Advances on Thermoelectrics for Energy Harvesting

Prof Douglas Paul
Director: James Watt Nanofabrication Centre

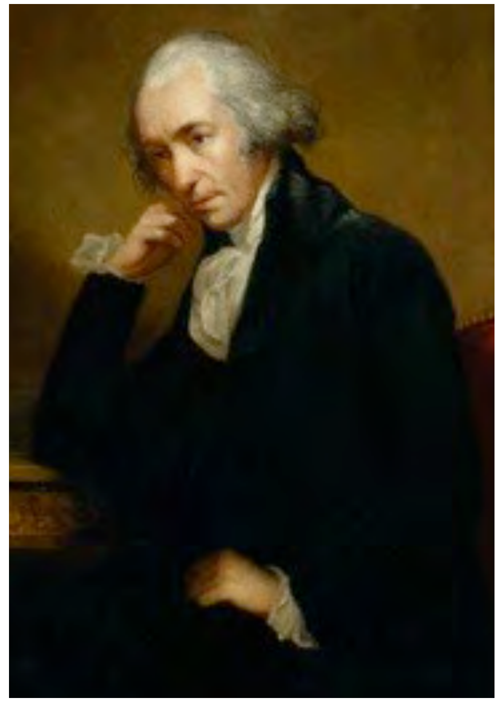
The University of Glasgow

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

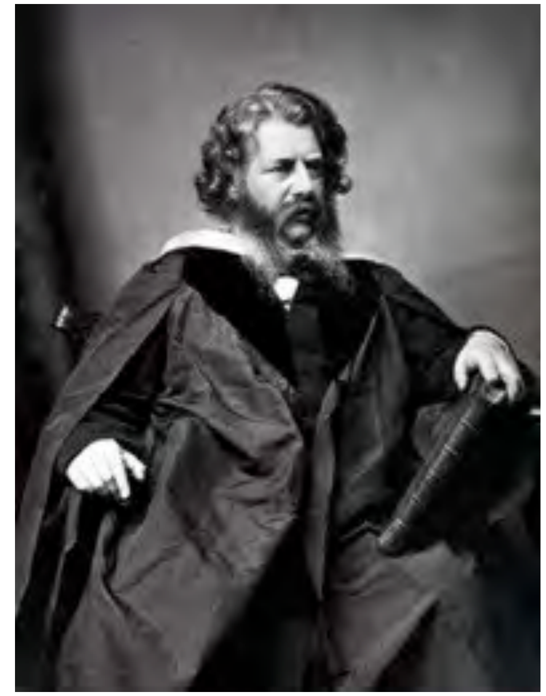
- 400 years in High Street
- Moved to Gilmorehill in 1870
- Neo-gothic buildings by Gilbert Scott

Famous Glasgow Scholars

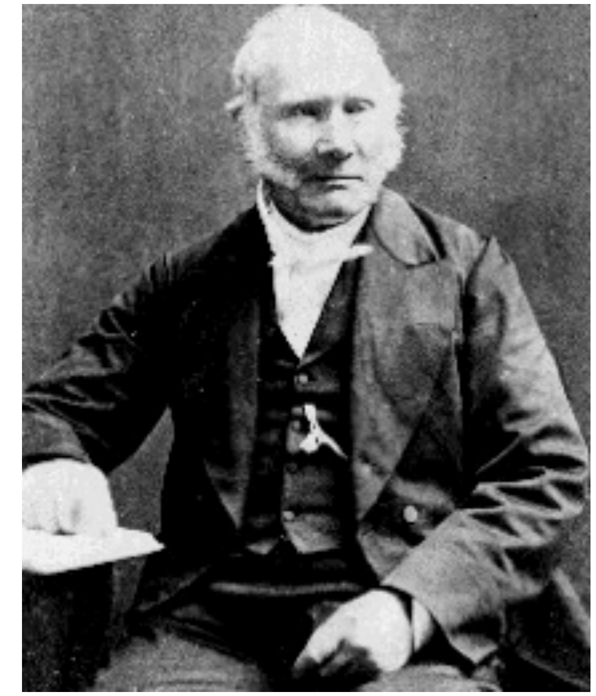
William Thomson (Lord Kelvin)



James Watt



William John Macquorn Rankine



Rev Robert Stirling

Rev John Kerr

Joseph Black

John Logie Baird

Adam Smith

University of Glasgow

James Watt's Laboratory

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

University of Glasgow

James Watt Nanofabrication Centre @Glasgow

- **750 m^2 cleanroom - pseudo-industrial operation**
- **14 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**

Vistec VB6 & EBPG5

E-beam lithography

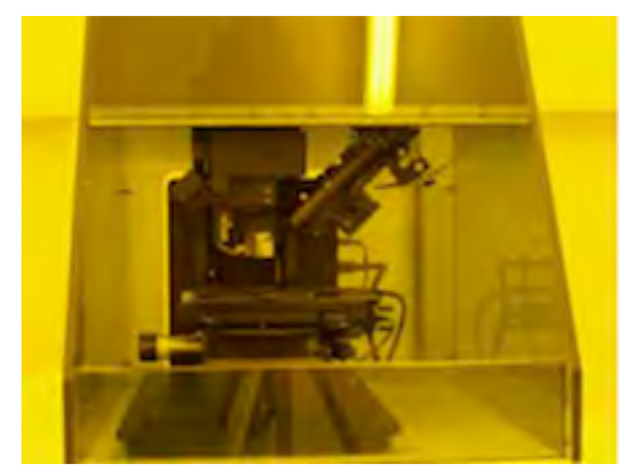
Süss MA6 optical lith

10 RIE / PECVD

5 Metal dep tools

4 SEMs: Hitachi S4700

Veeco: AFMs



Electron Beam Lithography Capability

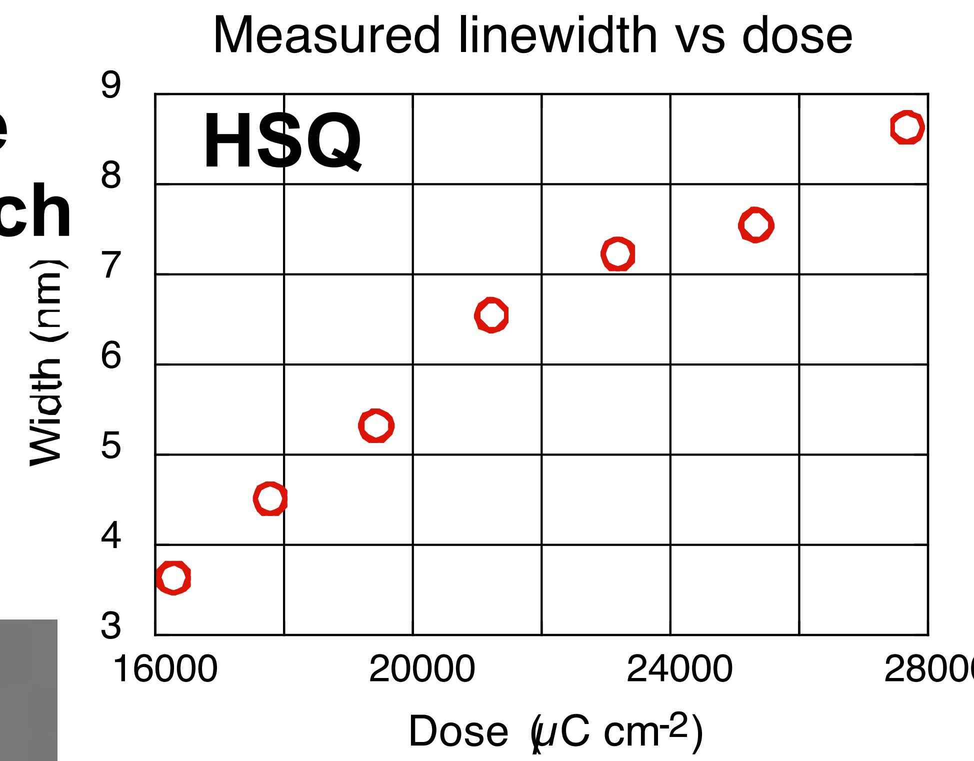
University of Glasgow

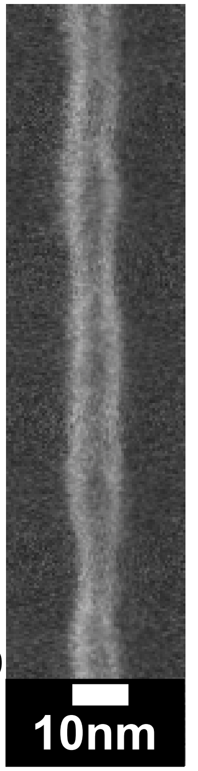
30 years experience of e-beam lithography

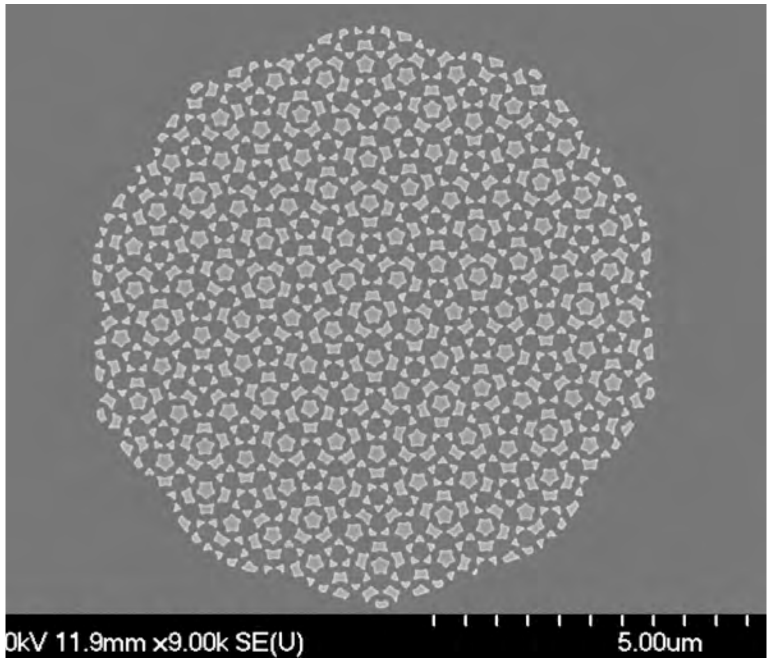
Vistec VB6

Vistec EBPG5

Sub-5 nm single-line lithography for research



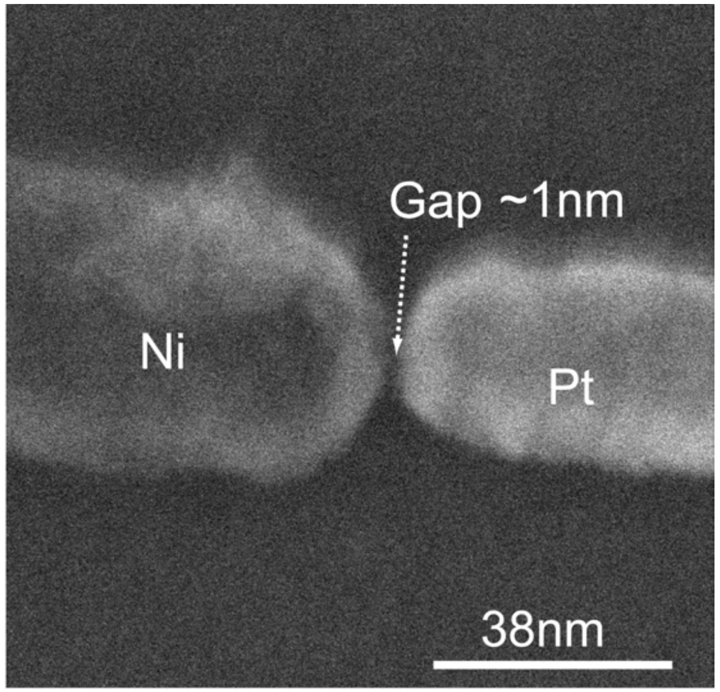




Penrose tile: layer-to-layer alignment 0.46 nm rms

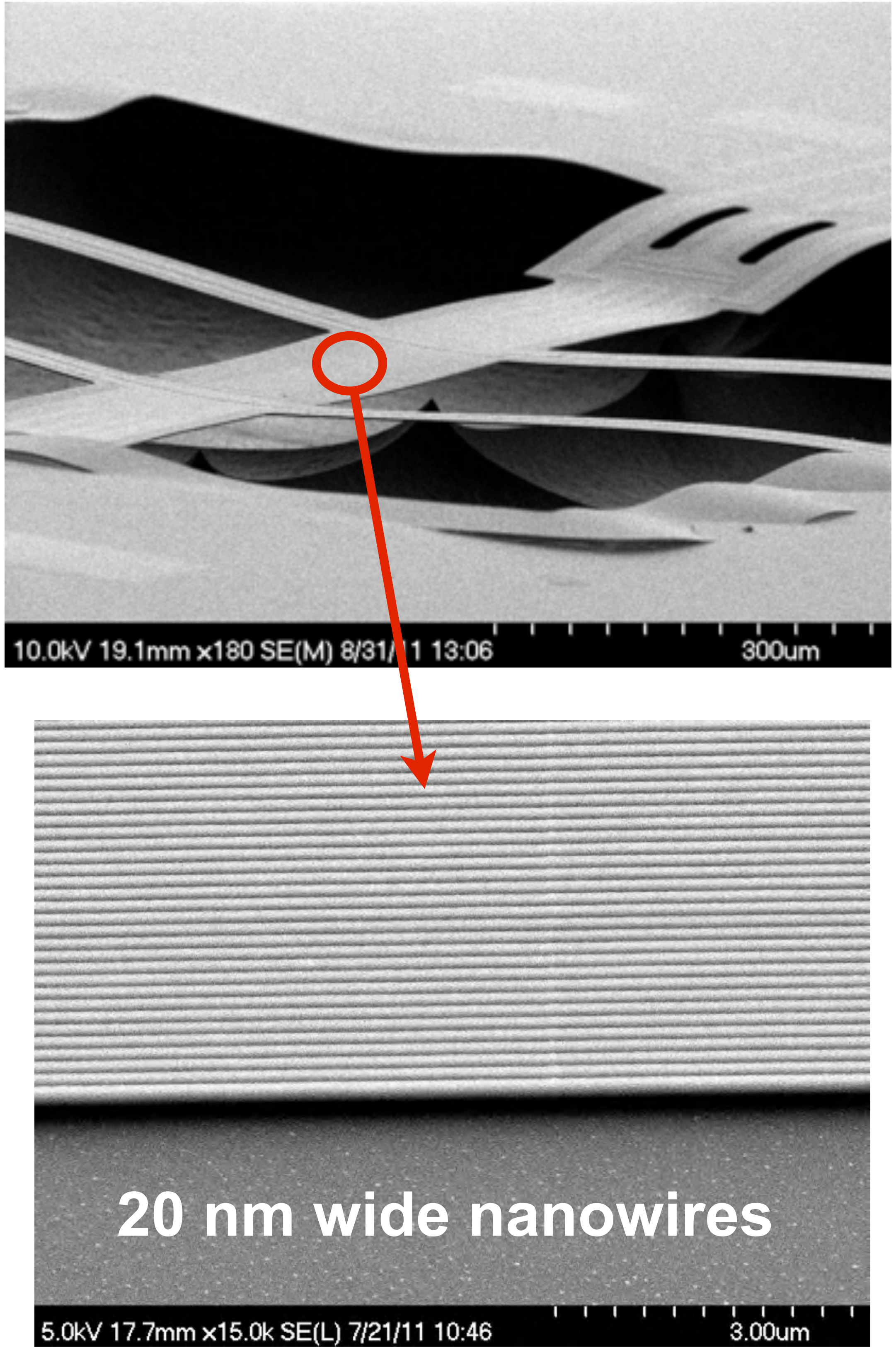
Alignment allows 1 nm gaps between different layers:

–> nanoscience: single molecule metrology



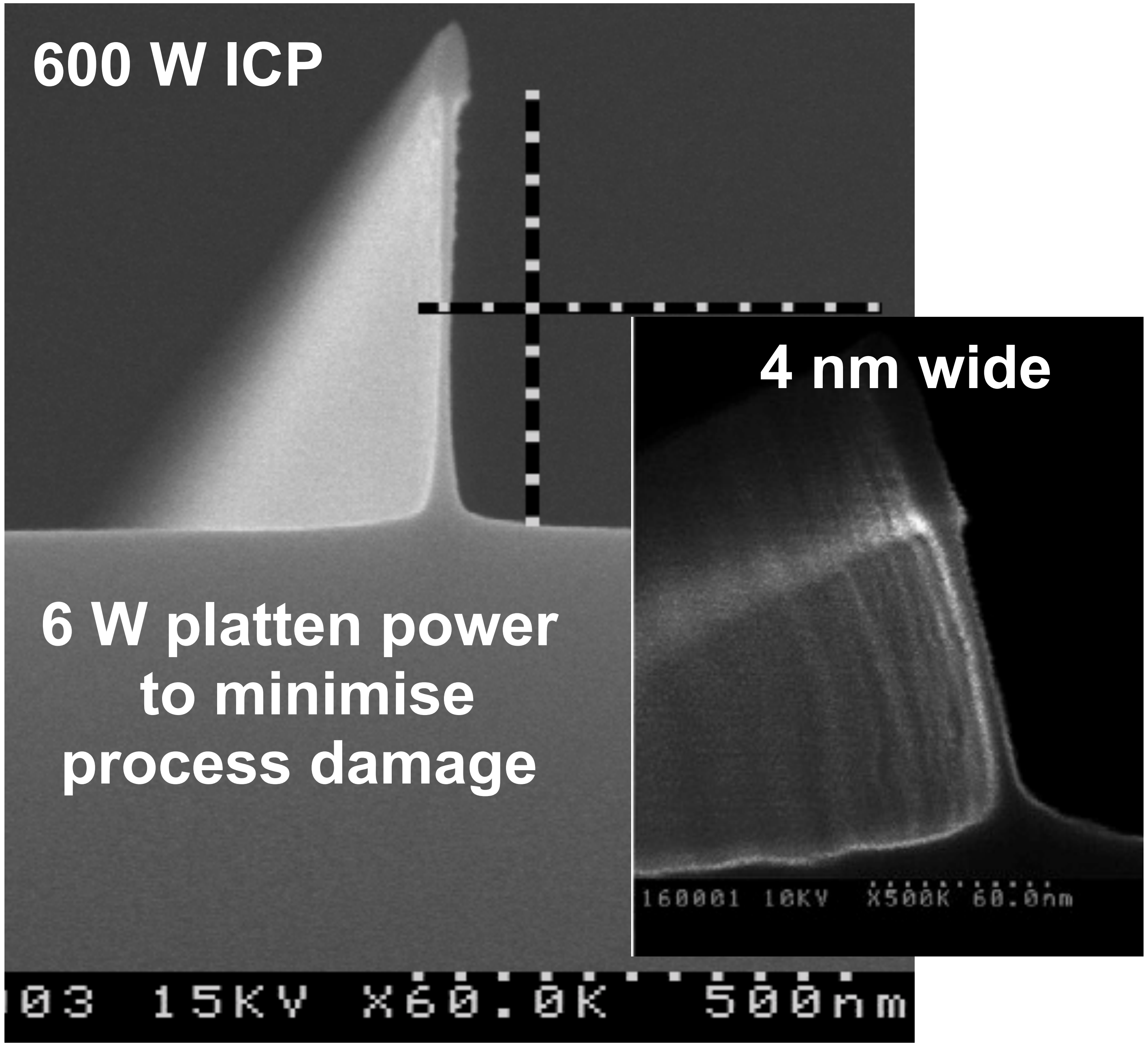
Pattern Transfer: 1D Silicon Nanowires

Lateral Nanowires

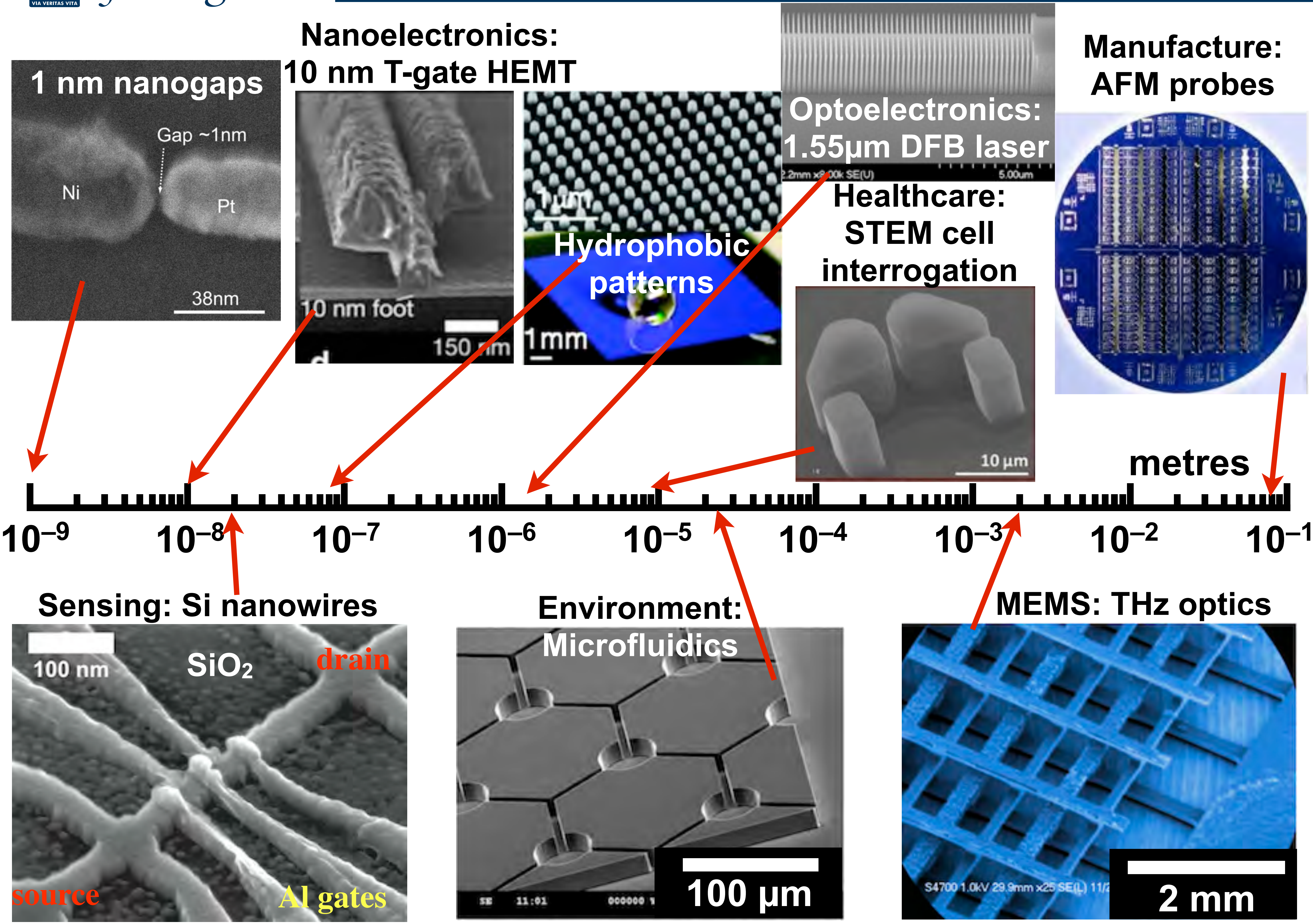


Vertical Nanowires

10 nm wide
500 nm tall
Si nanowire



Micro and Nanotechnology from Glasgow



University of Glasgow

Over 250 Industrial Partners & Customers

KELVIN NANOTECHNOLOGY

Wireless bioDevices

Intellemetrics

intense

SRC Semiconductor Research Corporation

numonyx

DMD DIAMOND MICROWAVE DEVICES LIMITED

e2v

Raytheon Systems Limited

BAE SYSTEMS

GSS GAS SENSING SOLUTIONS

M SQUARED

Unilever

SELEX GALILEO

elementsix

Micron

QinetiQ

IBM

National Semiconductor

AsahiKASEI

and

GWENT GROUP

syrris

oclaro

TeraView

toumaz

FIAT

CRF CENTRO RICERCHE FIAT

gsk GlaxoSmithKline

Honeywell

DOOSAN

Kodak

Doosan Babcock

Genetix

freescale semiconductor

COHERENT

epigem

LOGITECH Materials Technologists & Engineers

University of Glasgow

Who do we make devices for?

