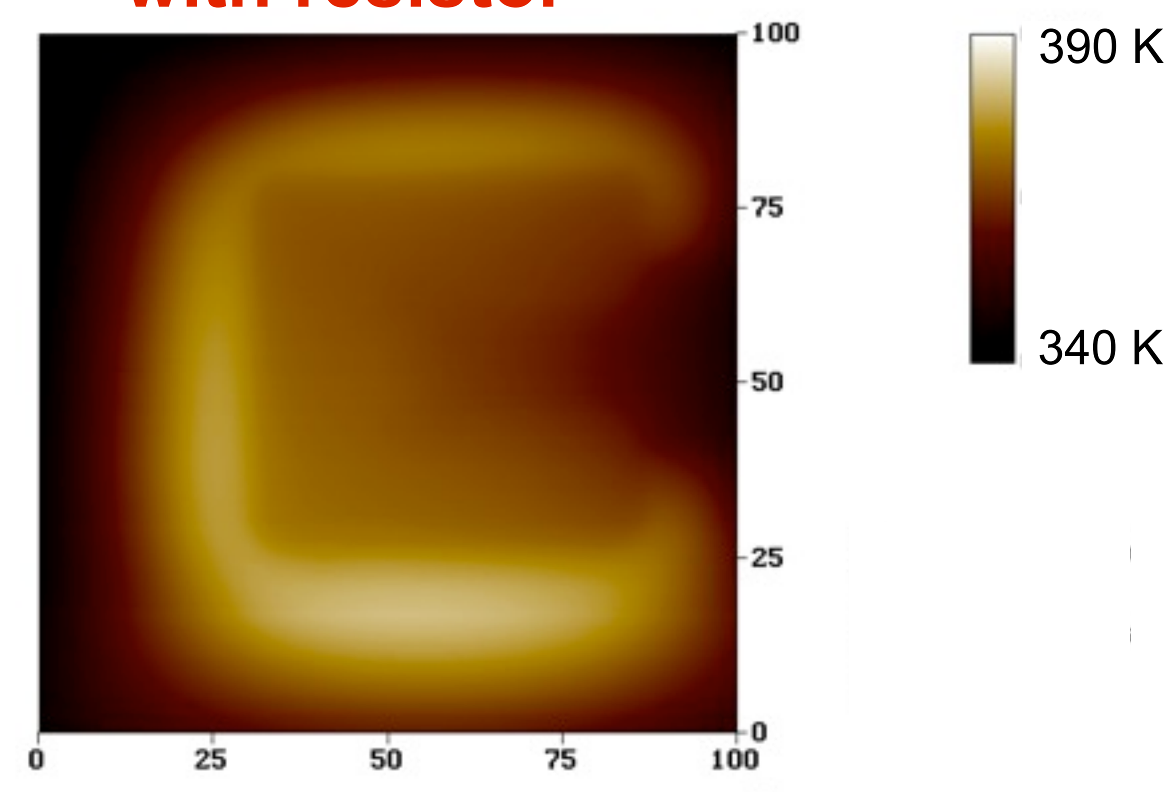






Electrically isolated Au spot: isothermal with resistor

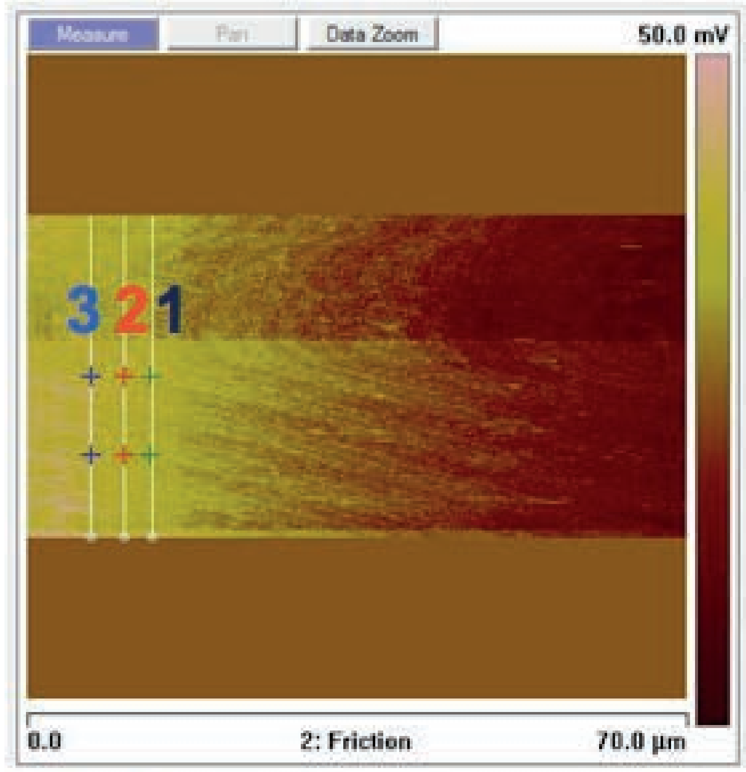


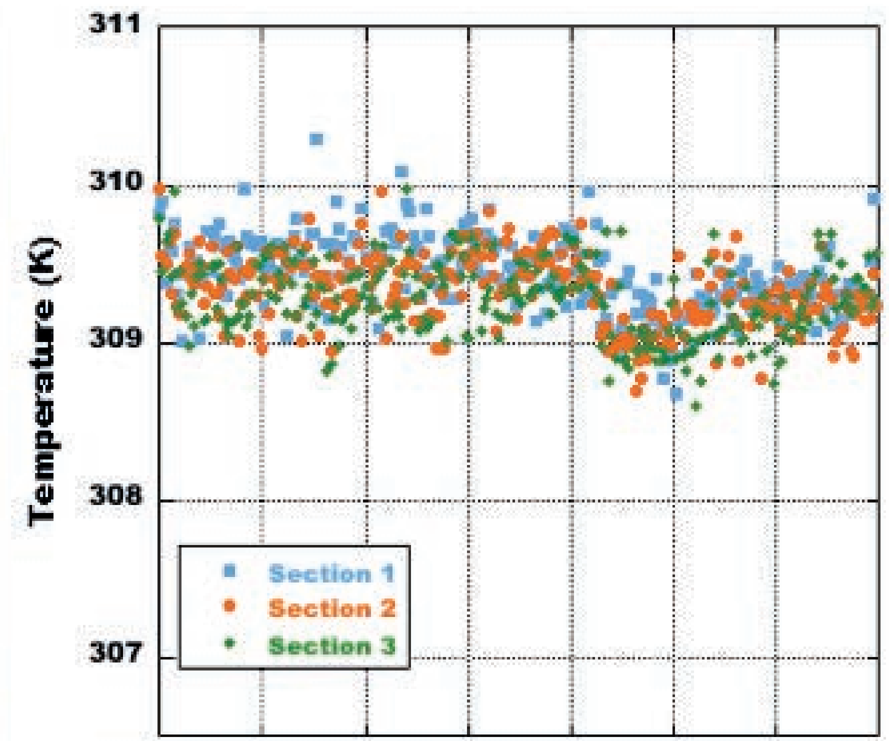


P. S. Dobson, et al., Rev. Sci. Inst. 76, 054901 (2006)

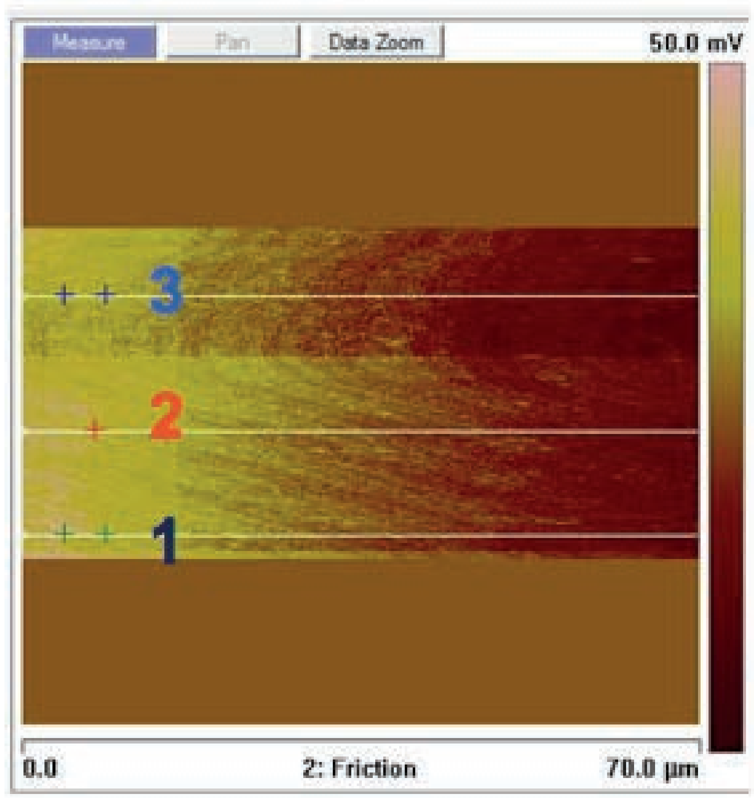
AFM Characterisation of Hall bar

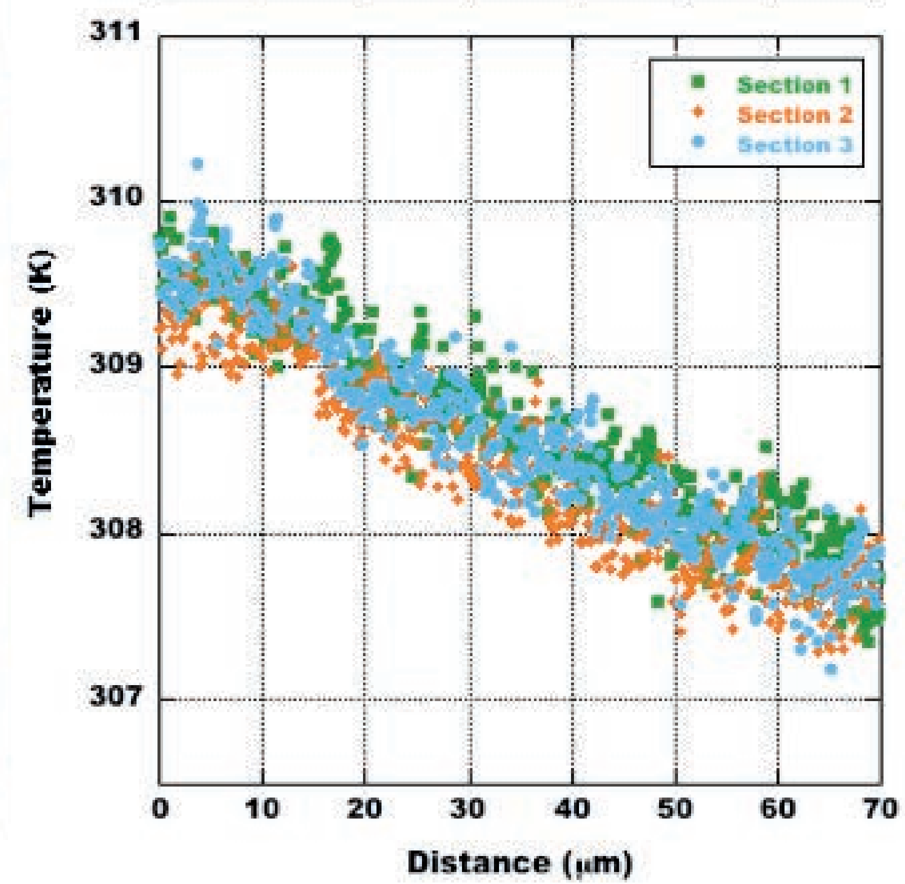
Thermal AFM across width



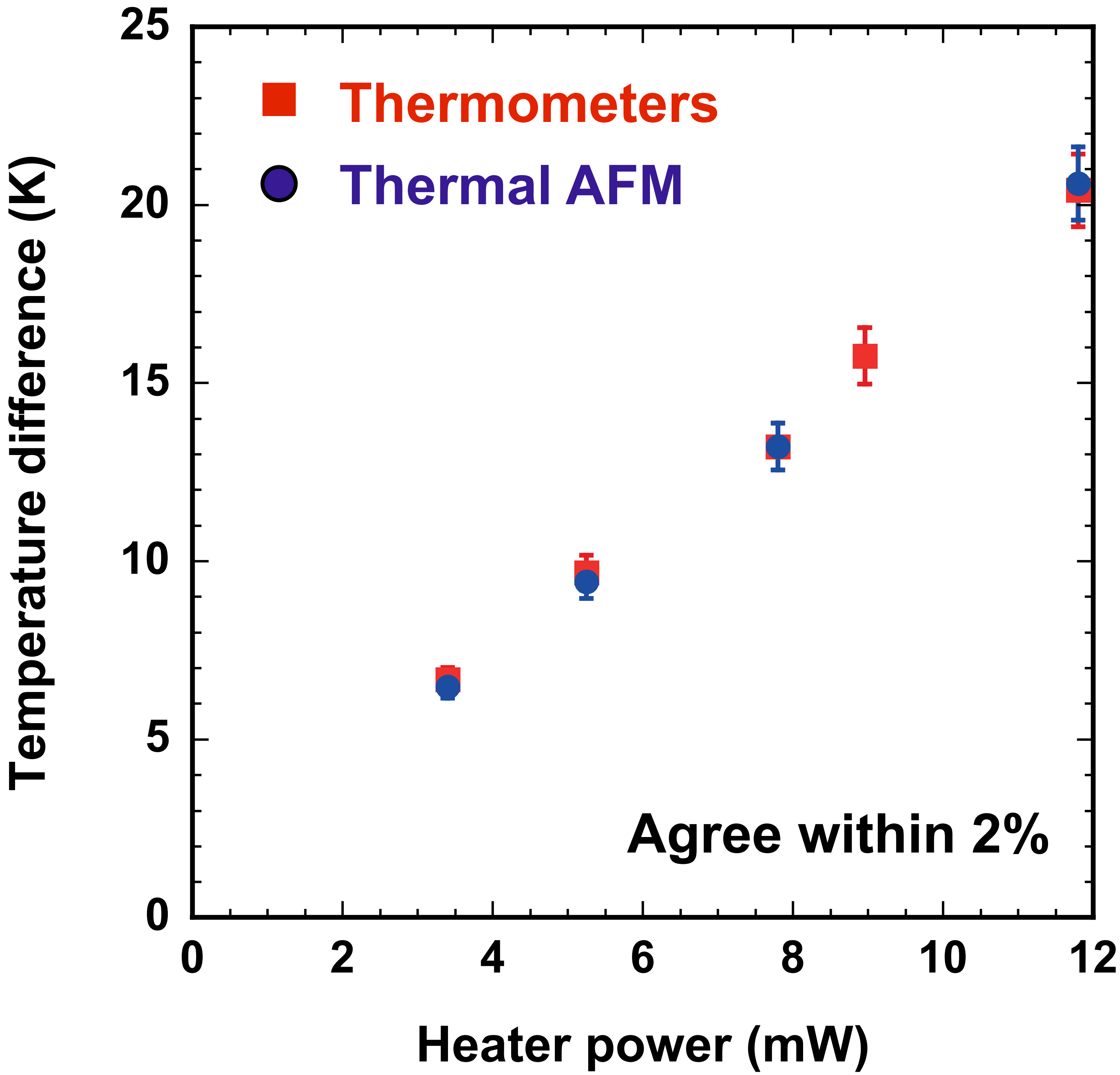


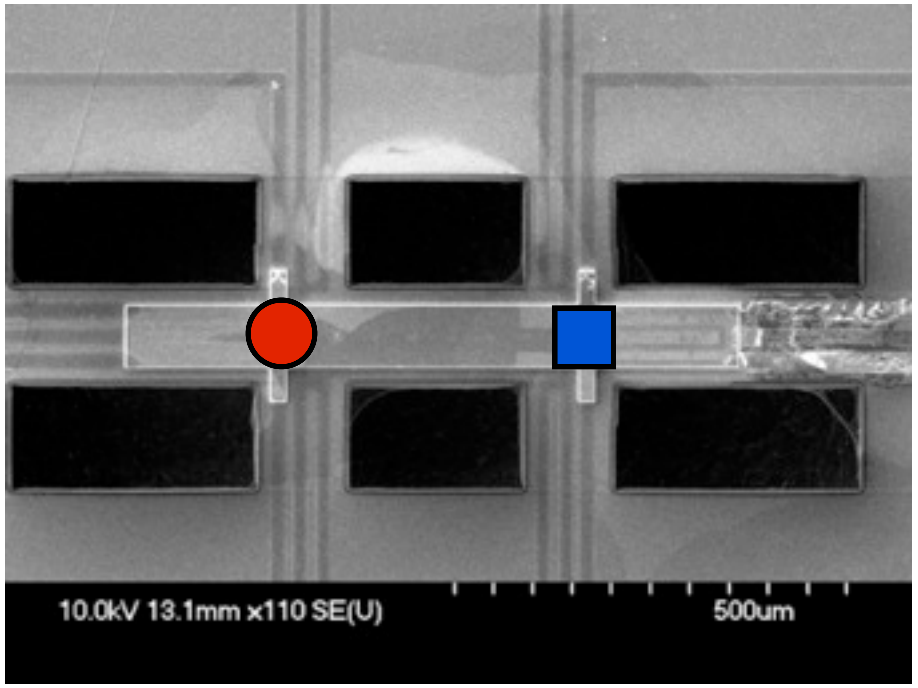
Thermal AFM along length





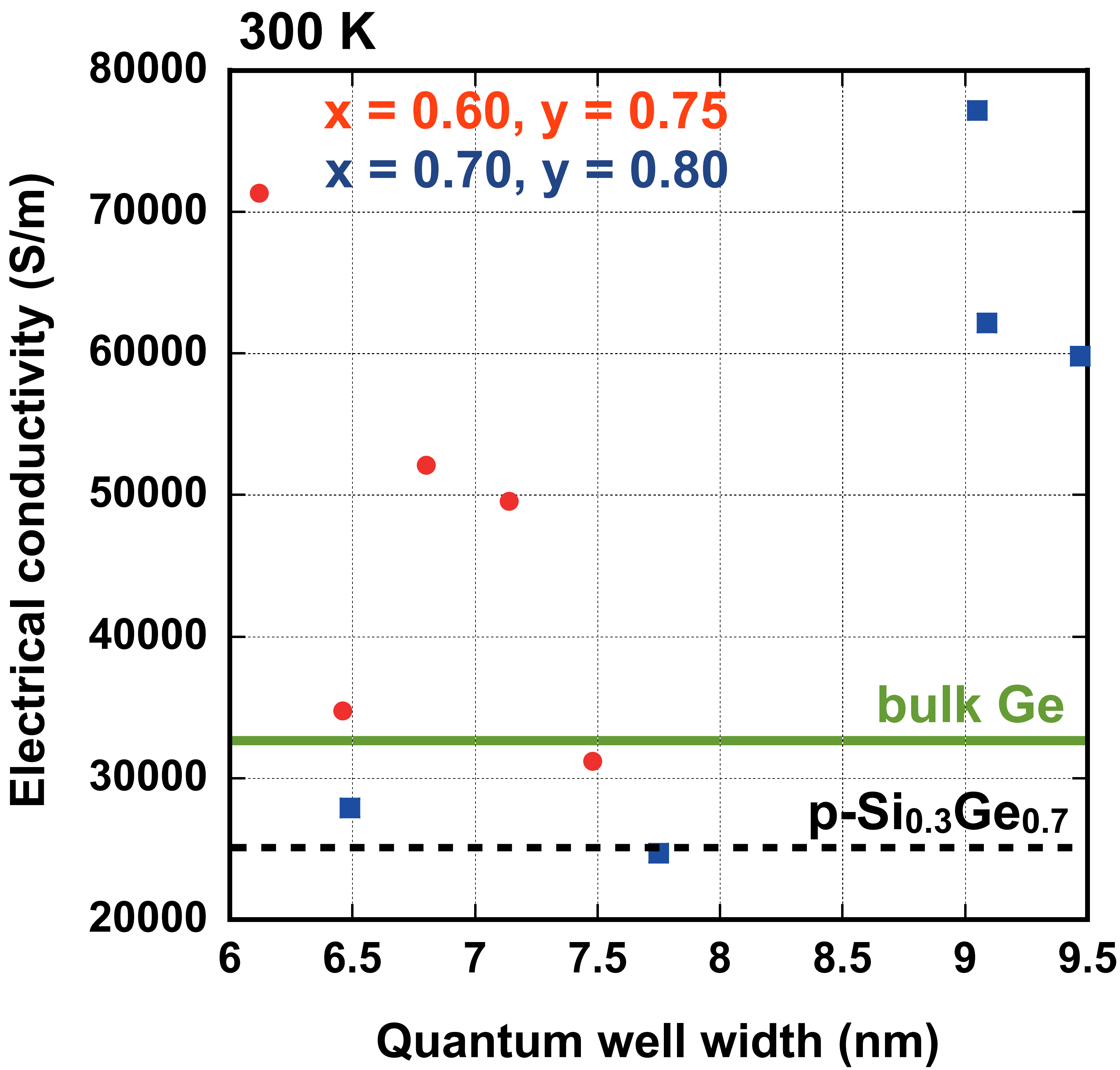
Comparison Between AFM & Thermometers

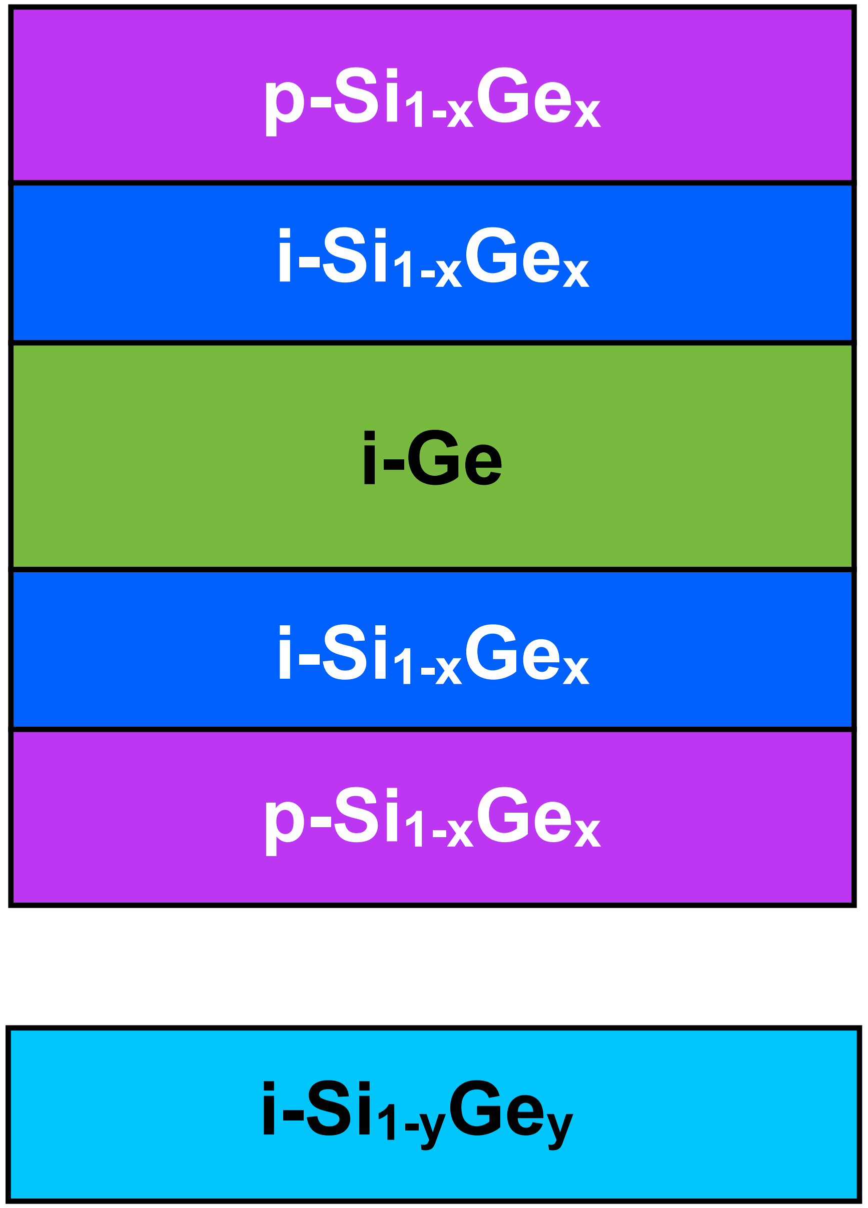




- We can measure temperature with sufficient accuracy

Electrical Conductivity vs QW Width

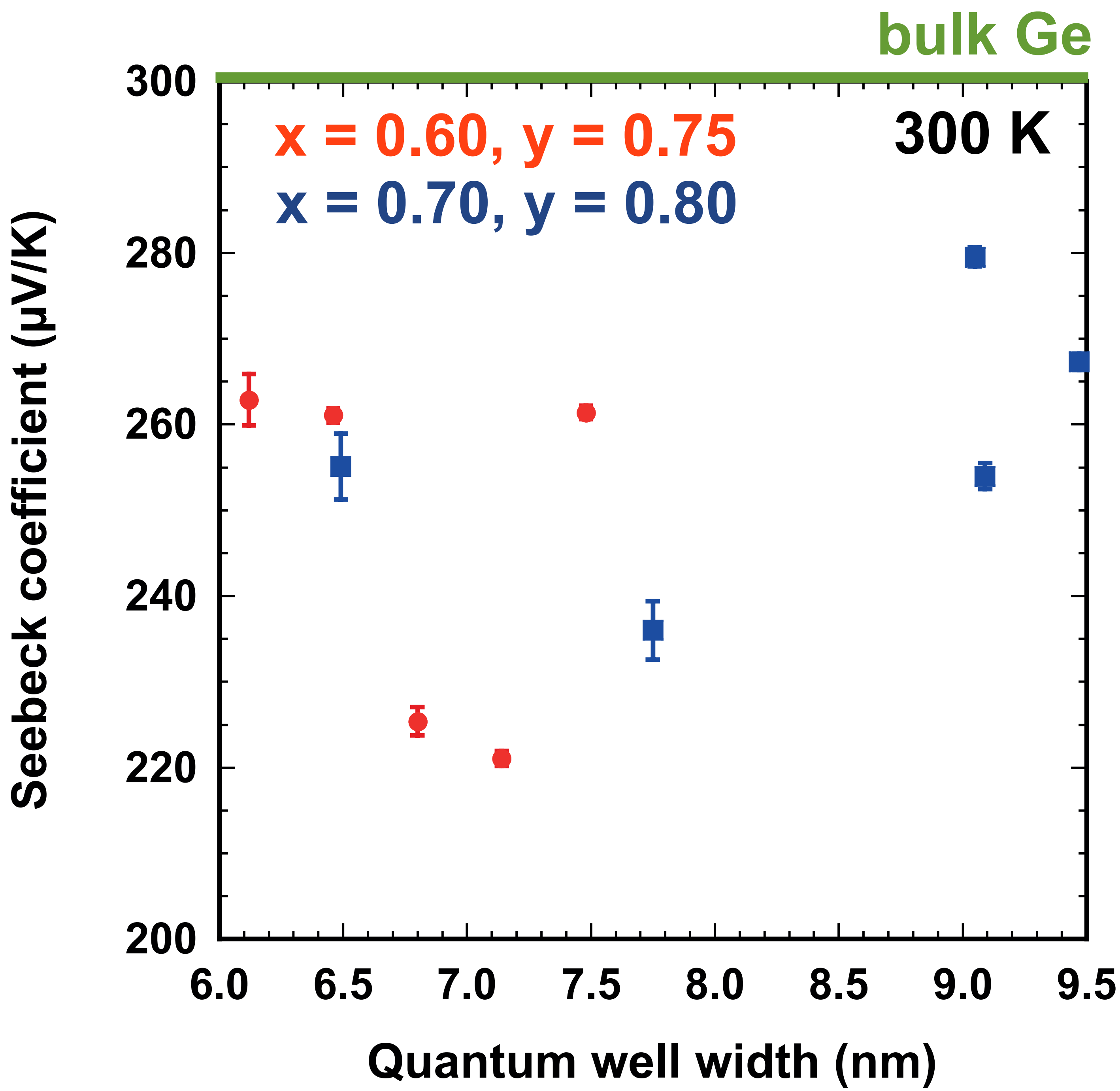