University of Cambridge
snf
Stanford University
Nano Research Lab
Nanoelectronics Research Lab UC Santa Barbara
UAM
University of Oxford
Berkeley University of California
University of Toronto
NRF UCLA Nanoelectronics Research Facility
Imperial College London
The University of Nottingham
The University Of Sheffield.
Vrije Universiteit Brussel
dmu.ac.uk De Montfort University Leicester
University of Bath
Politécnica "Ingeniamos el futuro"
Warwick
Politecnico di Milano
Johannes Kepler Universität Linz JKU
University of Strathclyde Glasgow
University of Southampton
University of Surrey
Queen's University Belfast
Technische Universität Kaiserslautern
Prifysgol Aberystwyth University
University of St Andrews
ETH Eidgenössische Technische Hochschule Zürich Swiss Federal Institute of Technology Zurich
UIB Universitat de les Illes Balears
Heriot Watt University
Institut d'Optique Graduate School
Universität Konstanz
Universidad de Salamanca
California NanoSystems Institute
University of Aberdeen
University of Bristol
imec
Università degli Studi di Pavia
UCL
Roma Tre Università degli Studi
Université Paris-Sud 11

Thermoelectrics History

- **History: Seebeck effect 1822**

heat –> electric current

- **Peltier (1834): current –> cooling**

- **Thomson effect: Thomson (Lord Kelvin) 1850s**

Thermoelectrics

- History: Seebeck effect 1822
  heat –> electric current
- Peltier (1834): current –> cooling
- Physics: Thomson (Lord Kelvin) 1850s
- Ioffe: physics (1950s), first devices 1950s - 1960s,
  commercial modules 1960s

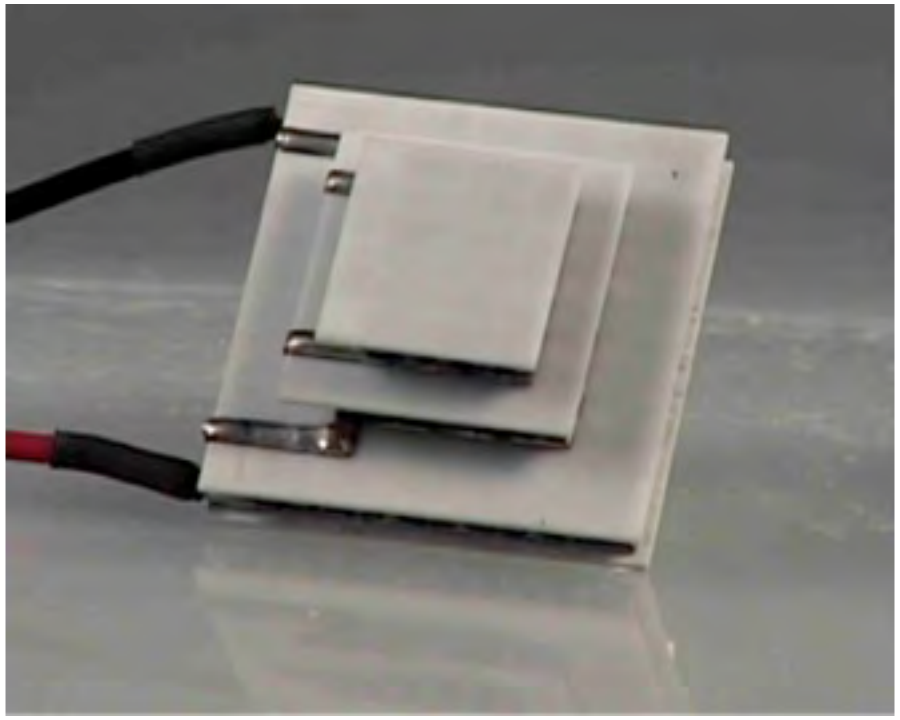
Present applications:

- Peltier coolers (telecoms lasers, rf / THz electronics, beer! etc...)
- Thermoelectric generators – some industrial energy harvesting
- 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 $\propto$ 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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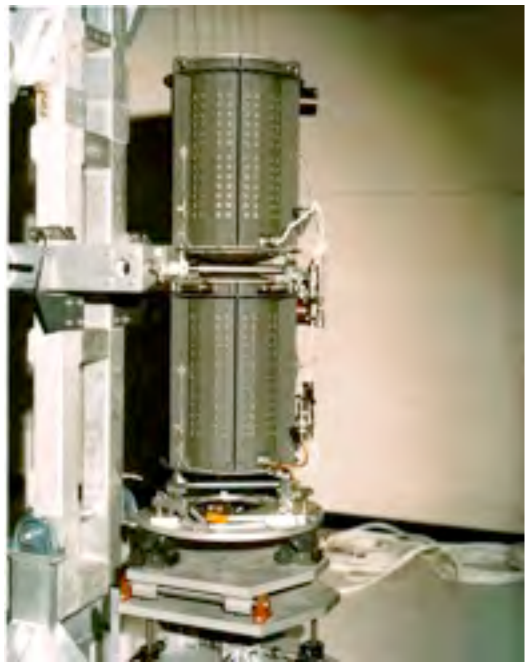
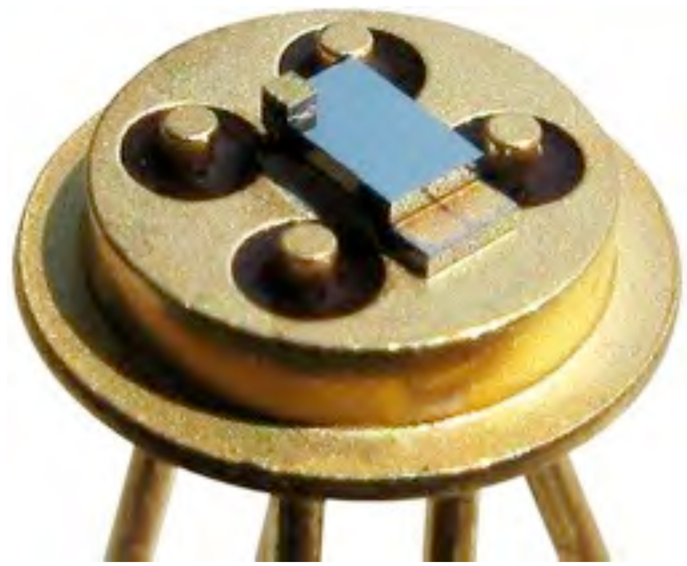
Thermoelectric Applications

NASA Voyager I & II



Peltier cooler: telecoms lasers

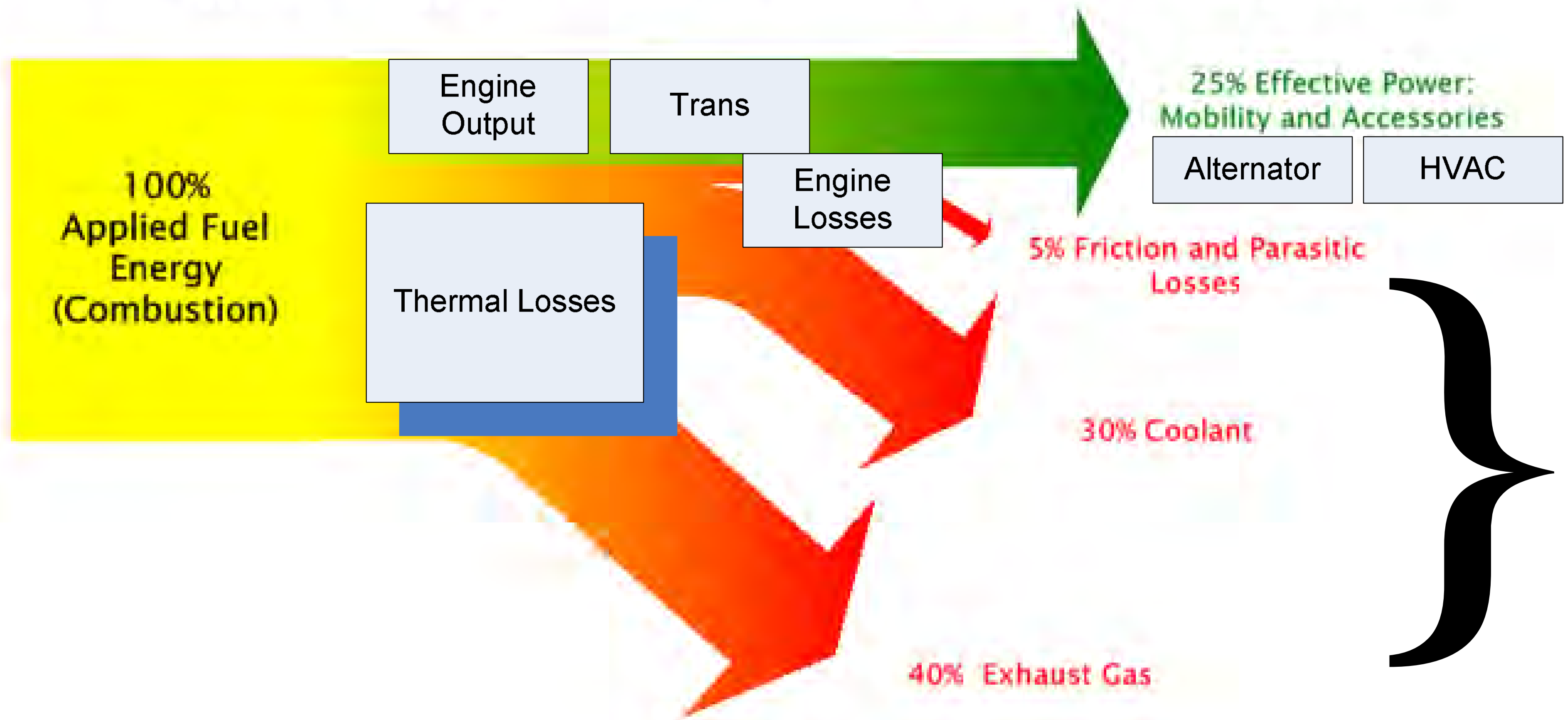


Cars: replace alternator

Temperature control for CO_2 sequestration

Powering autonomous sensors: ECG, blood pressure, etc.

Thermoelectric Energy Harvesting in Cars



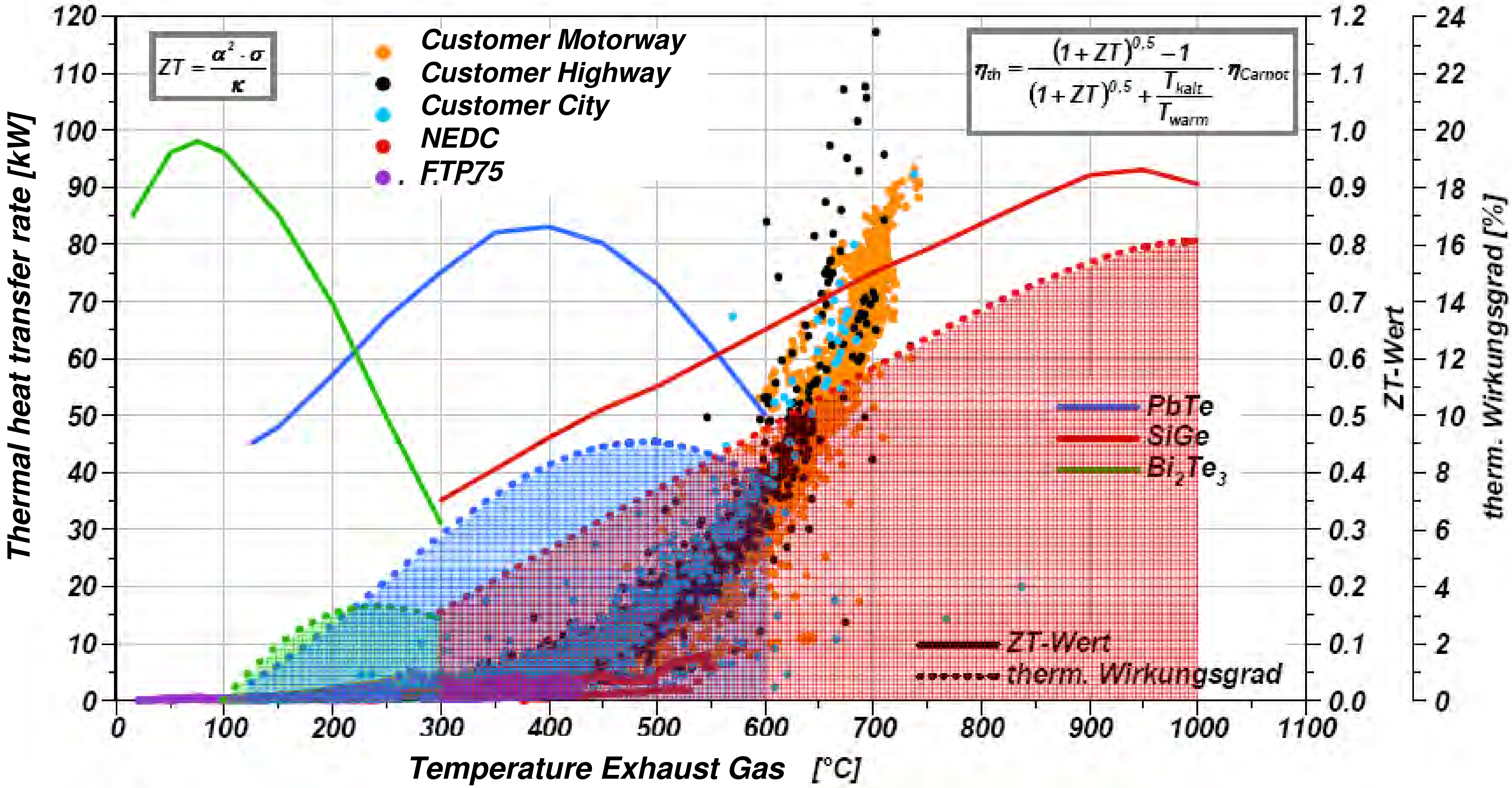
75% of waste = heat!

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

Thermoelectrics in Cars:

- Use waste heat energy (45% of fuel!)
- Can reduce fuel consumption ≤ 5%
- Provide efficient local cooling

Heat from Car Exhaust

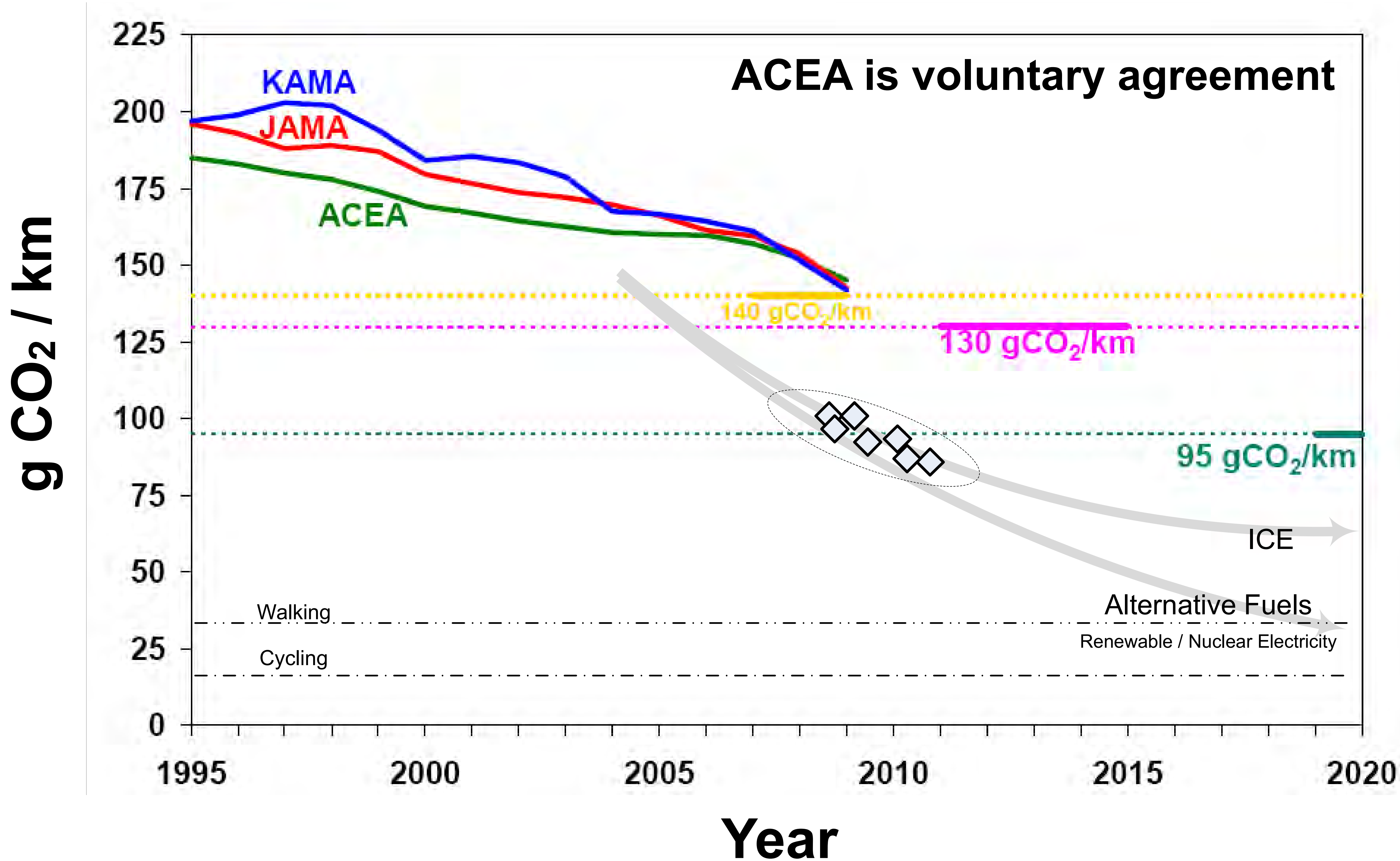


- PbTe the best present thermoelectrics for cars?

But
- Pb is toxic and banned, Te is unsustainable

BMW

Cars: CO_2 Emissions Legislation

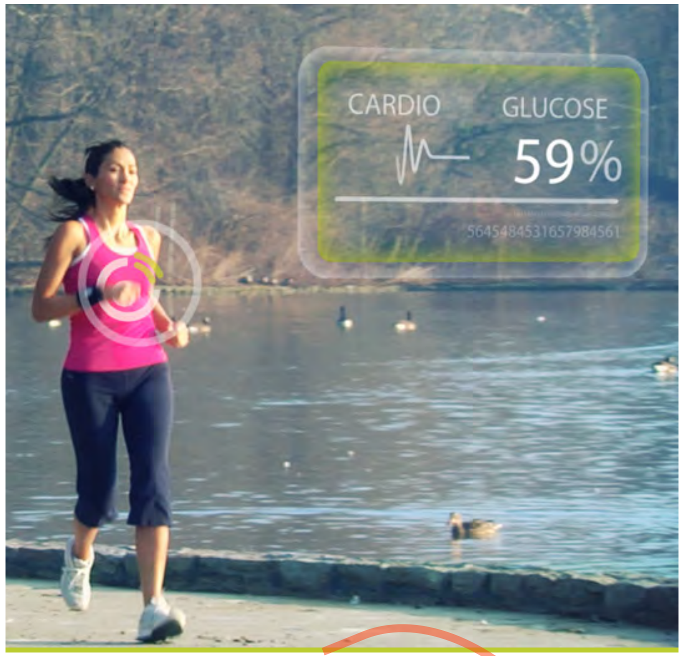


- **Legislation is driving thermoelectrics research**

M. Ellis, Jaguar-Land Rover

Energy Harvesting for Remote Sensing

Sports performance sensors



Flood sensors

Weather monitoring

Radio	> 10 mW
Processor	> 100 µW
Sensor	> 10 µW
Energy harvester	< 100 µW/cm^2 !!!

Aged well being sensors

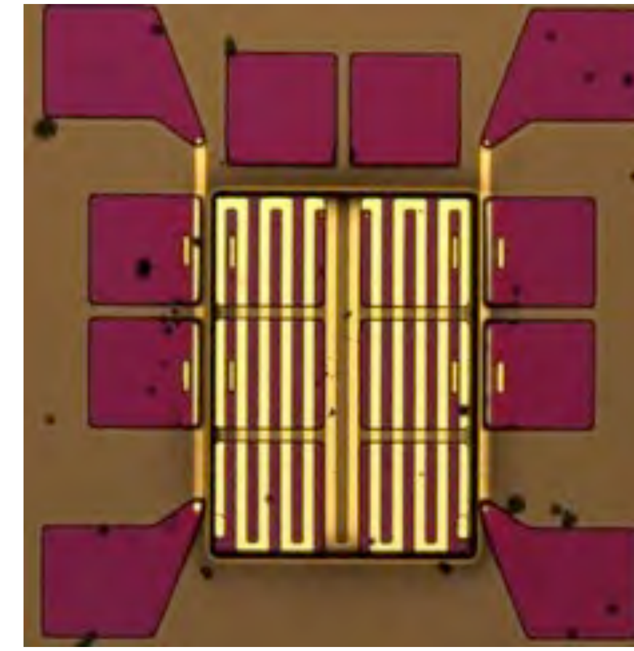
Battery free autonomous sensors: ECG, blood pressure, etc.

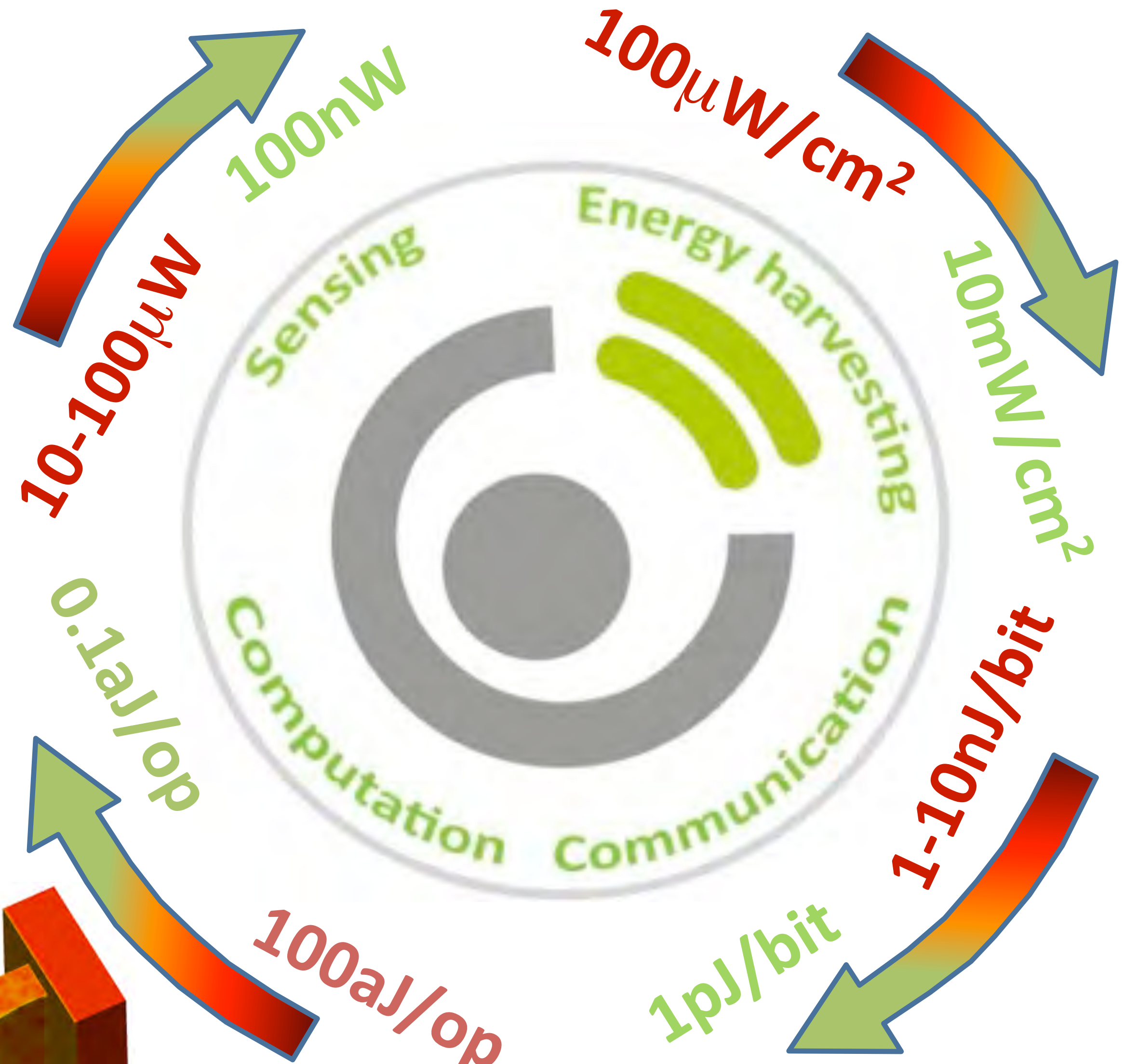
University of Glasgow

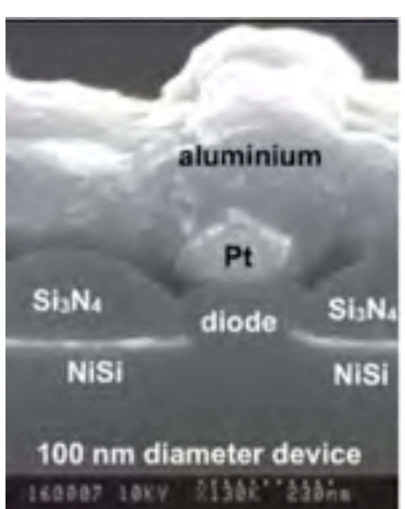
EC Flagship Pilot Guardian Angels

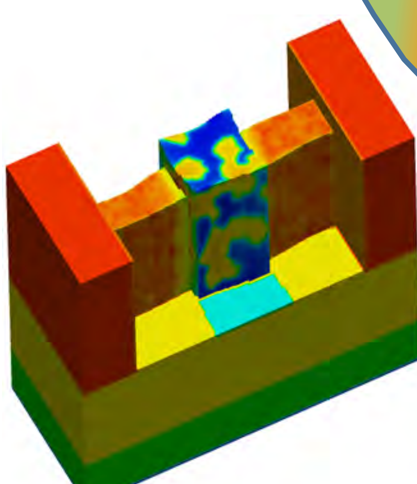
Biosensors and lab-on-a-pill

Thermoelectrics

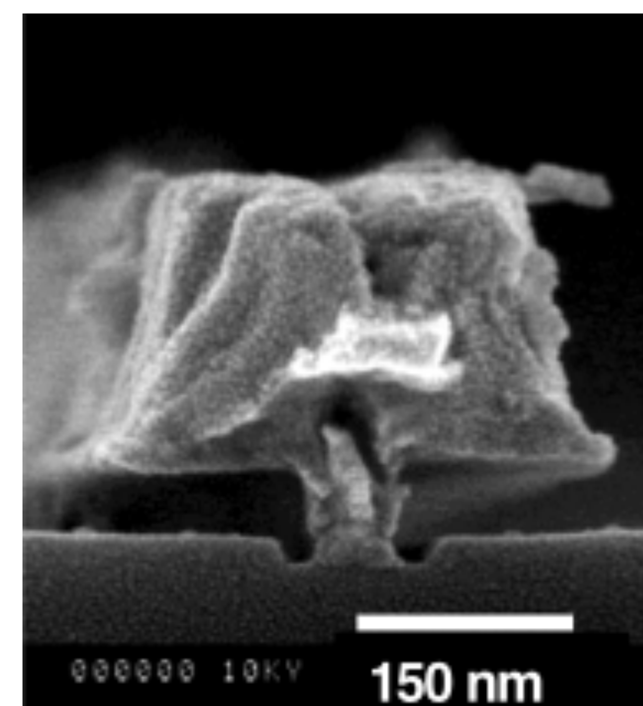








Nanoelectronics and device modelling

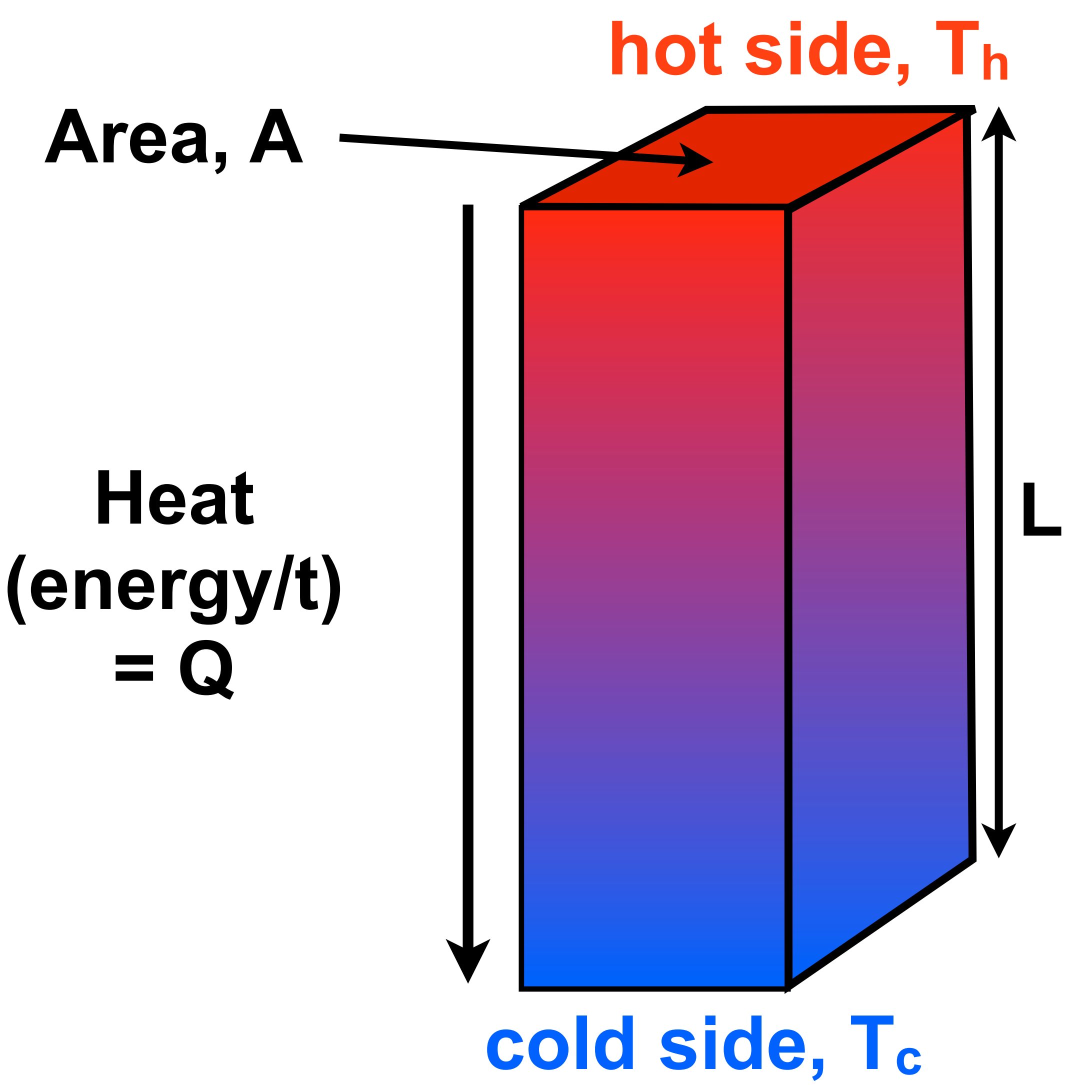


Ultralow power rf electronics

Background Thermal Physics

Fourier thermal transport

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

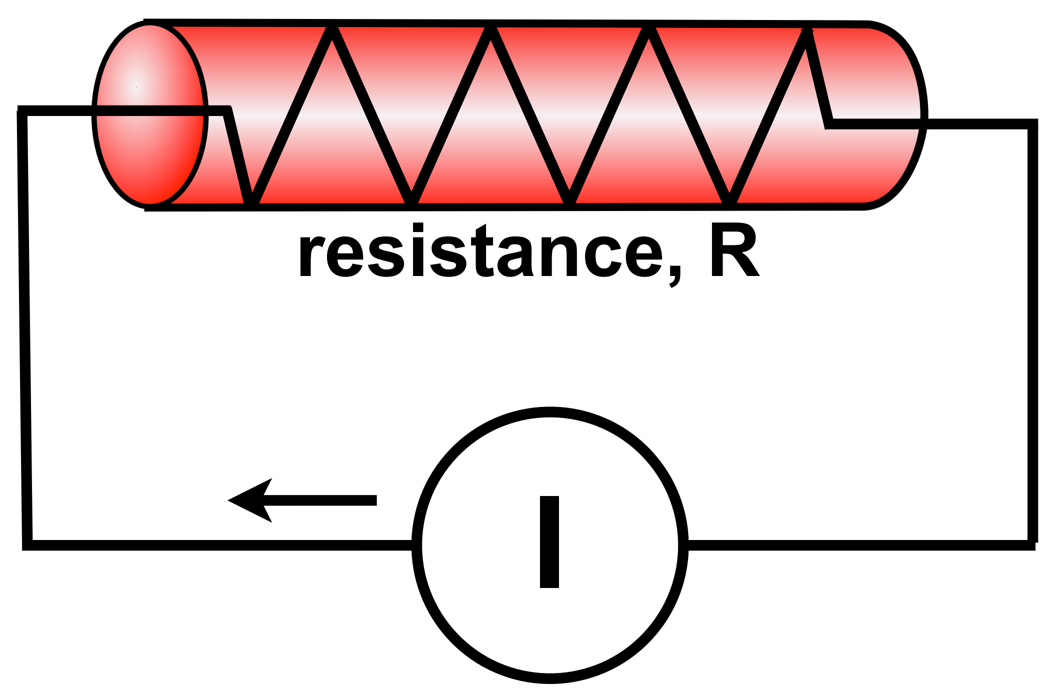


$$\mathbf{Q} = -\kappa \mathbf{A} \frac{\mathbf{T_c} - \mathbf{T_h}}{\mathbf{L}}$$