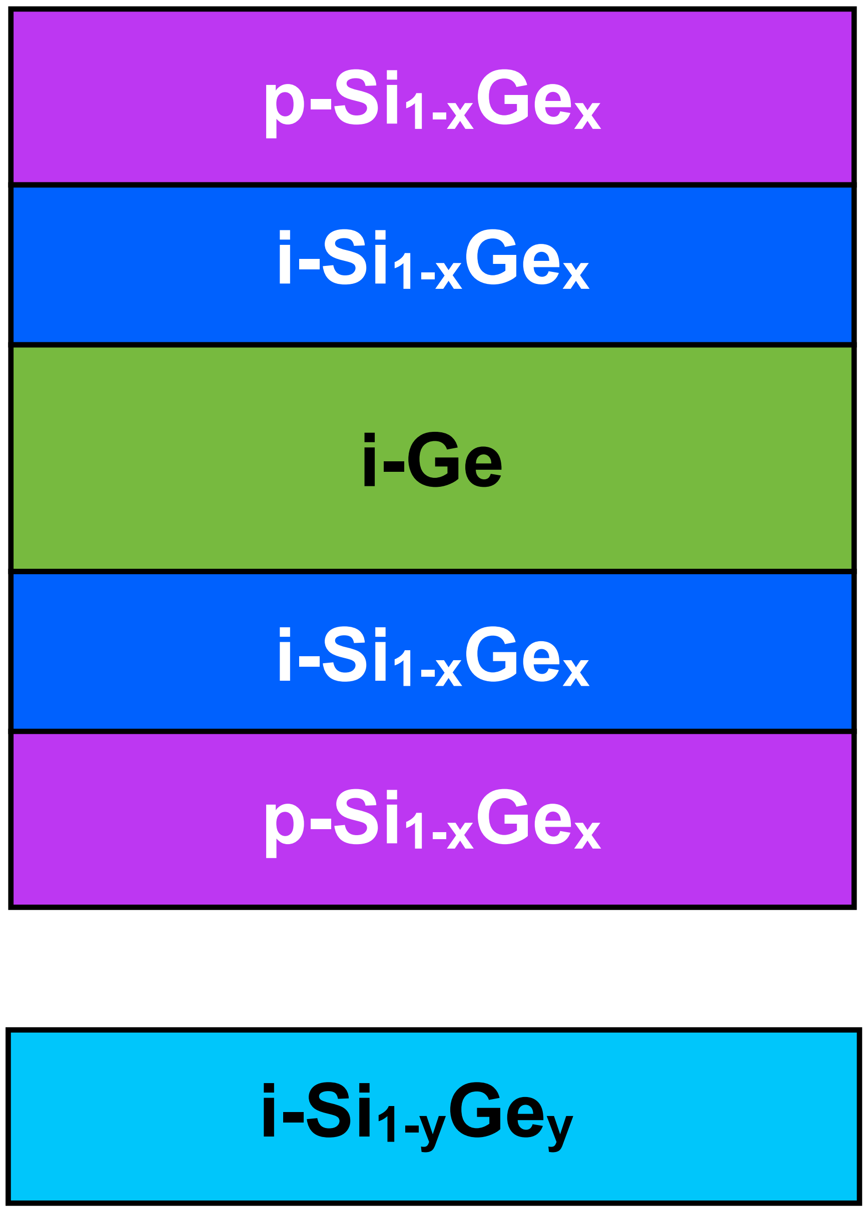


- Blue - higher density, Red - higher mobility

J. Appl. Phys. 113, 233704 (2013)

Seebeck Coeffcient

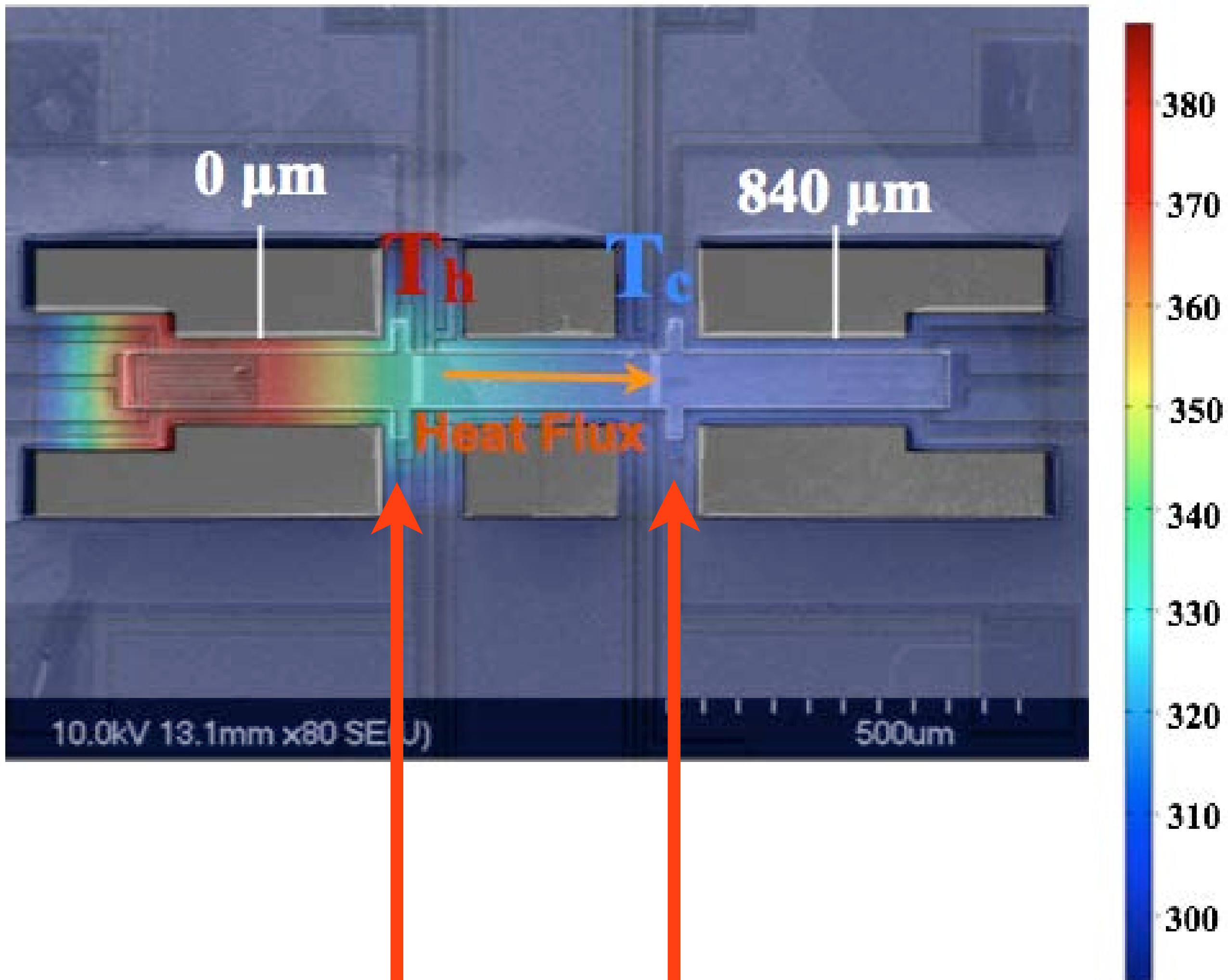


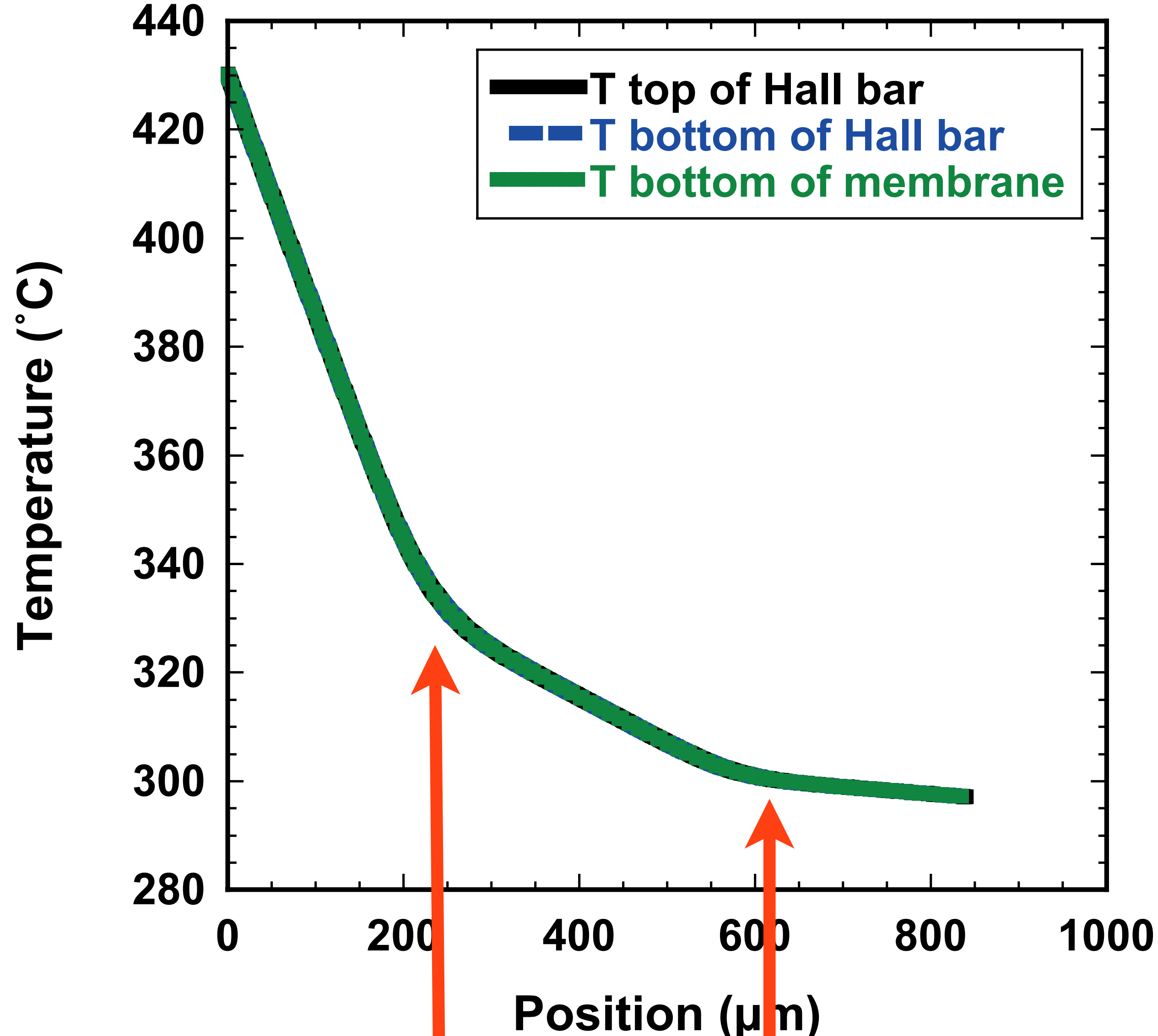


- p-$Si_{0.3}Ge_{0.7}$ α = 90 μV/K
- QWs too wide for Seebeck enhancements

J. Appl. Phys. 113, 233704 (2013)

Parasitic Thermal Channels

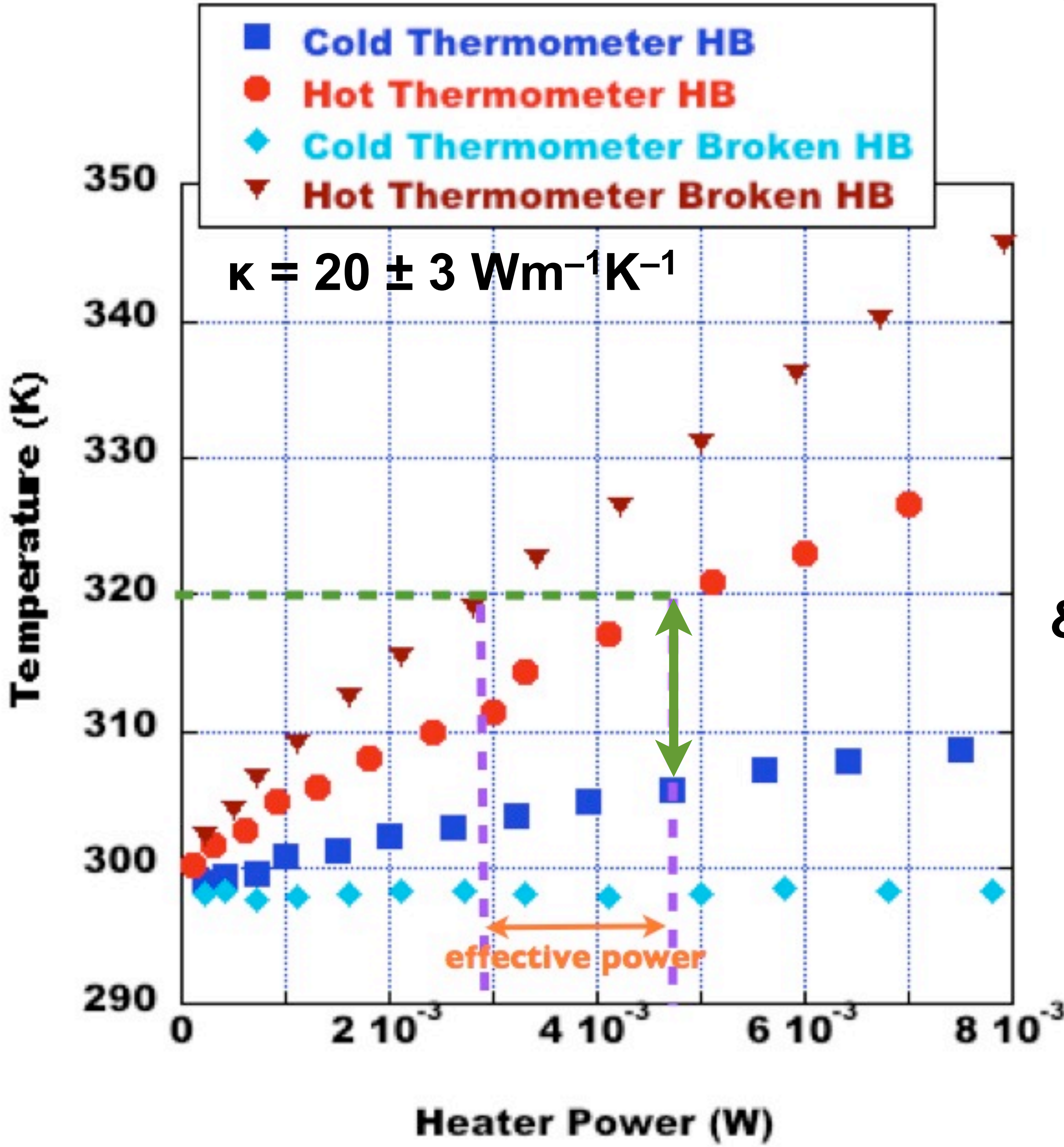




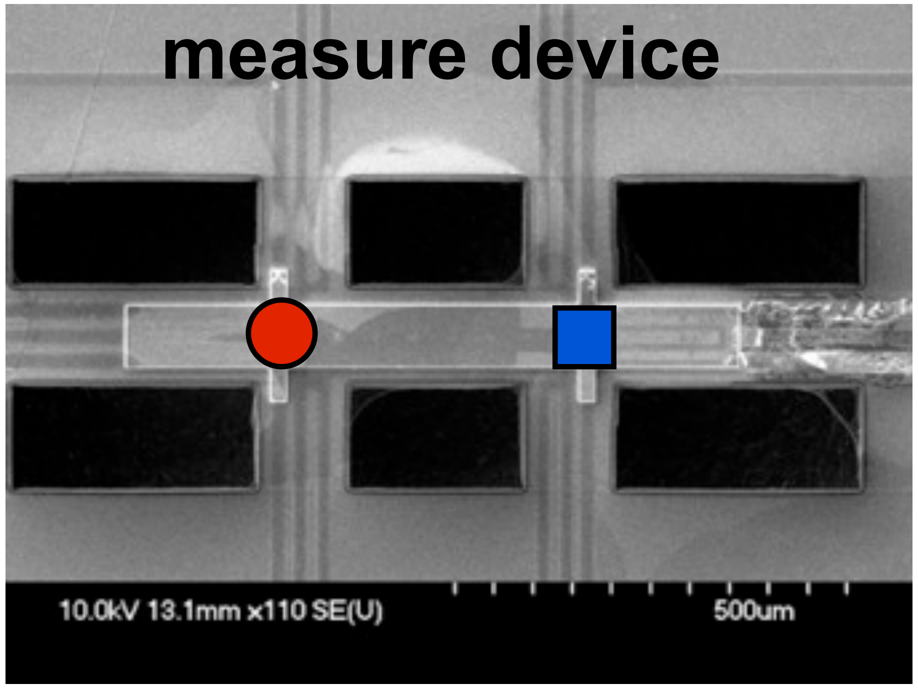
Thermometers

Thermometers

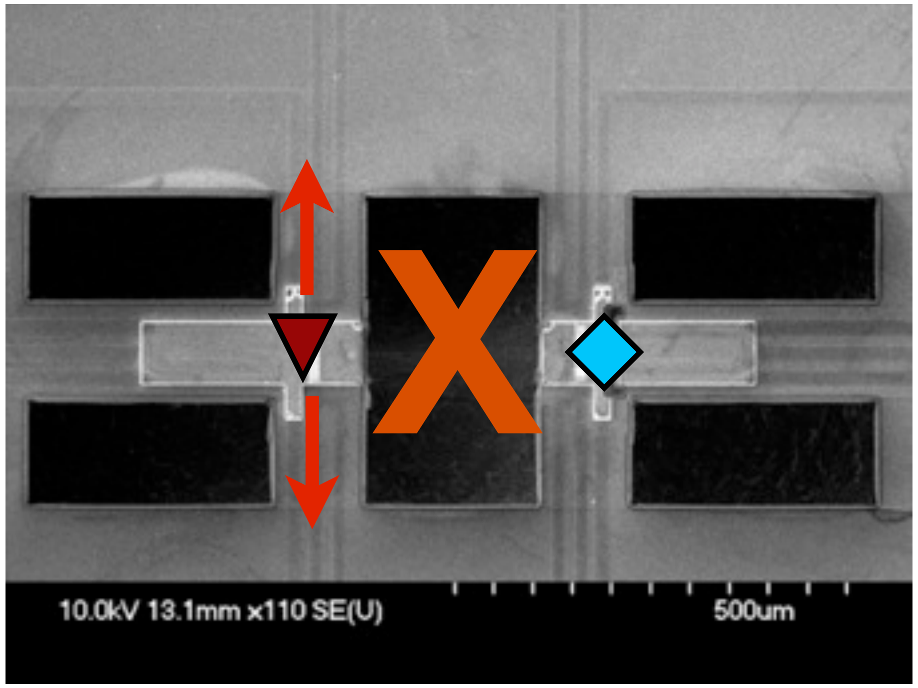
Thermal Conductivity Measurement



To obtain accurate heat flux

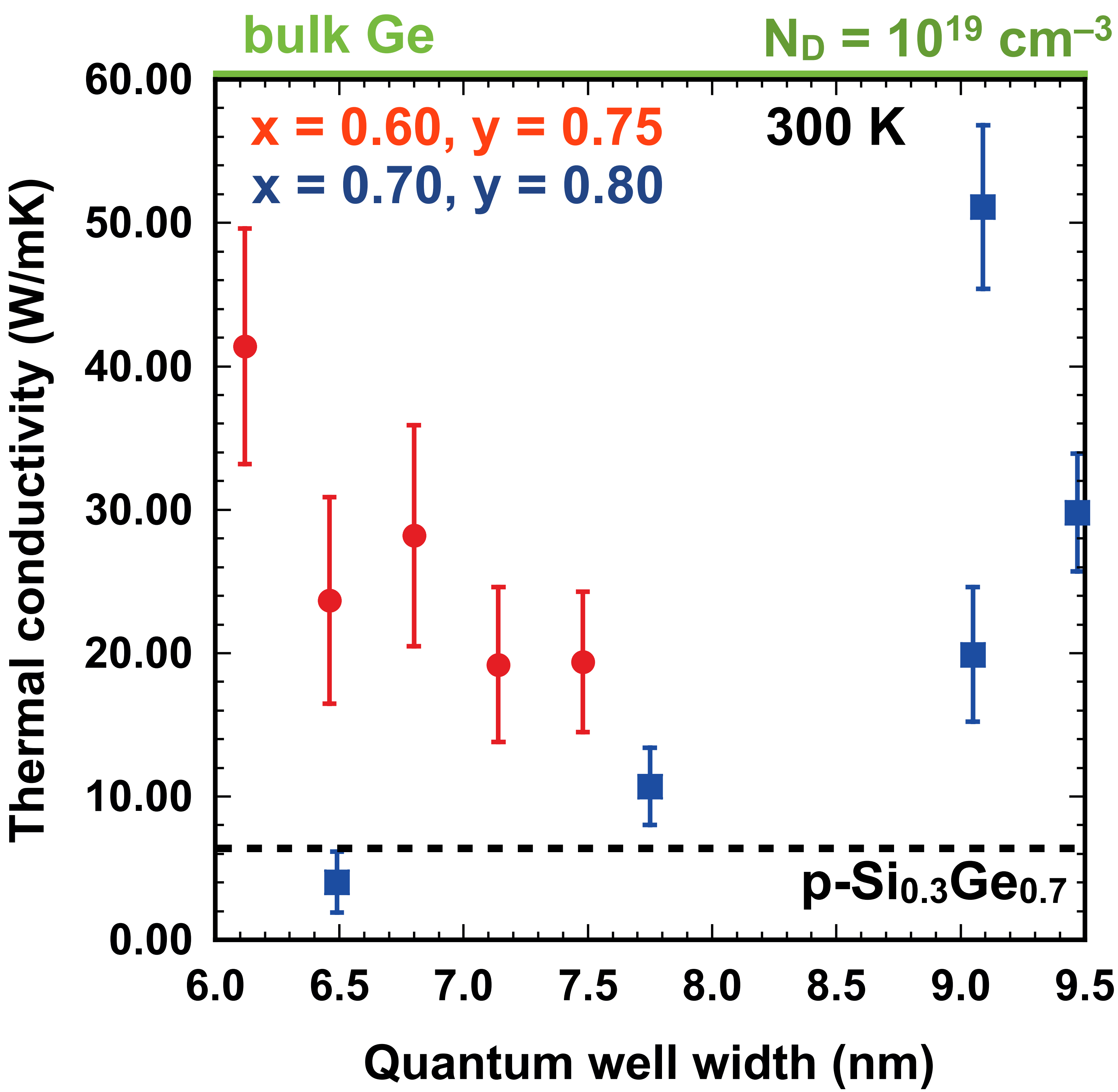


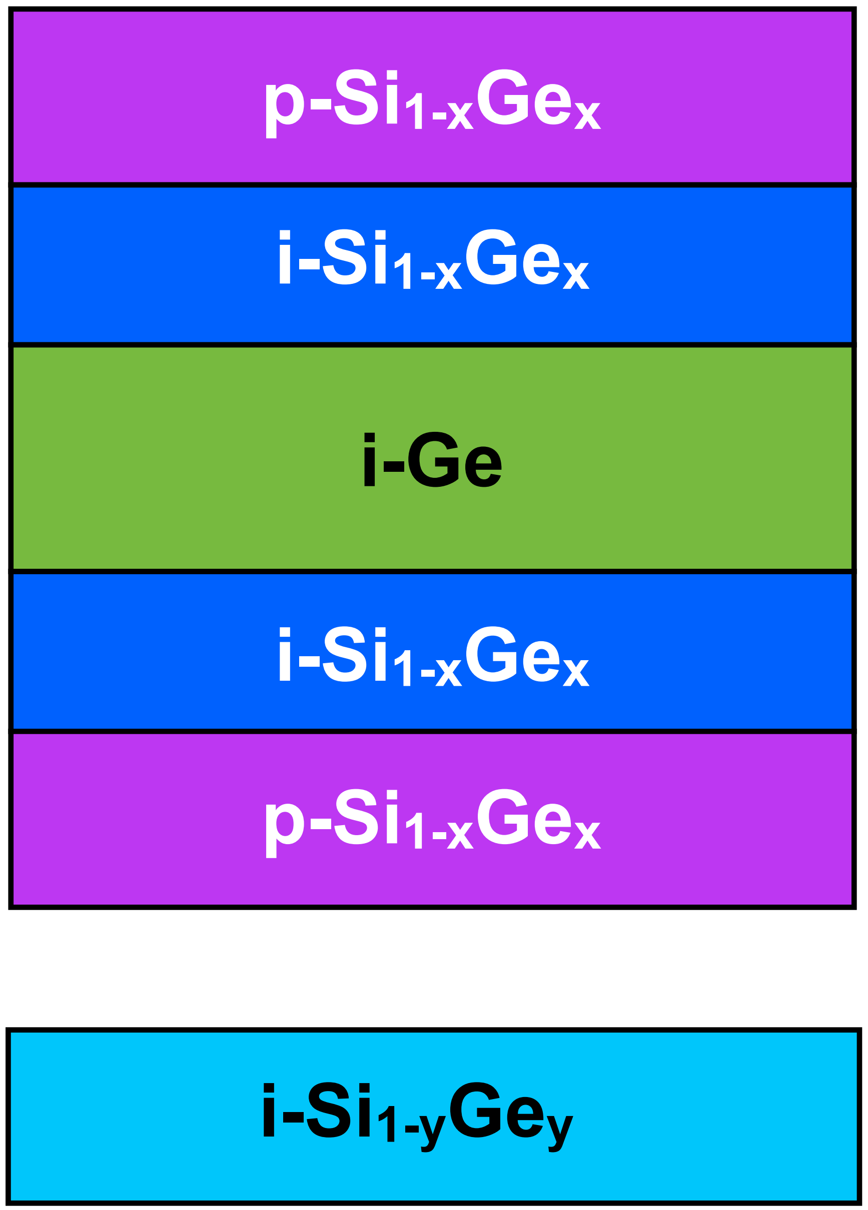
then remove device
& subtract thermal parasitics