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**

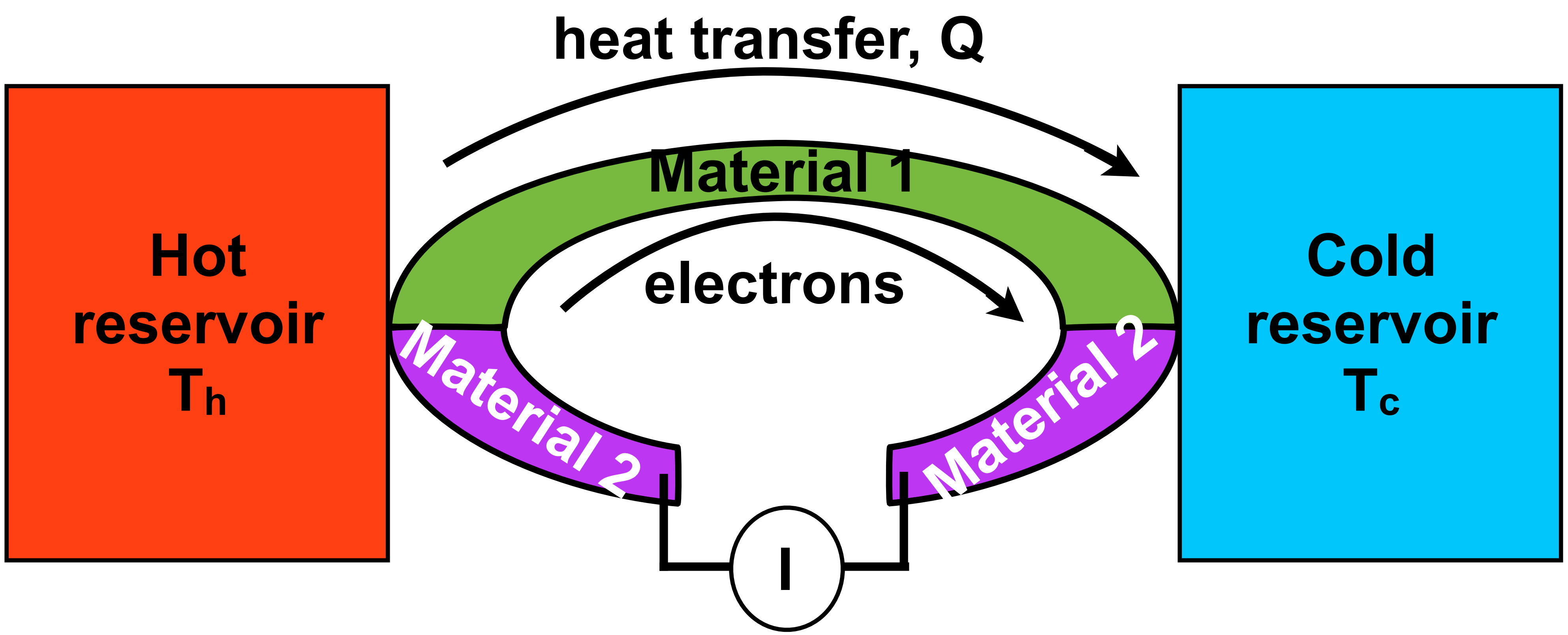
σ **= electrical conductivity**

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

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

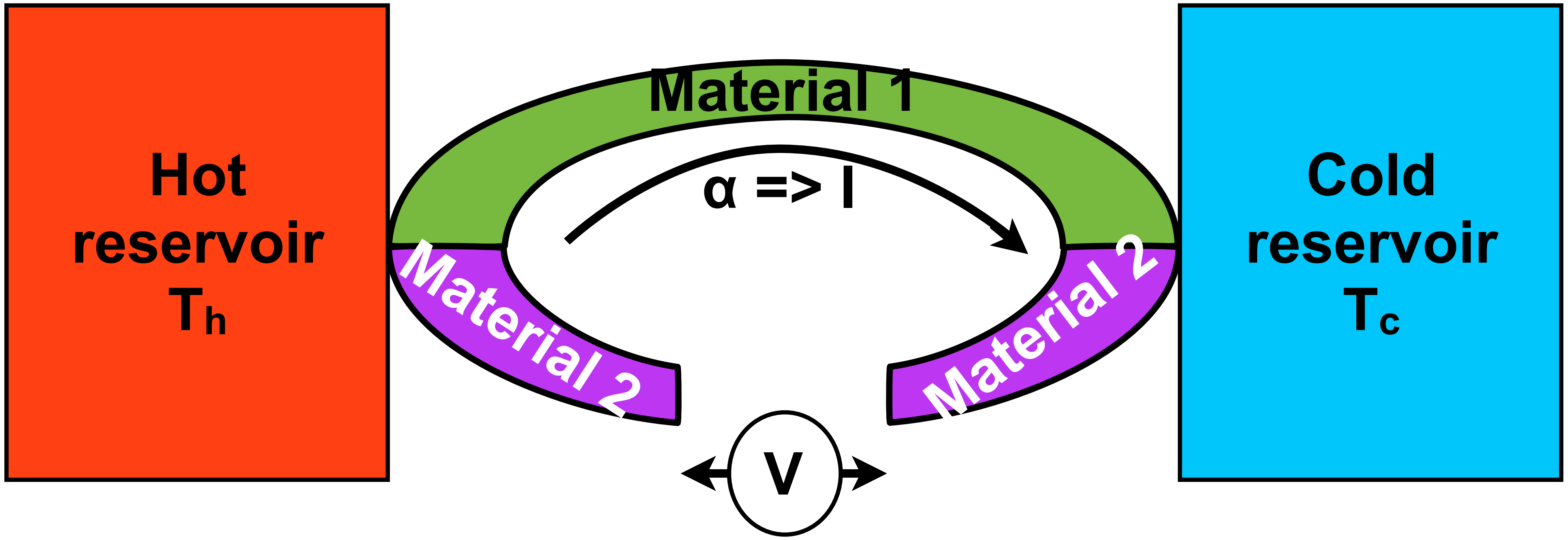
- $$\sigma = \int \sigma(\mathbf{E})\mathbf{dE} = \mathbf{q}\int \mathbf{g(E)}\mu(\mathbf{E})\mathbf{f(E)[1 - f(E)]dE}$$

- 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**

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

  τ **= momentum relaxation time**

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

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

For electrons in the conduction band, E_c of a semiconductor

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

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**

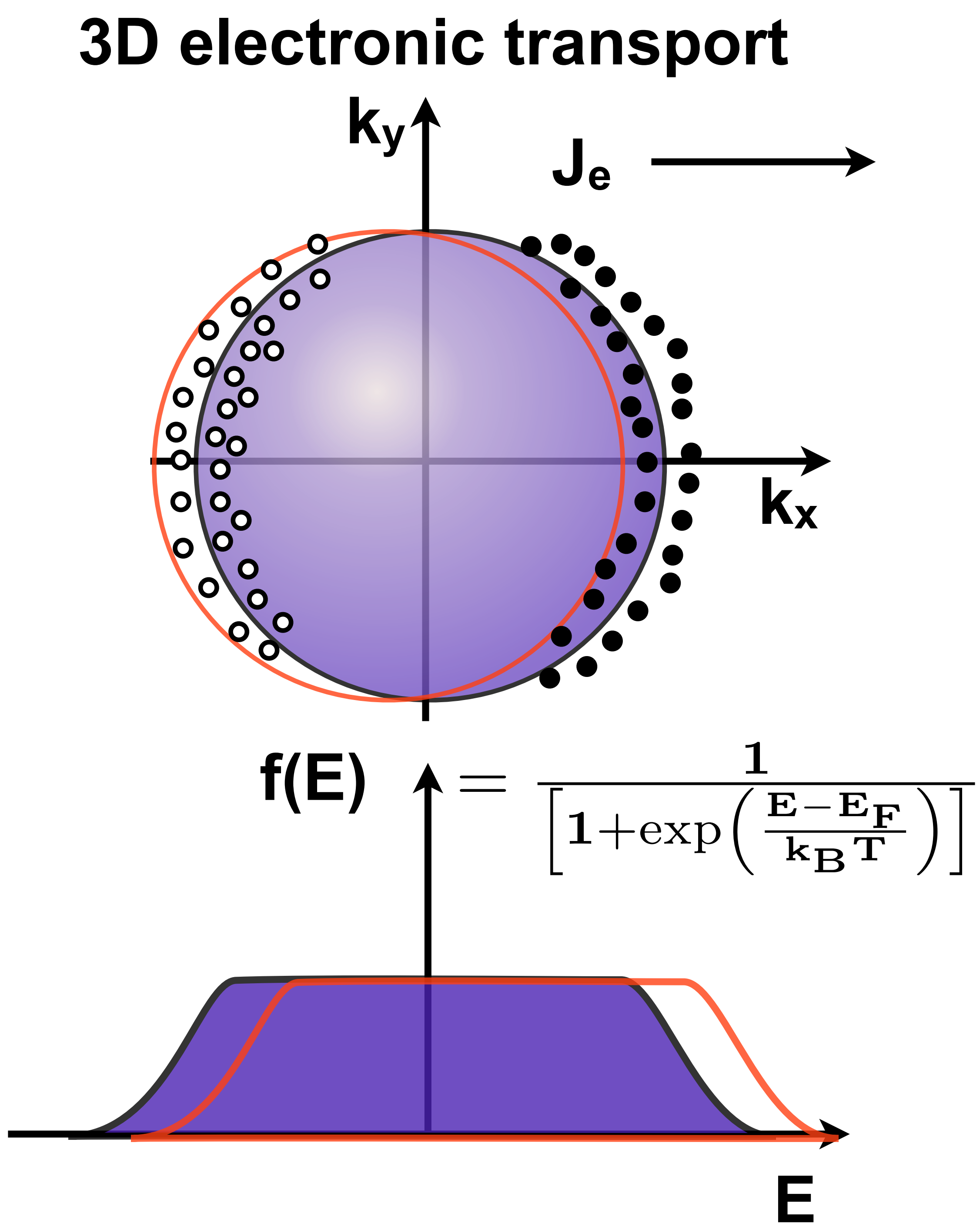
- $$\boxed{\alpha = -\frac{\pi^2}{3q} k_B^2 T \left[\frac{d\ln(\mu(E) g(E))}{dE} \right]_{E=E_F}}$$

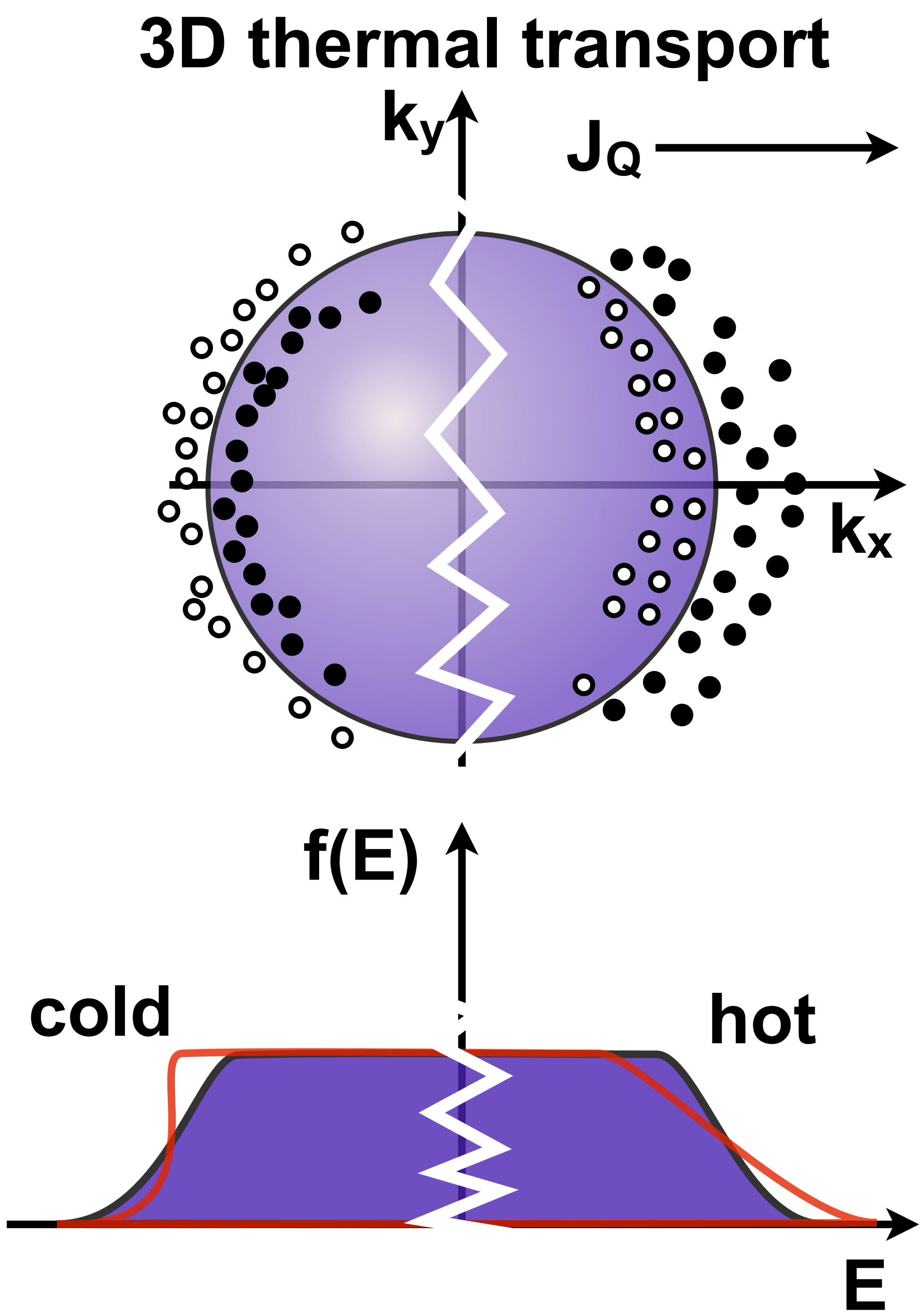
  (Mott's formula for metals)

  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

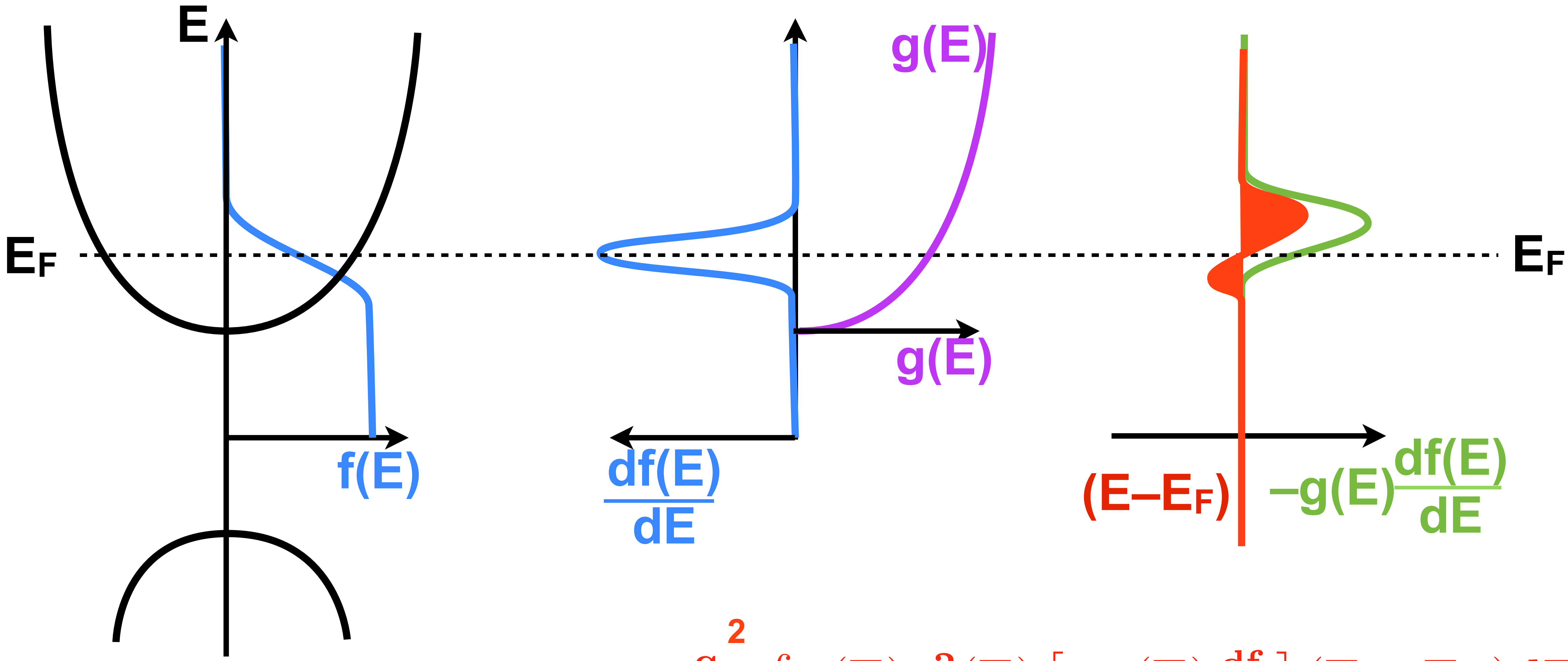




The Physics of the Thermoelectric Effect

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

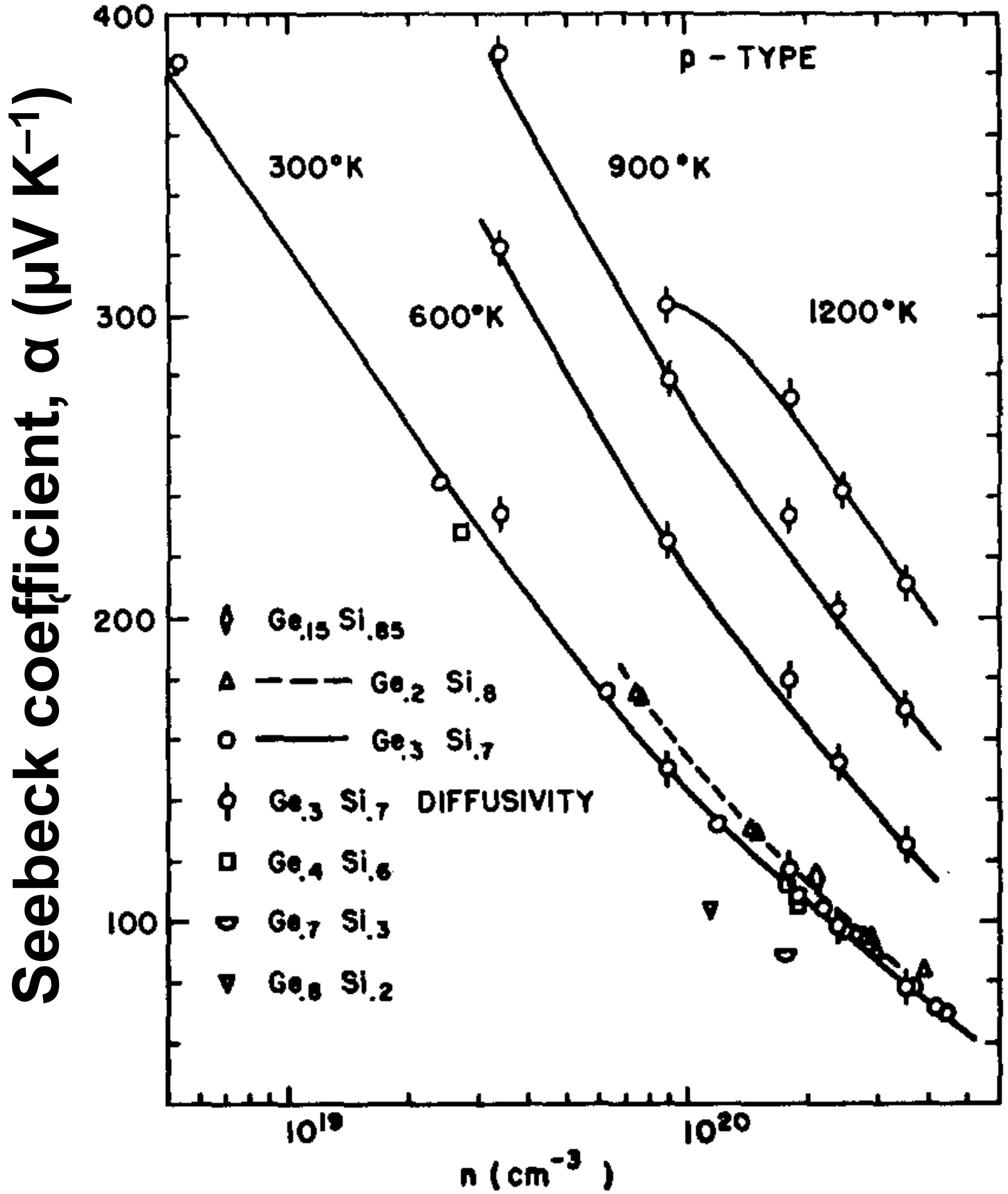
$$\sigma = \frac{q^2}{3}\int \tau(E)\nu^2(E)\left[-g(E)\frac{df}{dE}\right] dE$$



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

- Thermoelectric power requires asymmetry in red area under curve

Semiconductor Example: SiGe Alloys

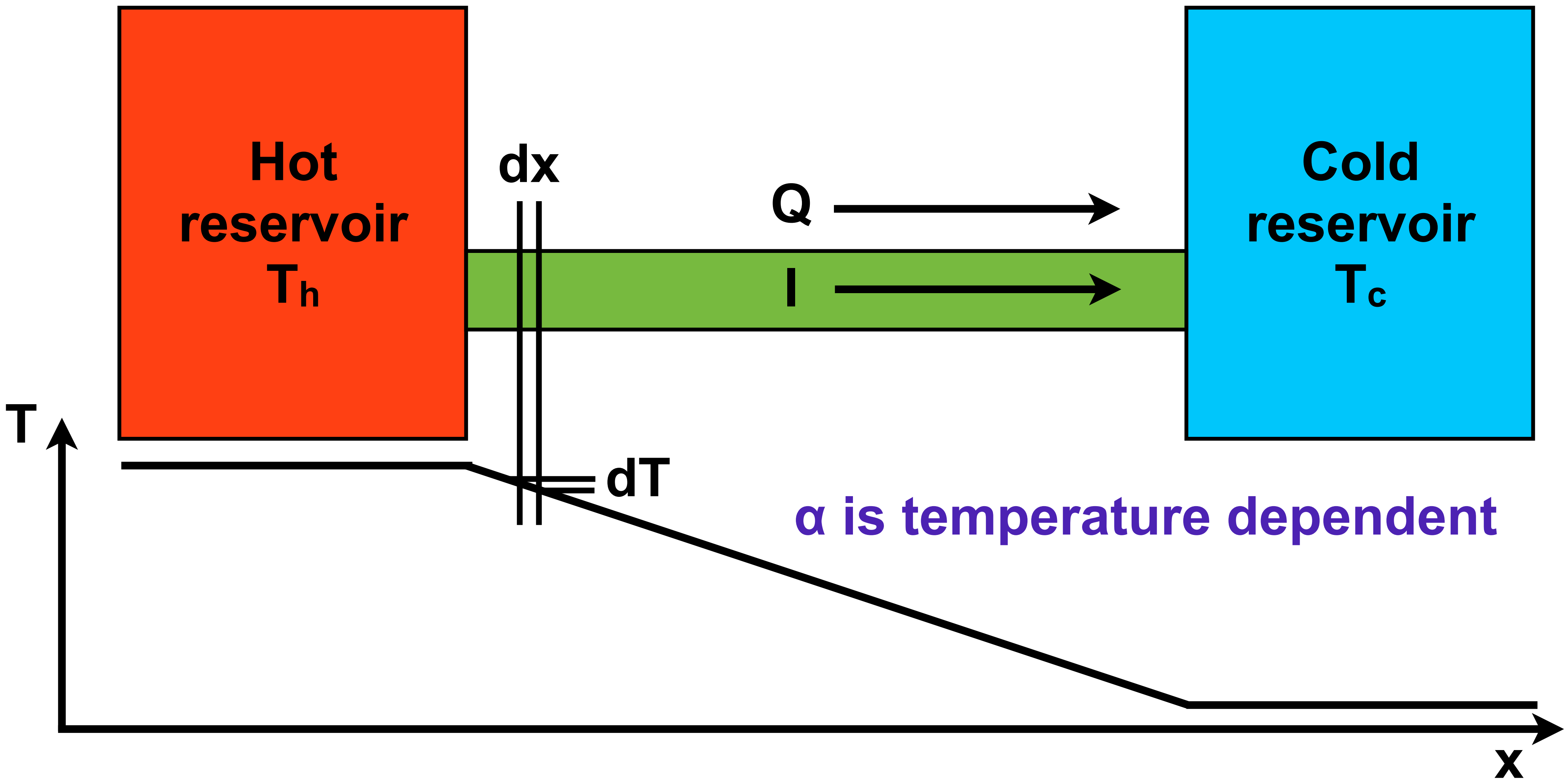


- Mott criteria ~ 2×10^{18} cm^{-3}
- Degenerately doped p-$Si_{0.7}Ge_{0.3}$
- α decreases for higher n
- For SiGe, α increases with T