Evaluation of heat flux that is physically transported in the structure

Thermal Conductivity vs QW Width

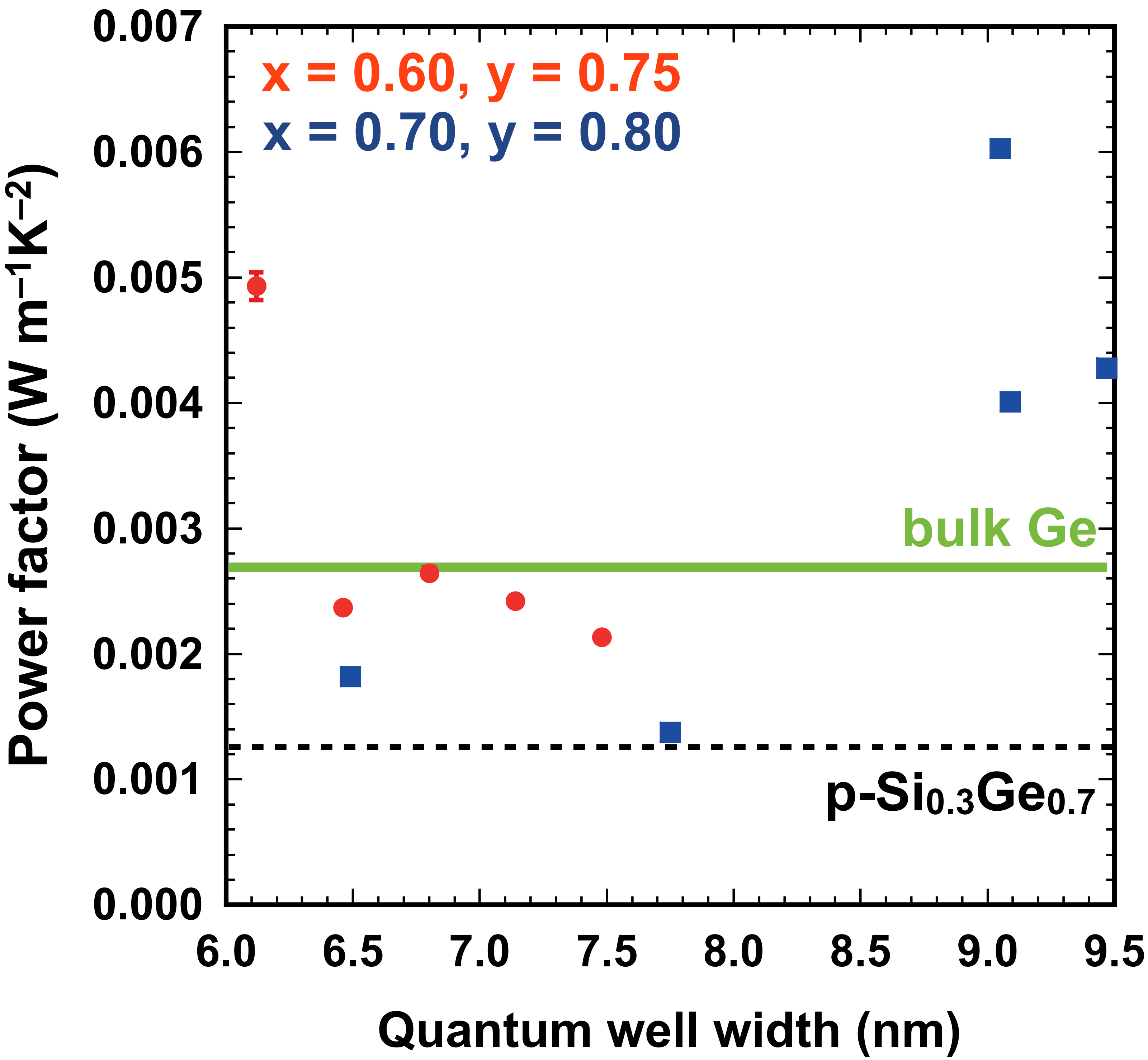


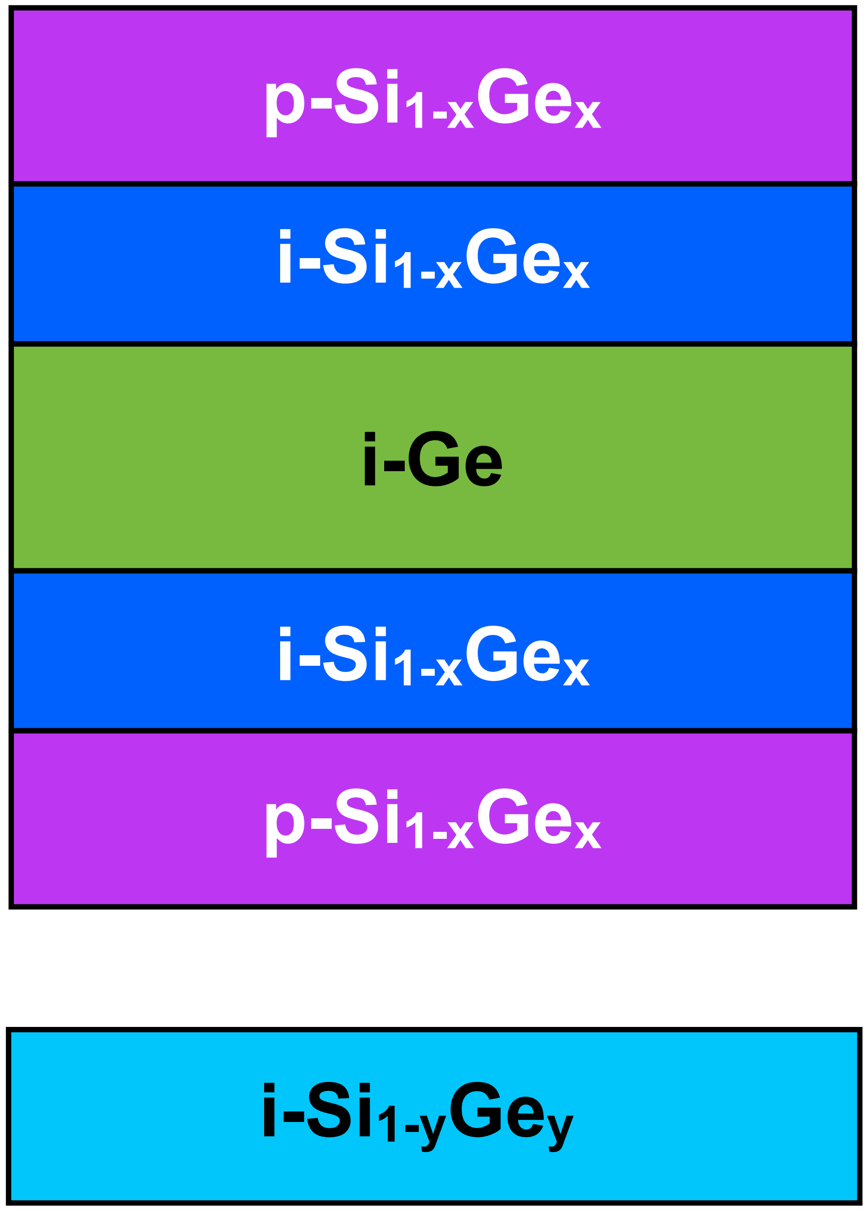


- Additional phonon scattering as QW width reduces

J. Appl. Phys. 113, 233704 (2013)

Power Factor

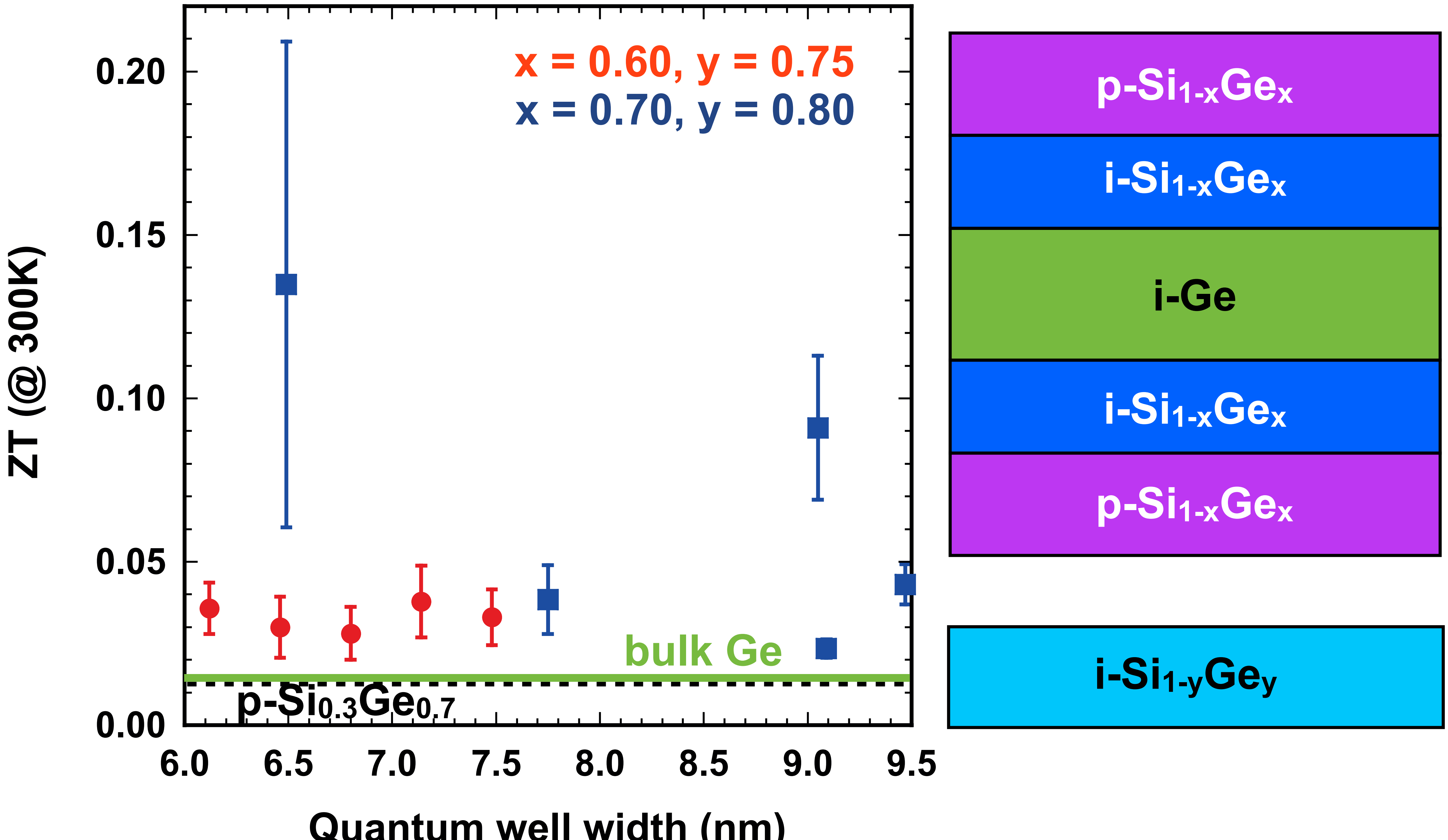




- Modulation doping allows significant higher power factors than bulk

J. Appl. Phys. 113, 233704 (2013)

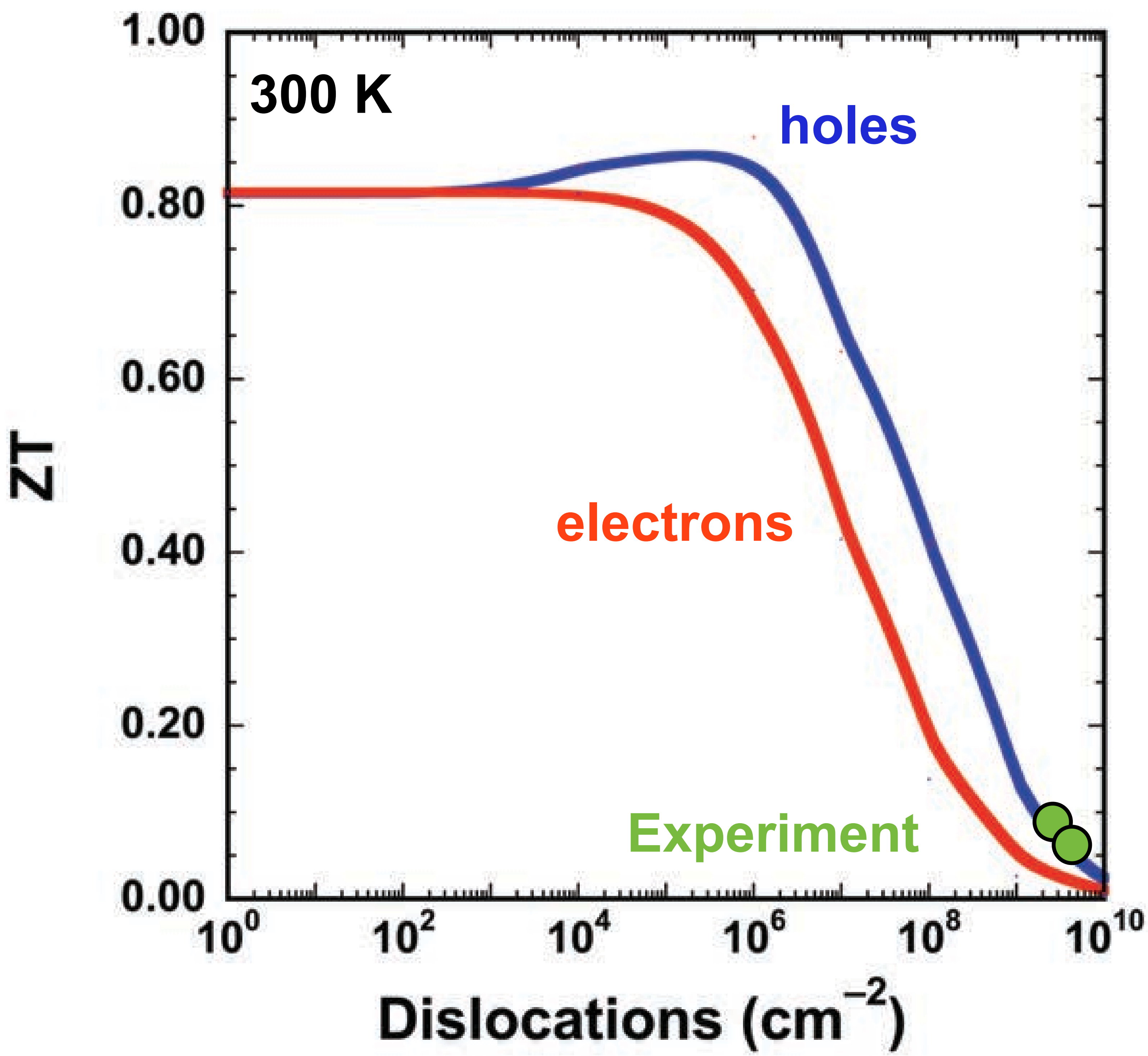
ZT at 300 K



- Order of magnitude improved ZTs with 6 times higher power factors than bulk $Si_{0.3}Ge_{0.7}$ at 300 K

J. Appl. Phys. 113, 233704 (2013)

Experiment versus Theory



Modelling for 9 nm QW

New thin buffers have TDD ~ 5 x 10^7 cm^{-2}

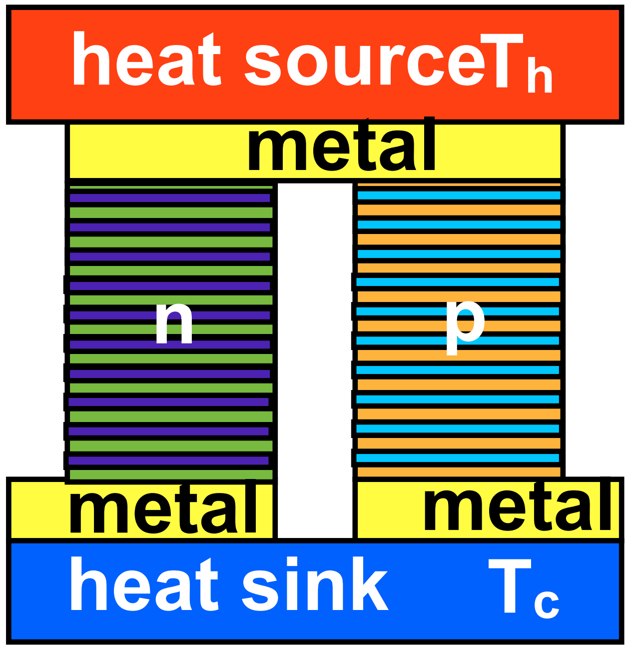
Theory suggest ZT ~ 0.5

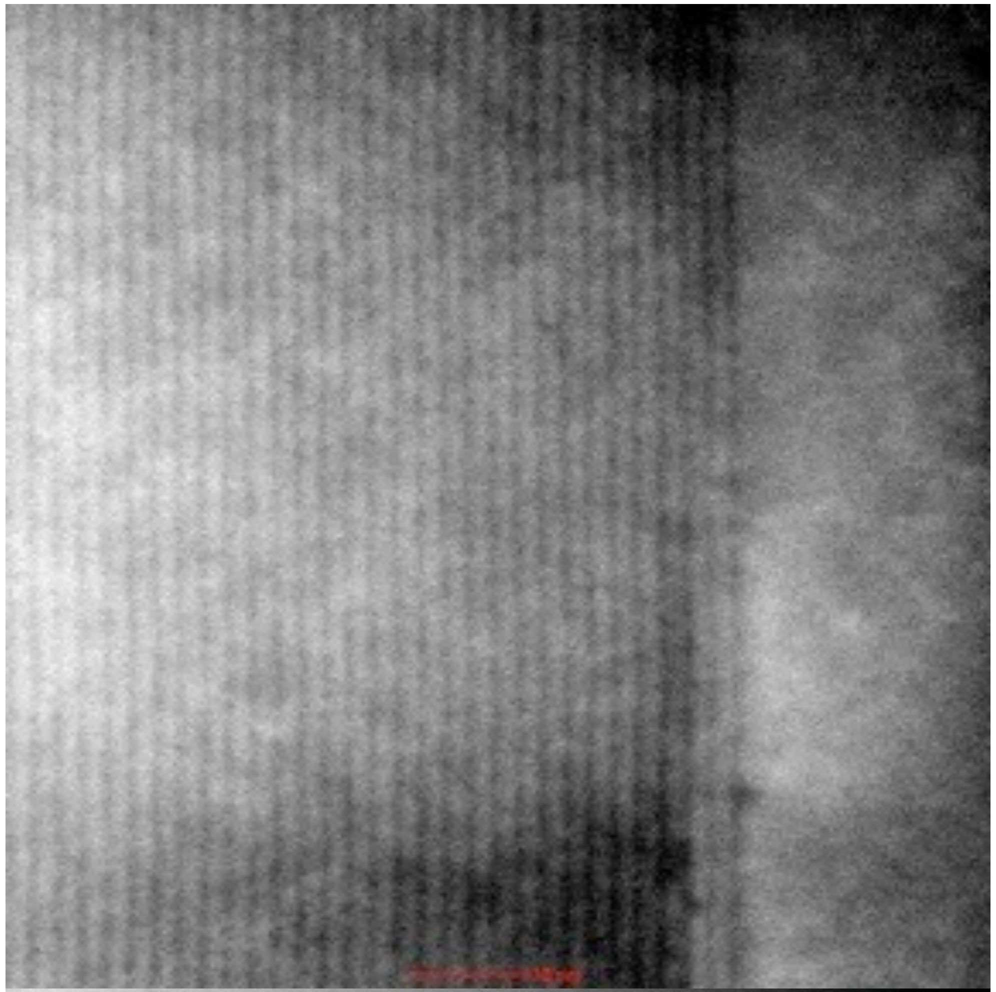
J. Appl. Phys. 113, 233704 (2013)

J.R. Watling & D.J. Paul, J. Appl. Phys. 110, 114508 (2011)

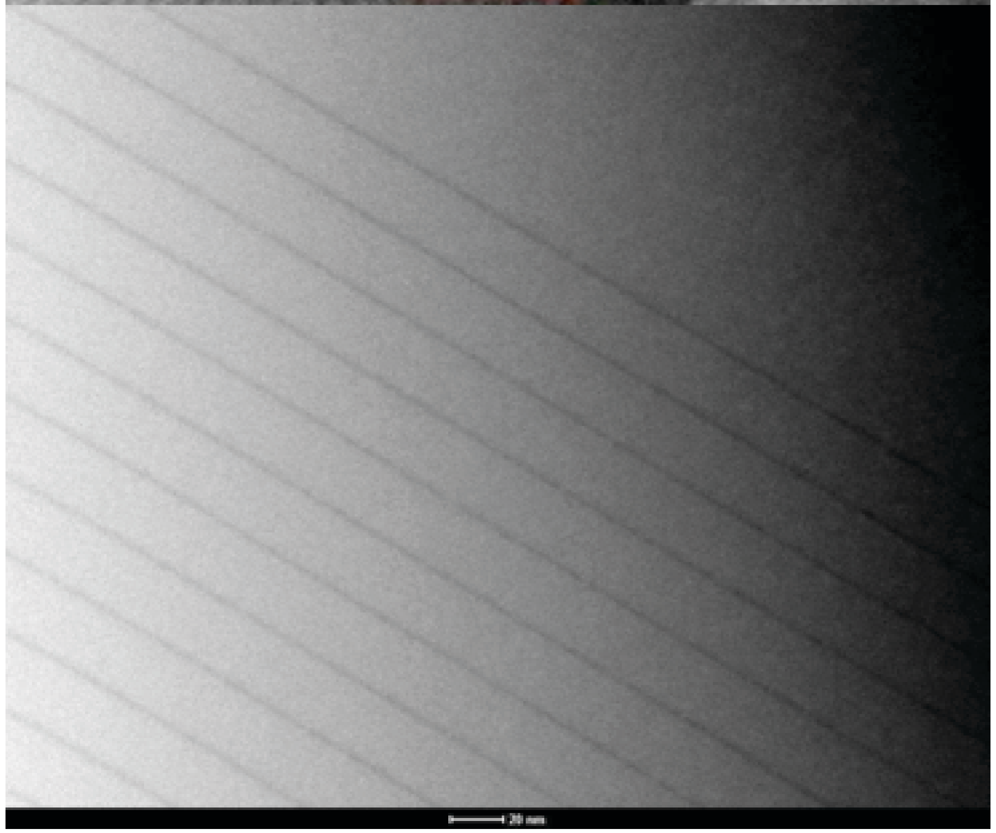
Vertical SiGe Designs

Vertical superlattice





narrow QWs



wide QWs

Vertical (Cross-plane) Superlattice TEs

- 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

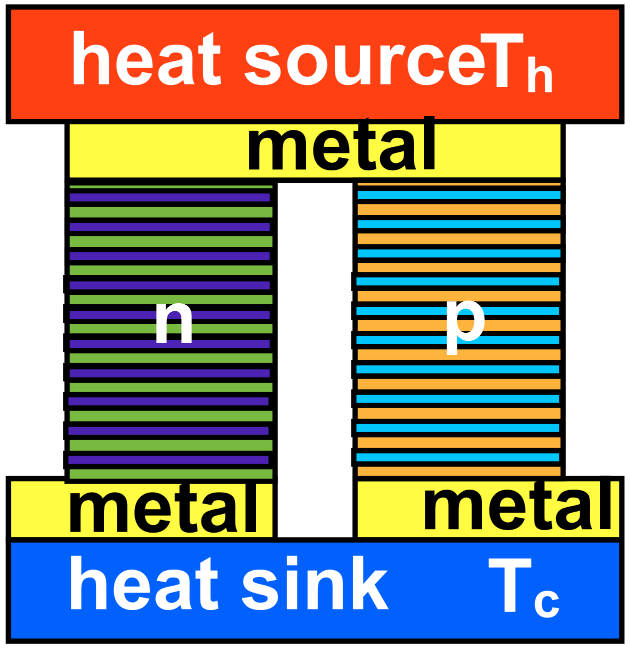
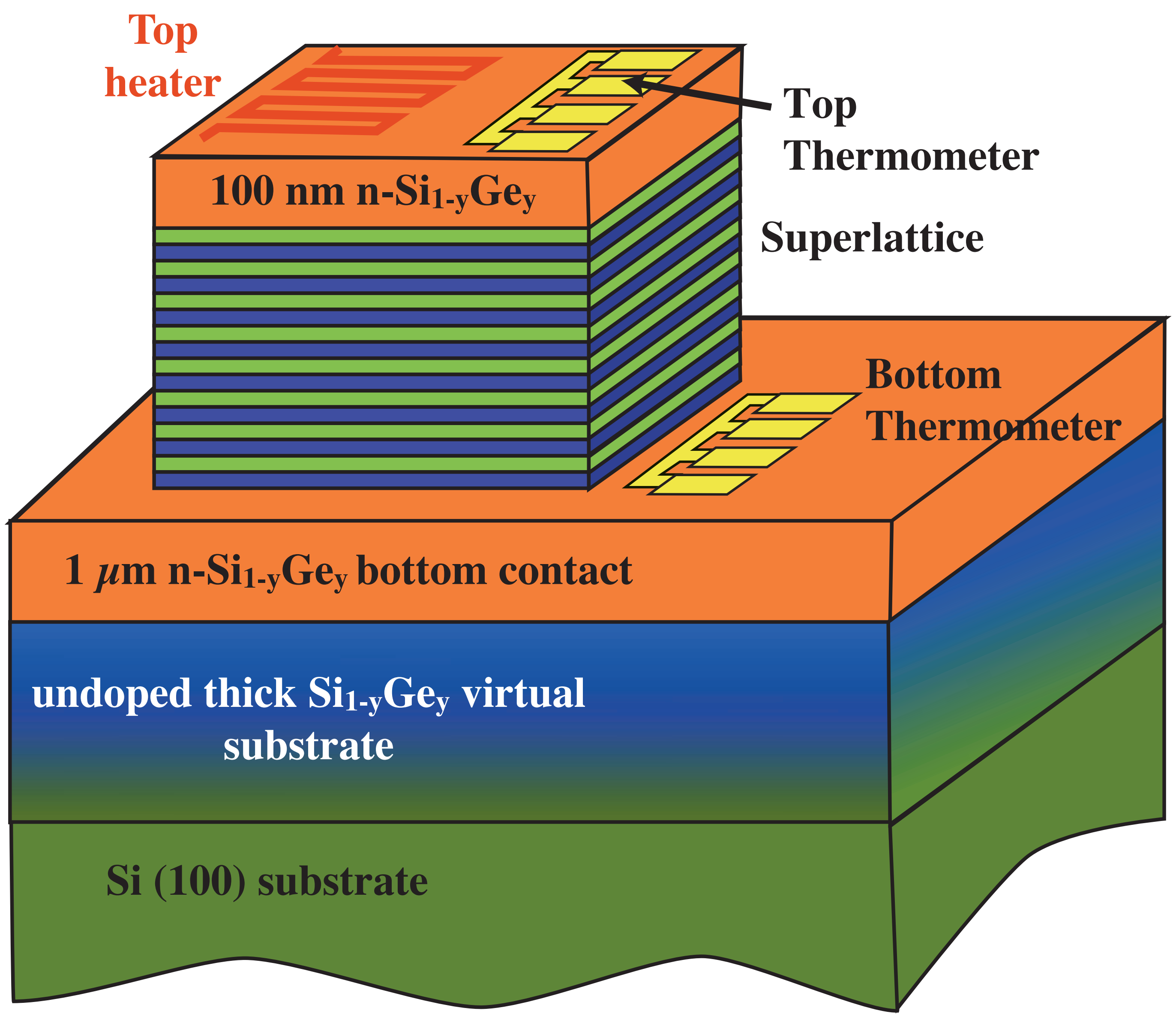
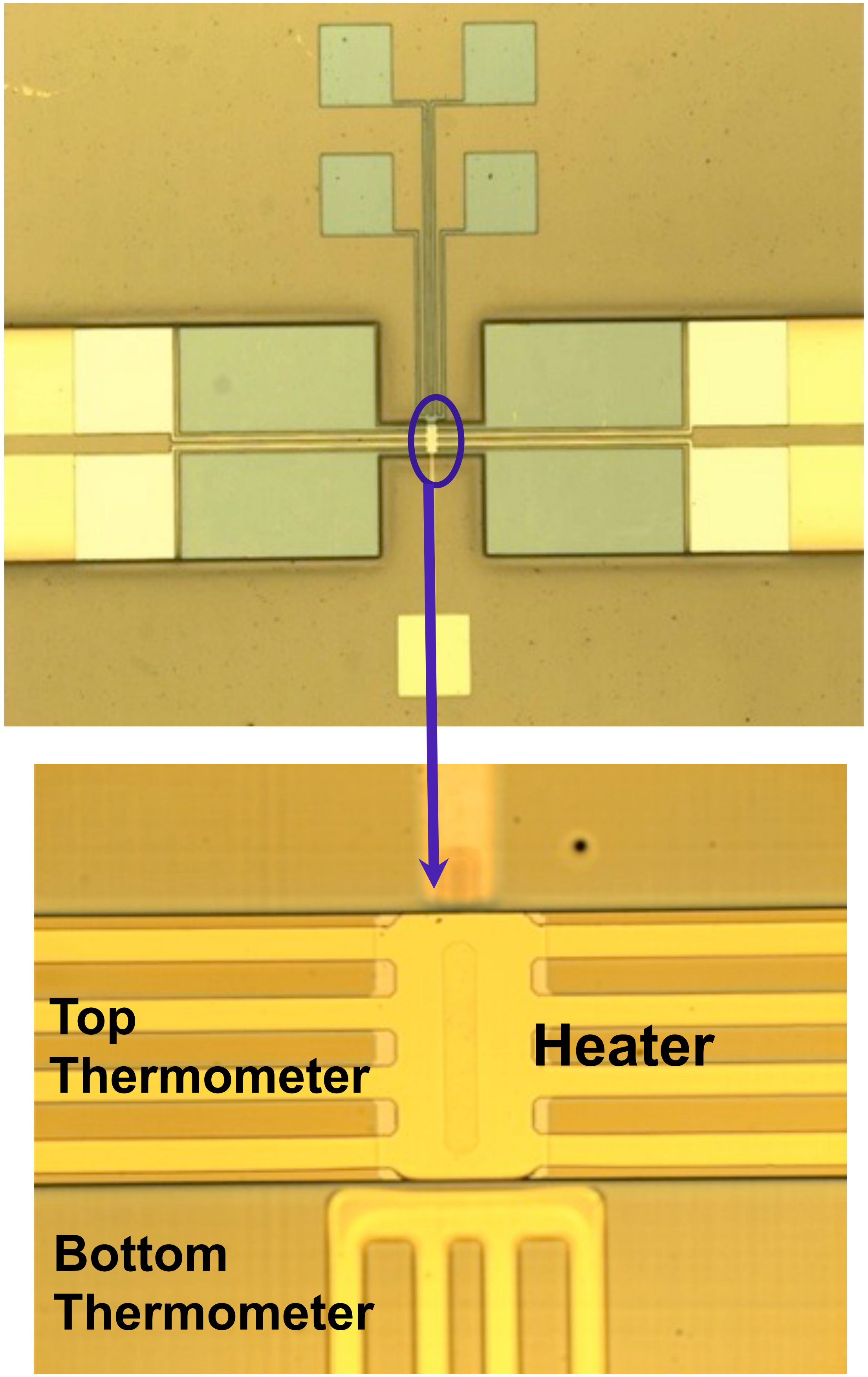


Figure of merit

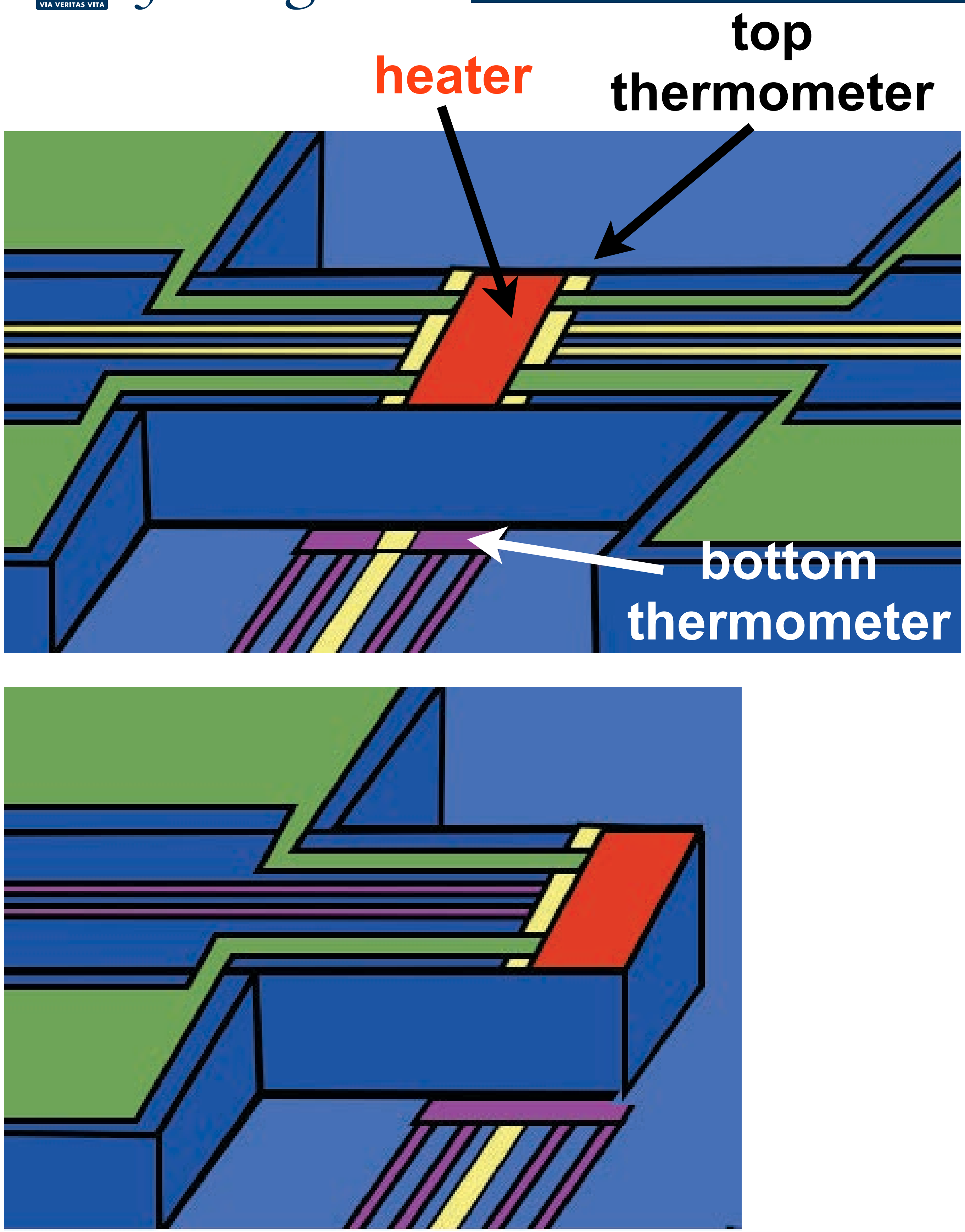
$$\mathrm{ZT} = \frac{\alpha^2 \sigma}{\kappa} \mathrm{T}$$

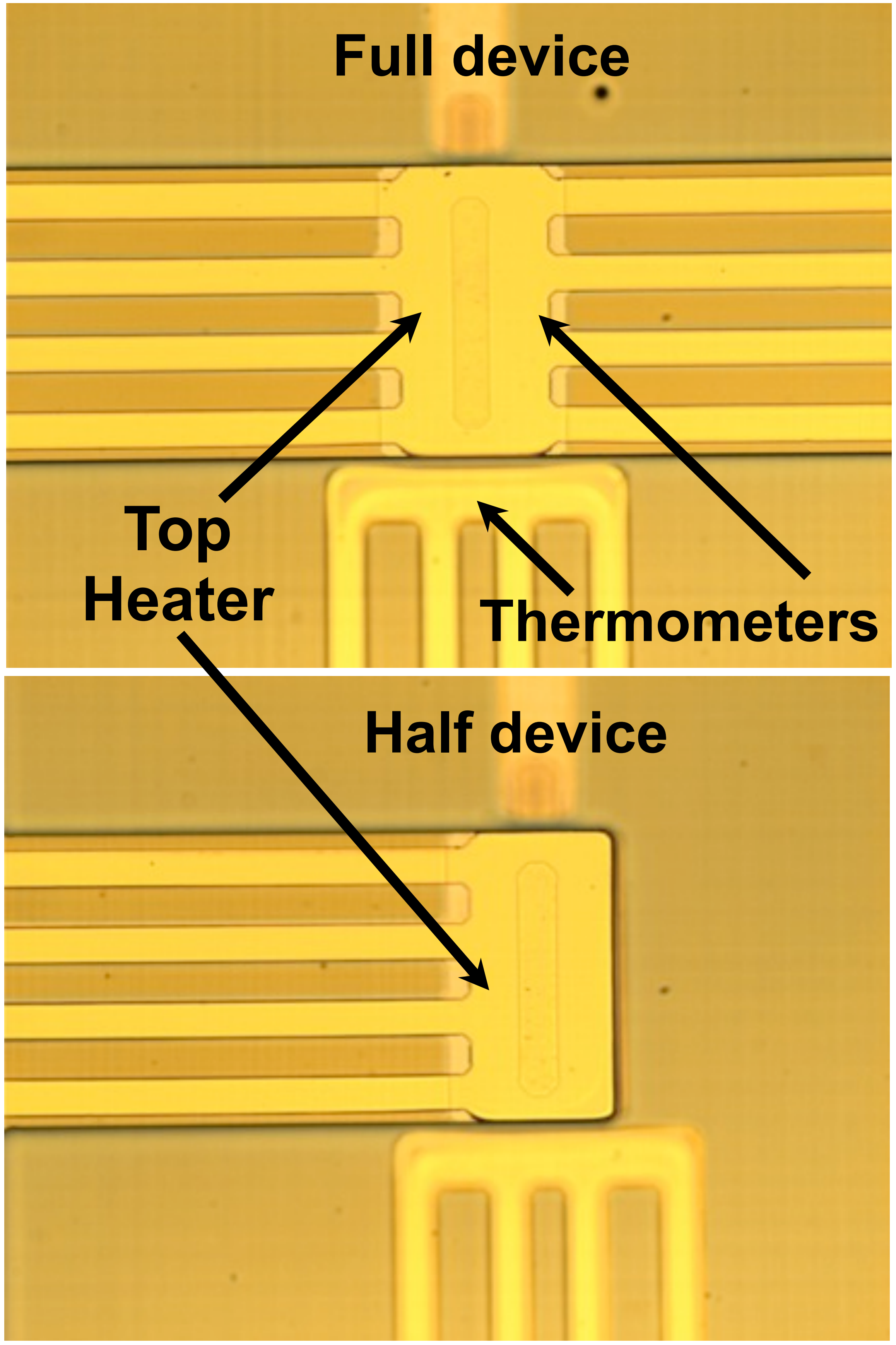
Vertical Electrical & Thermal Characterisation





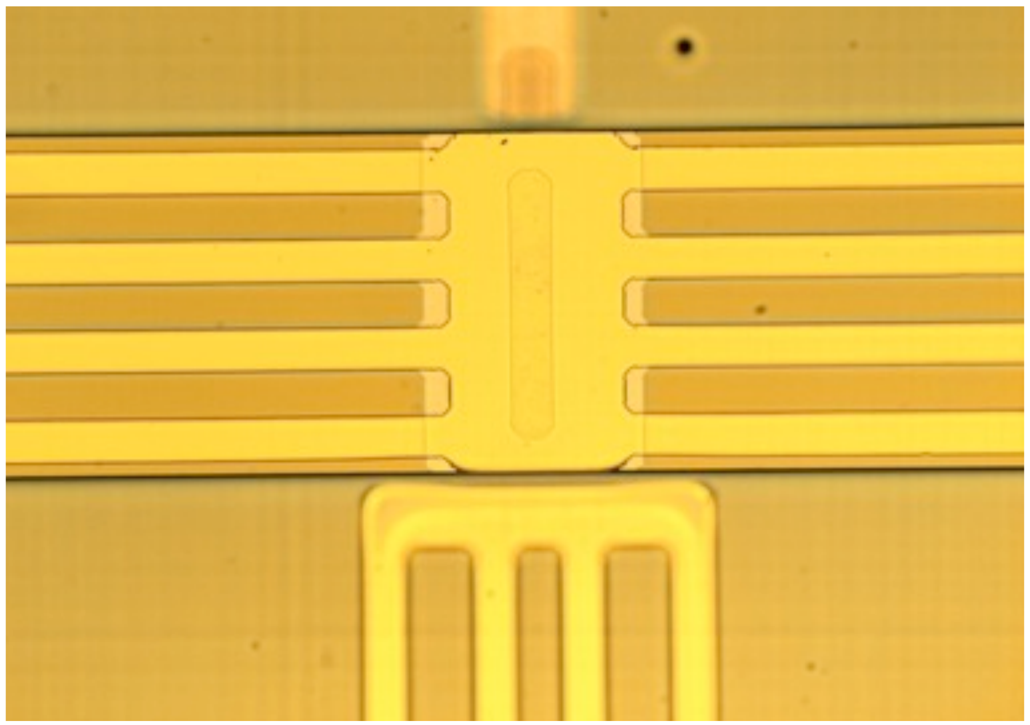
Vertical Thermal Conductivity Measurement



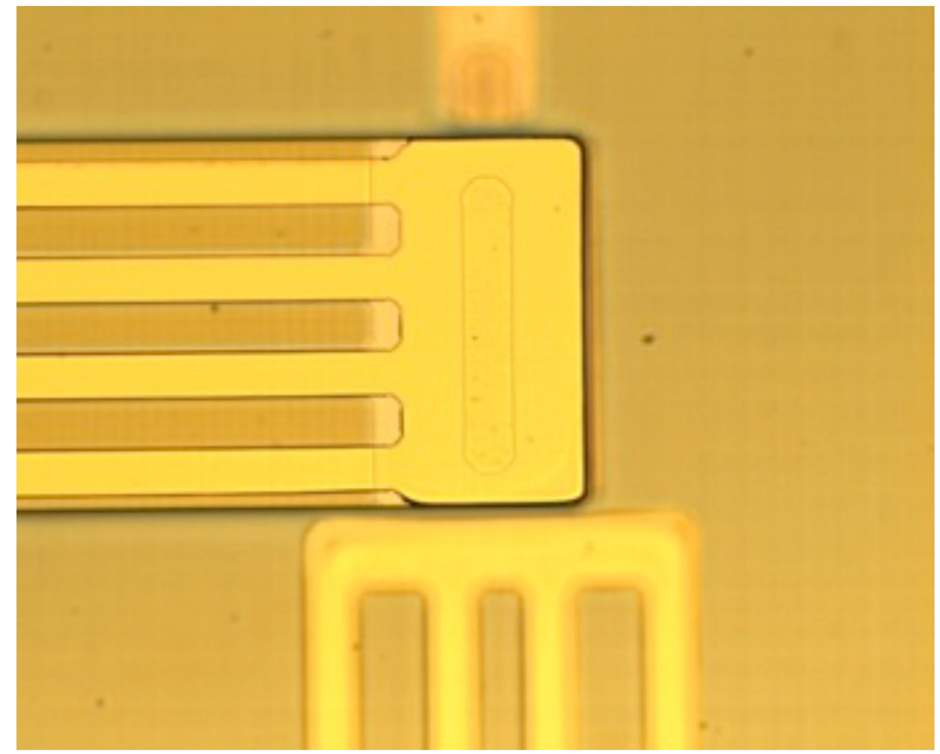


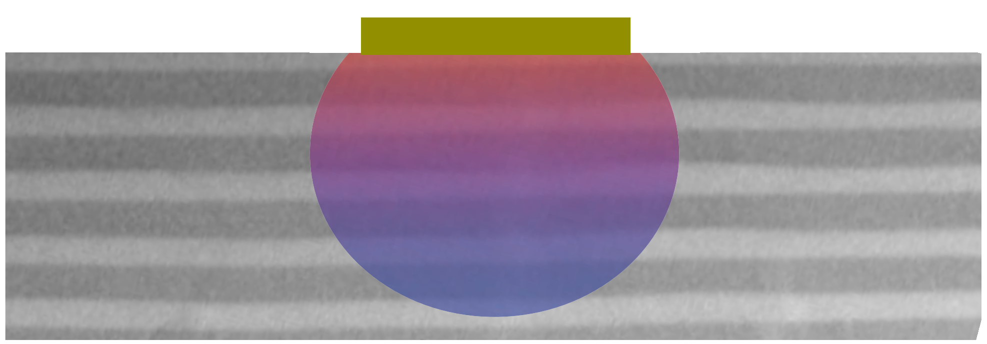
Vertical Heat Flux Estimation

Full device

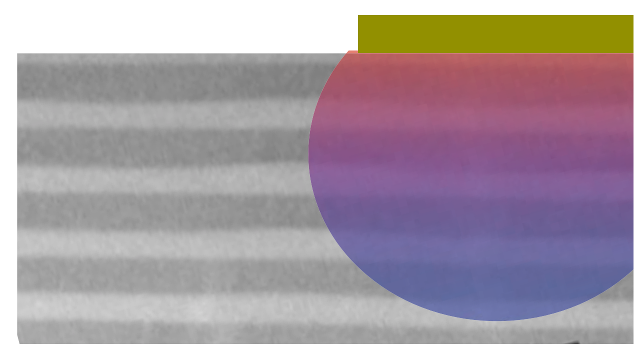


Half device

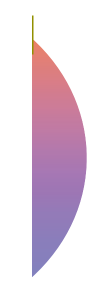




Isotropic structure



half structure

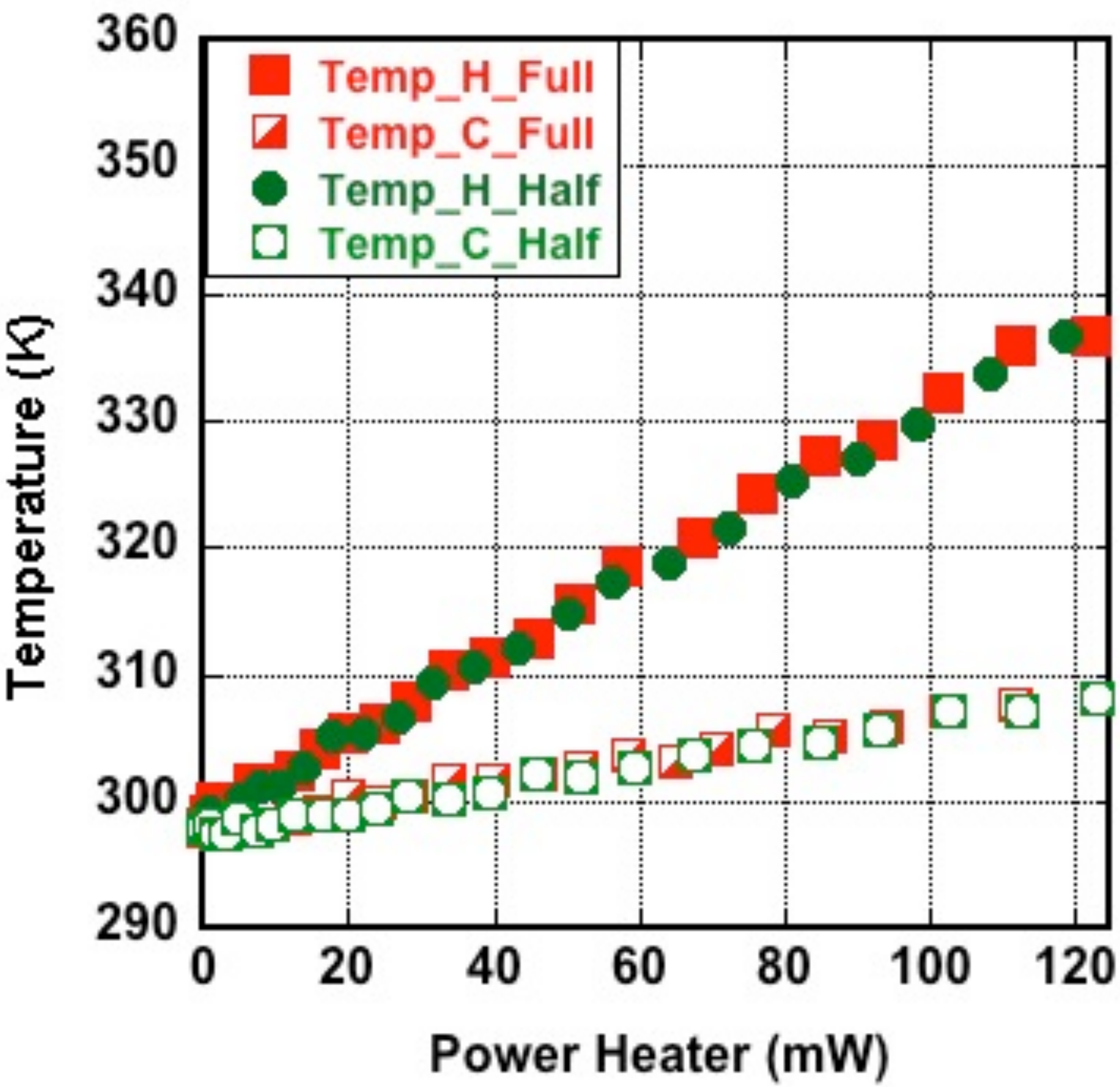


lateral parasitic contribution

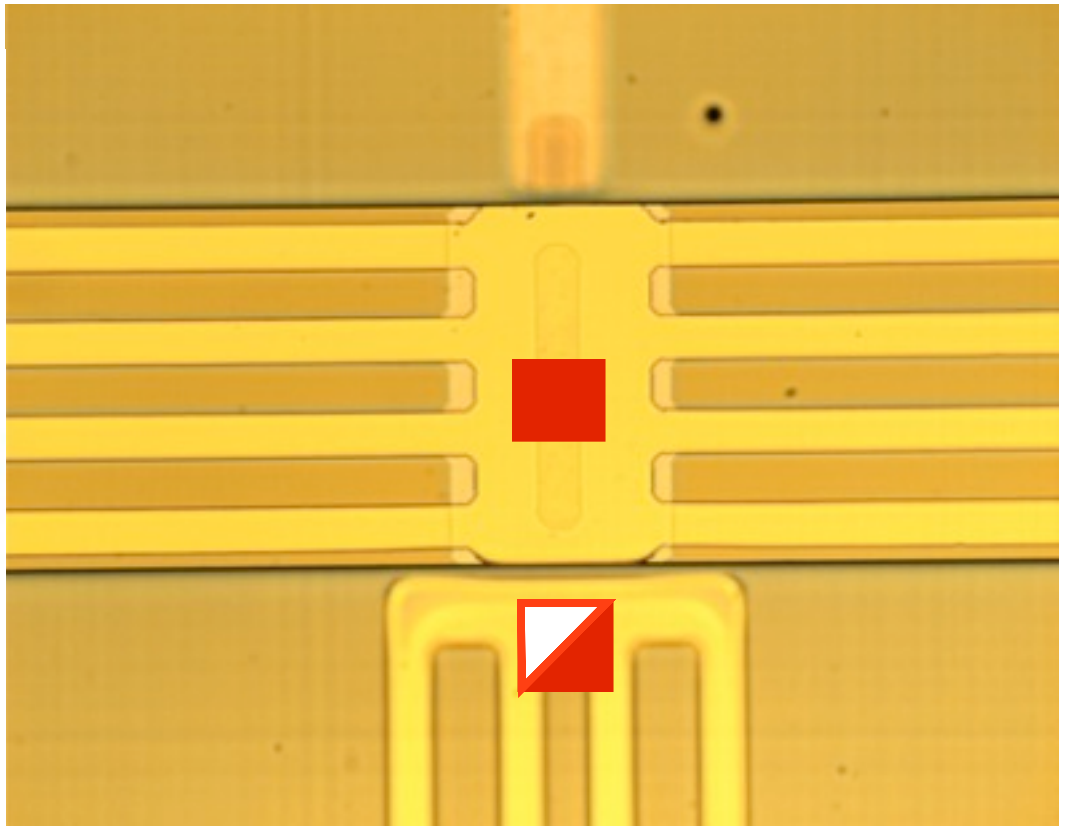
- Half structure allows parasitics to be removed for accurate heat flux