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

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

The Thomson Effect



α is temperature dependent

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

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

units: V/K

The Kelvin Relationships

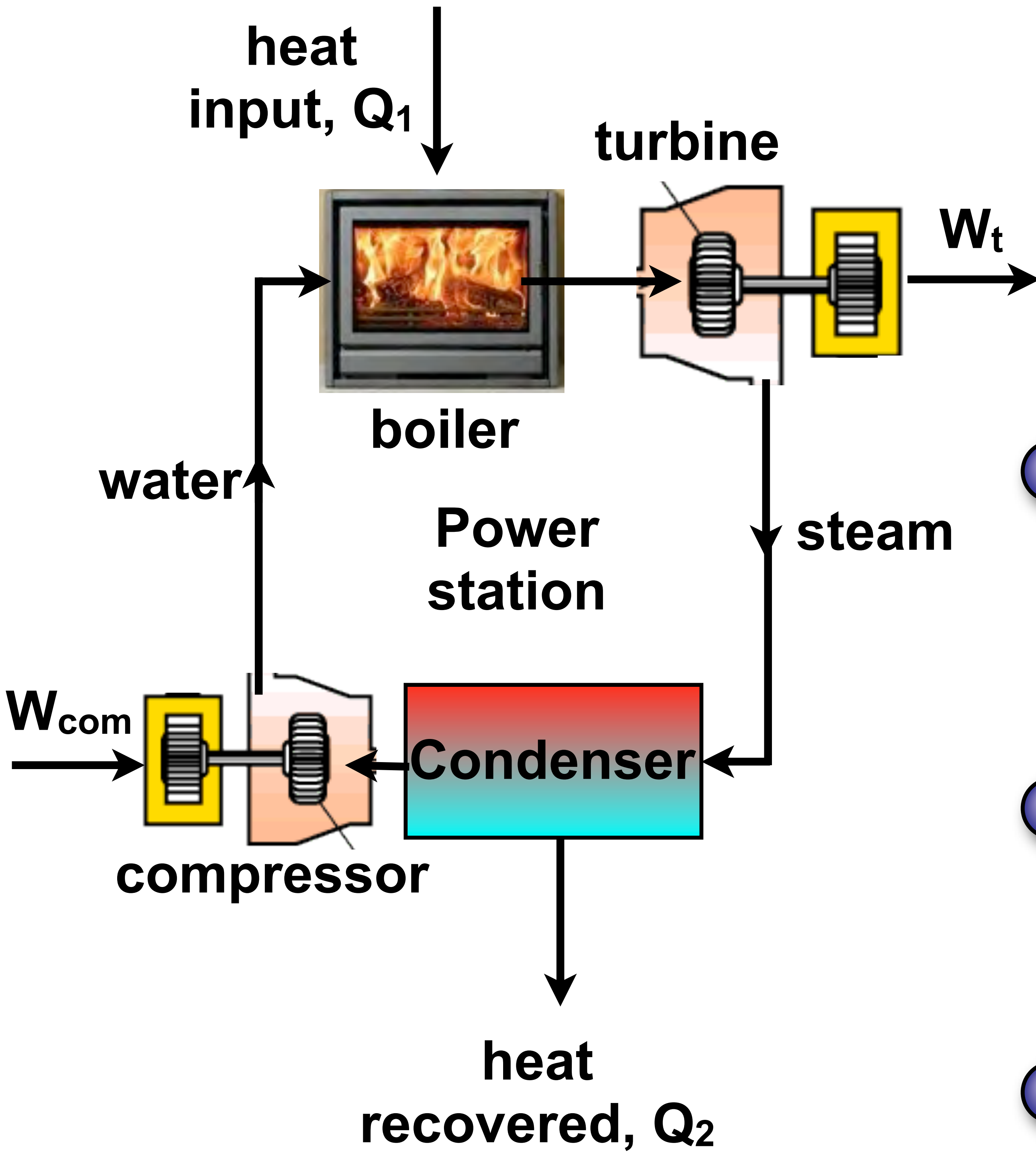
- Derived using irreversible thermodynamics

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

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

- 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

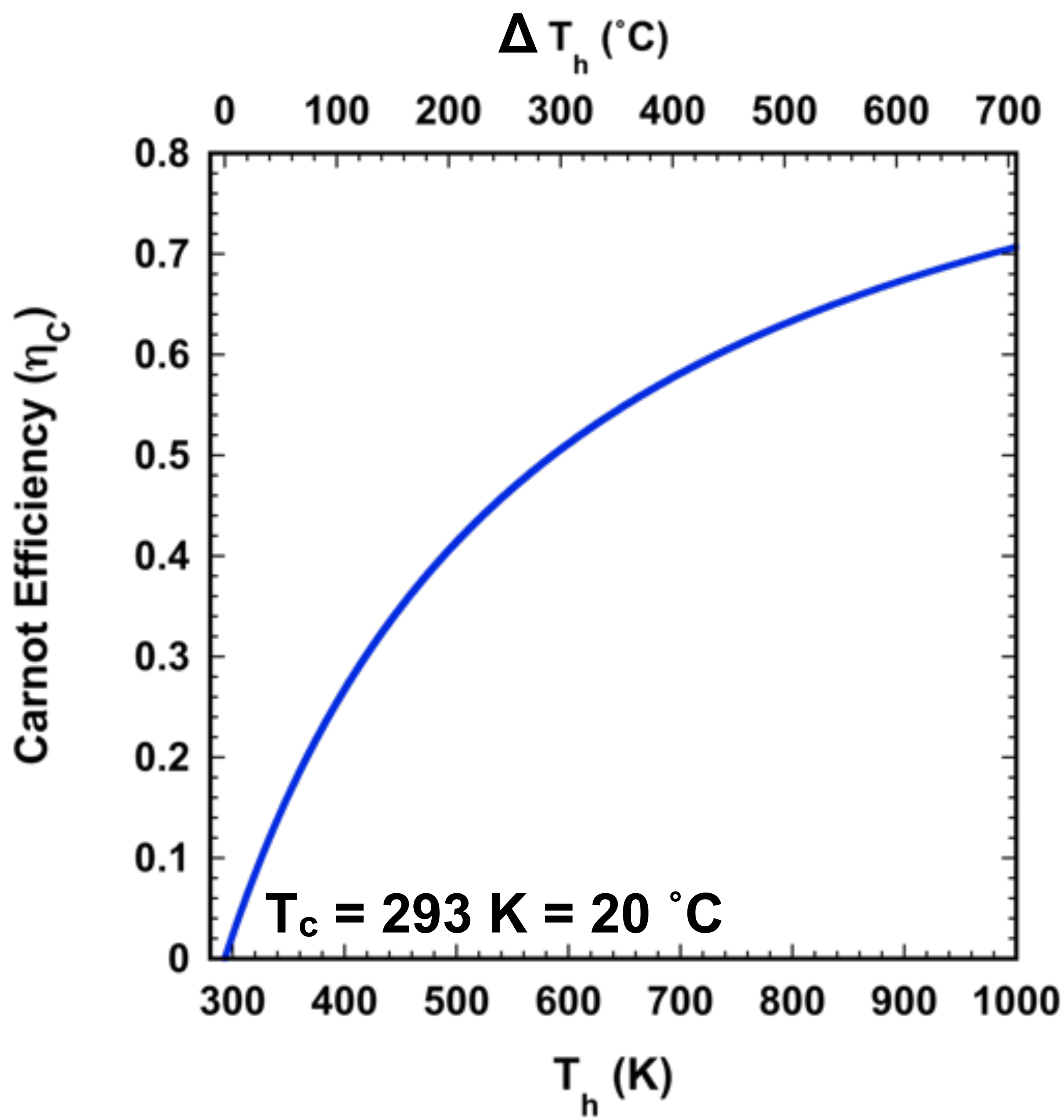
Efficiency =

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

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

Carnot: maximum η only depends on T_c and T_h

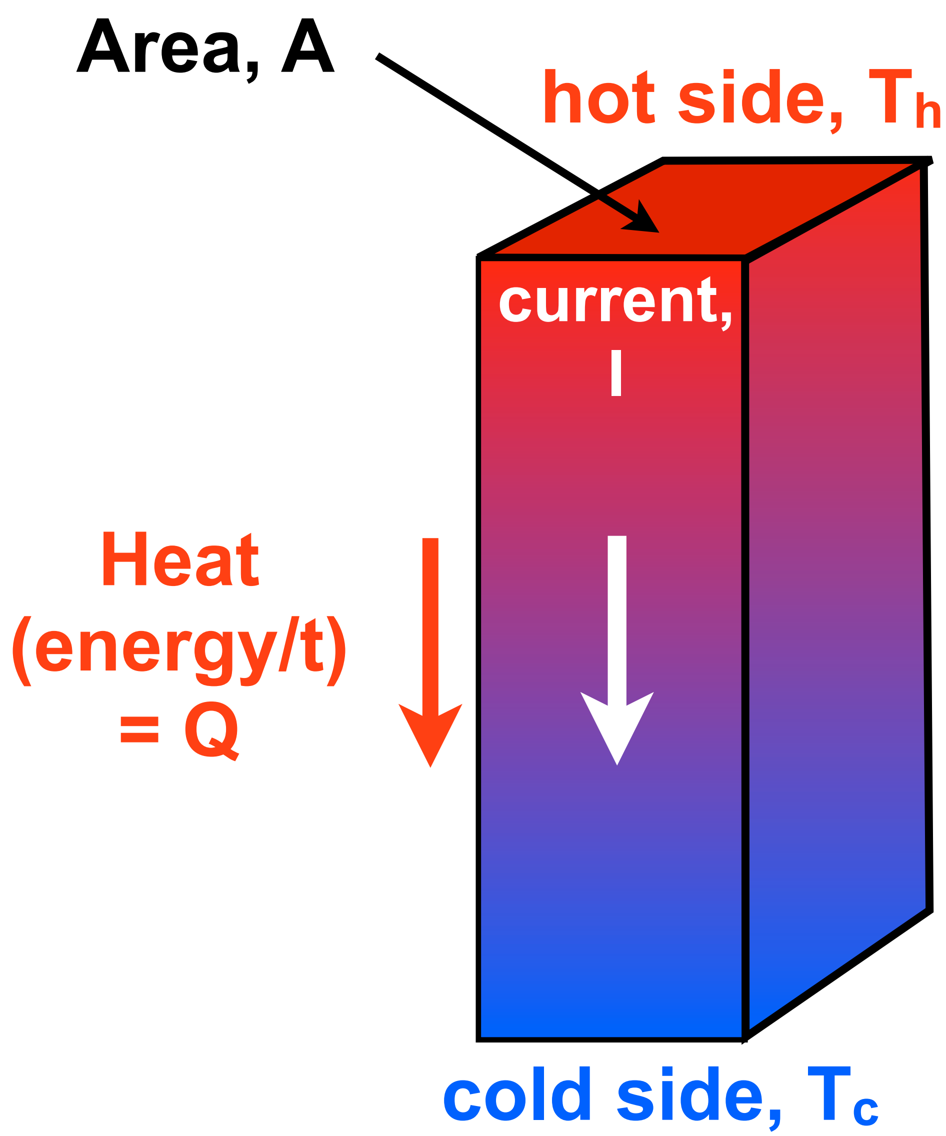
$$\boxed{\eta_c = 1 - \frac{T_c}{T_h}}$$



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)

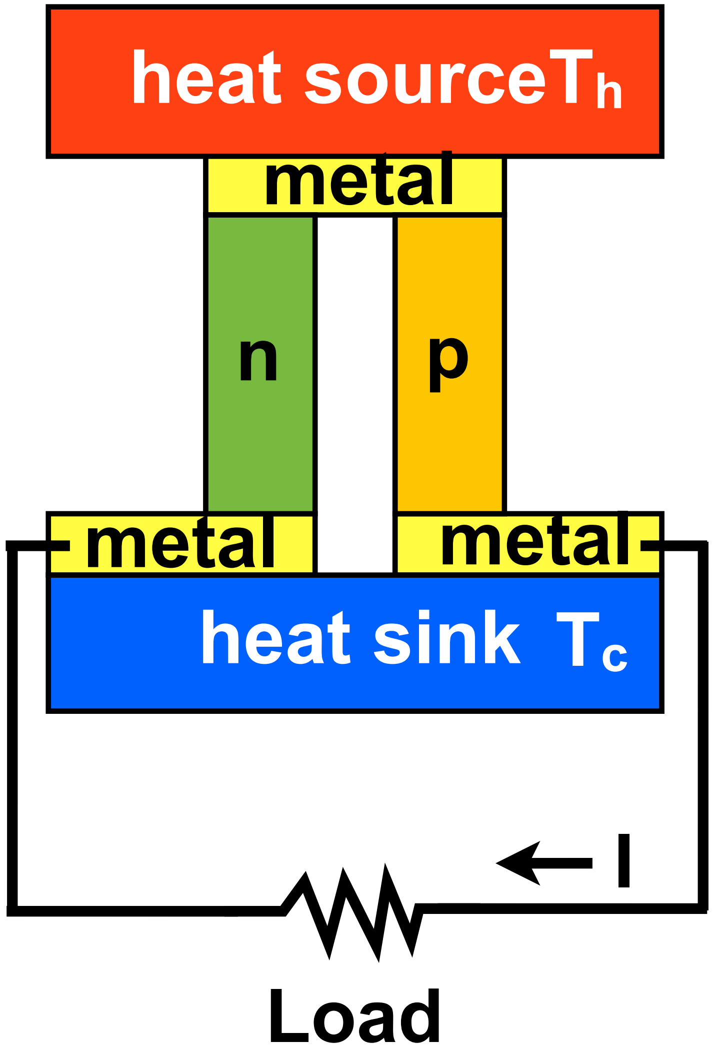
- $$\frac{\mathbf{Q}}{\mathbf{A}} = \mathbf{\Pi J} - \kappa \nabla \mathbf{T}$$

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

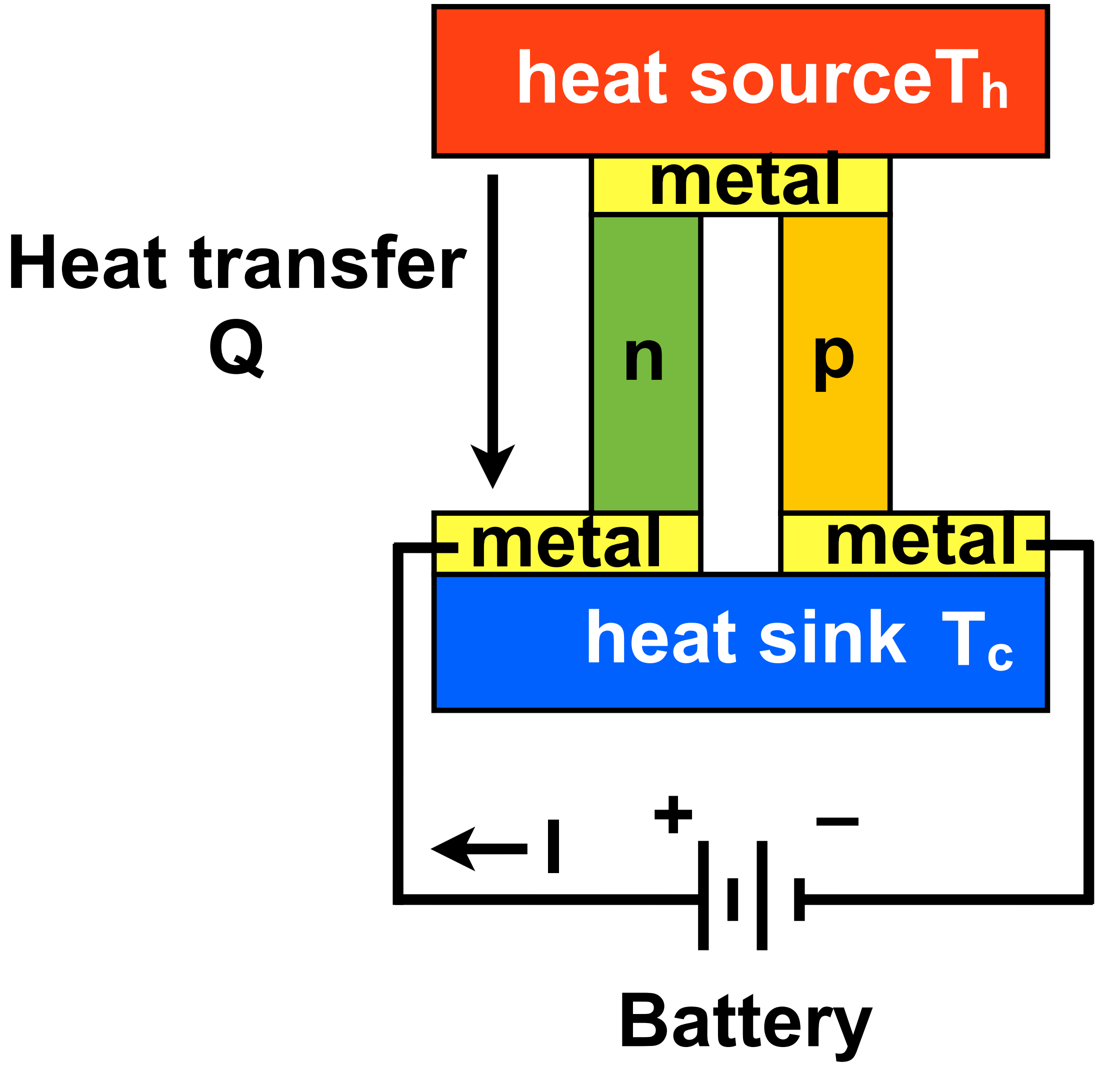
$$\boxed{\mathbf{Q} = \alpha \mathbf{IT} - \kappa \mathbf{A} \nabla \mathbf{T}}$$

Semiconductors and Thermoelectrics

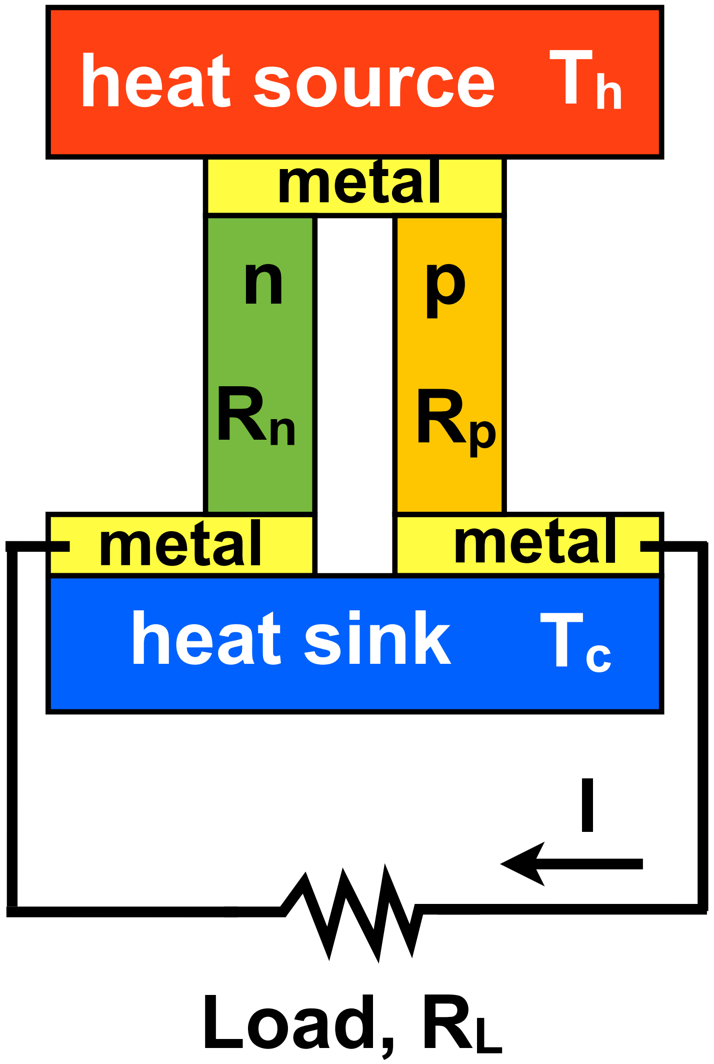
Seebeck effect: electricity generation



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 $= \kappa A \left(T_h - T_c\right) - \frac{1}{2} I^2 R$

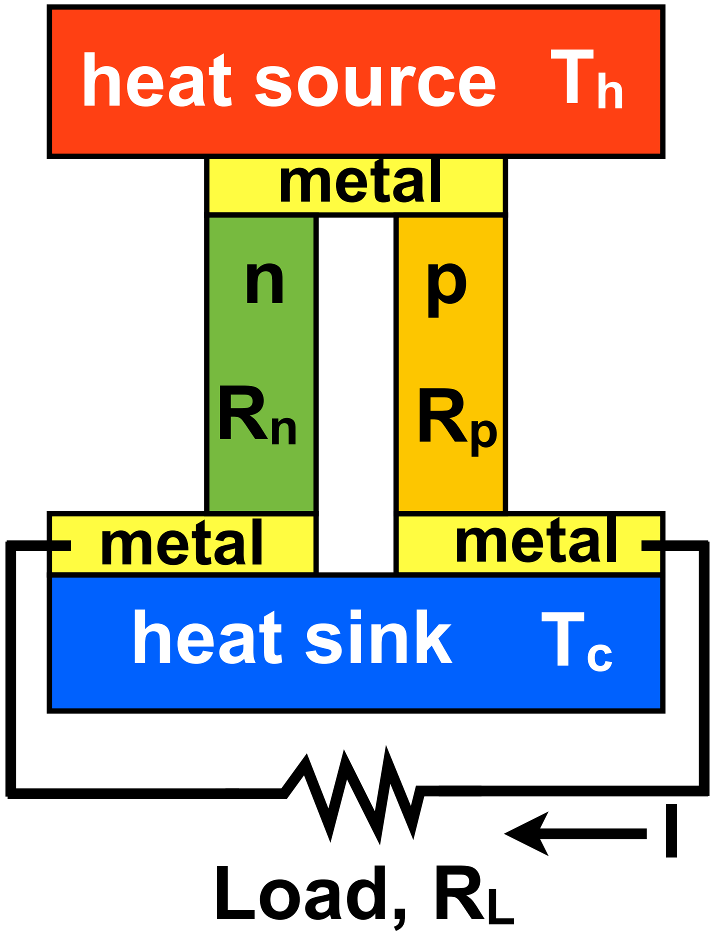
NB half Joule heat returned to hot junction