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

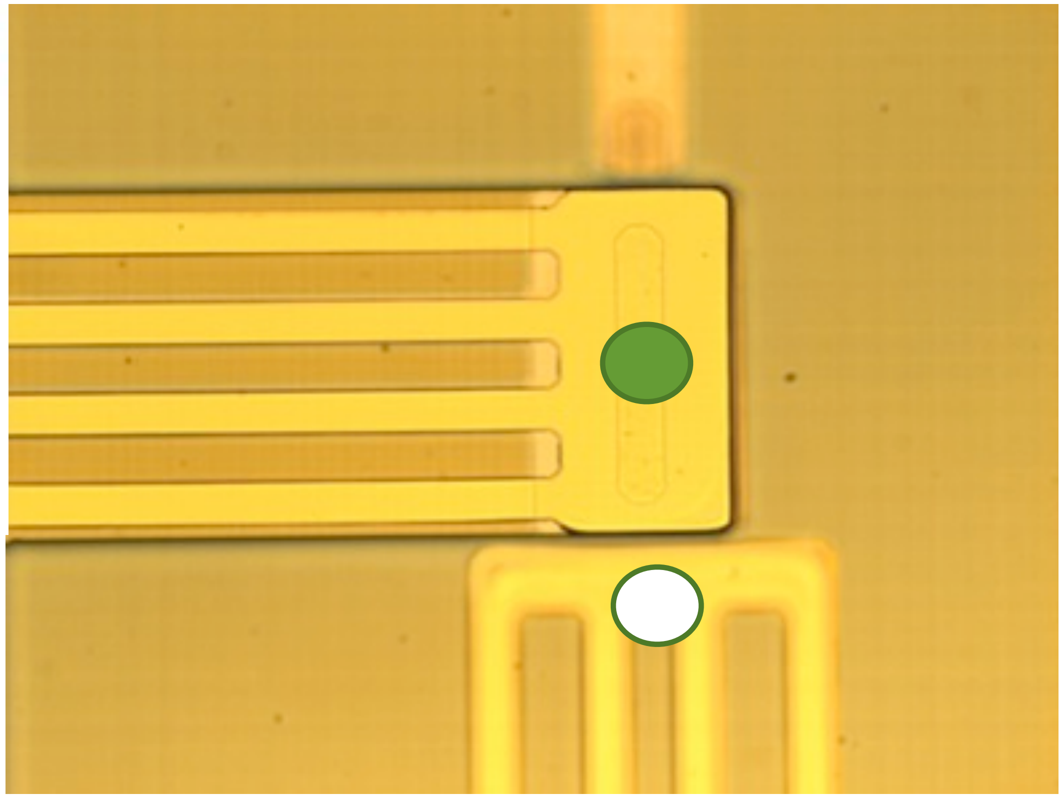
Thermal Conductivity Measurement



Full device

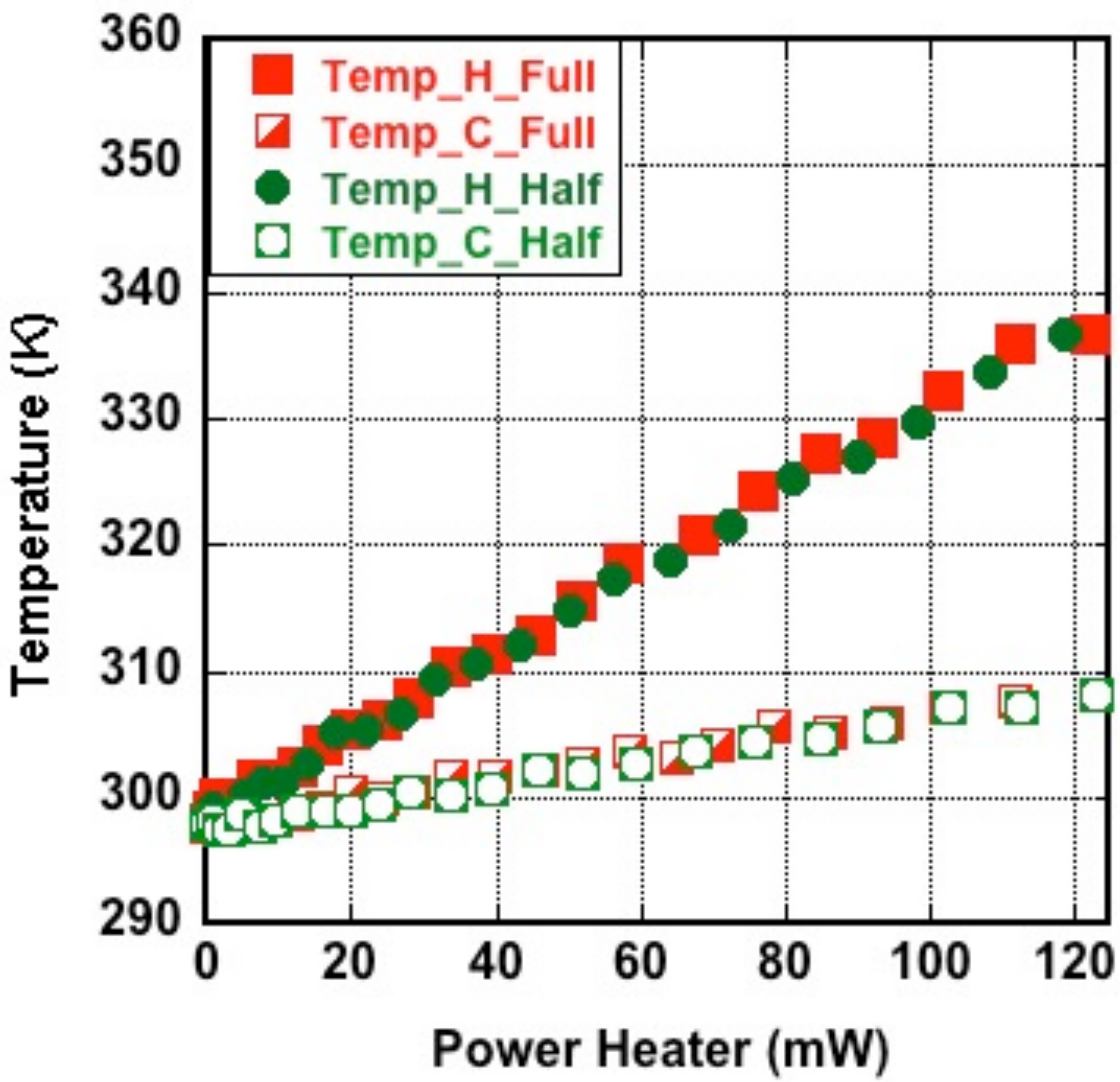


Half device



Vertical Thermal Conductivity

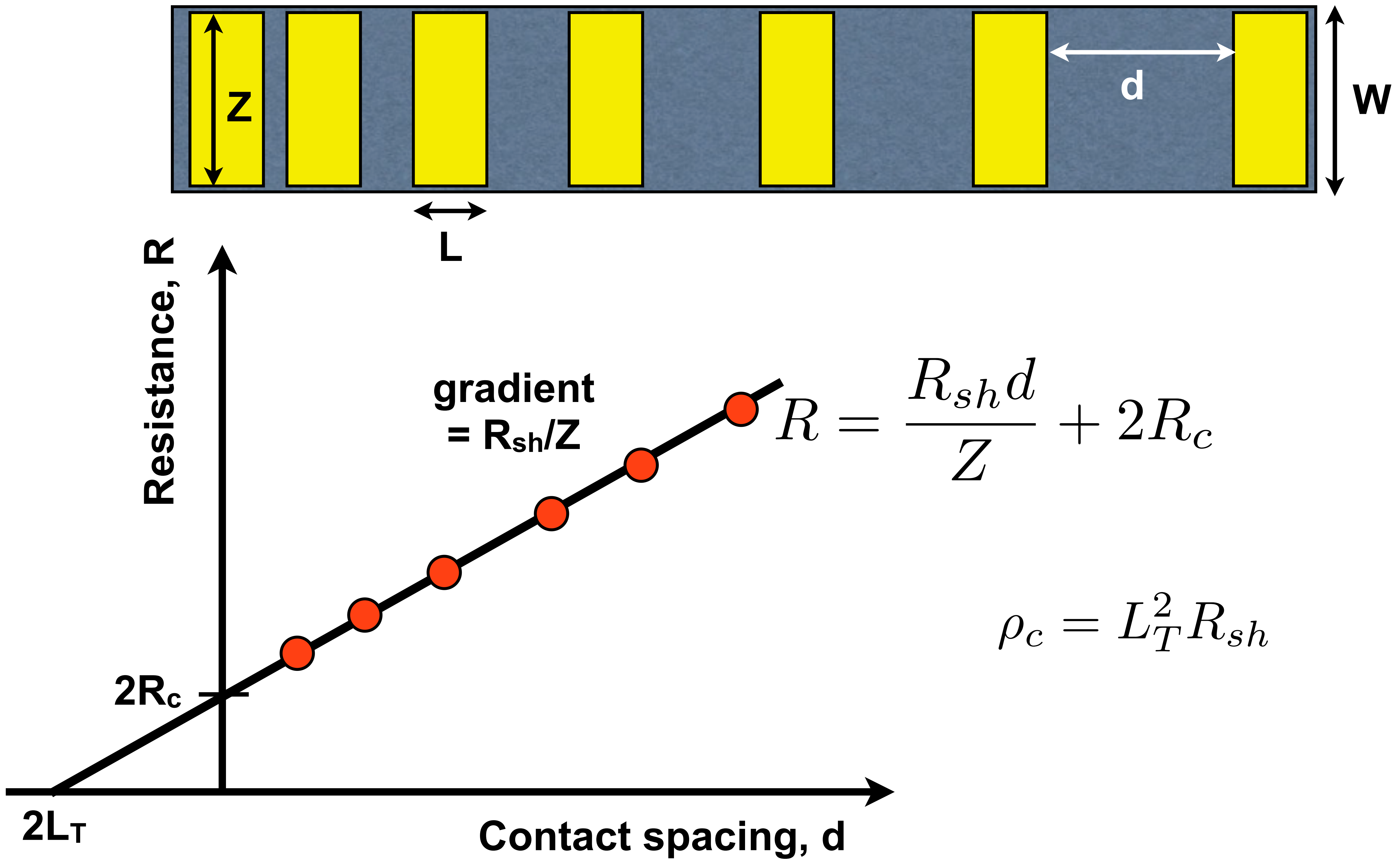
independent heater & thermometer



sample	Thermal conductivity (W/mK)
8950	5.06 ± 0.43
8957	5.56 ± 0.25
8961	5.07 ± 0.03

- Significantly lower κ compared to lateral material

Transfer Line Measurements (TLMs)

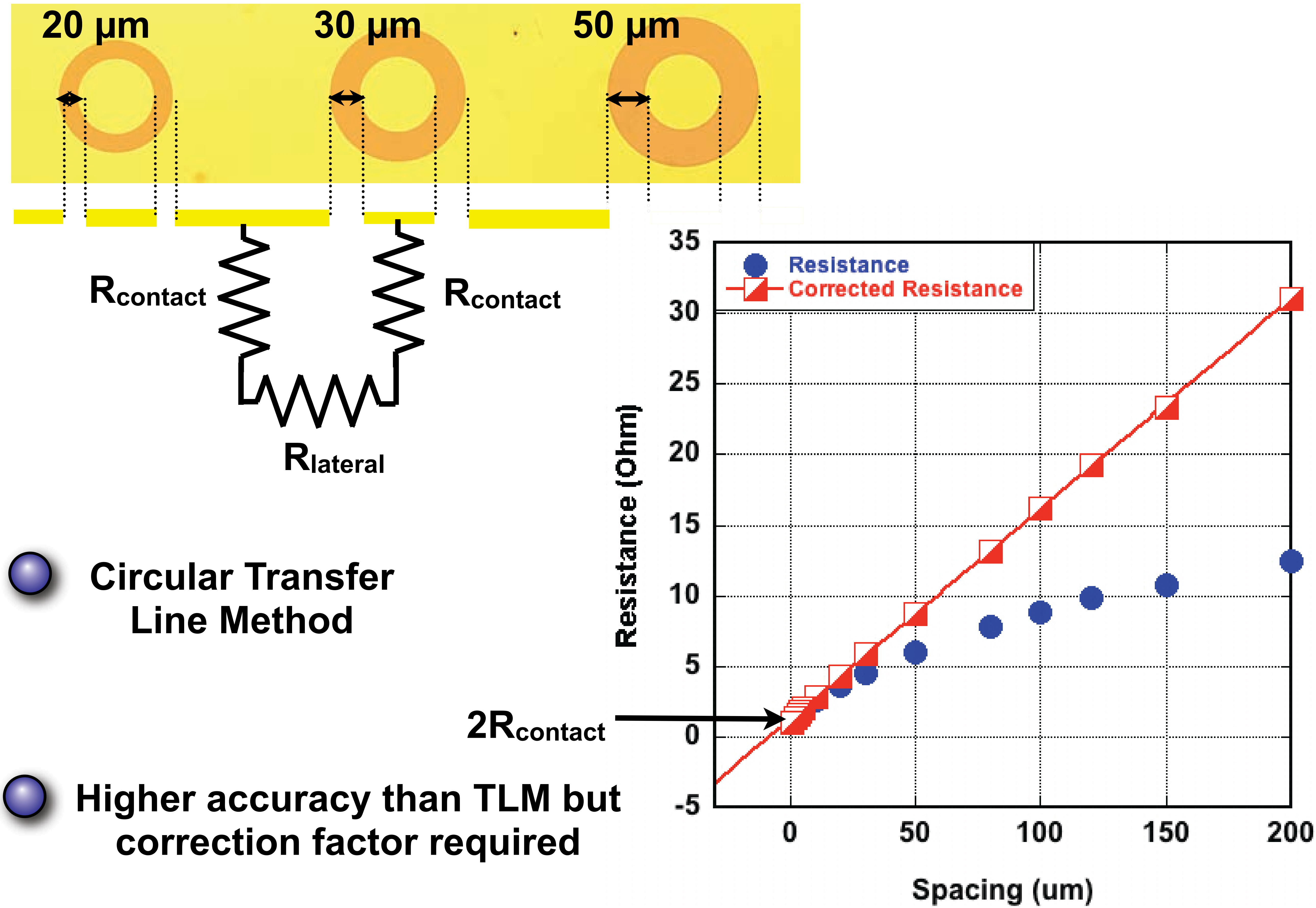


$$R = \frac{R_{sh} d}{Z} + 2R_c$$

$$\rho_c = L_T^2 R_{sh}$$

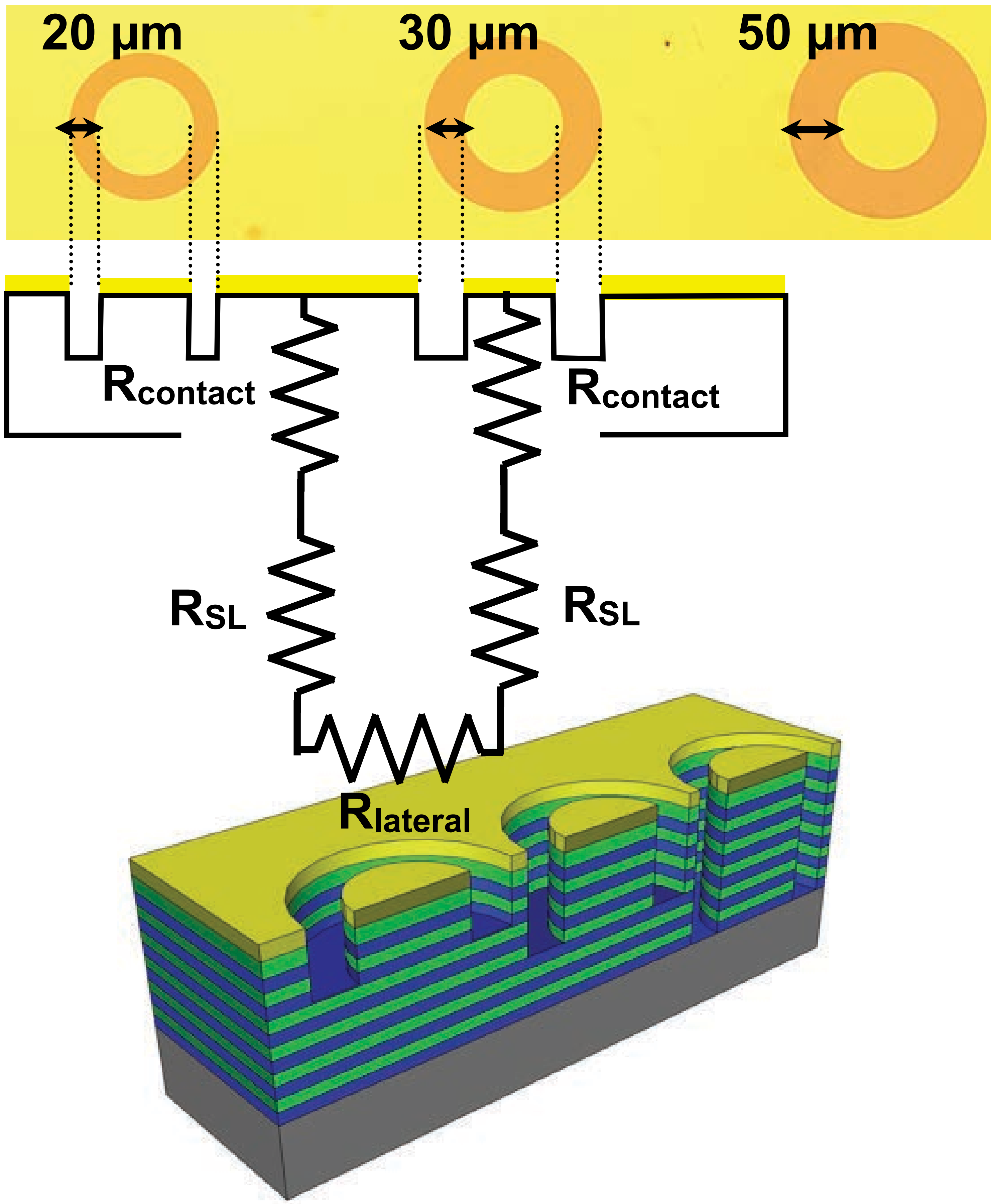
- Any misalignment or gaps results in errors –> circular TLMs

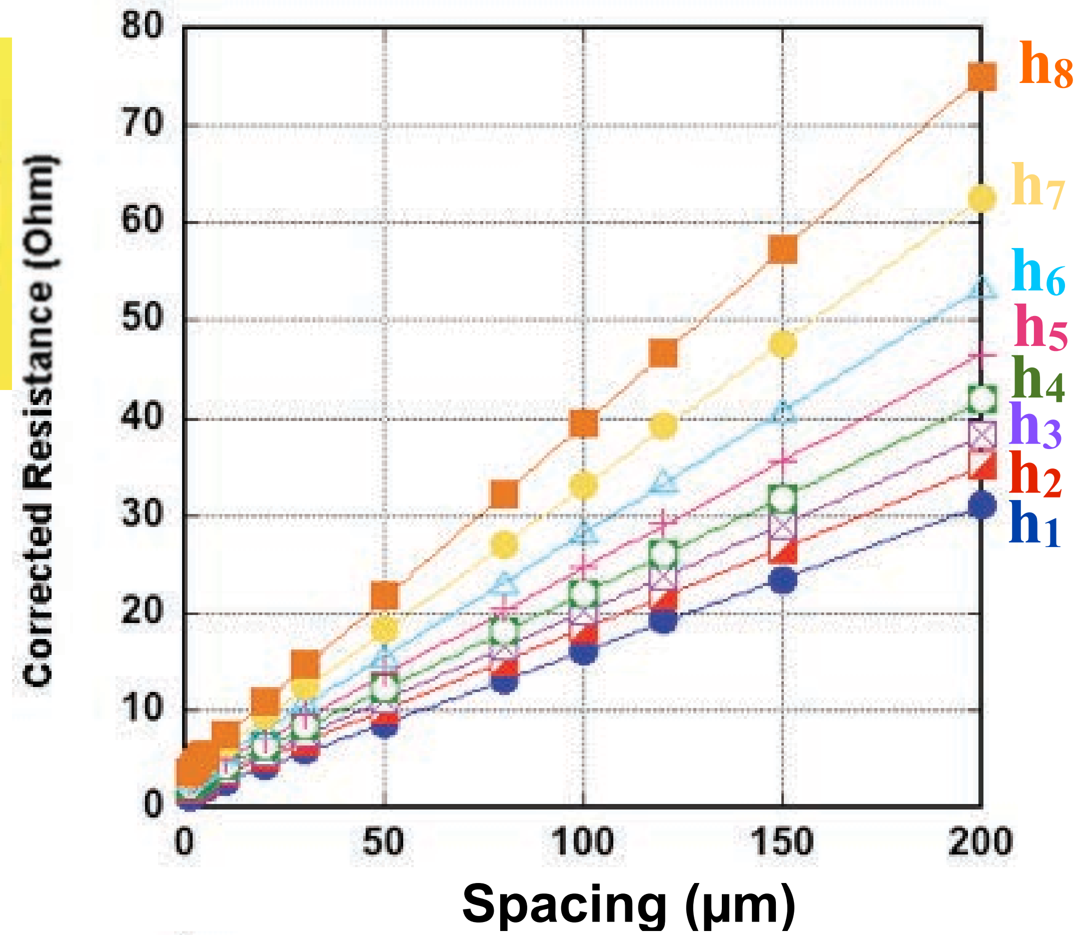
Vertical Electrical Conductivity I

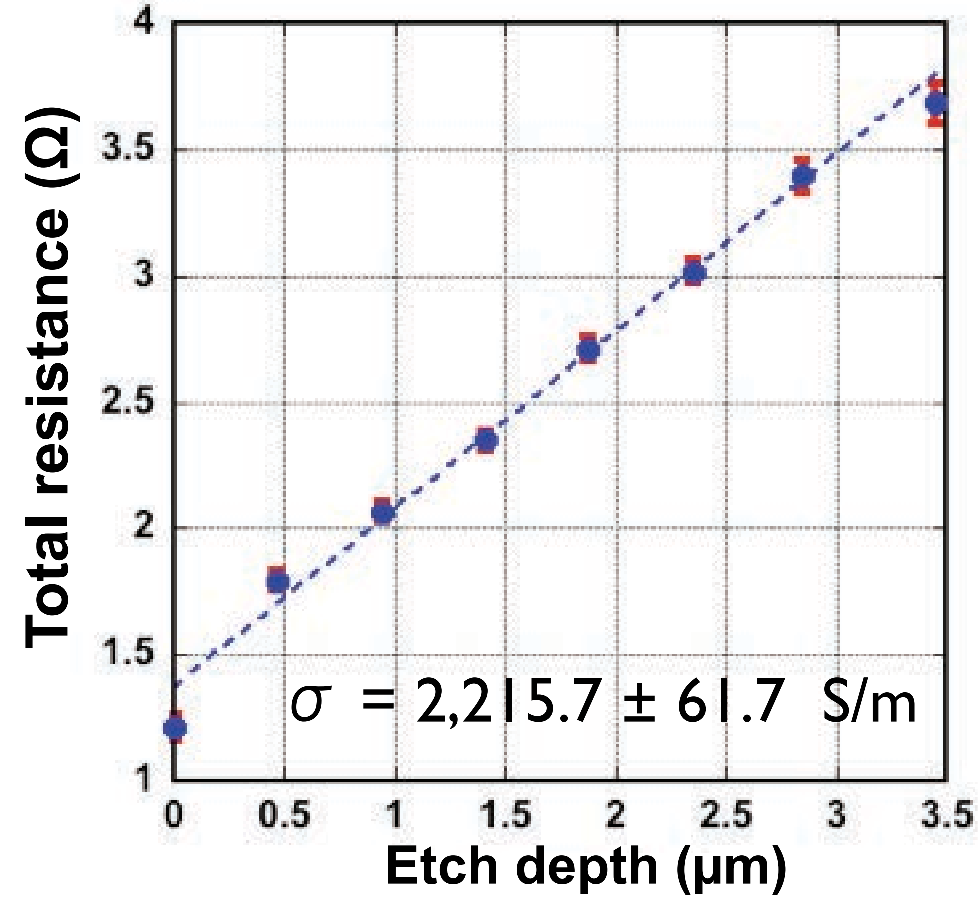


- Circular Transfer Line Method
- Higher accuracy than TLM but correction factor required

Vertical Electrical Conductivity II





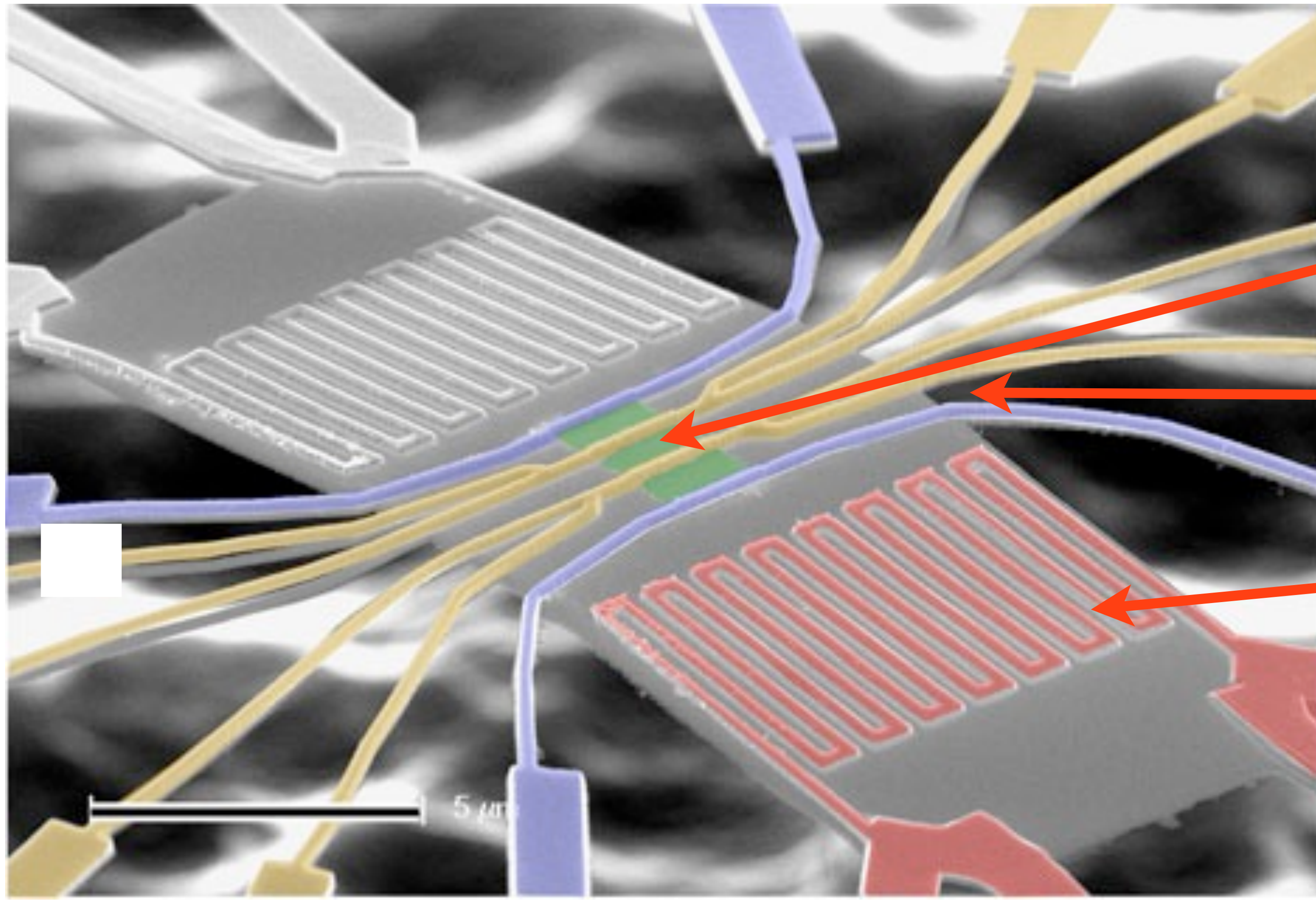


p-type Superlattice Material Summary

Sample	QW width (nm)	σ (S/m)	κ (W/mK)	α (μV/K)	ZT	$\alpha^2\sigma$ ($Wm^{-1}K^{-2}$)
8950_H4	2.85	8,633	5.1	399	0.081	0.0013
8957_G4	2.85	14,099	5.6	113	0.009	0.00017
8961_E4	1.1	13,805	5.1	91.8	0.007	0.00012
p-Si	bulk	11,100	148	148	0.00049	0.00243
p-Ge	bulk	30,300	59.5	300	0.014	0.00272
p-$Si_{0.3}Ge_{0.7}$	bulk	25,000	6.3	90	0.01	0.00126

- p-type doping ~10^{19} cm^{-3}
- Interface roughness scattering dominating results

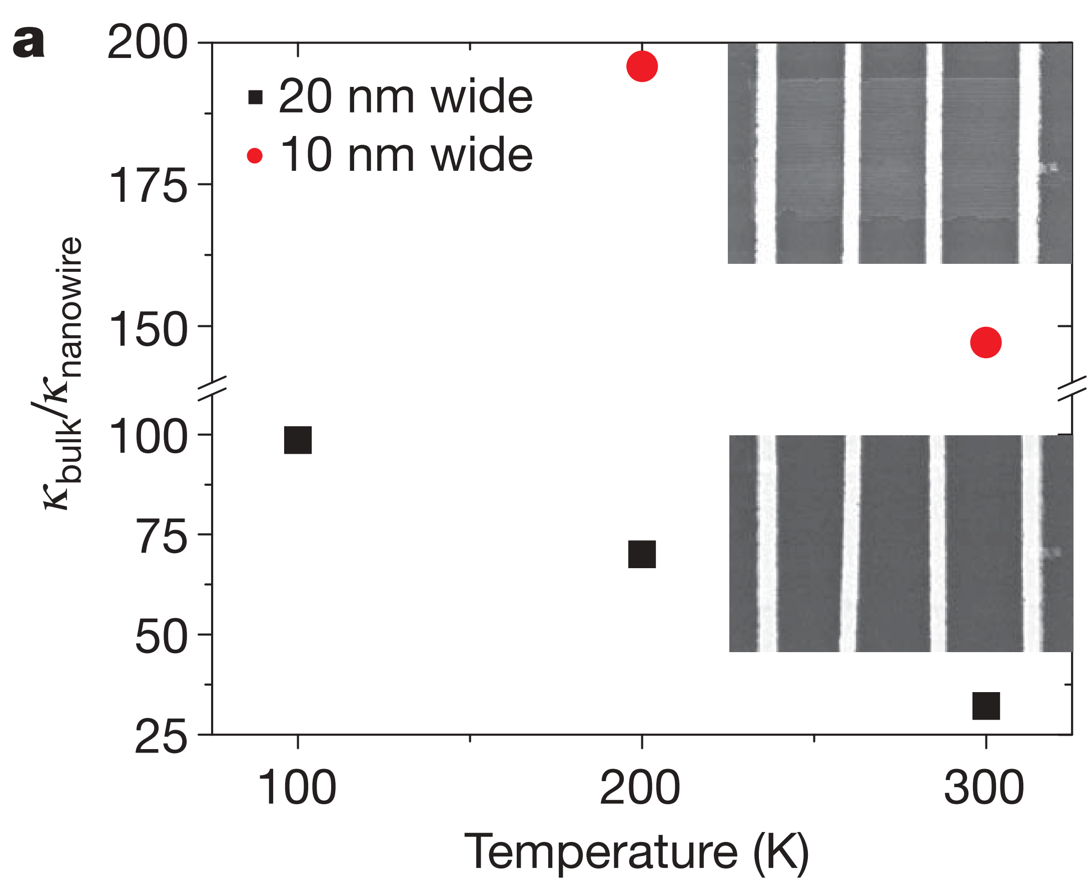
1D Nanowires



4 terminal Si nanowires

Substrate removed by etching

Heaters



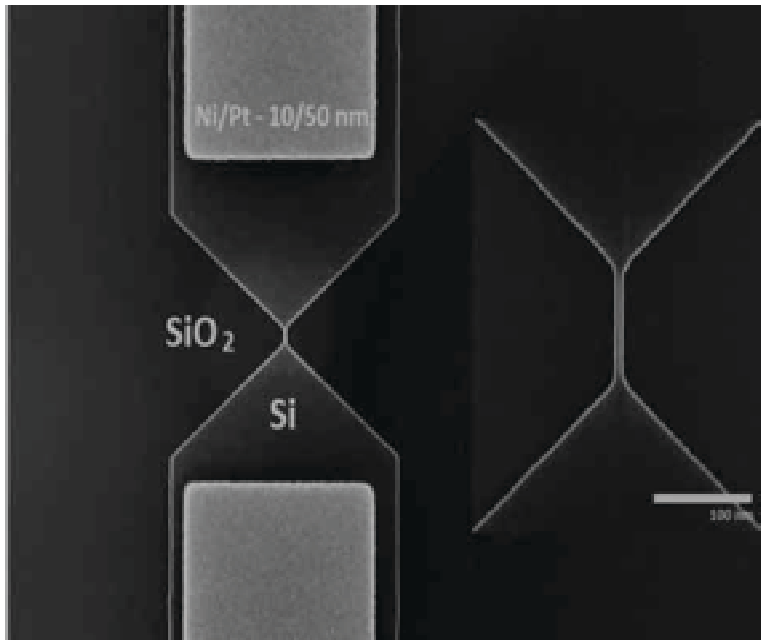
A.I. Boukai et al., Nature 451, 168 (2007)