Thermoelectric Conversion Efficiency

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

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

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



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

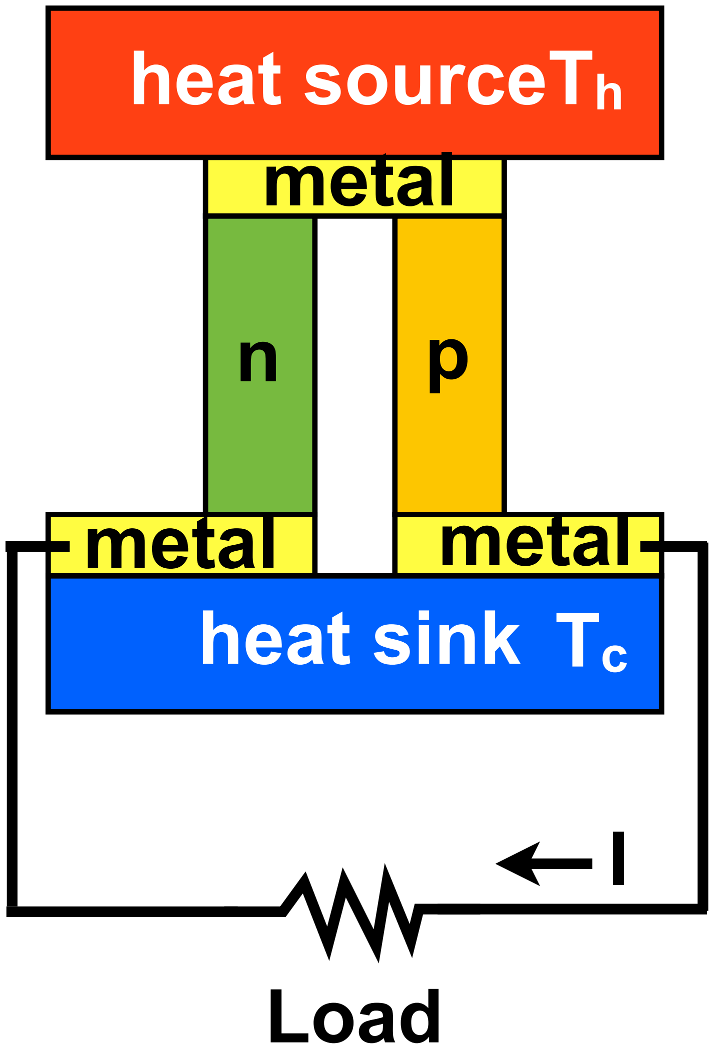
$$T = \frac{1}{2}(T_h + T_c)$$

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

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

= Carnot x Joule losses and irreversible processes

Thermoelectric Power Generating Efficiency



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

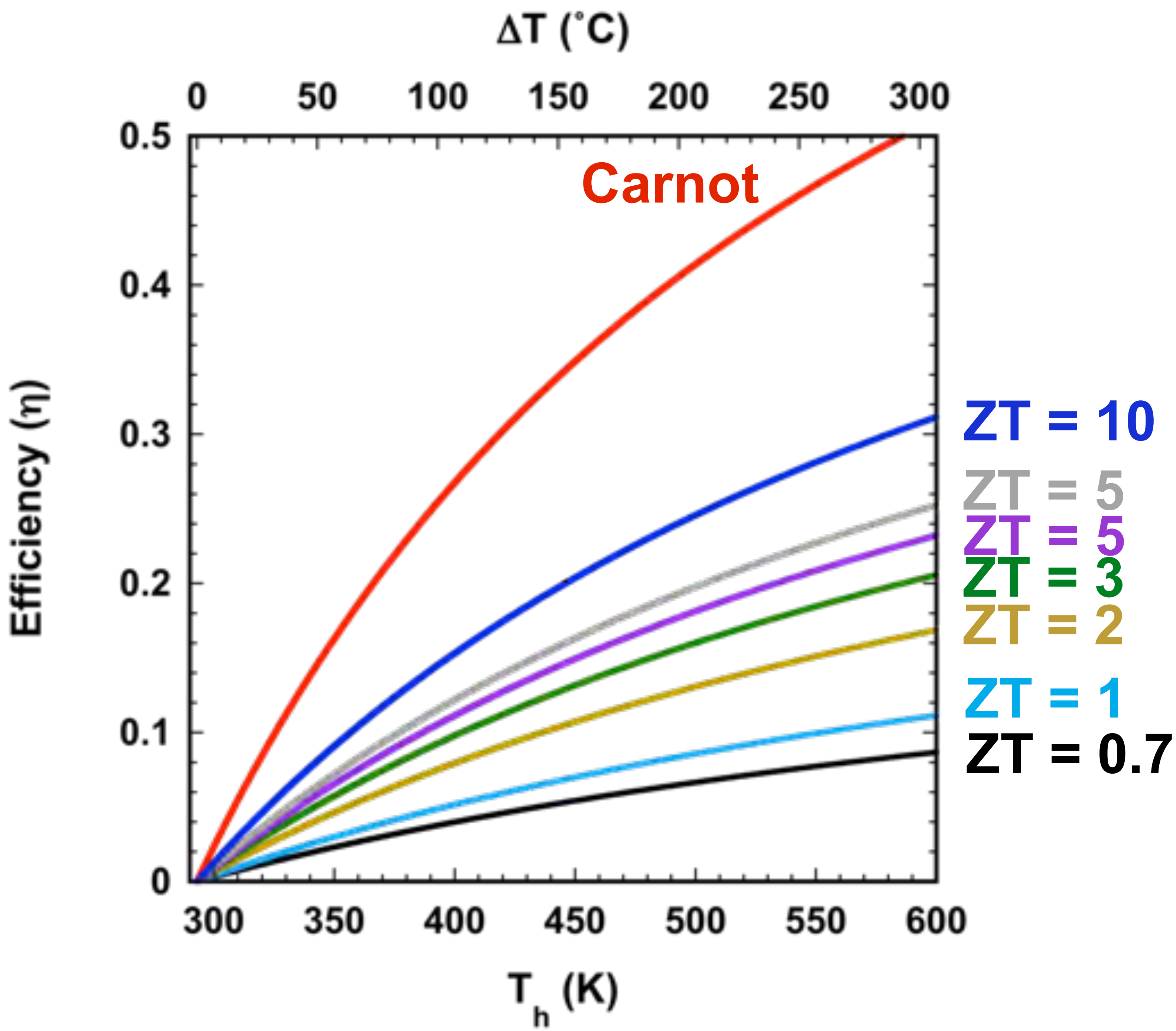
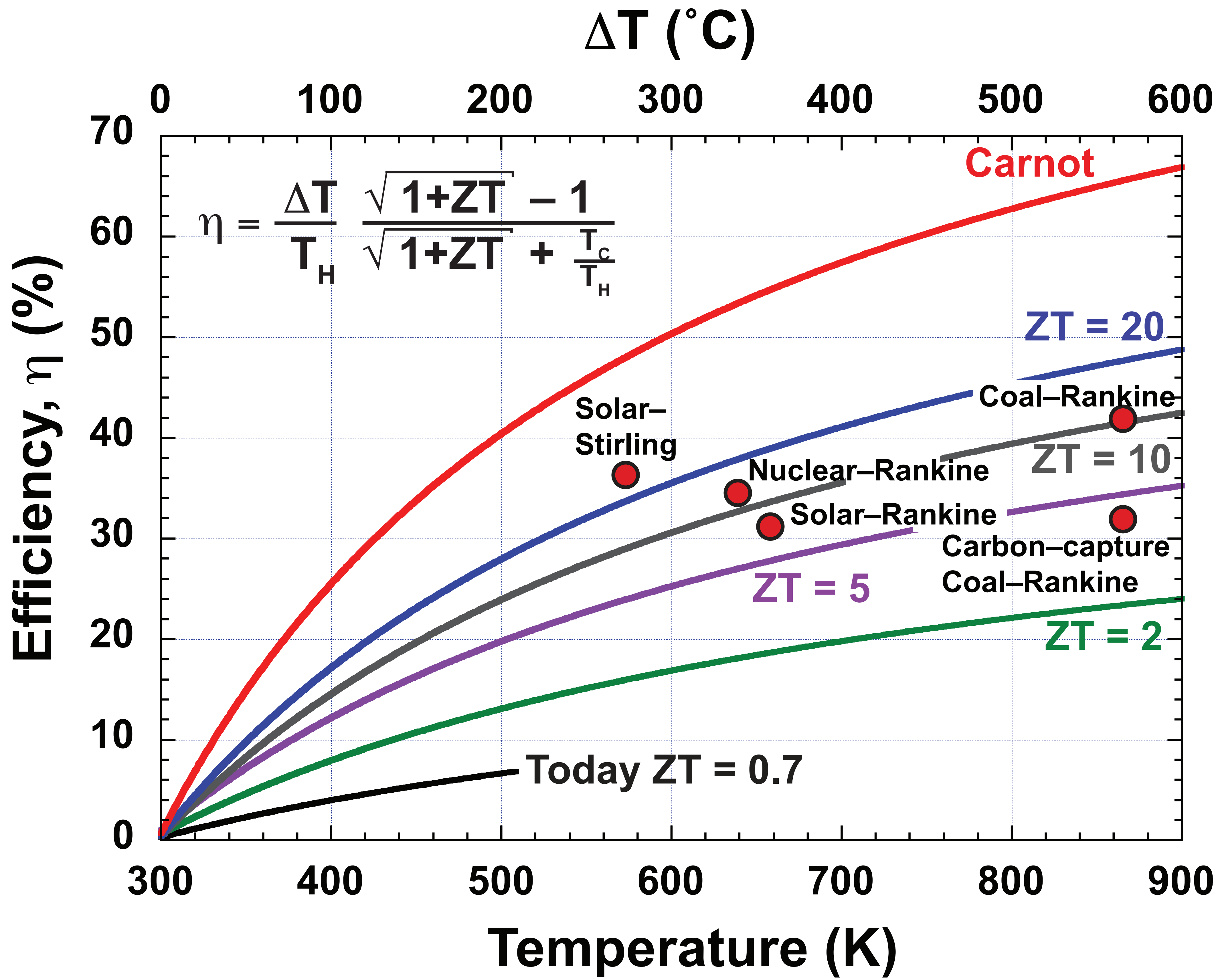


Figure of merit

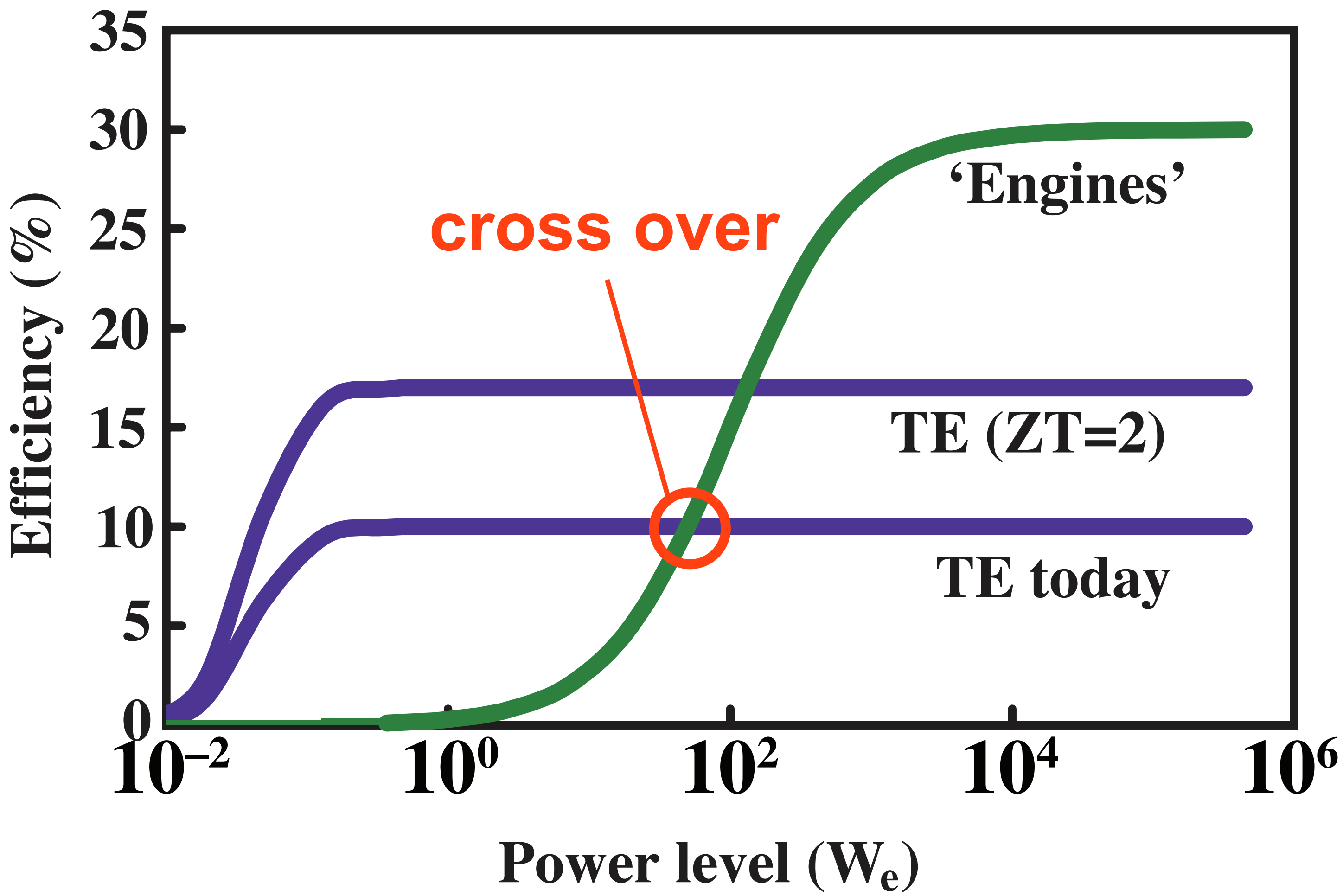
$$\mathrm{ZT} = \frac{\alpha^2\sigma}{\kappa}\mathrm{T}$$

Thermodynamic Efficiency



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)

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)

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

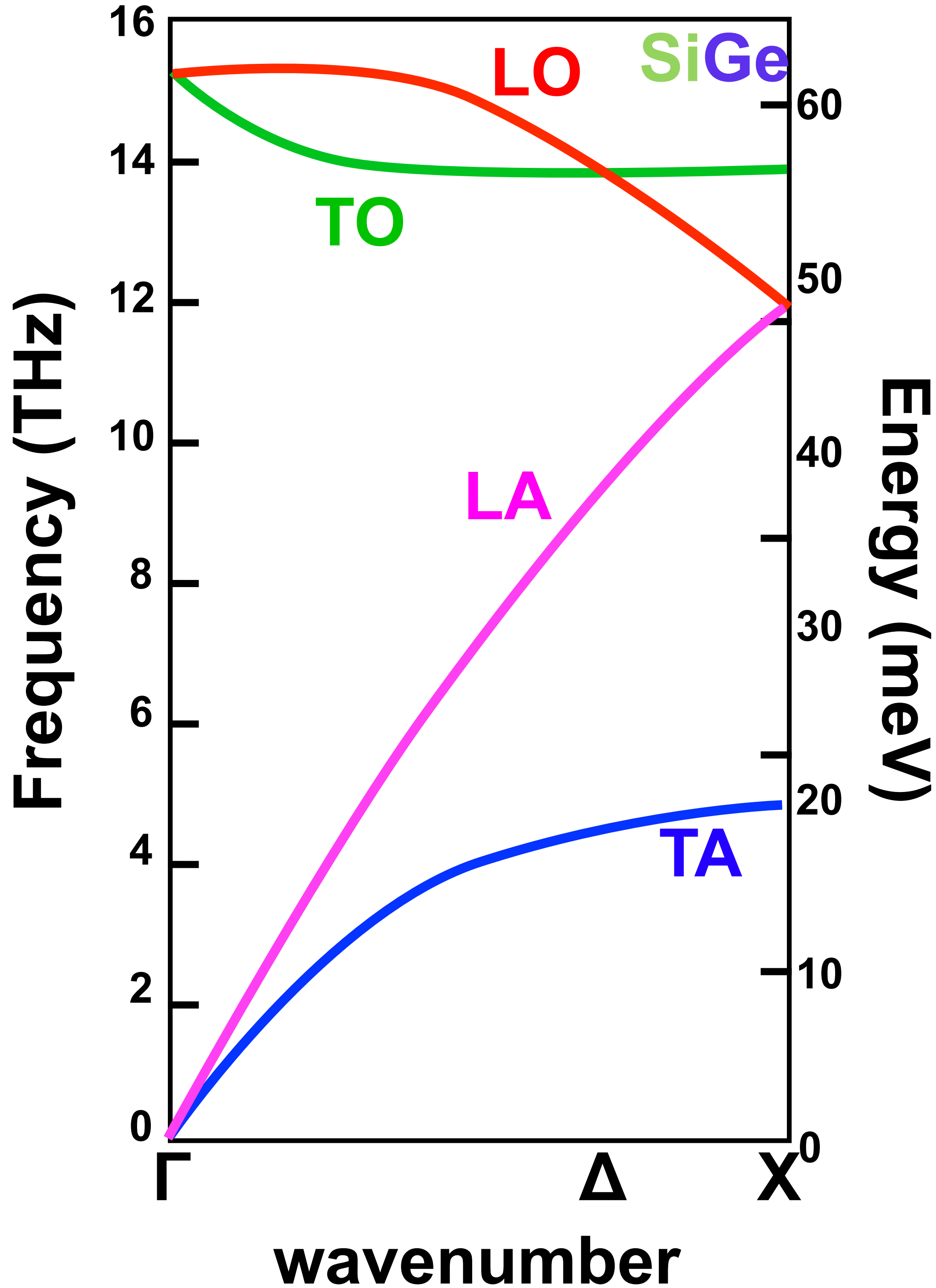
- For high carrier densities in semiconductors (degenerate)

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

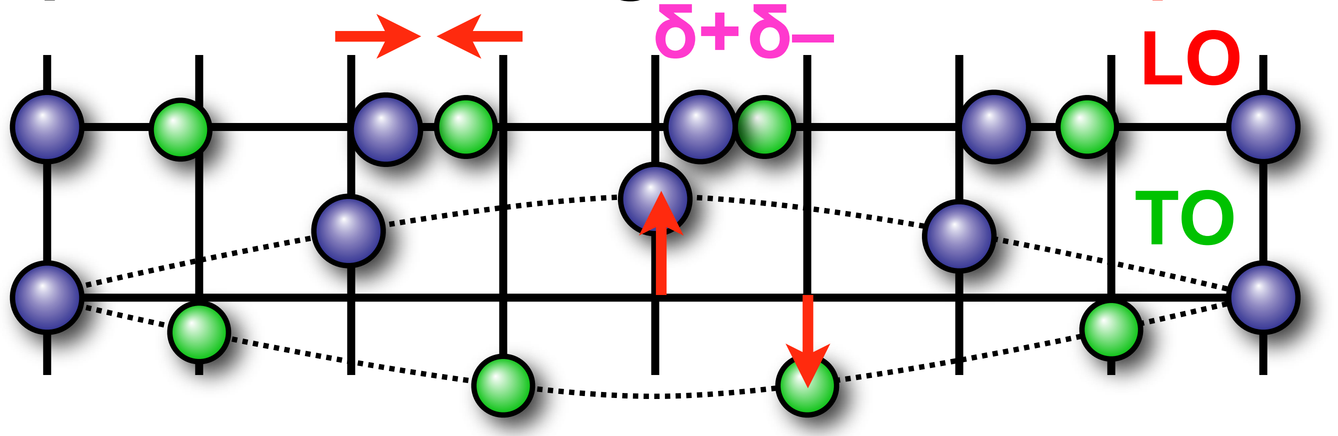
- Good thermoelectric materials should ideally have $\kappa_{\mathbf{el}} \ll \kappa_{\mathbf{ph}}$

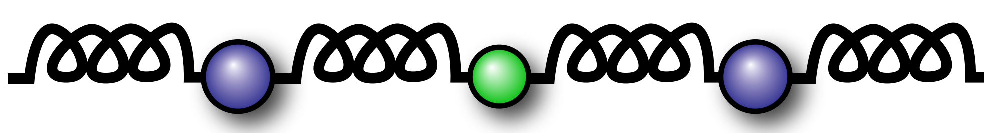
  i.e. electrical and thermal conductivities are largely decoupled

Phonons: Lattice Vibration Heat Transfer



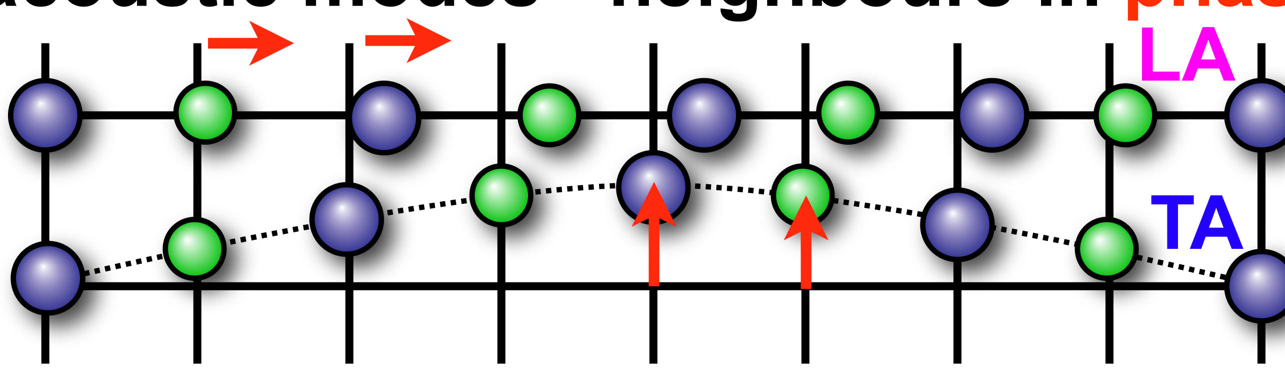
optic modes - neighbours in antiphase





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:

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

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:

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

$\tau(E)$ = 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 = Lorentz number
= 2.45 x 10^{-8} W-ΩK^{-2}

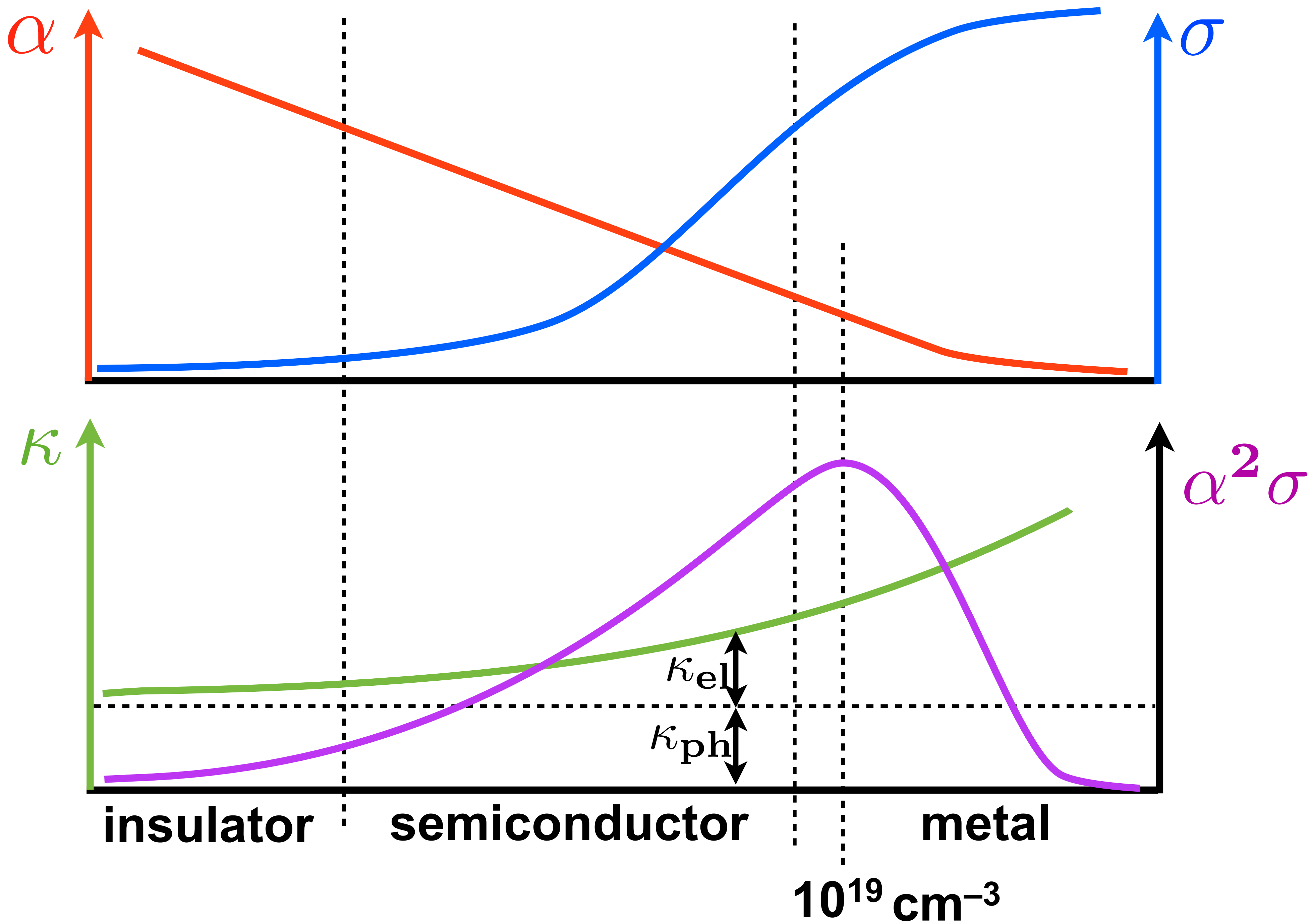
$$\boxed{\mathbf{ZT} = \frac{\mathbf{3}}{\pi^{\mathbf{2}}} \left(\frac{\mathbf{q}\alpha}{\mathbf{k_B}} \right)^{\mathbf{2}} = 4.09 \times 10^{7}\ \alpha^{\mathbf{2}}}$$

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

Exceptions:

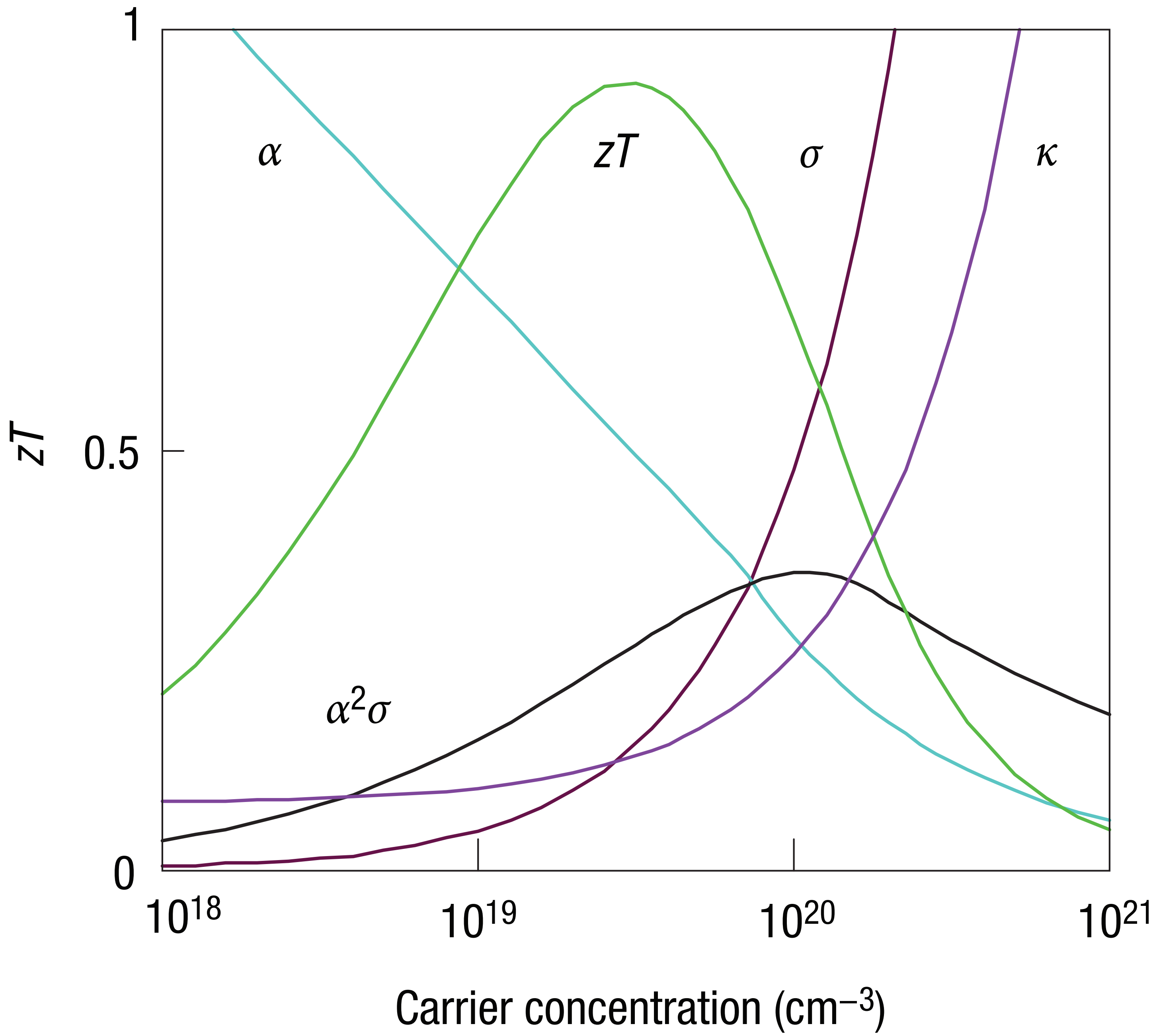
- most exceptions systems with $\kappa_{\mathrm{el}} \ll \kappa_{\mathrm{ph}}$
- some pure metals at low temperatures
- alloys where small κ_{el} results in significant κ_{ph} contribution
- certain low dimensional structures where κ_{ph} can dominate