University of Glasgow

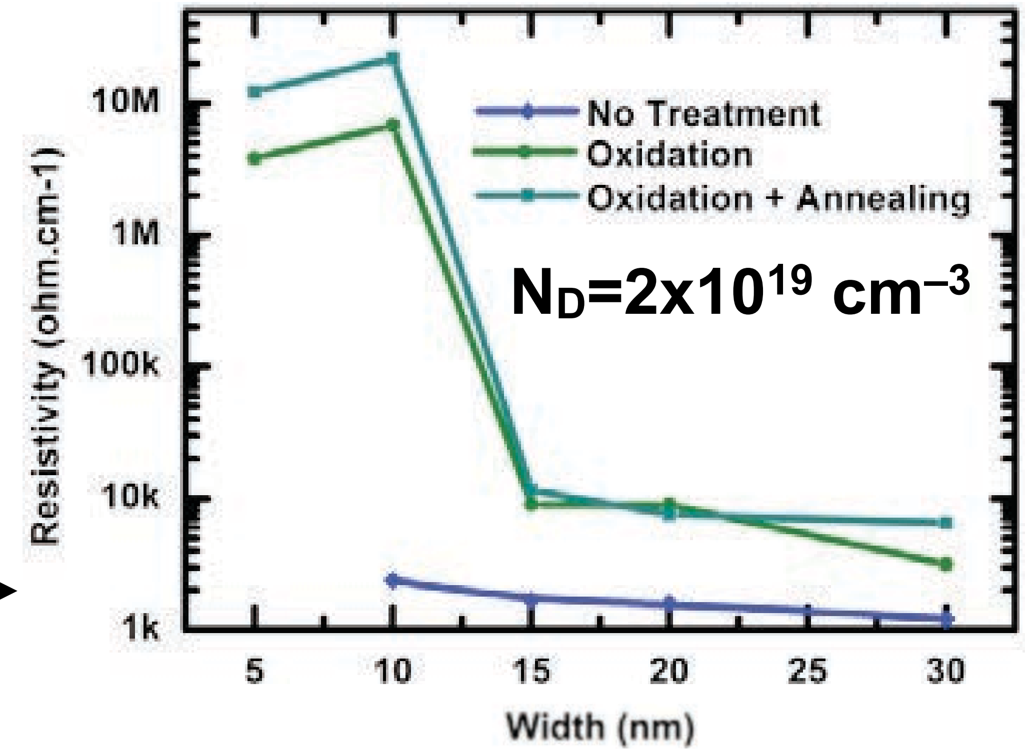
Si Nanowires: Electrical resistivity

- At Glasgow SET process scaled for 300 K operation (DSTL & MOD interest)

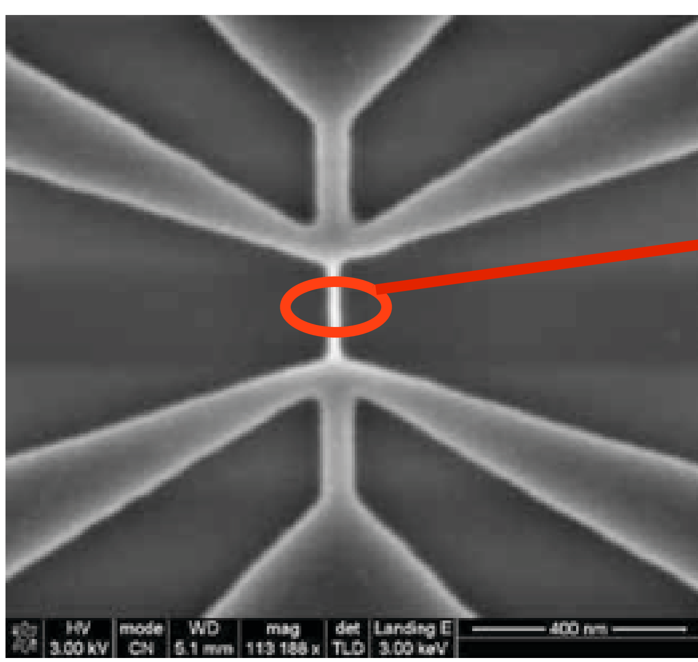
2 contacts nanowire



Fully characterised process modules >98% yield

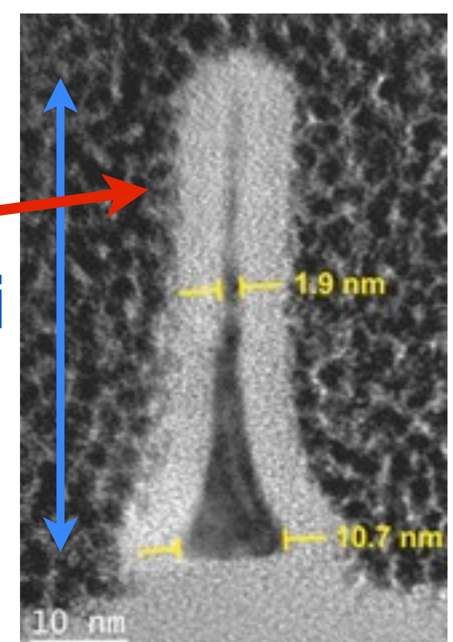


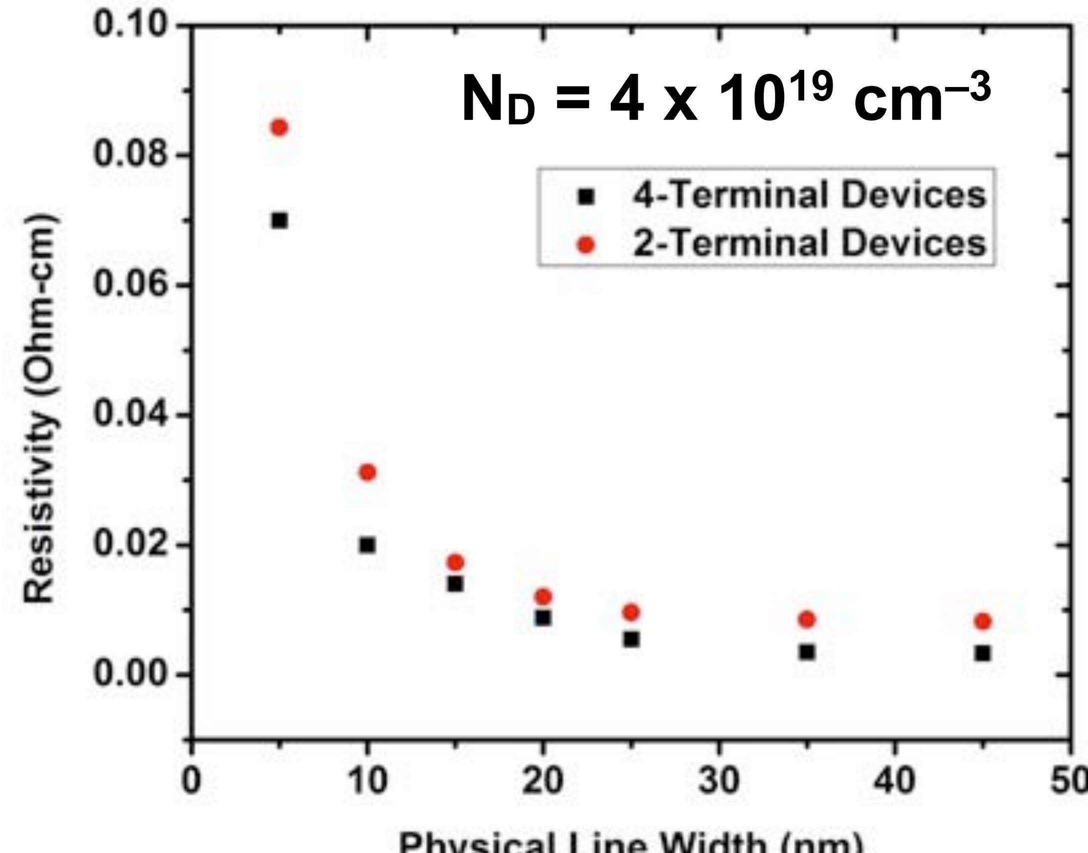
4 terminal contact nanowire



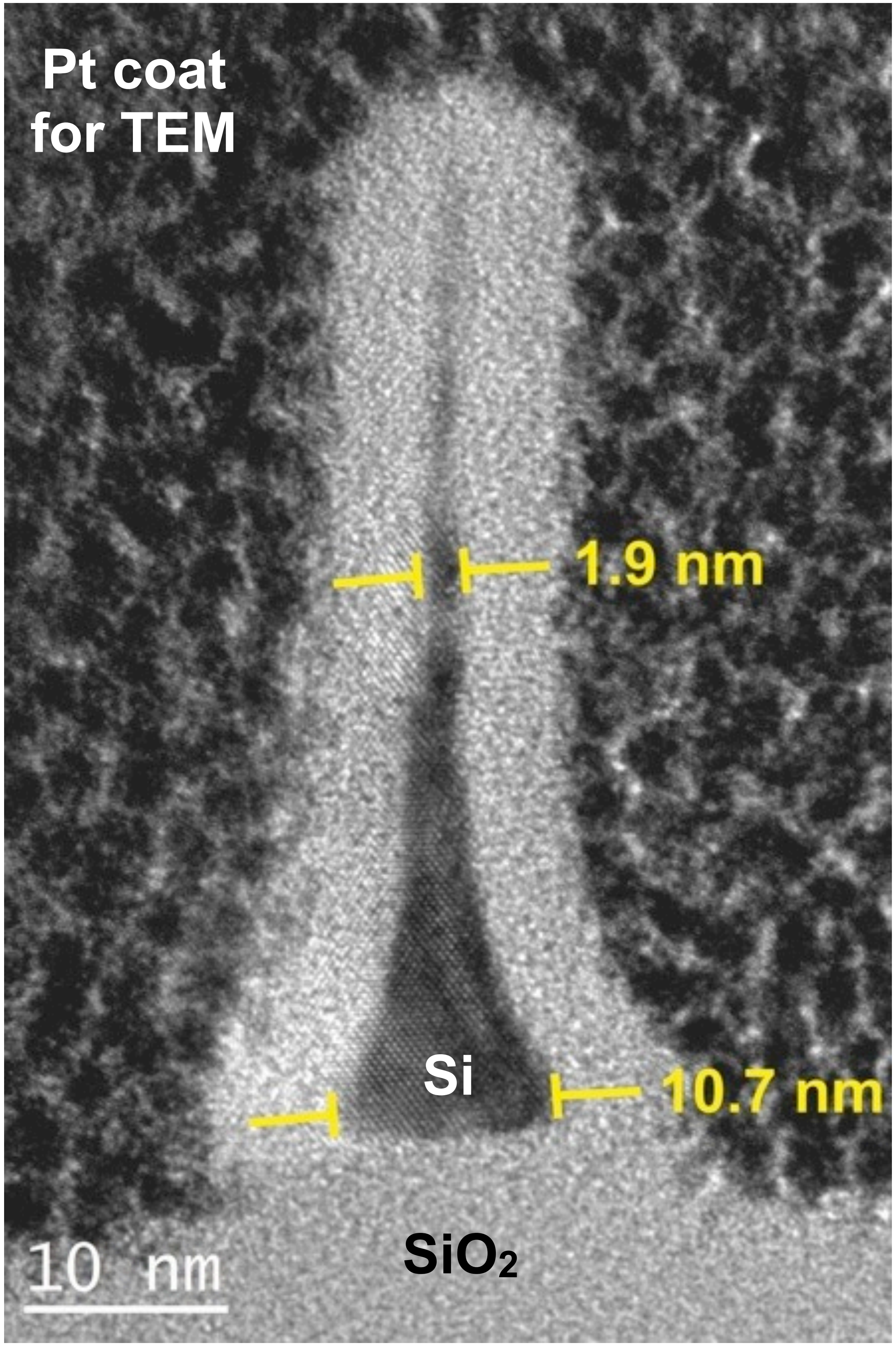
50 nm Si SOI

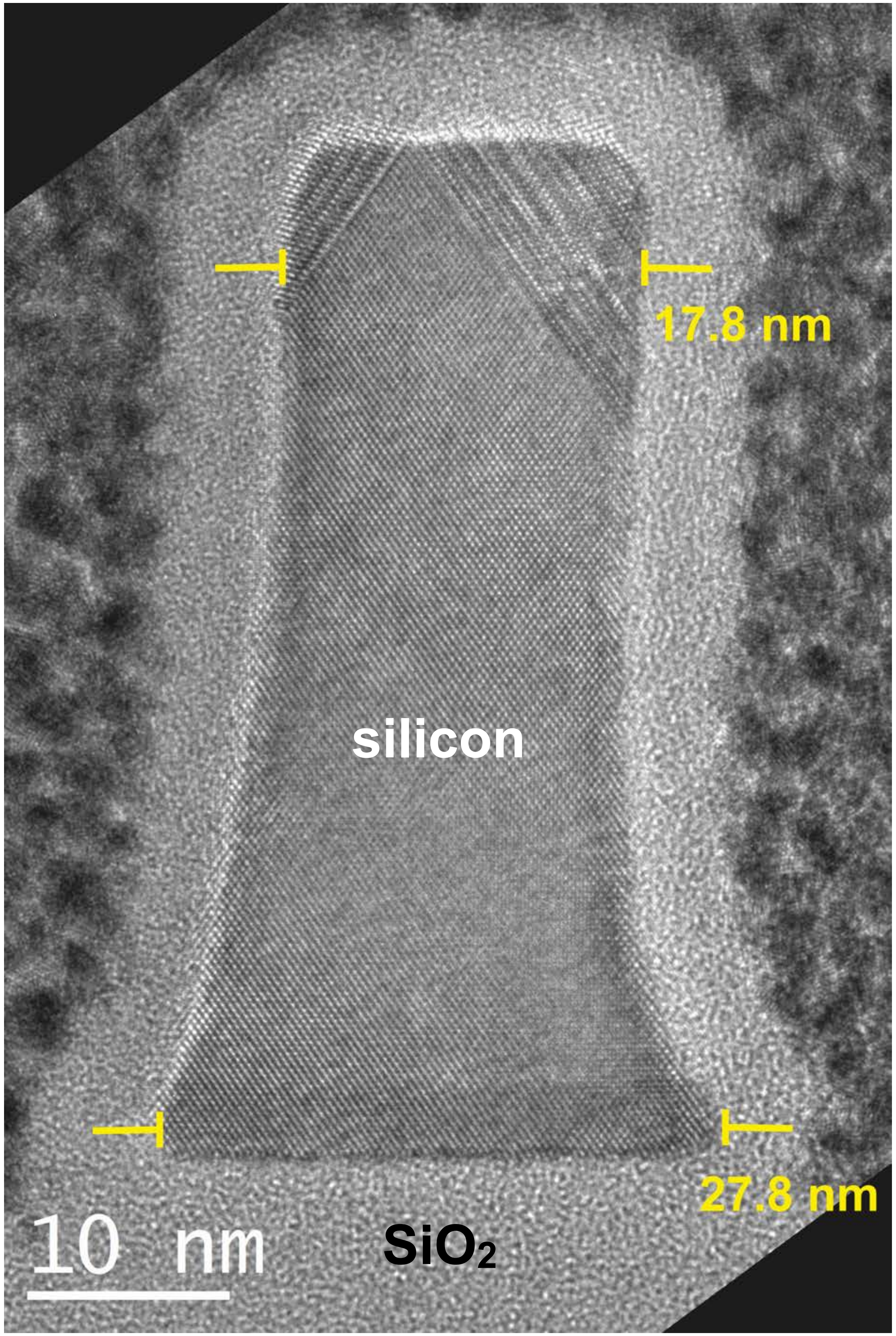
Cross section



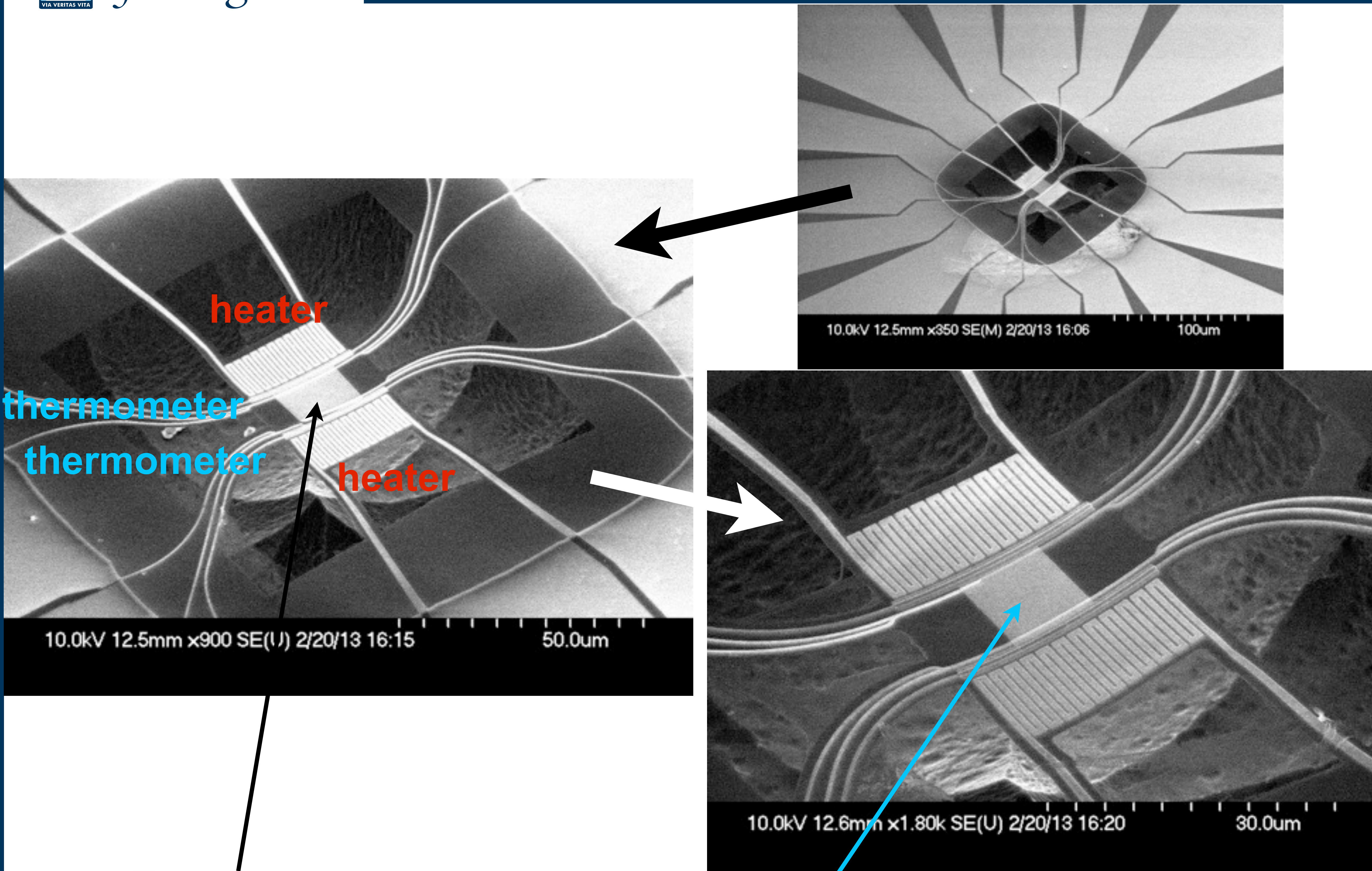


Si Nanowires: How many atoms wide?





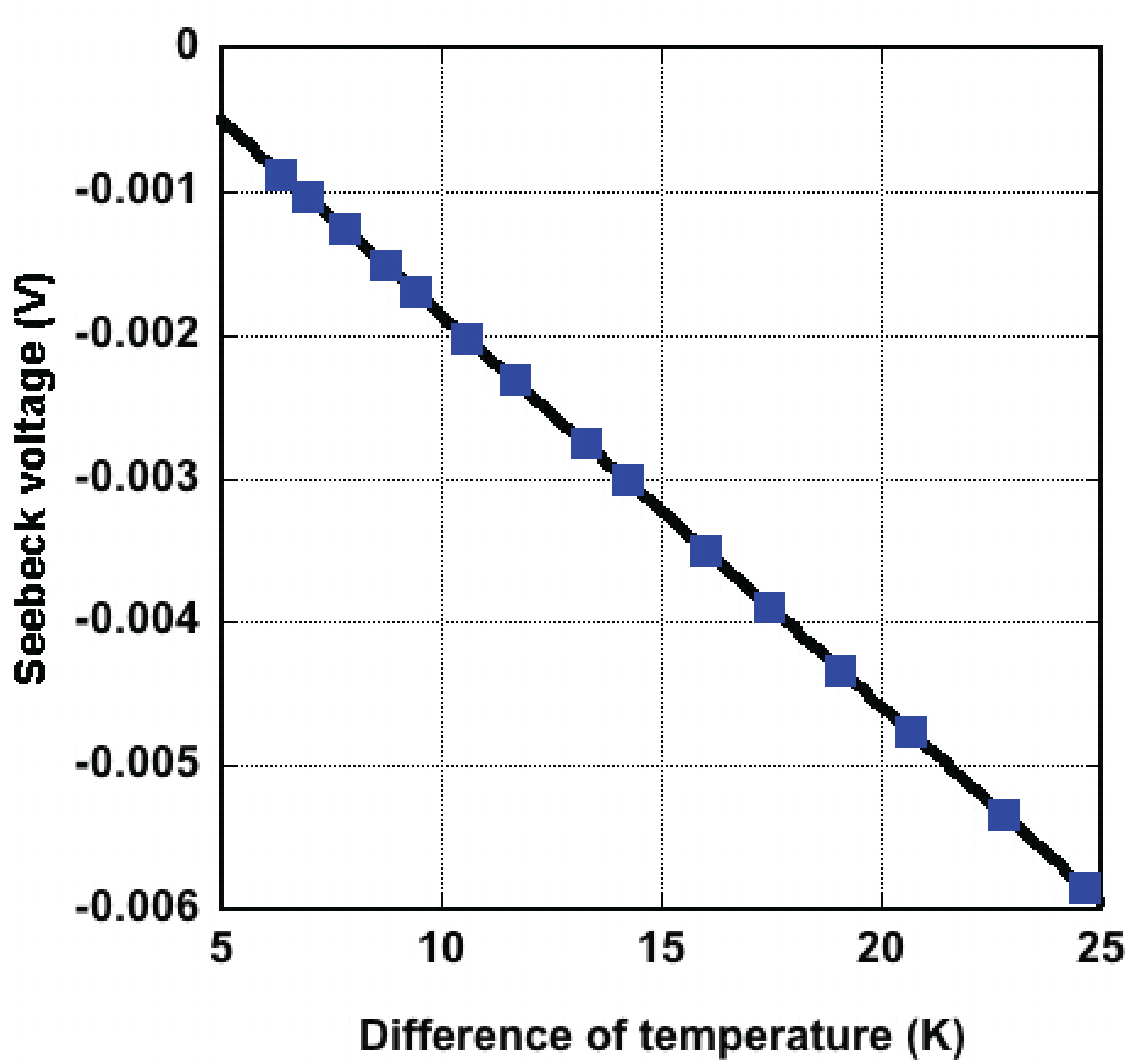
Nanowire Fabrication on Suspended Hall Bar



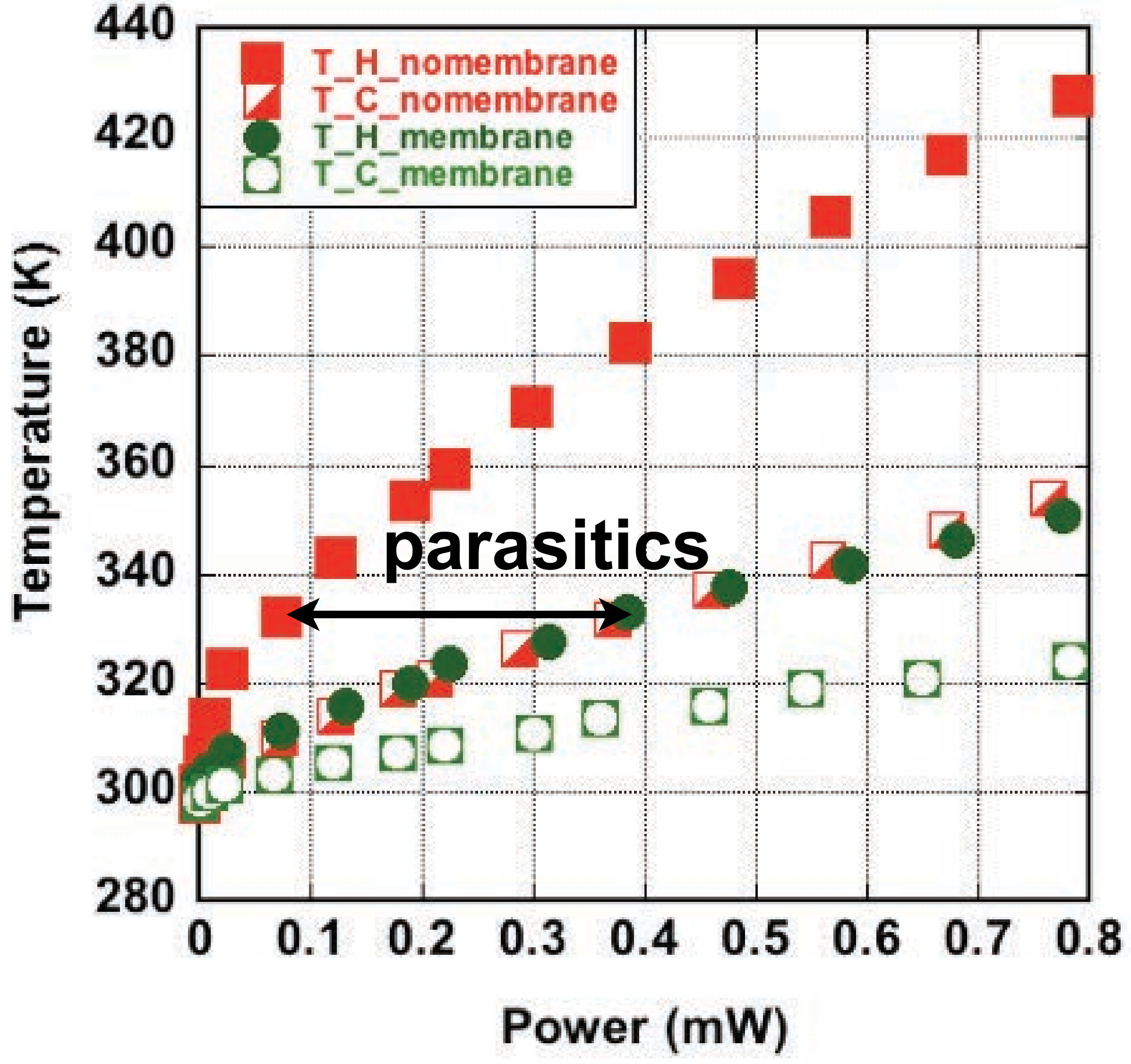
- **100 x 20 nm wide Si nanowires with integrated heaters, thermometers and electrical probes**