Thermoelectric vs Doping of Semiconductors



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

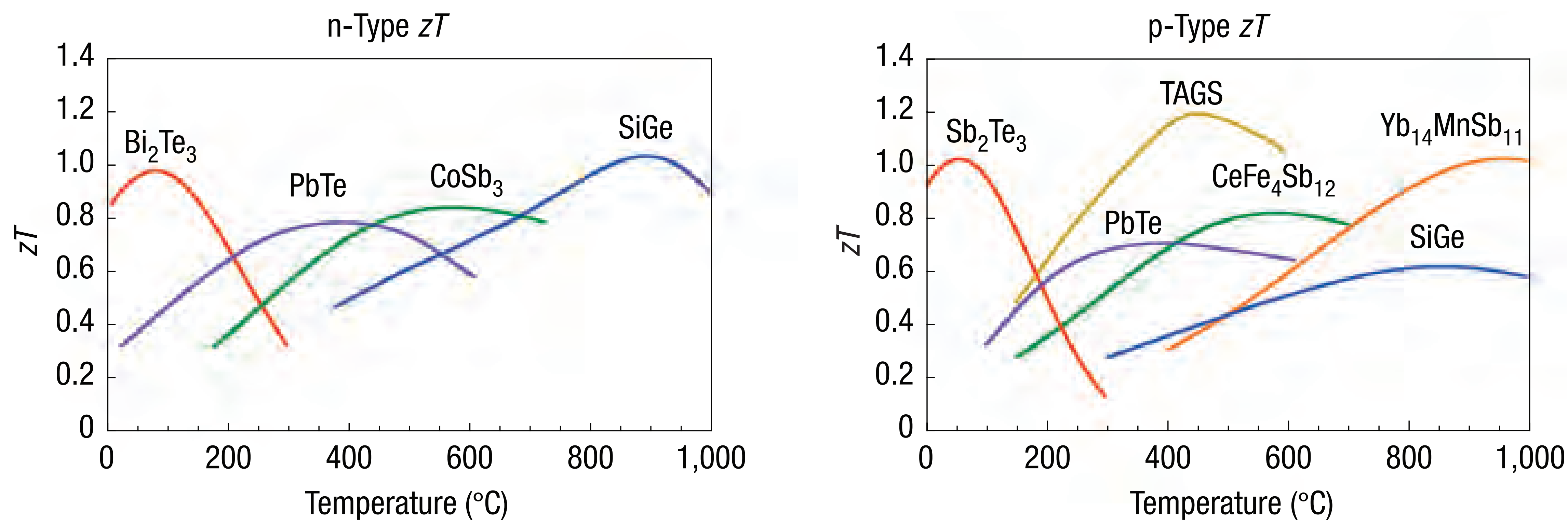
Bi_2Te_3 ZT Optimisation Through Doping



- **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

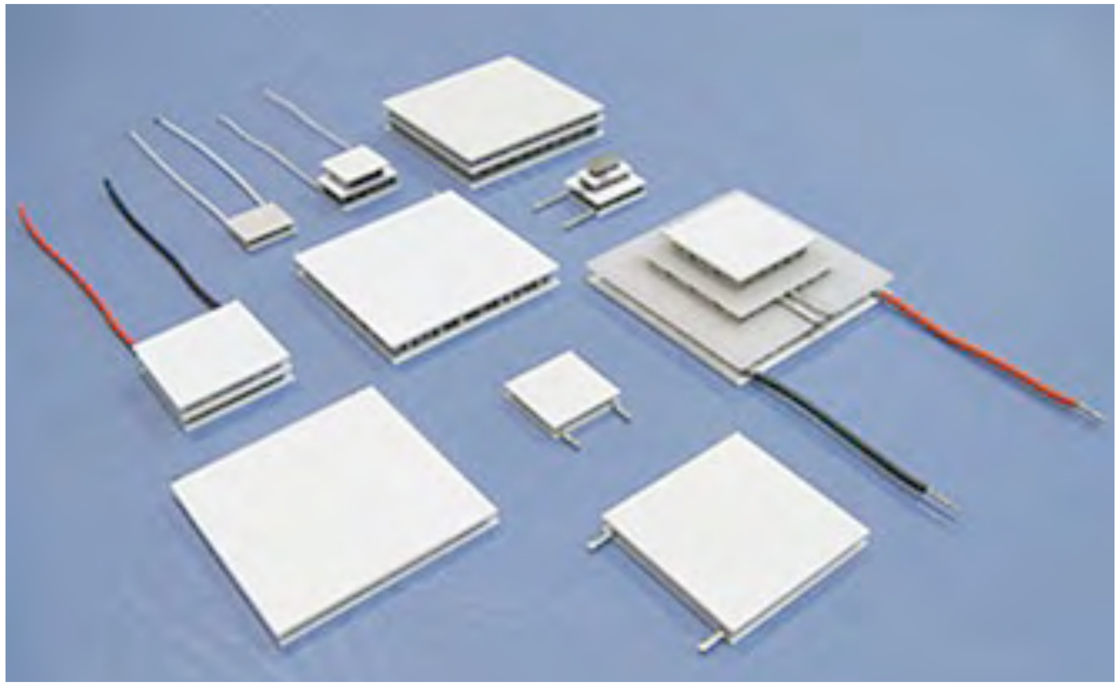


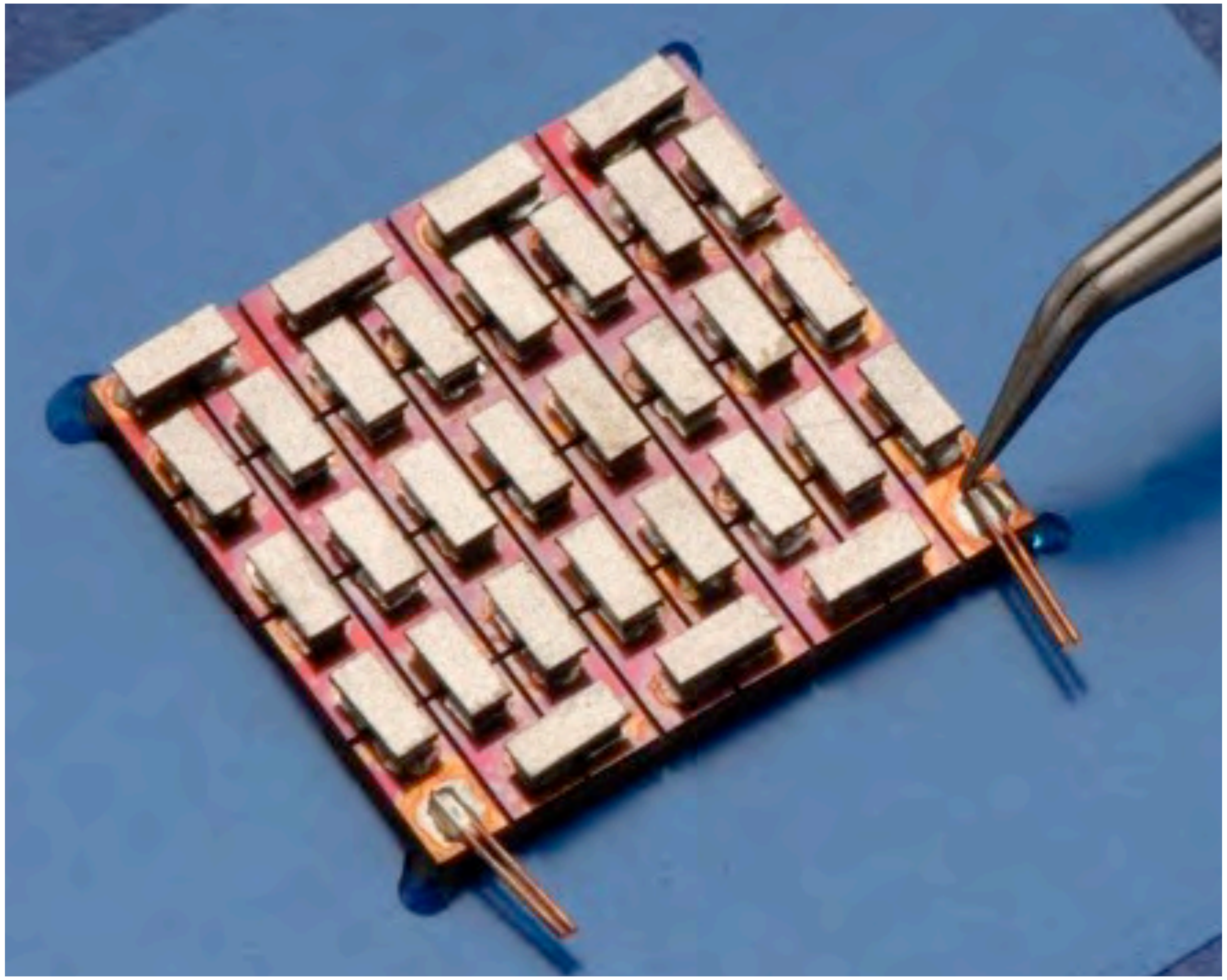
Nature Materials 7, 105 (2008)

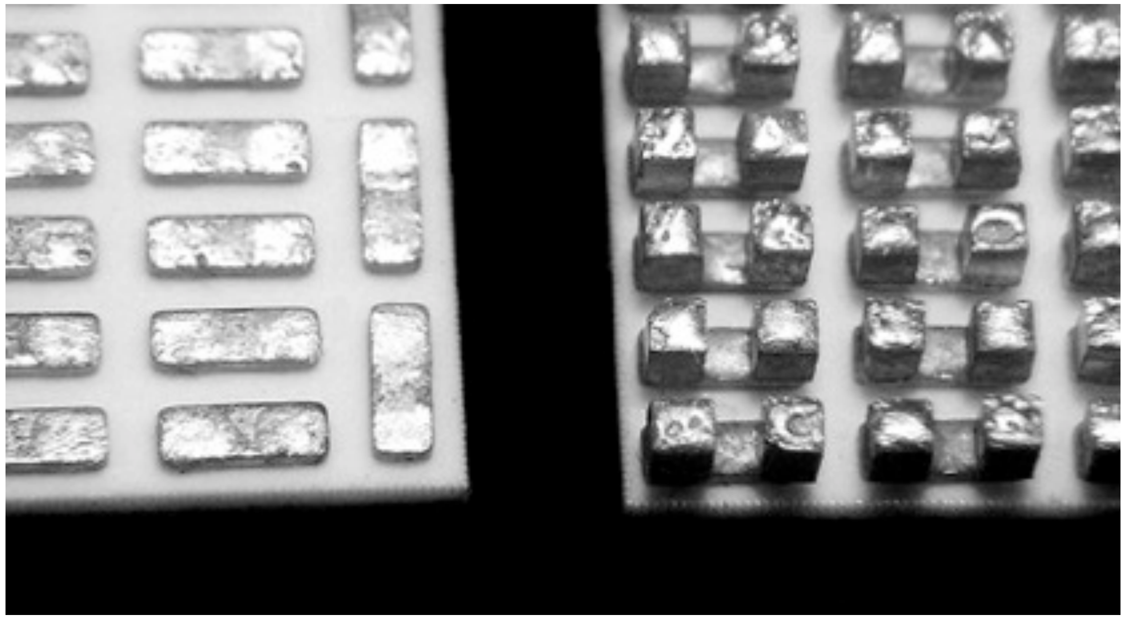
- **Bulk n-Bi_2Te_3 and p-Sb_2Te_3 used in most commercial thermoelectrics & Peltier coolers**
- **But tellurium is 7th rarest element on earth !!!**
- **Bulk $Si_{1-x}Ge_x$ (x~0.2 to 0.3) used for high temperature satellite applications**

Thermoelectric Generators / Peltier Coolers

Bulk n-Bi_2Te_3 and p-Sb_2Te_3 devices

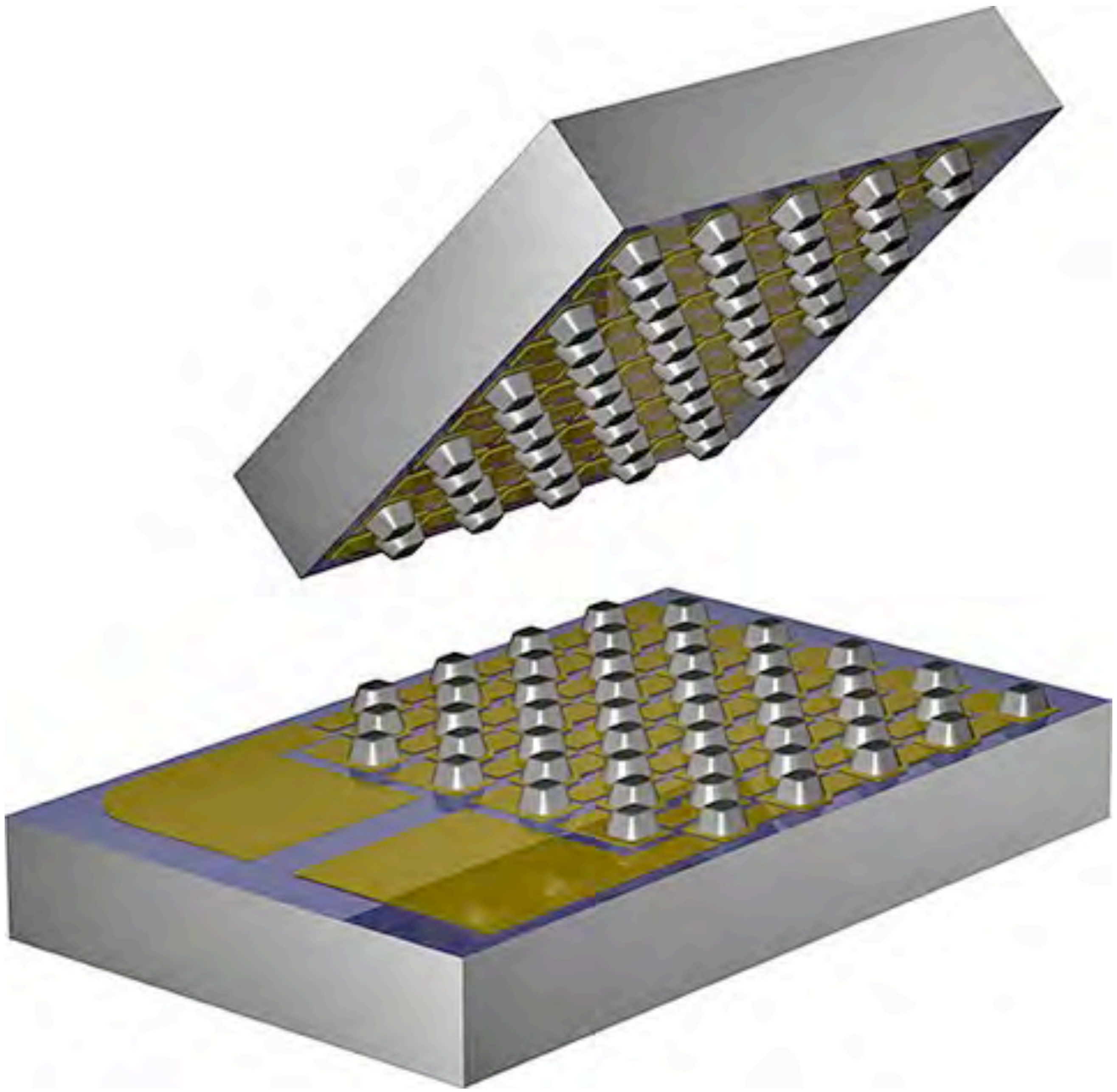


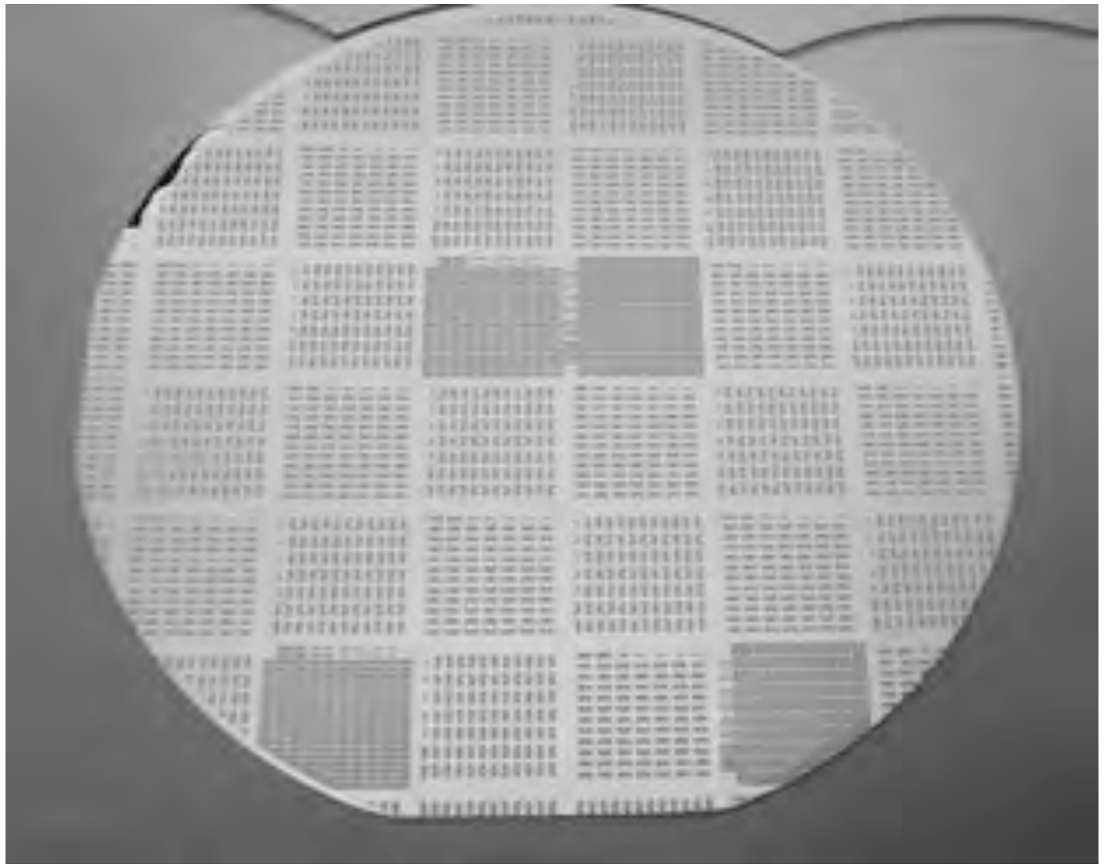


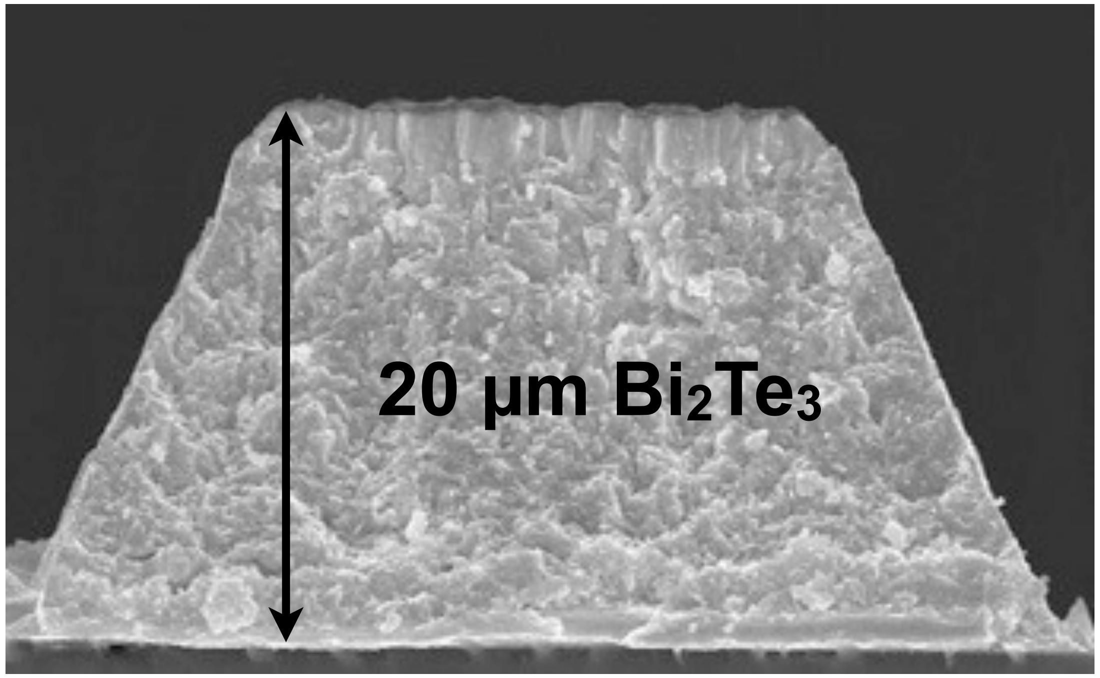


- **Variations in solder diffusing up legs results in variable module ZT**

Micropelt: Microfabricated Bi_2Te_3 Technology



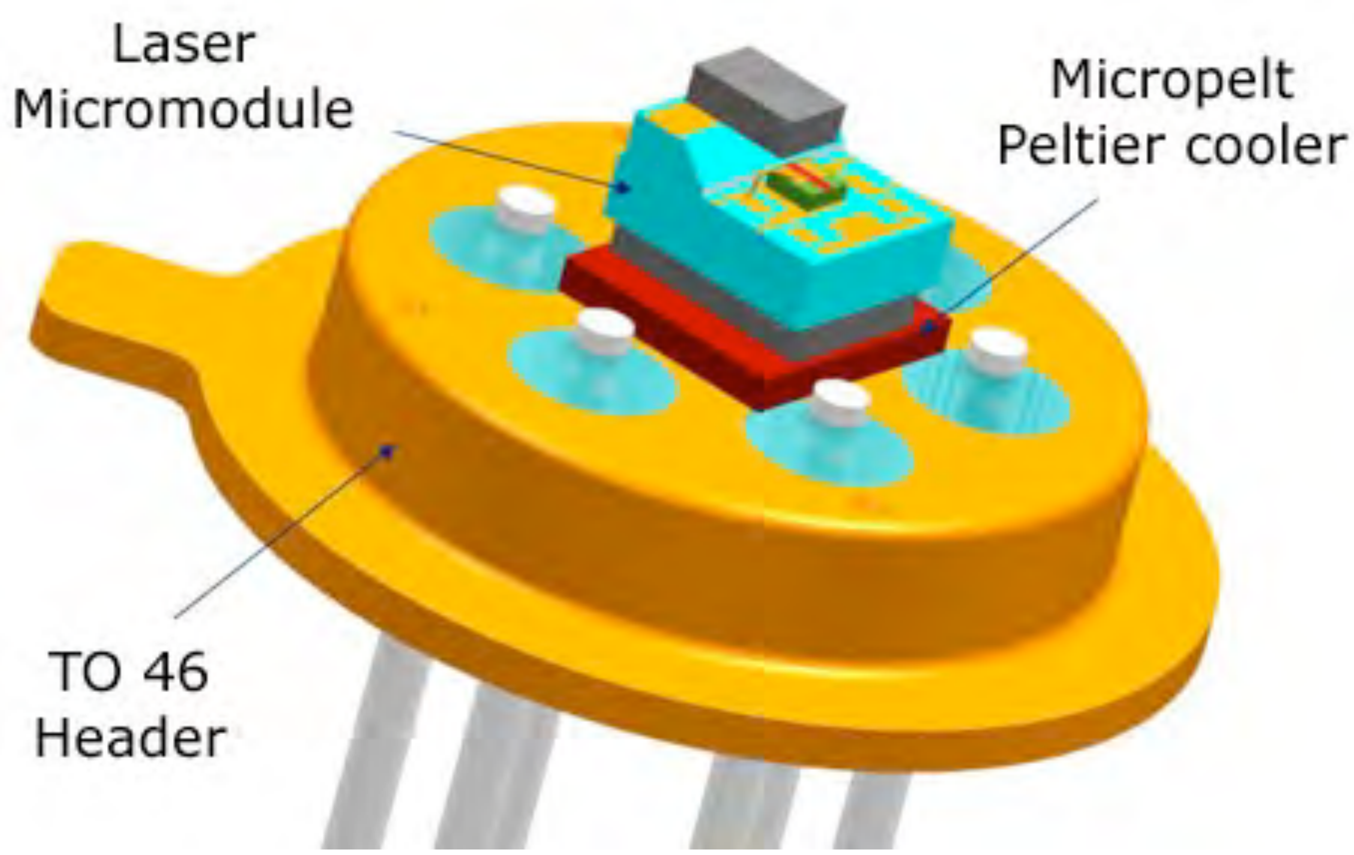


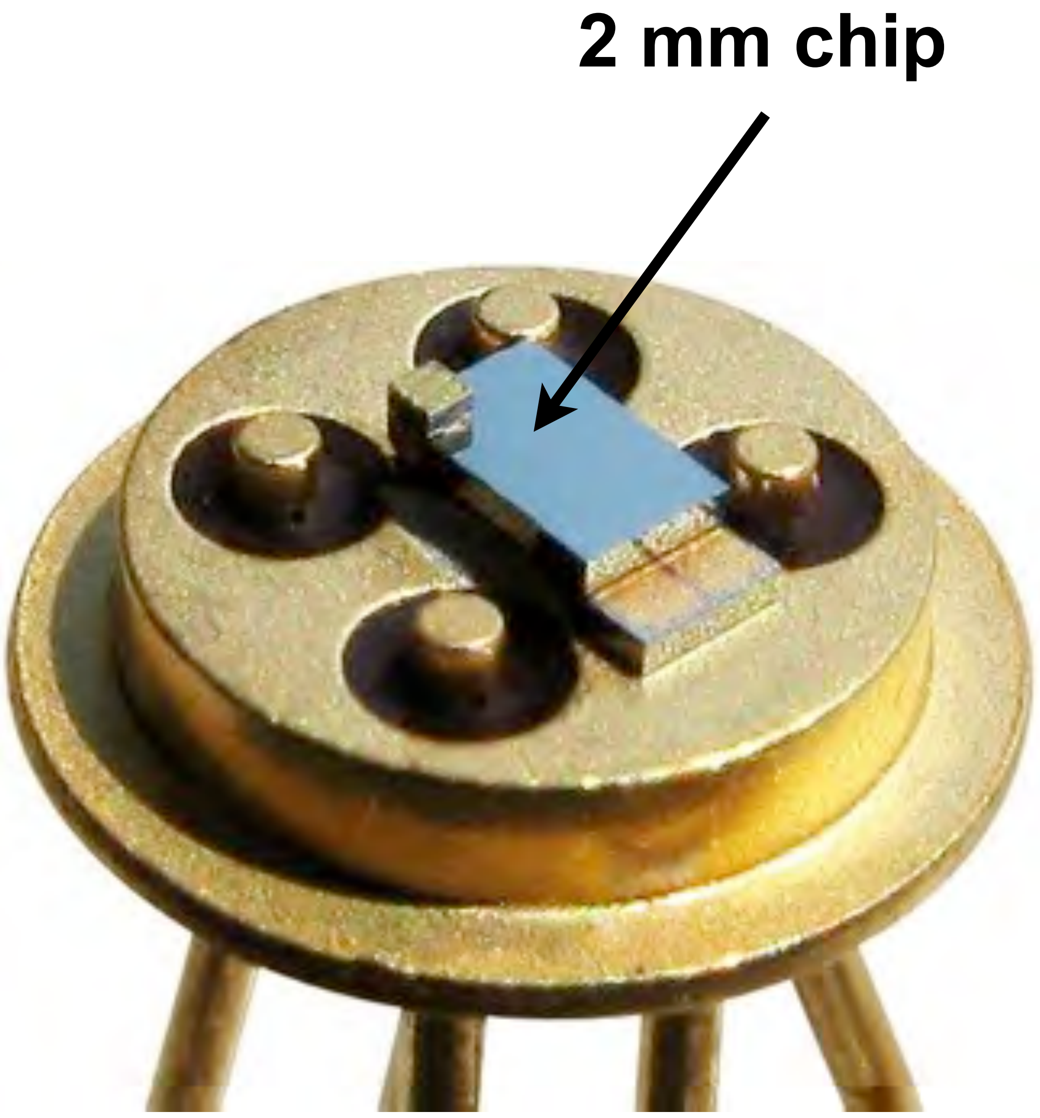


http://www.micropelt.com/

Micropelt Peltier Coolers for Lasers

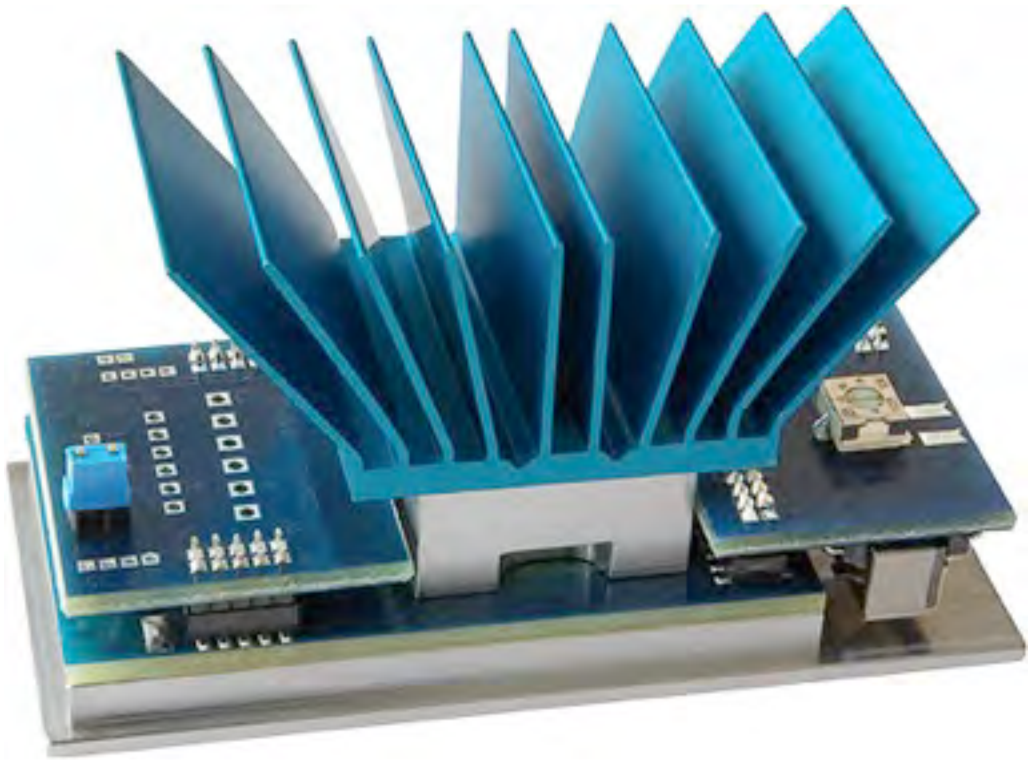
- **Microfabricated Bi_2Te_3 thermoelectric devices**



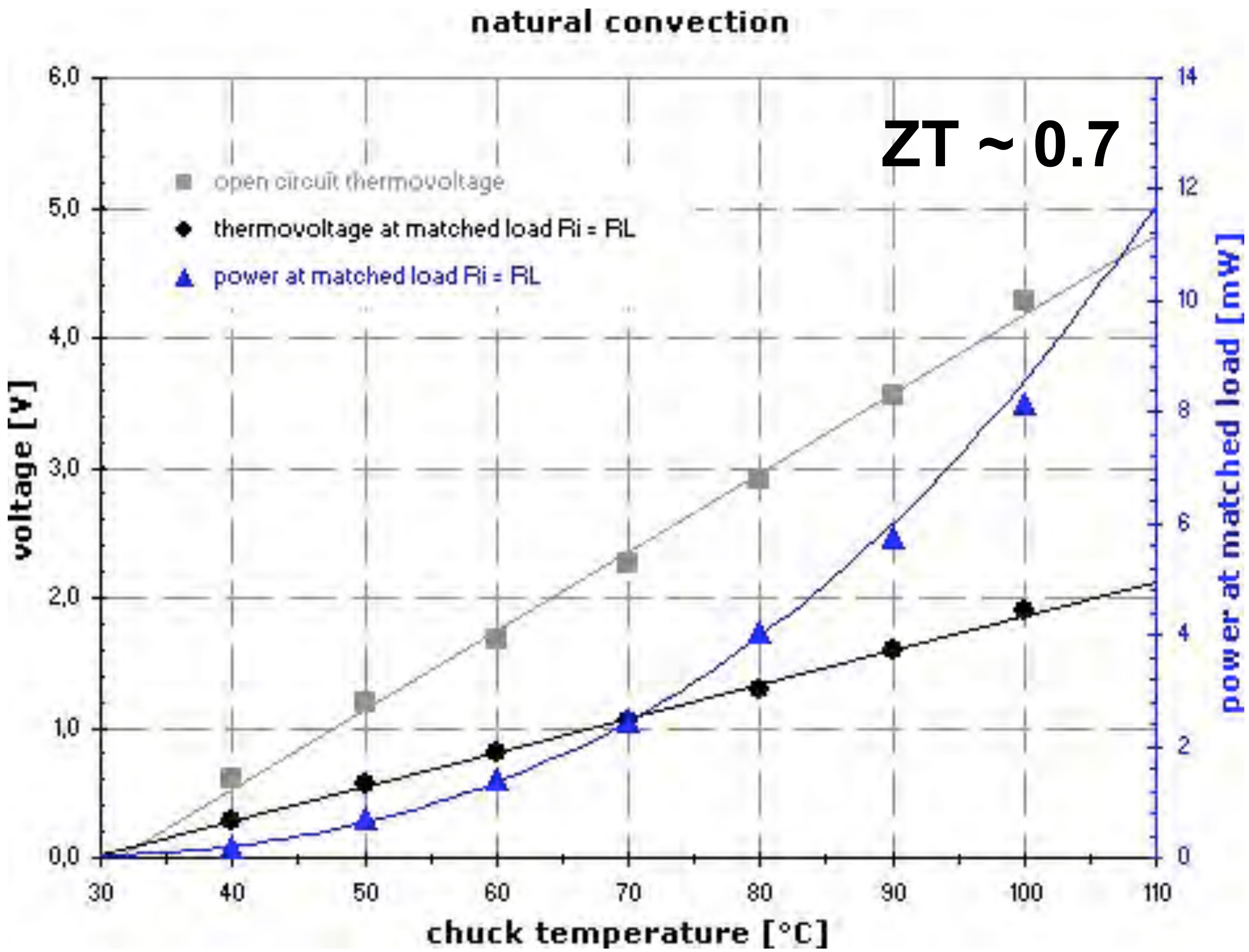


http://www.micropelt.com/

Micropelt Bi_2Te_3 Thermoelectric Energy Harvester

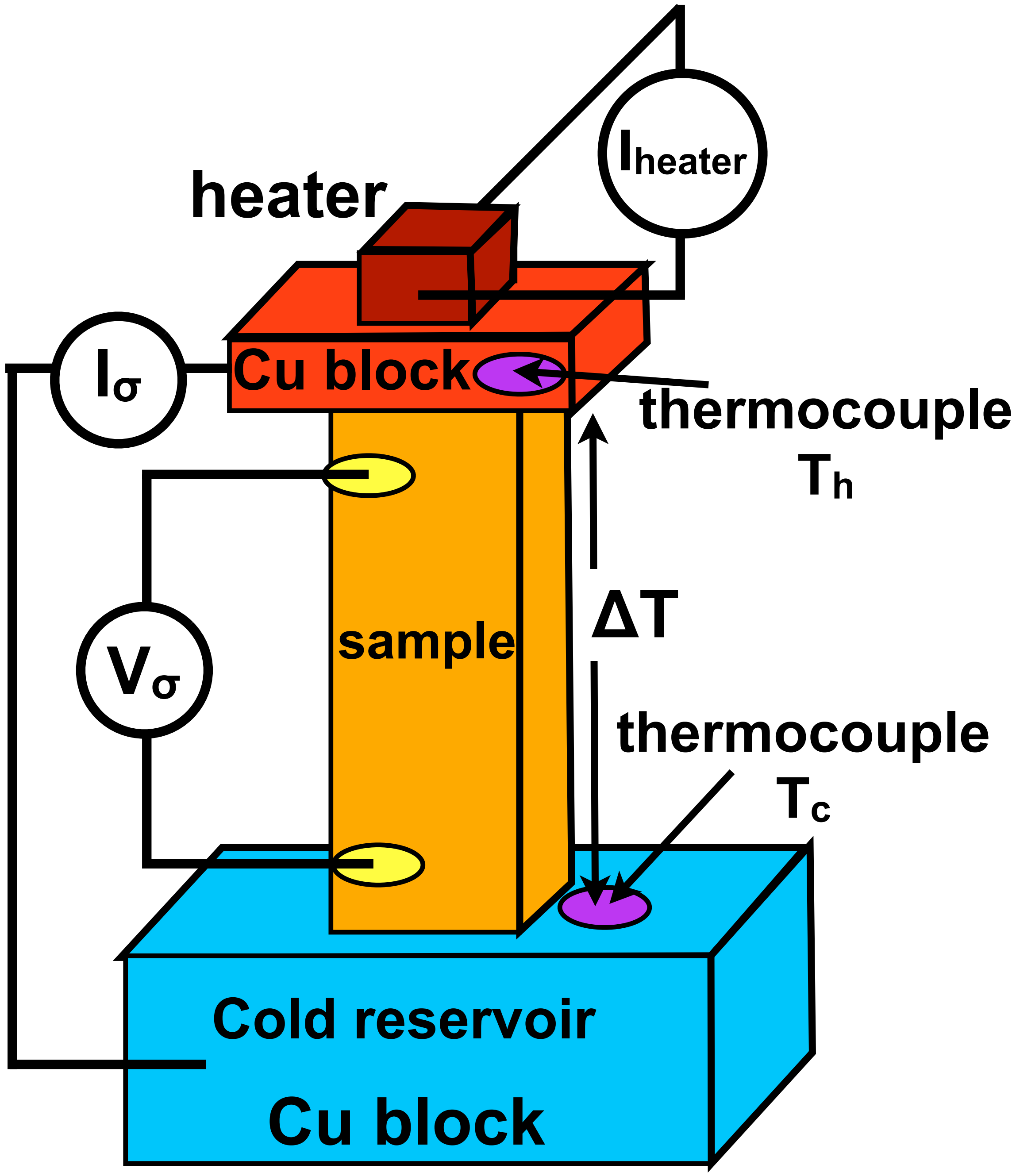


3.4 mm x 3.4 mm thermoelectric chip



http://www.micropelt.com/

Measuring Seebeck Coefficient



- Physically heat one side of sample
- Cold sink on other side of sample
- Thermocouples top and bottom to measure ΔT
- 4 terminal electrical measurements
- α and σ easy to measure
- Thermal conductivity, κ very difficult to measure

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

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

  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%

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)

Length Scales: Mean Free Paths

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

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

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

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

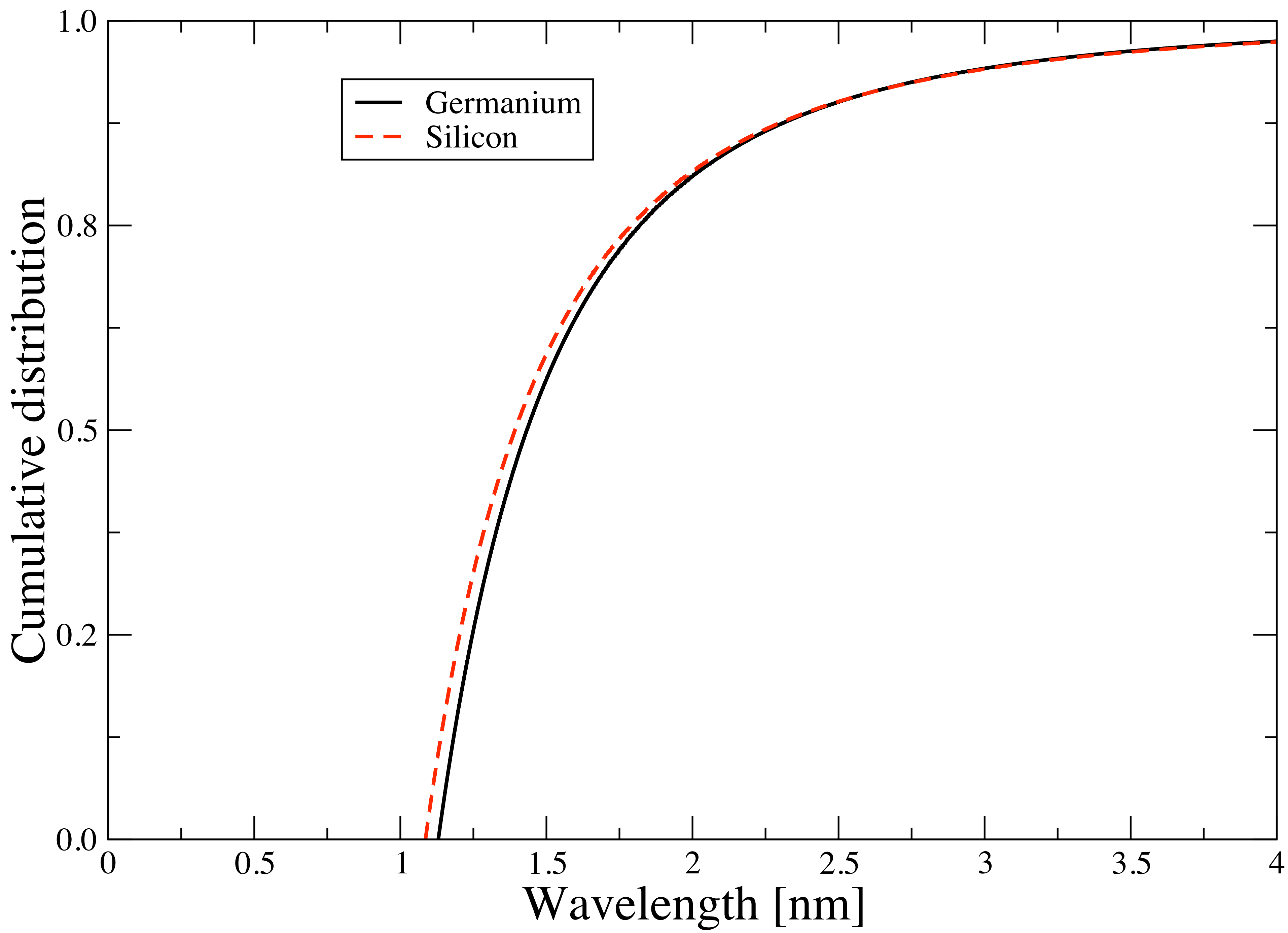
- A structure may be 2D or 3D for electrons but 1 D for phonons (or vice versa!)

Phonon Mean Free Paths

Material	Model	Specific Heat ($x10^6$ $Jm^{-3}K^{-1}$)	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:

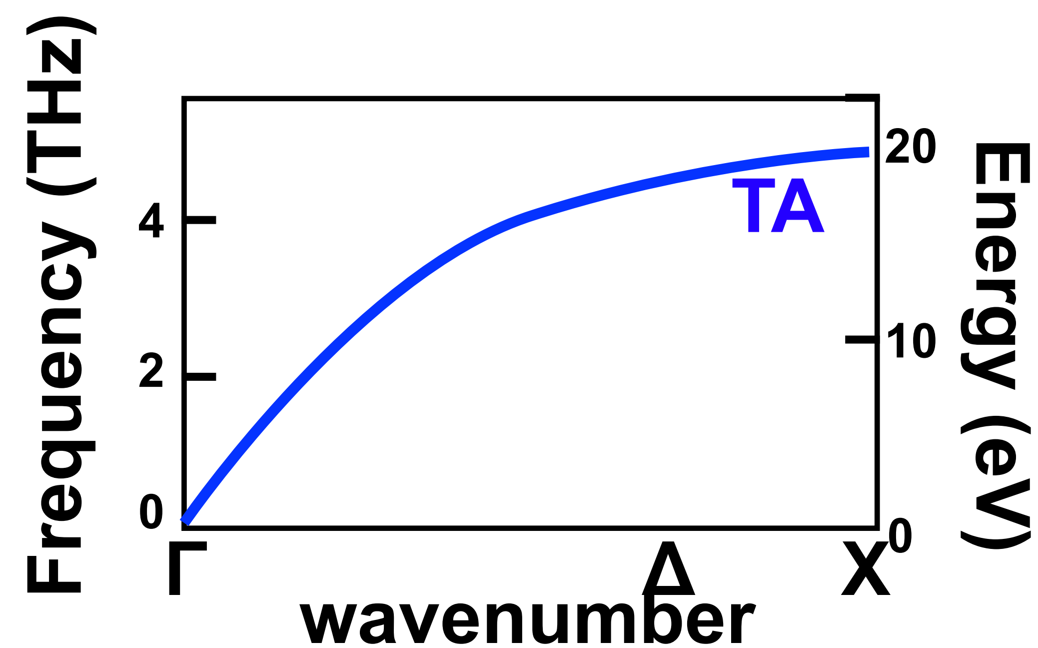
- Require structures below the phonon mean free path (10s nm)

Phonon Bandgaps:

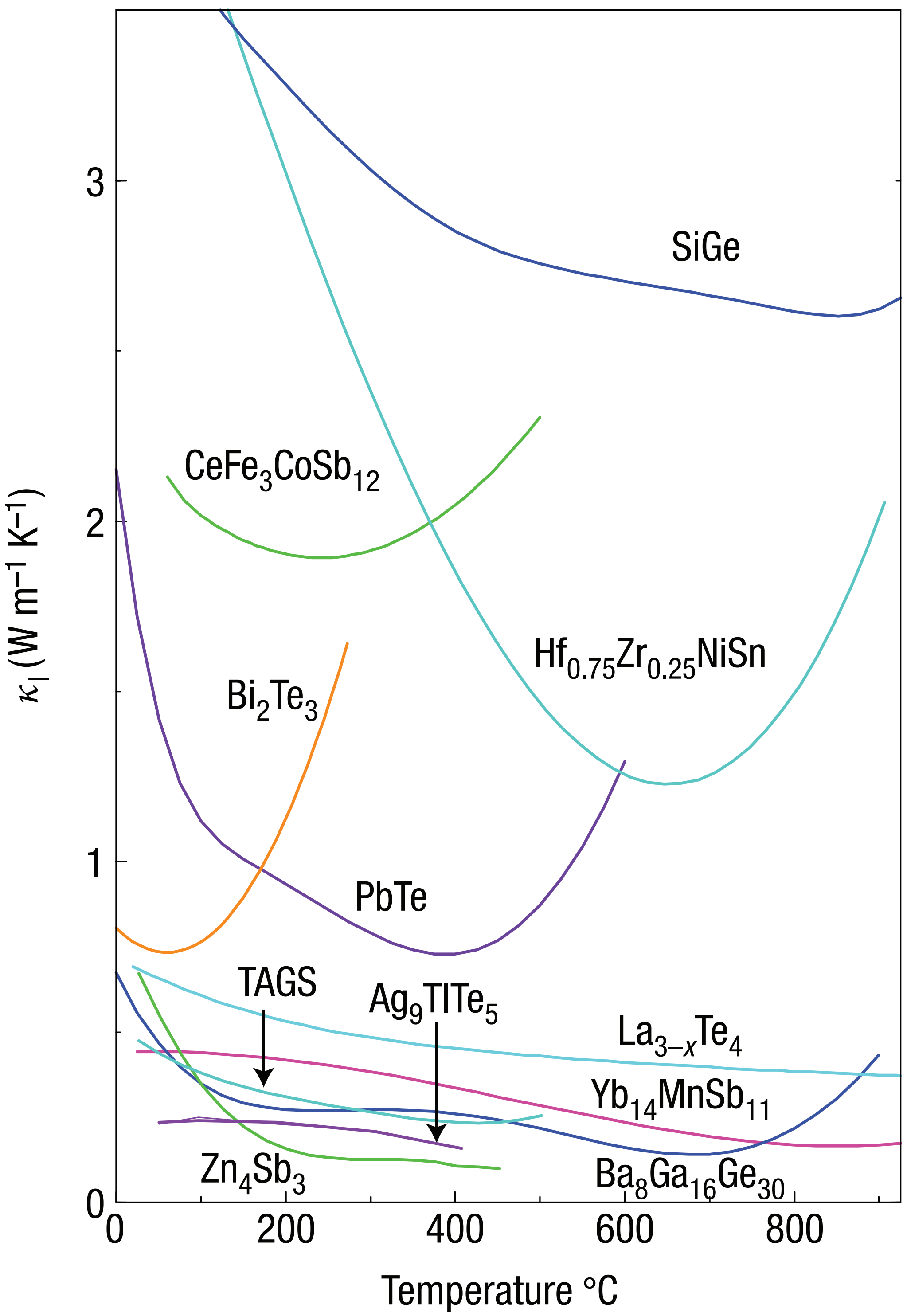
- Change the acoustic phonon dispersion –> stationary phonons or bandgaps

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

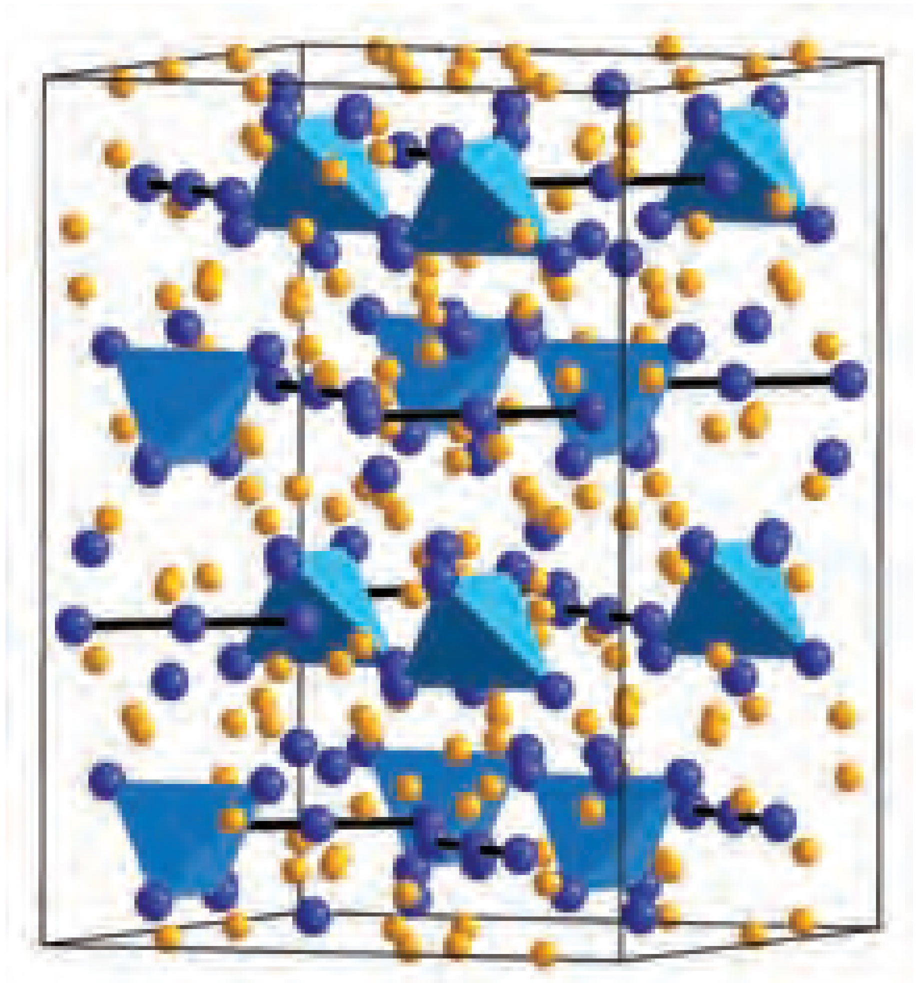
- Phonon group velocity $\propto \dfrac{dE}{dk_q}$



Complex Crystal Structures: Reducing κ_{ph}



Skutterudite structure: filling voids with heavy atoms

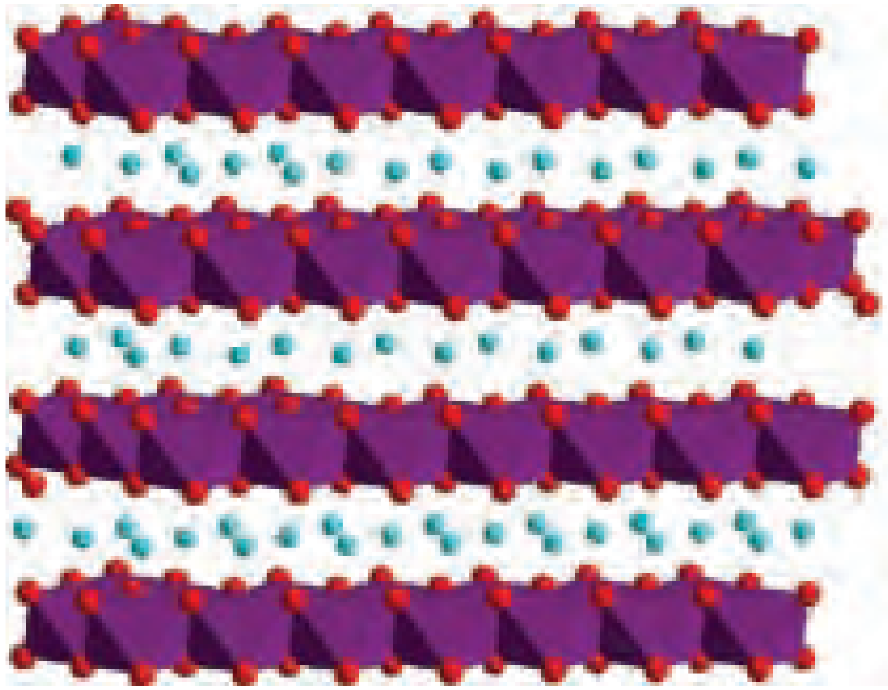


p-$Yb_{14}MnSb_{11}$ – ZT ~ 1 @ 900 ˚C

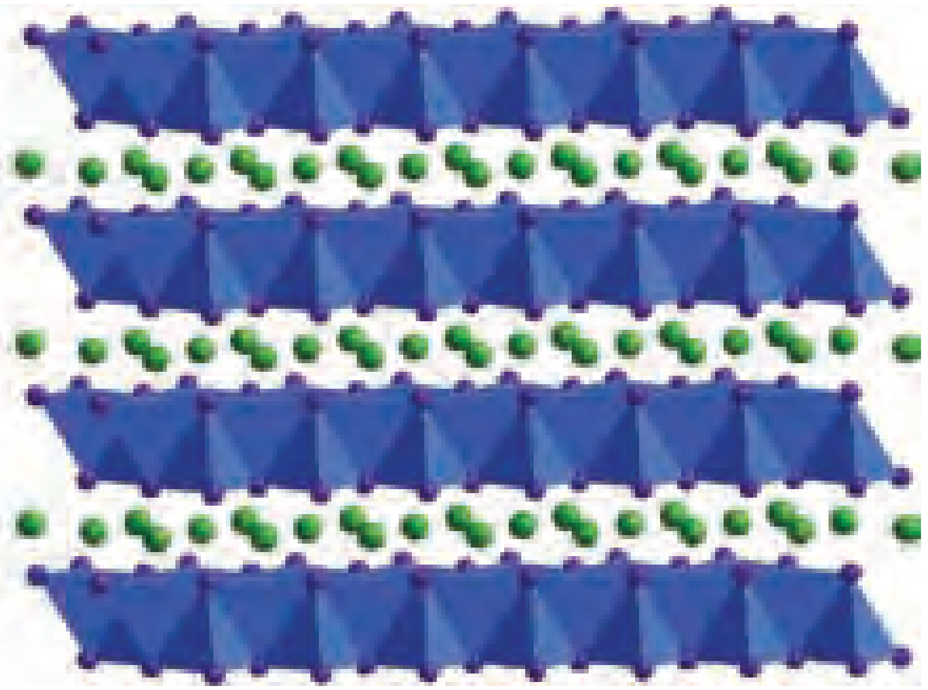
G.J. Snyder et al., Nat. Mat. 7, 105 (2008)