Seebeck and Thermal Conductivity

Seebeck coefficient



Thermal conductivity = total – parasitics

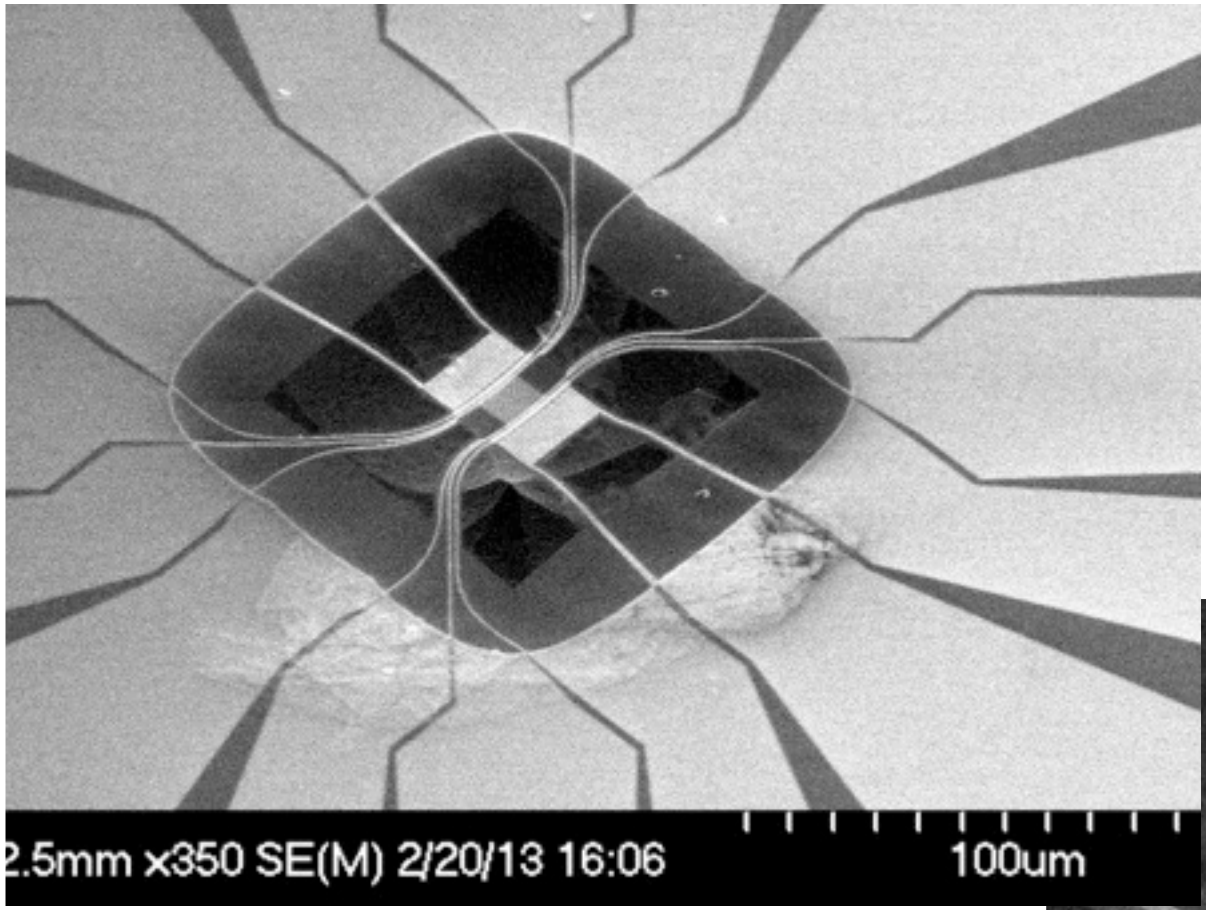


- $\alpha = -271.4\ \mu V/K$
- x3 enhancement over n^+-Si
- $\kappa = 7.78\ Wm^{-1}K^{-1}$
- x20 enhancement over n^+-Si

45 nm Wide n-Silicon Nanowires

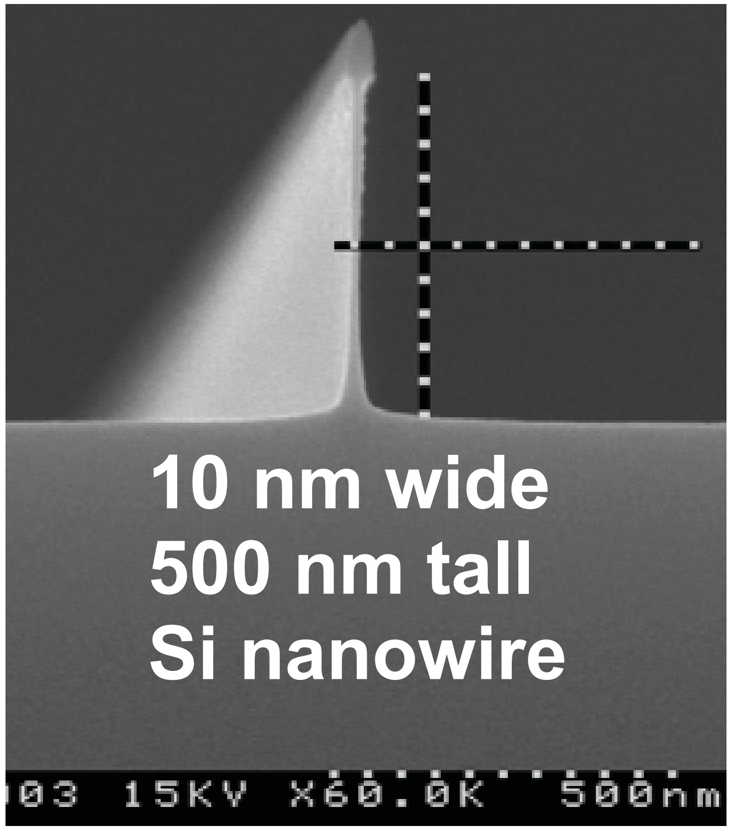
@ 300 K:

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

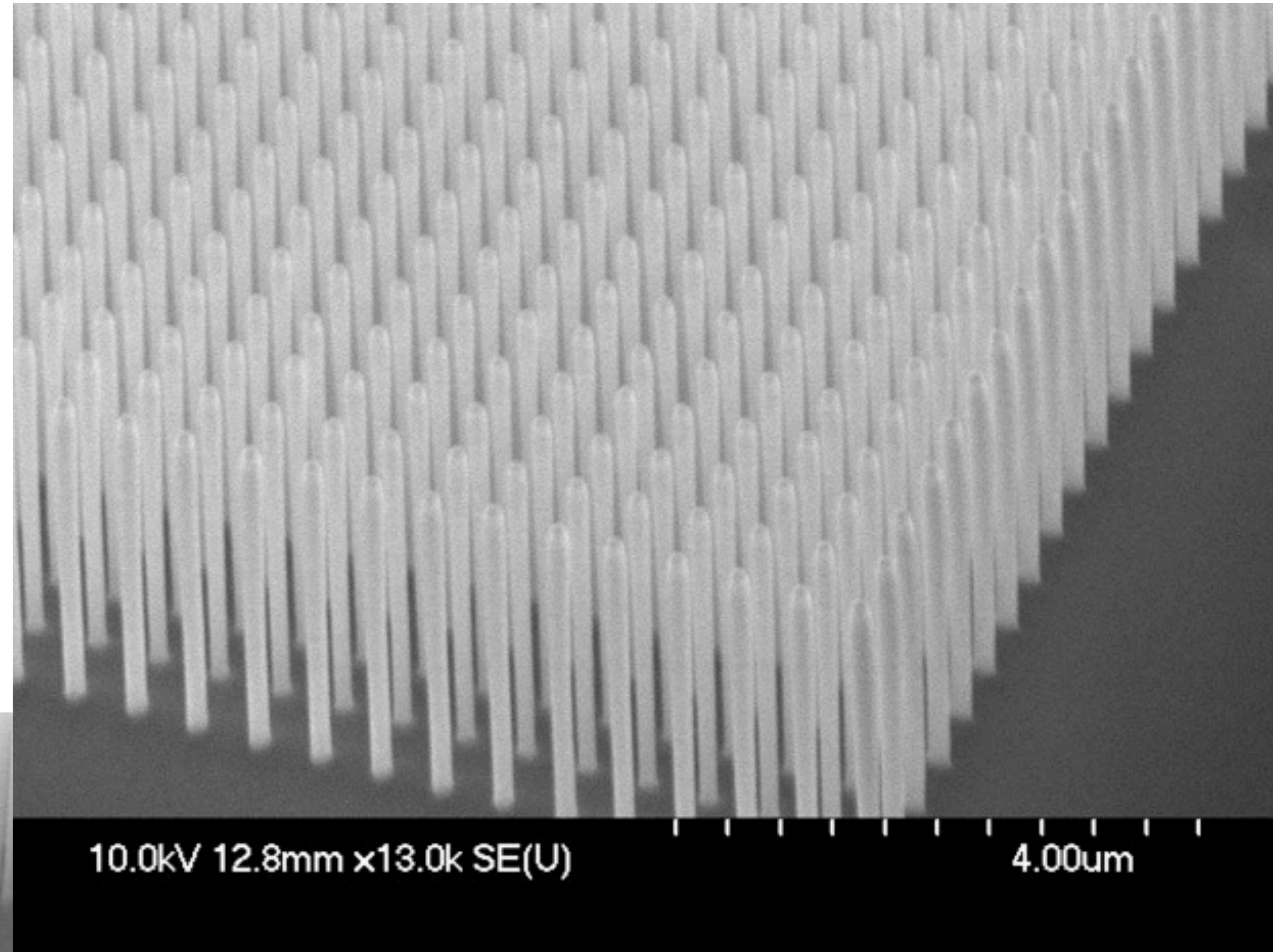


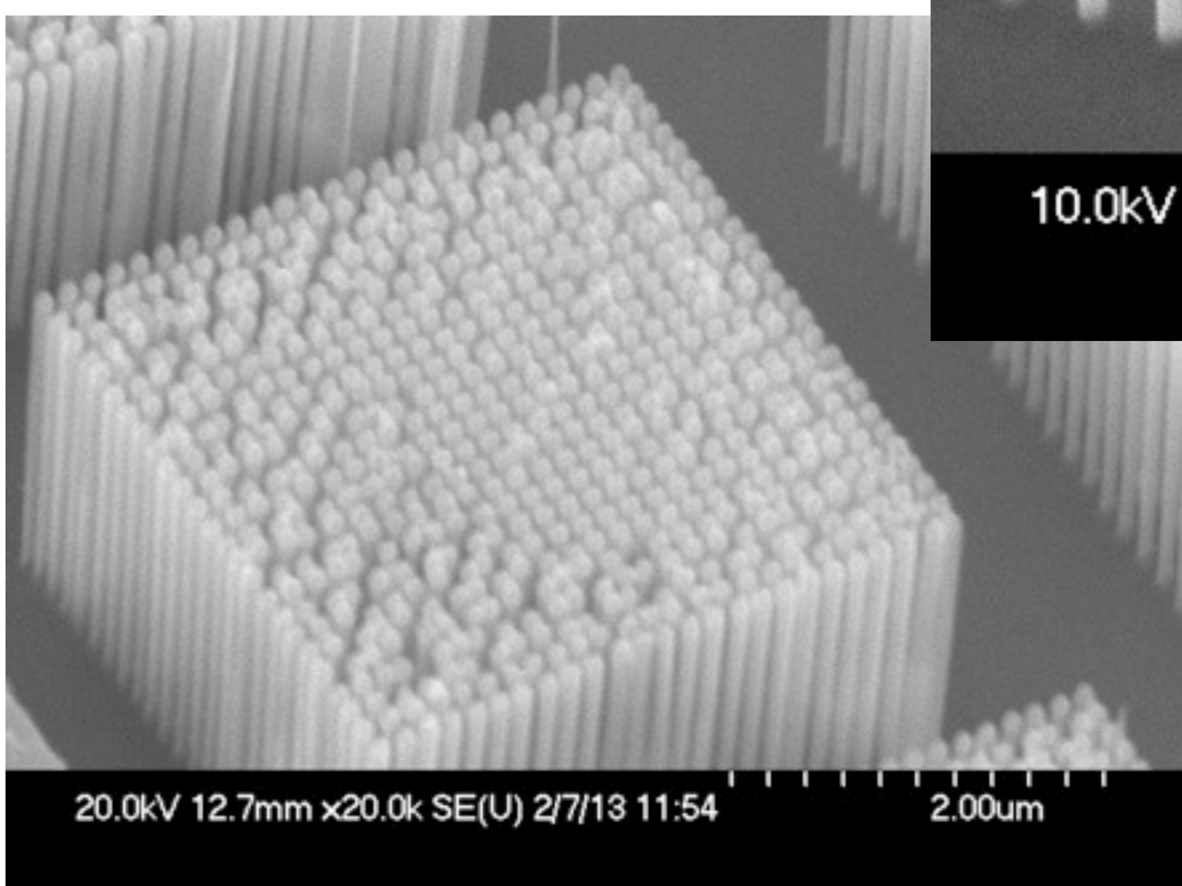
- ZT enhanced by x117
- $\alpha^2\sigma$ = 1.49 mW m^{-1}K^{-2}
- What enhancements with SiGe ?

Nanowire Module Development



Si etch



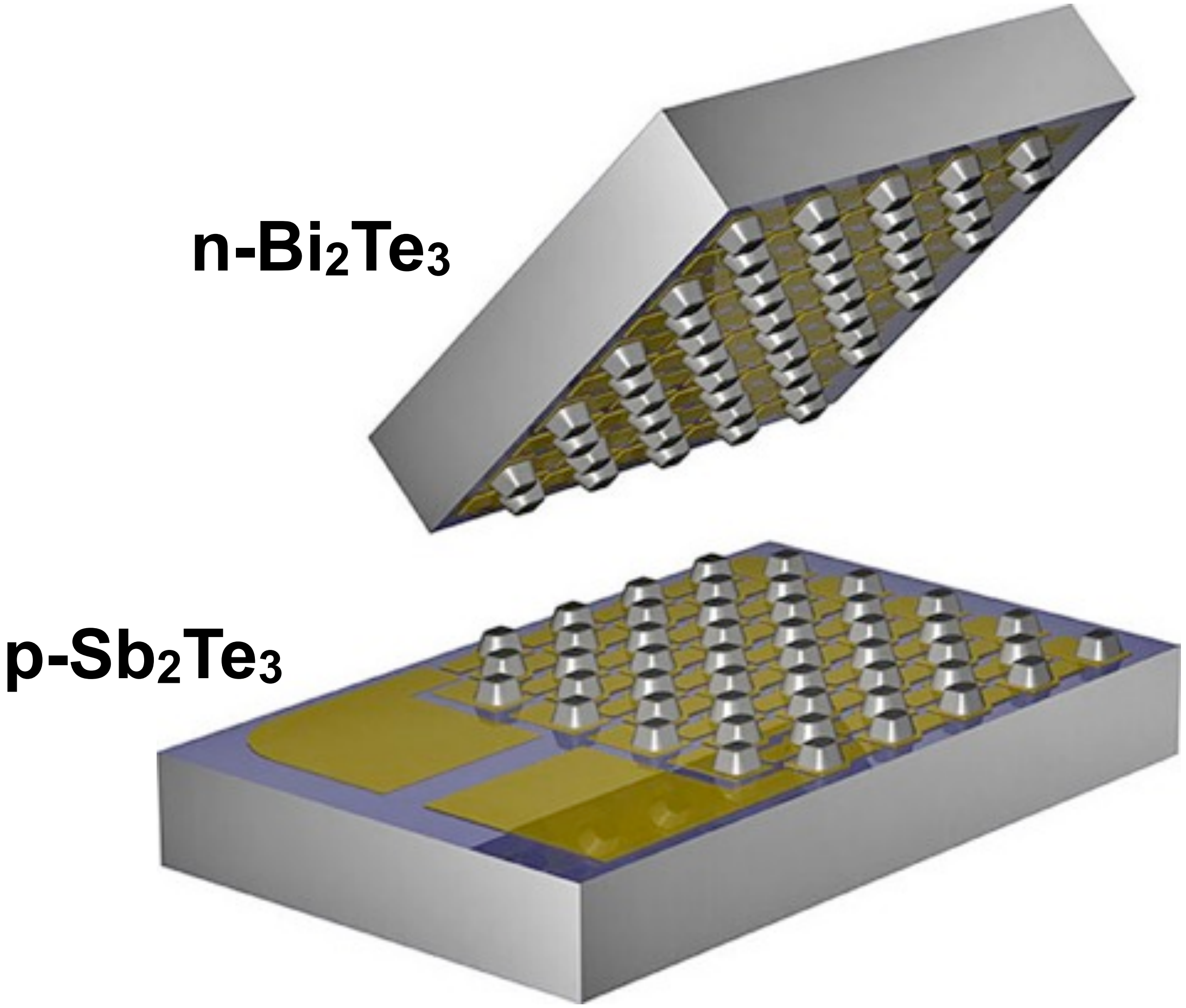


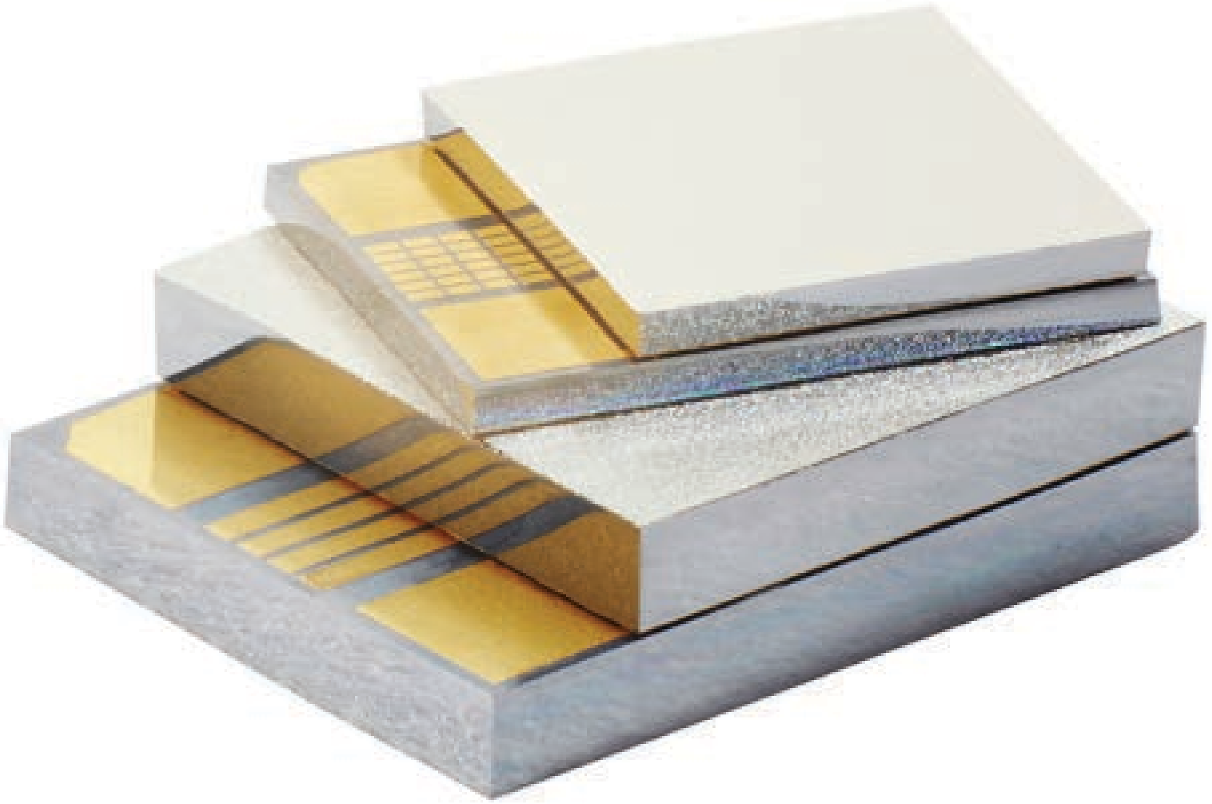
High density nanowires

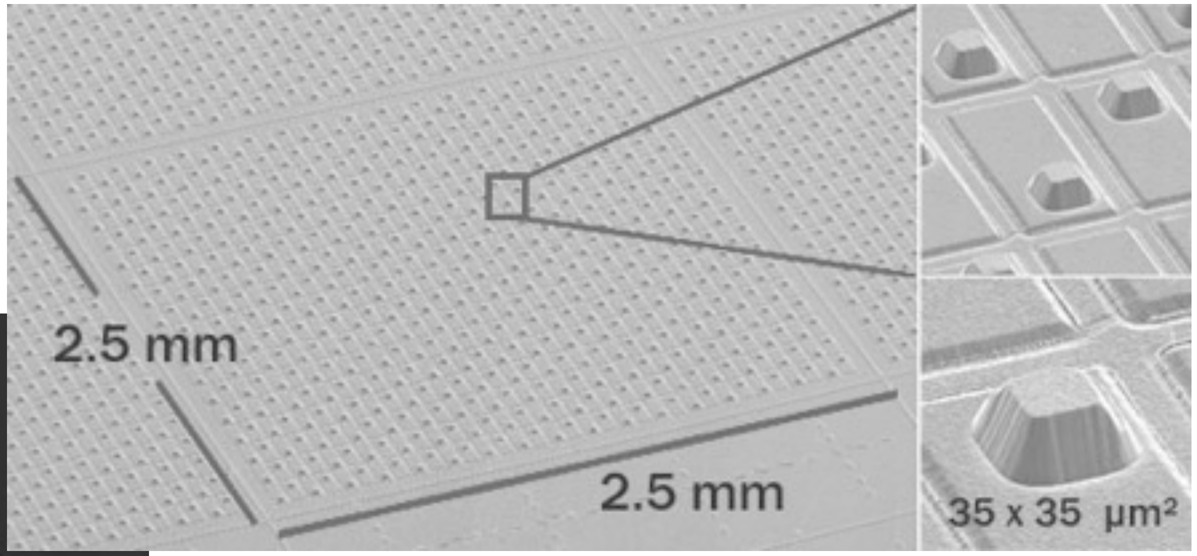
50 nm Ge/SiGe nanowires

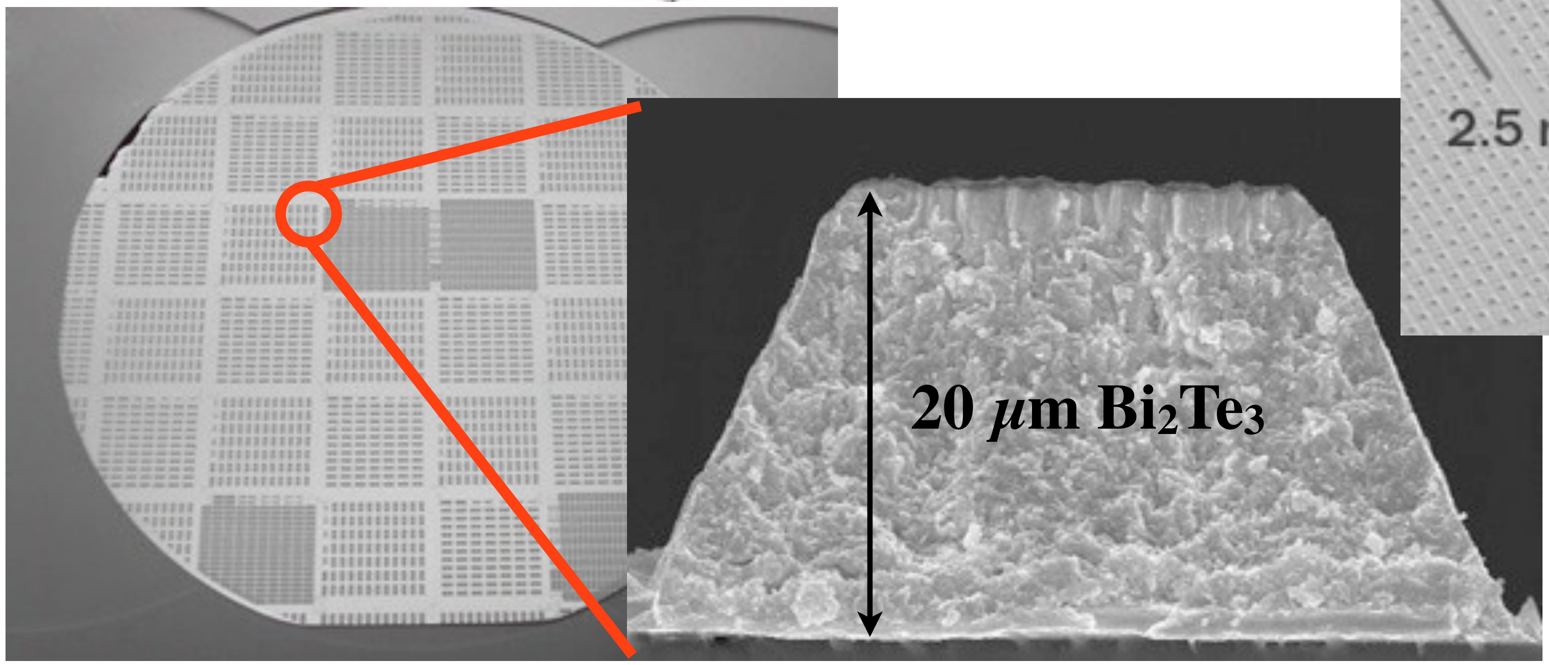
4 µm deep etched

Micropelt Microfabrication of BiTe Alloys



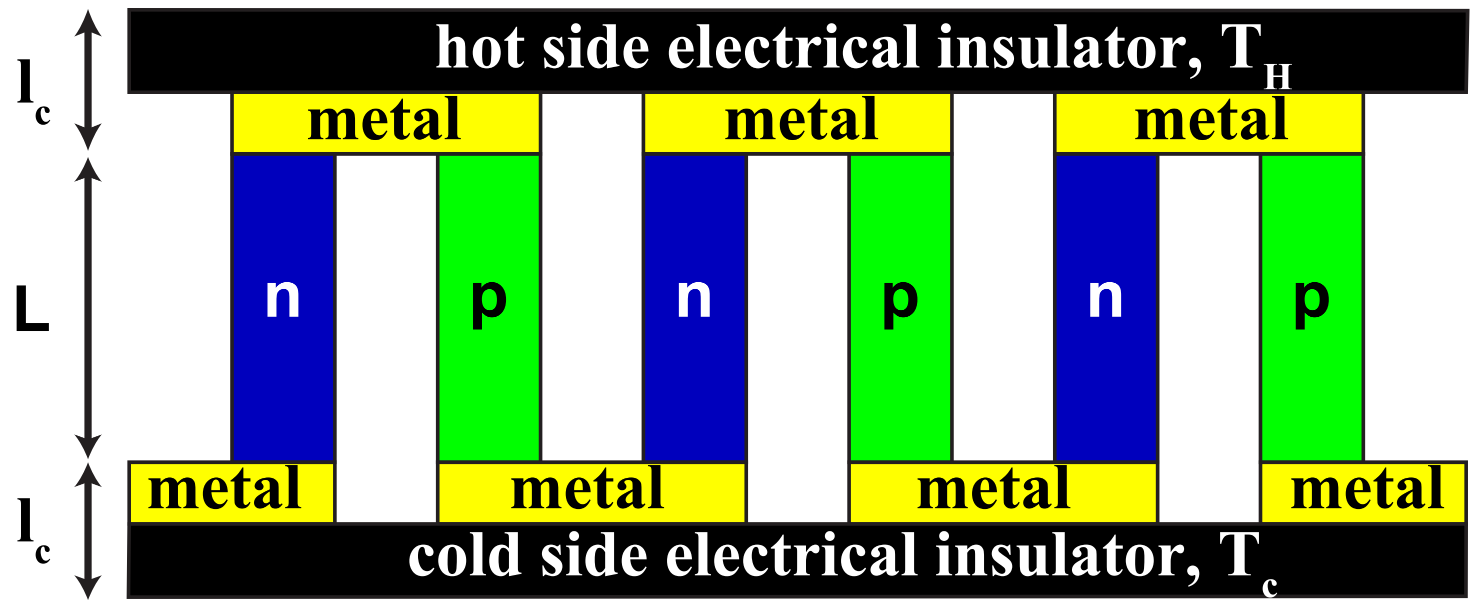






http://www.micropelt.com/

System Design: Power Output



A = module leg area

L = module leg length

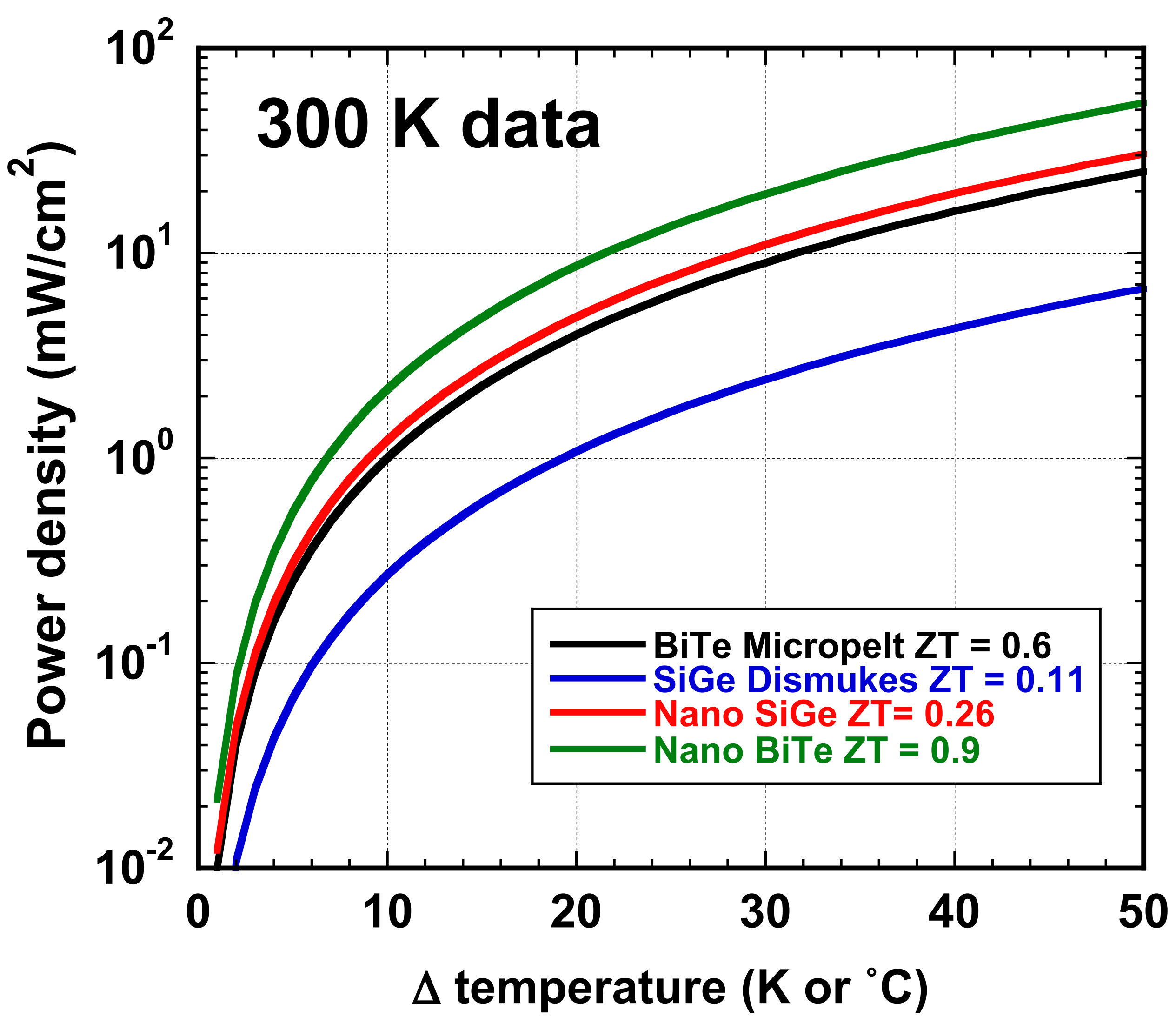
N = number of modules

κ_c = thermal contact conductivity

ρ_c = electrical contact resistivity

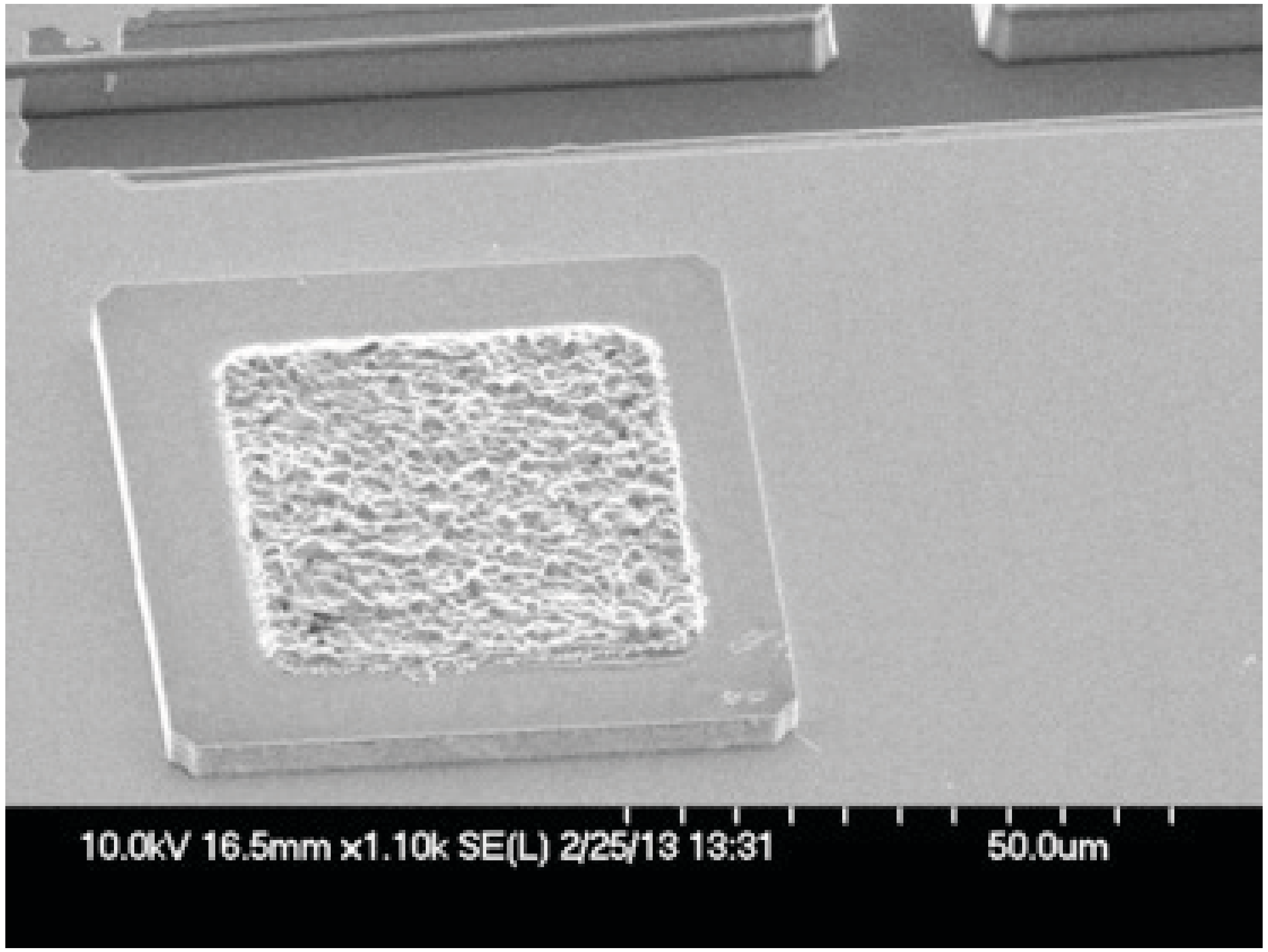
$$P = \frac{\alpha^2 \sigma A N \Delta T^2}{2(\rho_c \sigma + L)\left(1 + 2\frac{\kappa l_c}{\kappa_c L}\right)^2}$$

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

Indium Bump Bonding

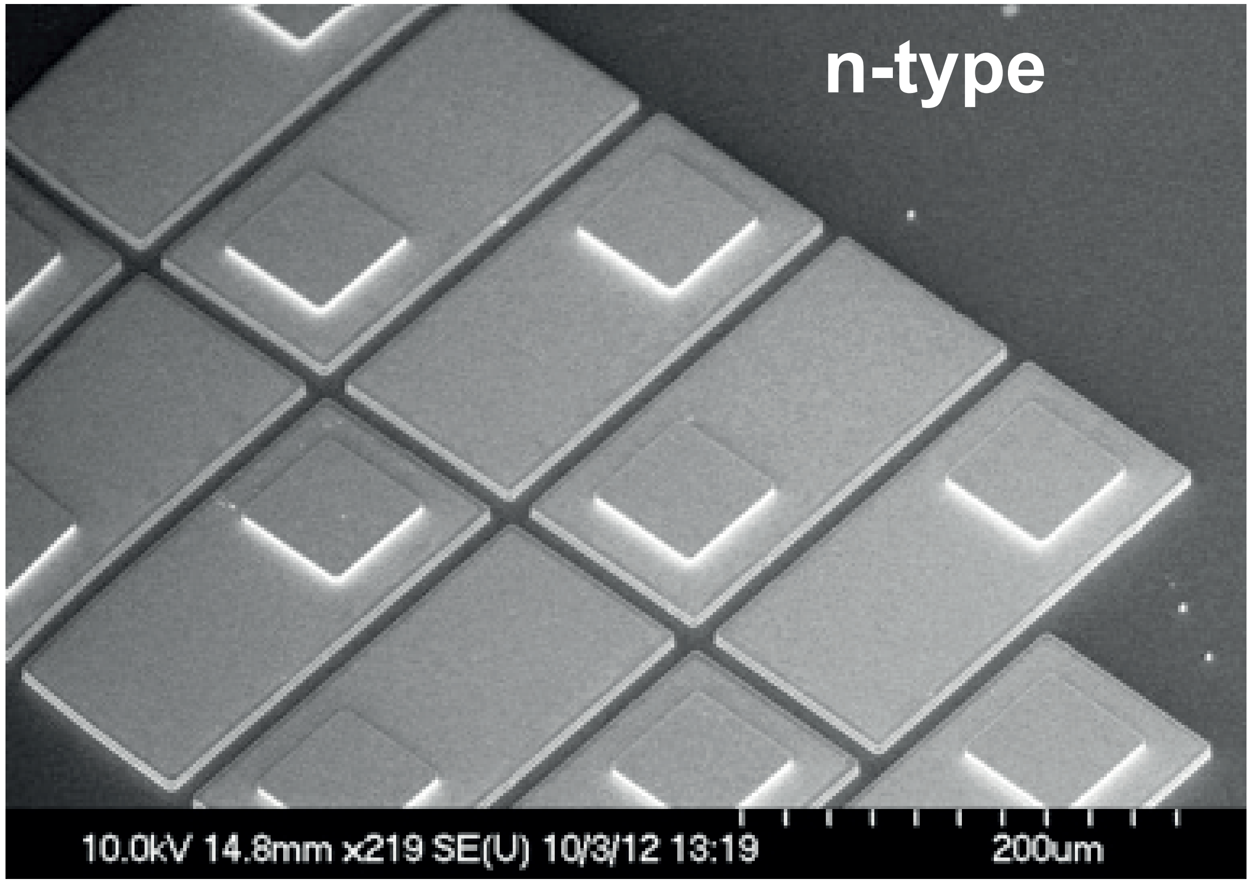


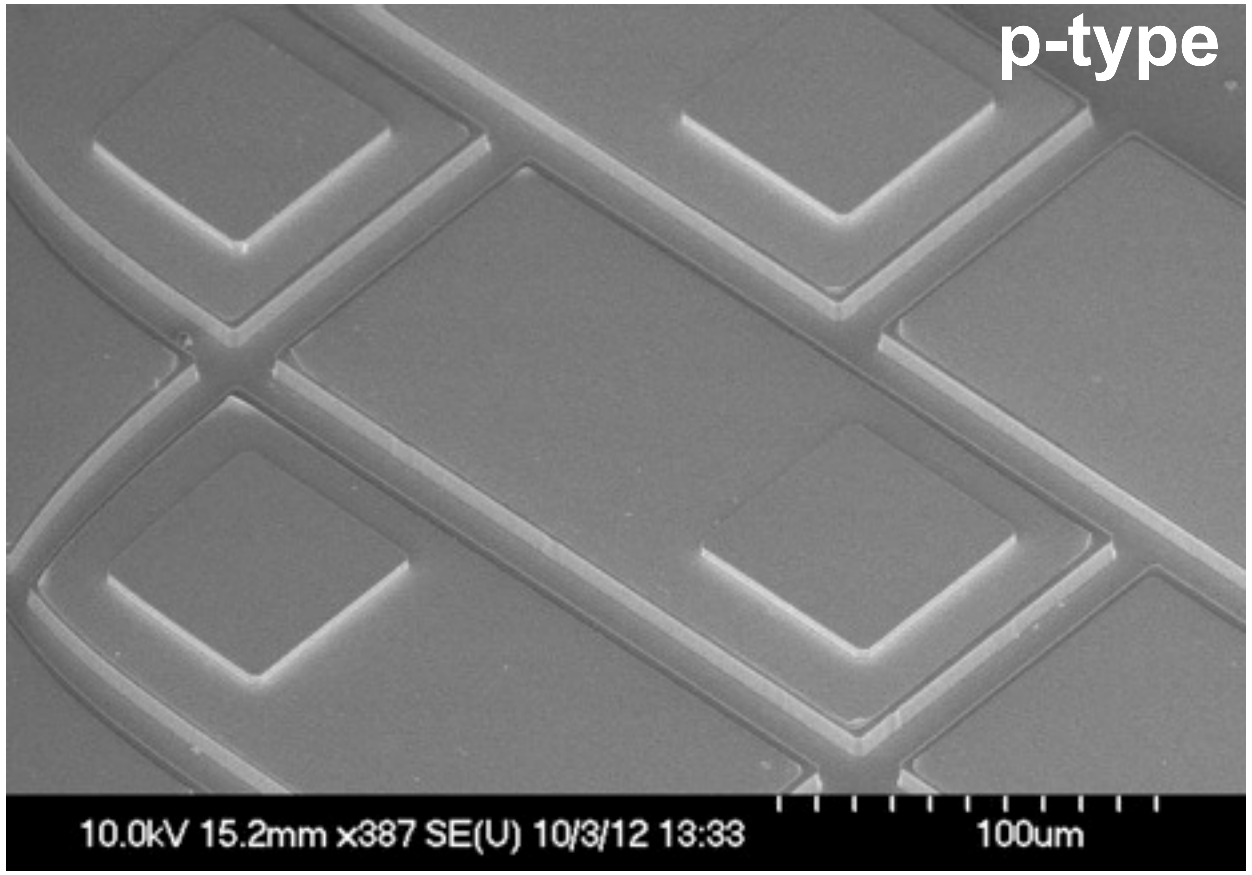
- 2 µm thick In allows bump bonding on legs down to 25 µm diameter

- Limitation: operation is limited to ≤ 125 ˚C

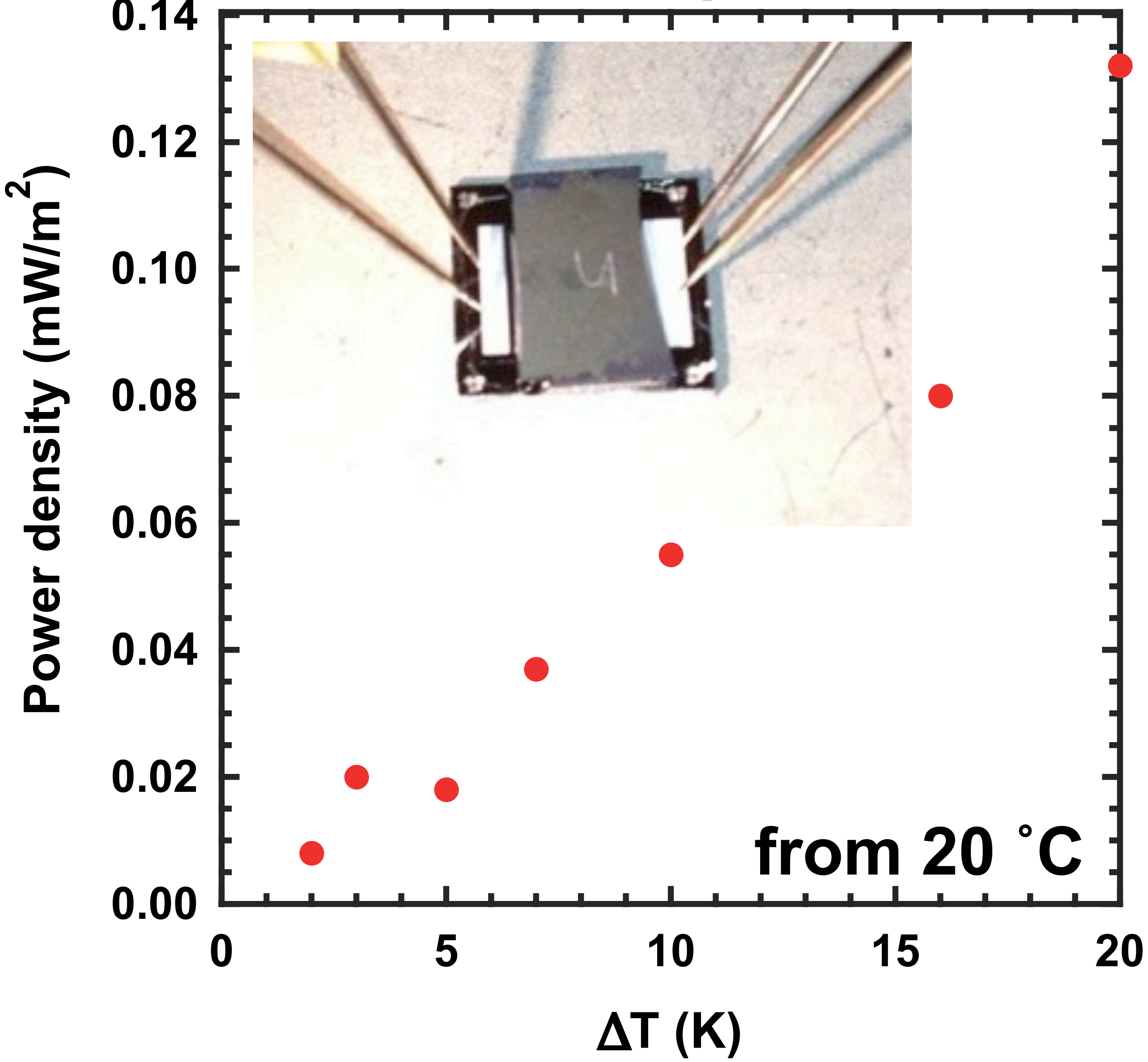
- Investigating new bump process for operation to ≤ 500 ˚C

Module Power Density





Single n- and p-type legs indium bump bonded

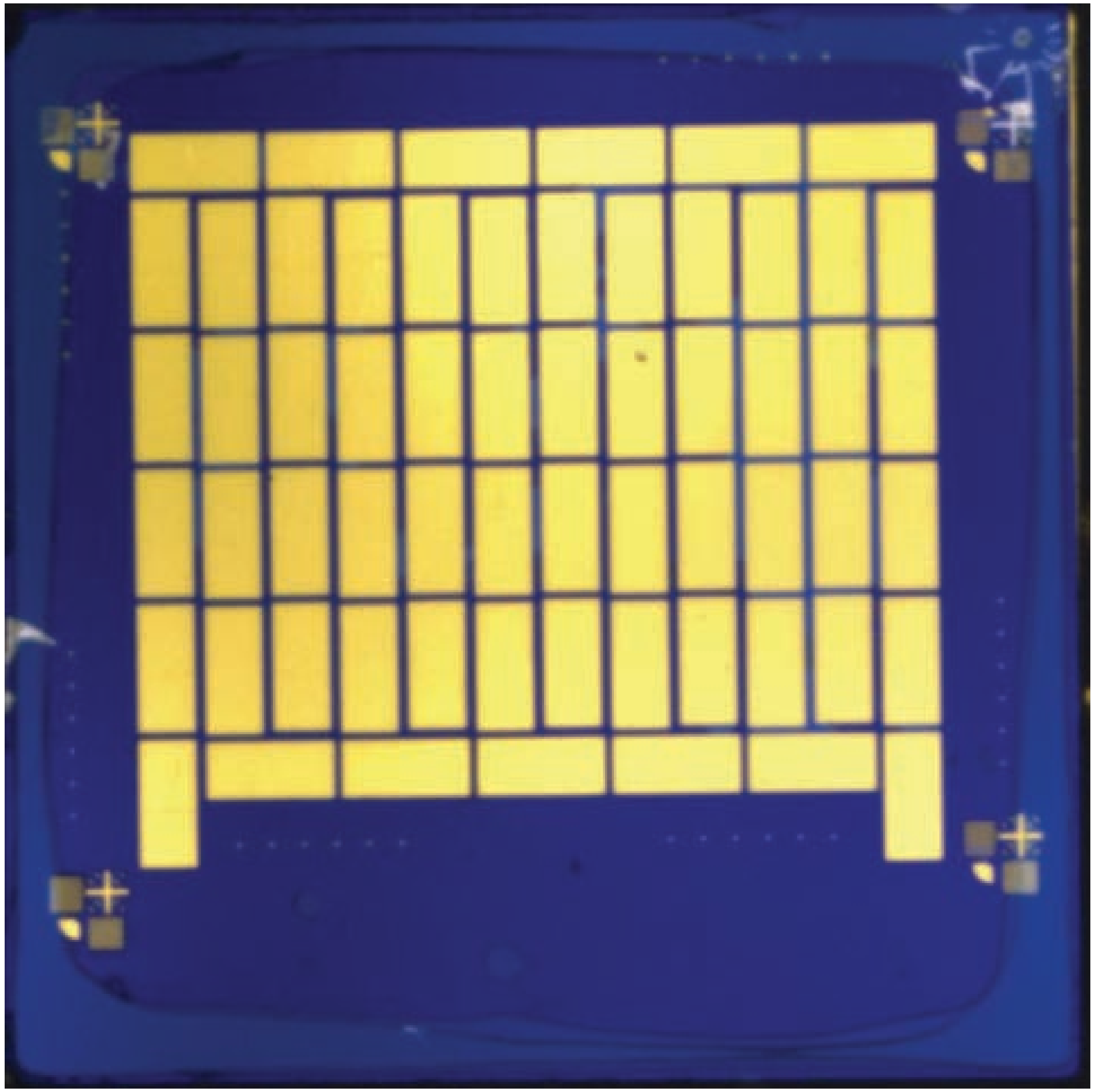


Early results on poor ZT material to develop module technology

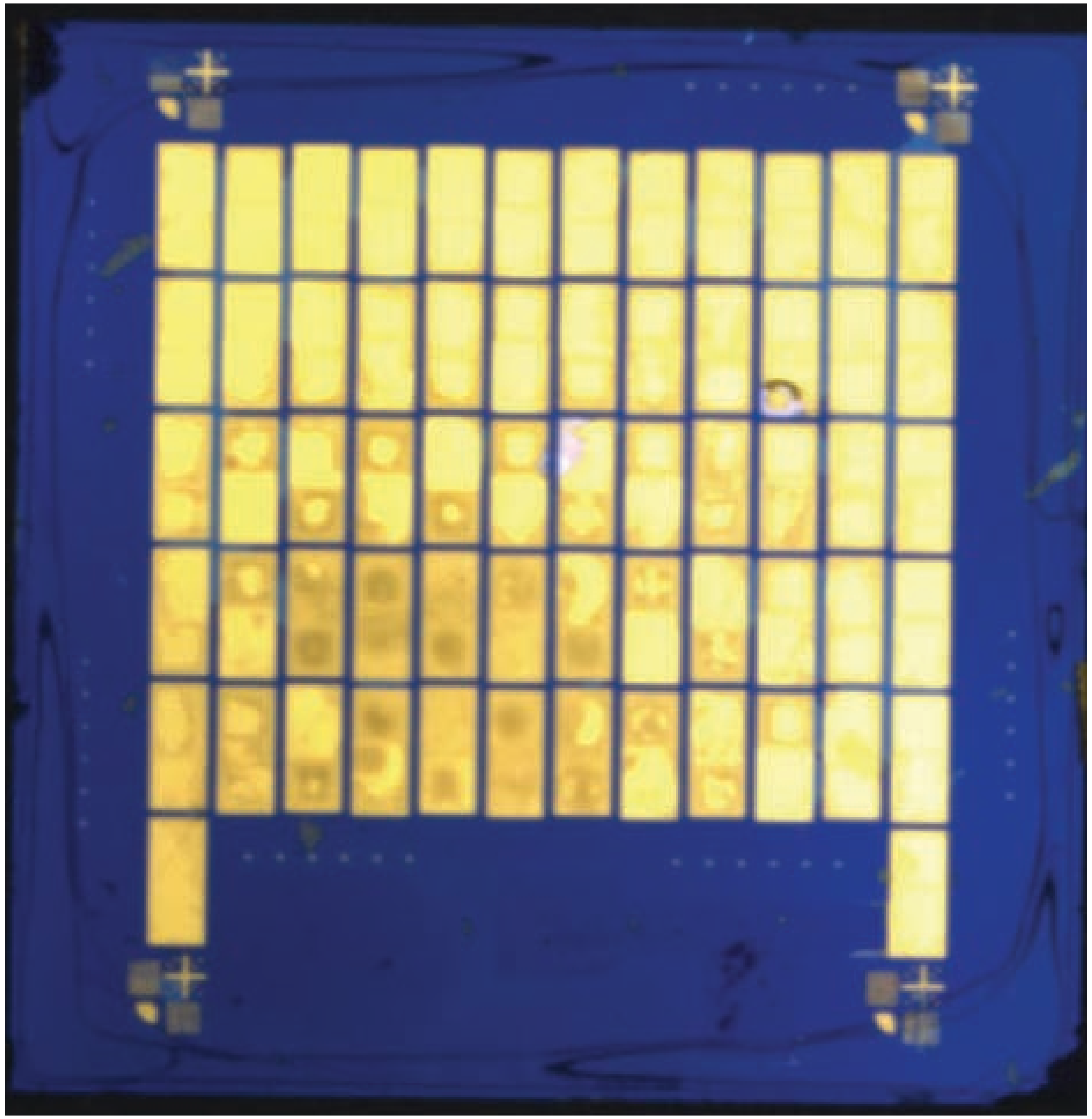
Enormous room for optimisation

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

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Further Information

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