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

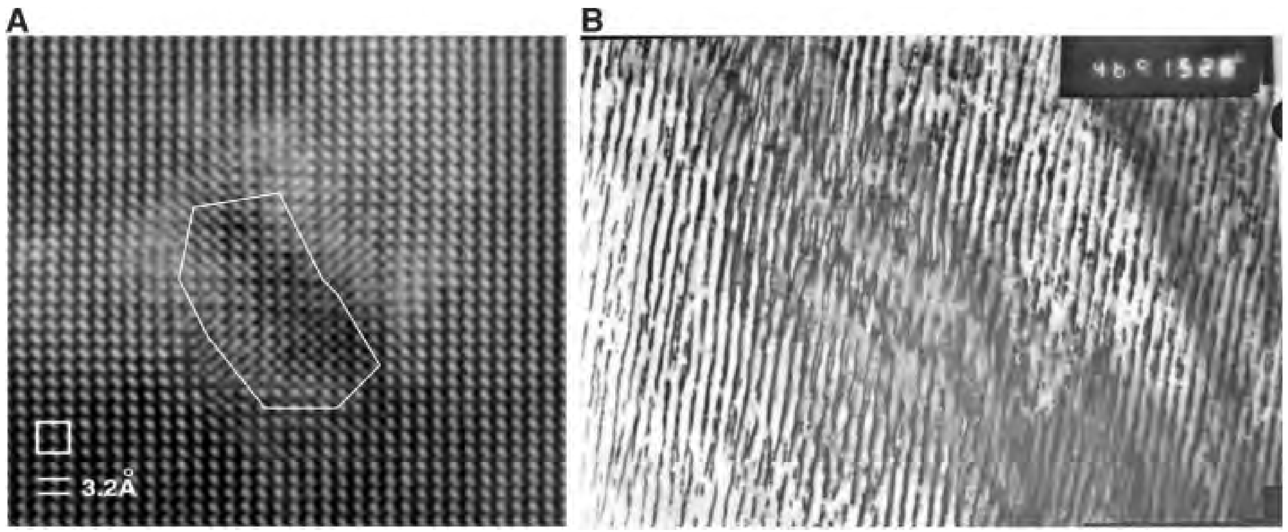


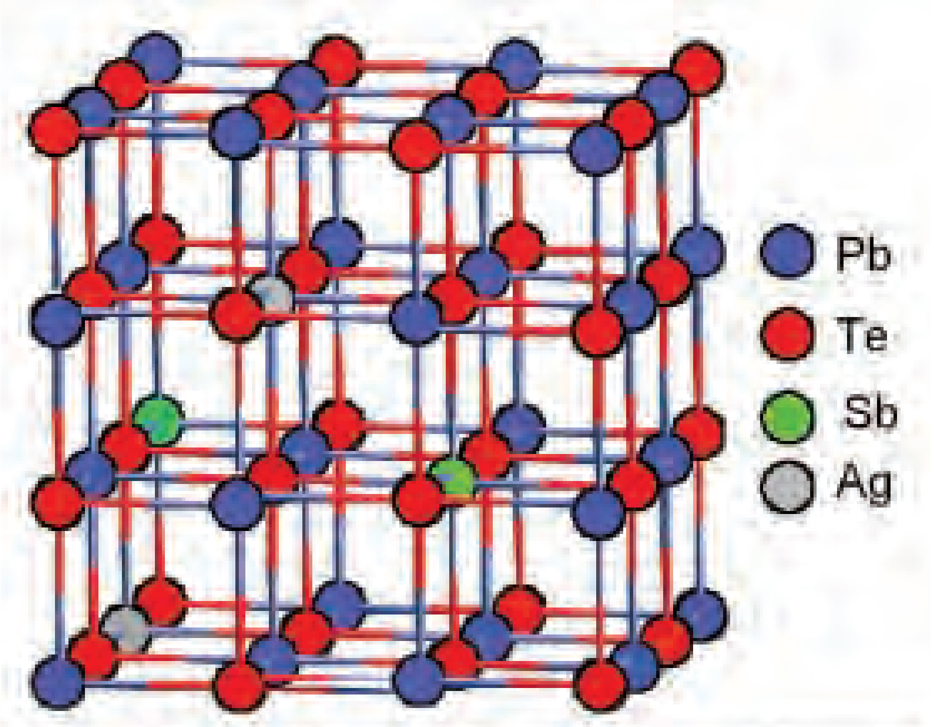
$Ca_xYb_{1-x}Zn_2Sb_2$

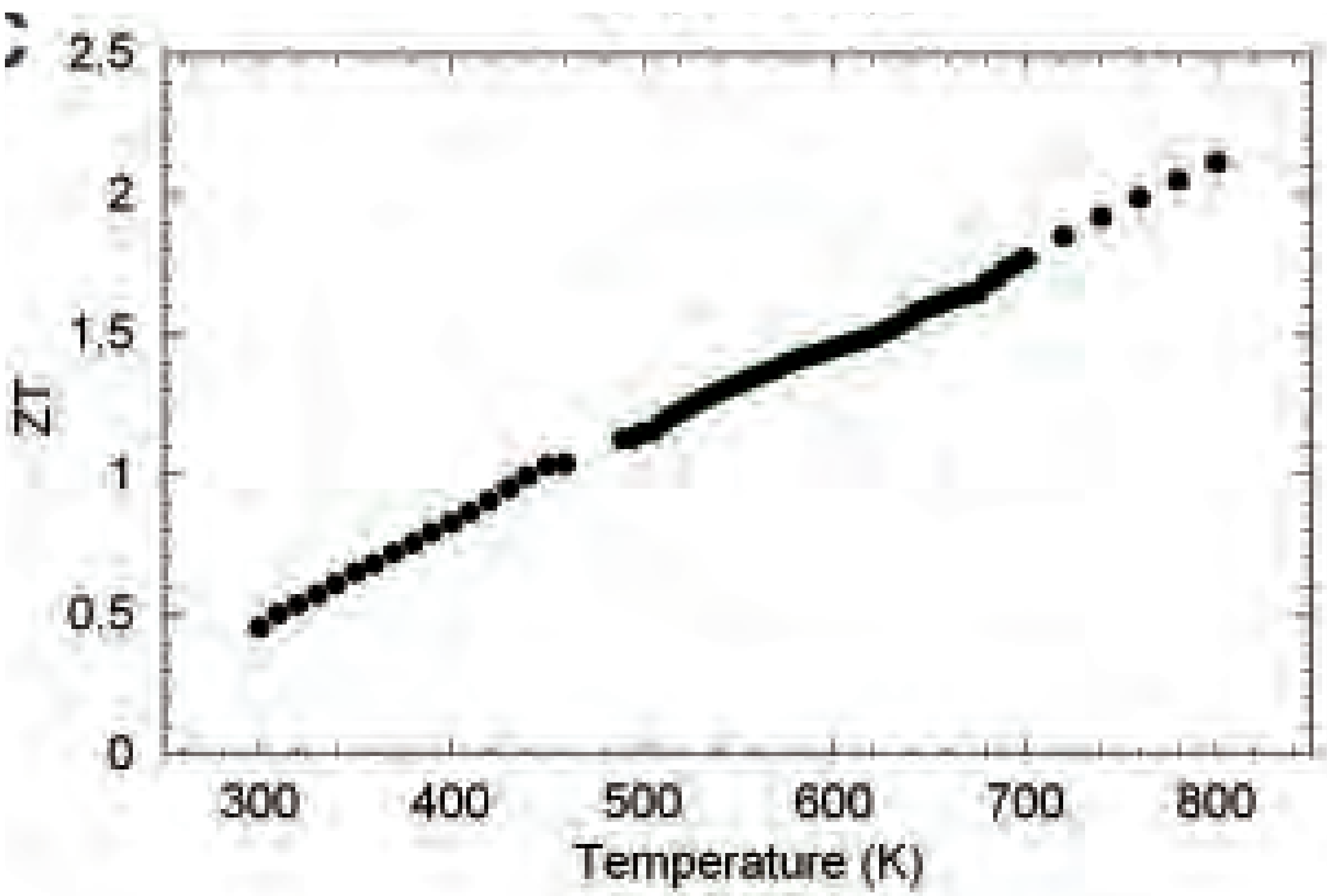
- Only small improvements to ZT observed

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

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







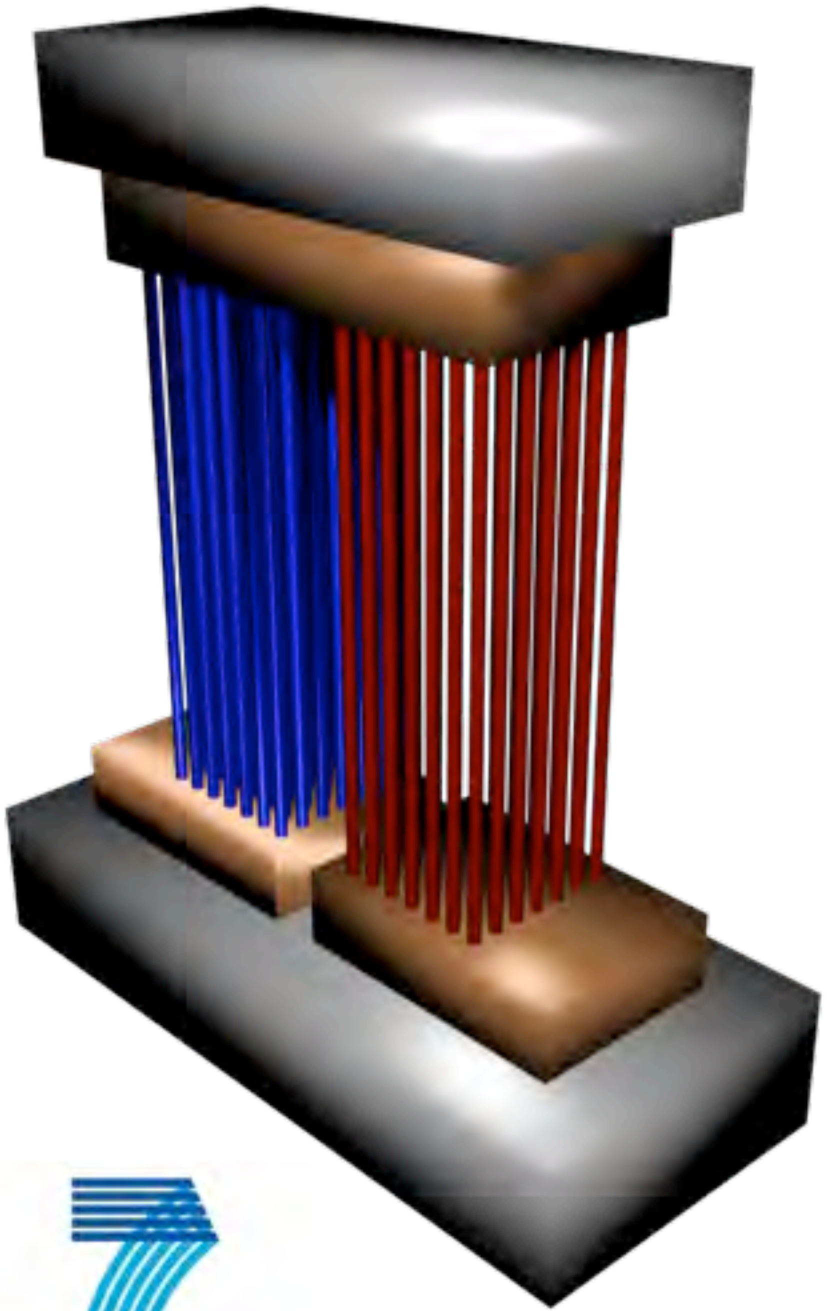
α = –335 μVK^{-1}
σ = 30,000 S/m
κ = 1.1 Wm^{-1}K^{-1}
at 700 K

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

University of Glasgow

GREEN Silicon

Generate Renewable Energy Efficiently using Nanofabricated Silicon (GREEN Silicon)



D.J. Paul, J.M.R. Weaver, P. Dobson & J. Watling

University of Glasgow, U.K.

G. Isella, D. Chrastina & H. von Känel

L-NESS, Politecnico de Milano, Como, Italy

J. Stangl, T. Fromherz & G. Bauer

University of Linz, Austria

E. Müller

ETH Zürich, Switzerland

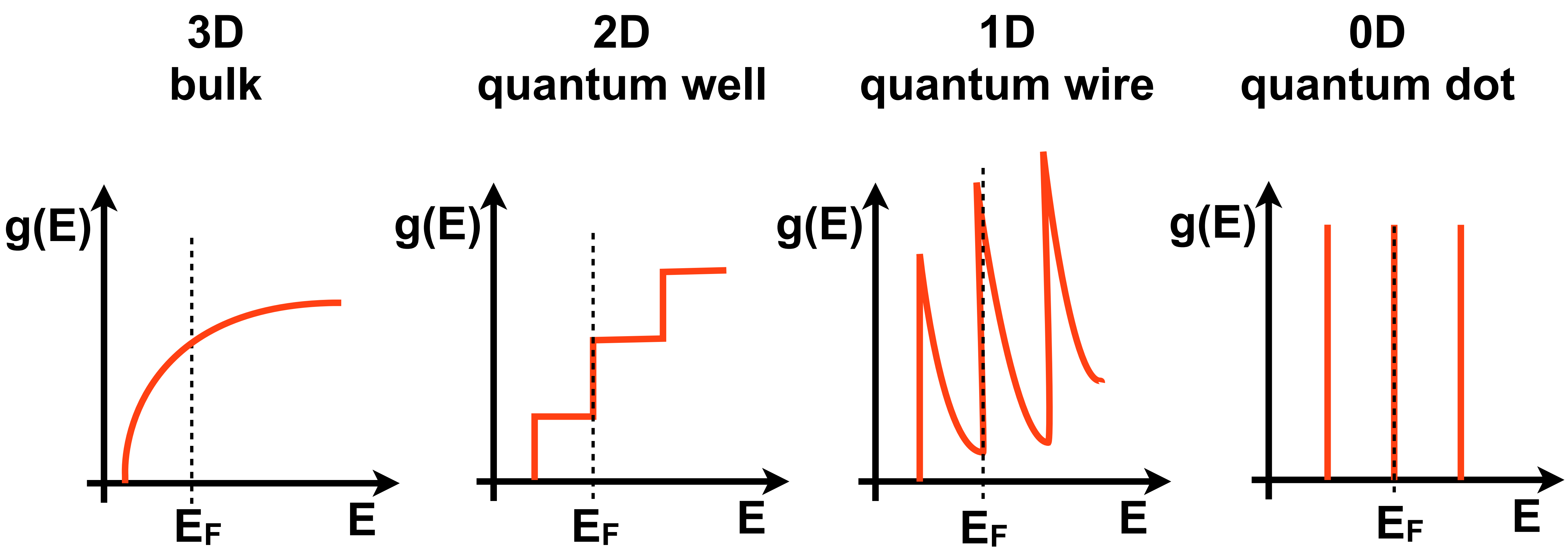
SEVENTH FRAMEWORK PROGRAMME

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

Seebeck Enhancement at Low Dimensions

- **Increase α through enhanced DOS:**

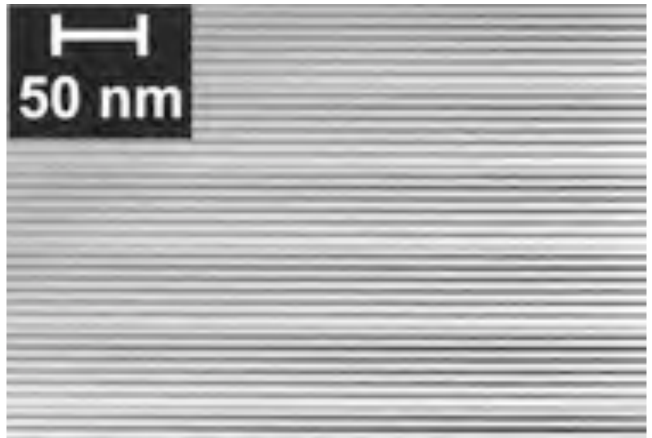
$$\alpha = -\frac{\pi^2}{3q} k_B^2 T \left[\frac{d\ln(\mu(E)g(E))}{dE} \right]_{E=E_F}$$



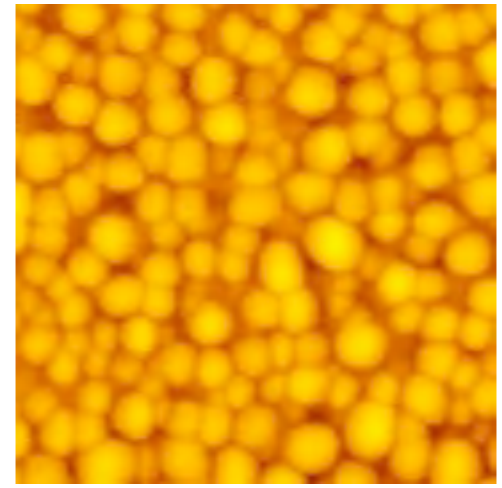
α increasing

GREEN Silicon Approach

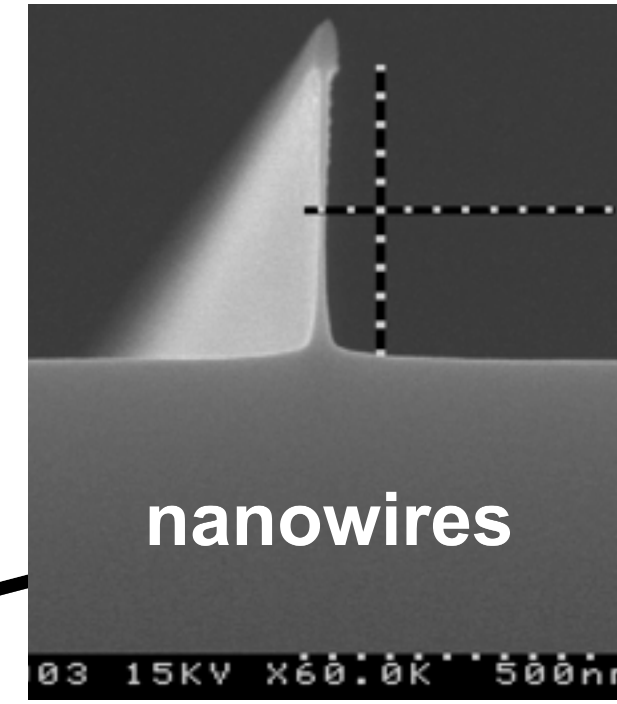
Low dimension technology



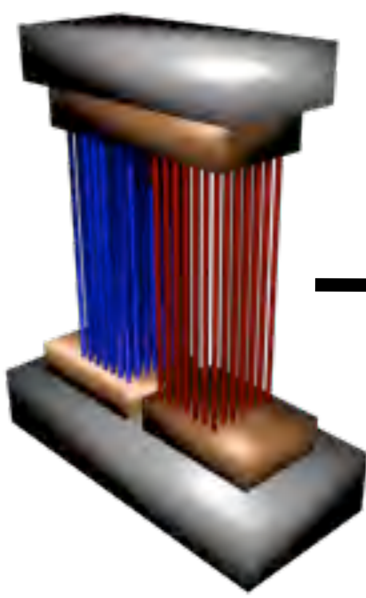
superlattices

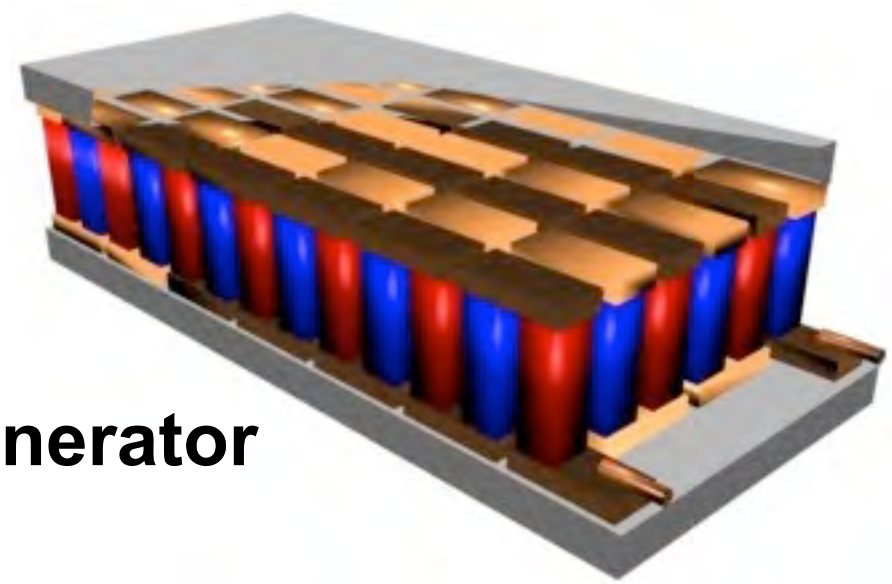


quantum dots



Module

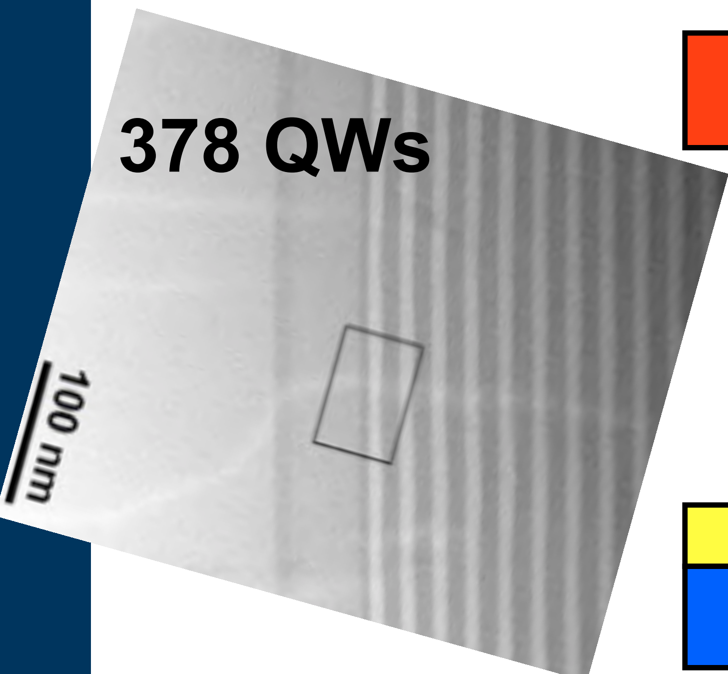




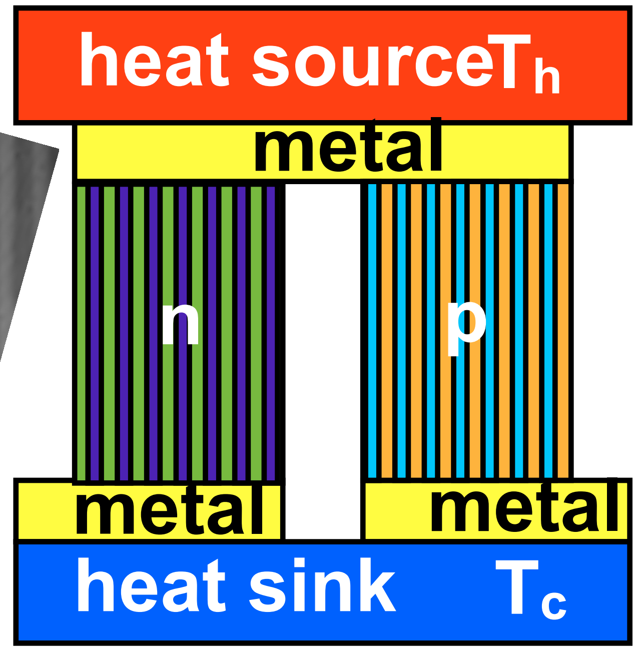
Generator

- **Si/SiGe technology –> cheap and back end of line compatible**

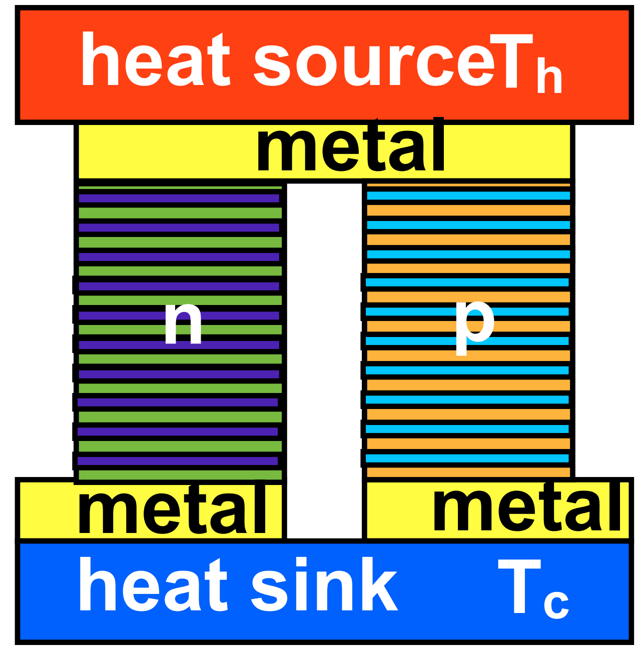
Thermoelectric Low Dimensional Structures

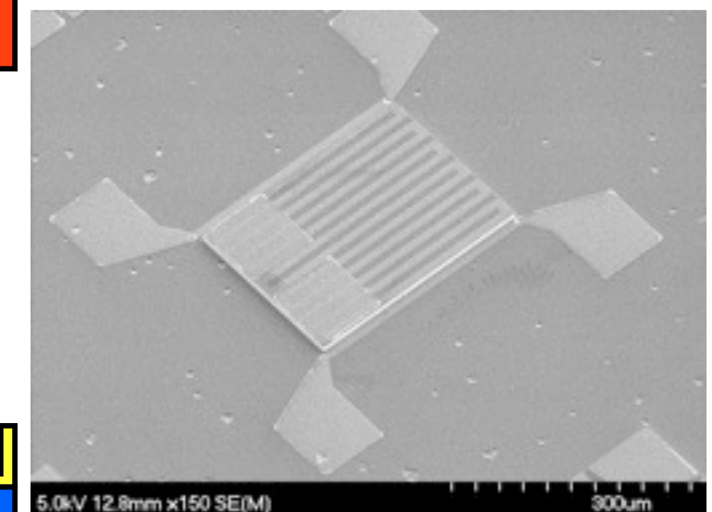


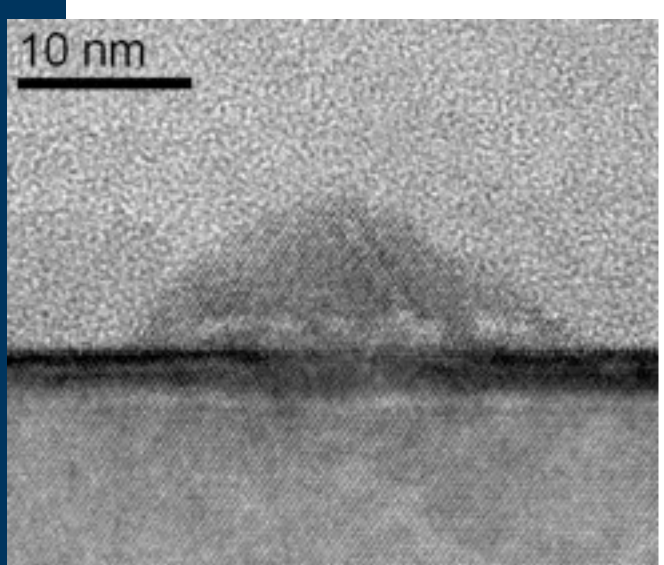
Lateral superlattice



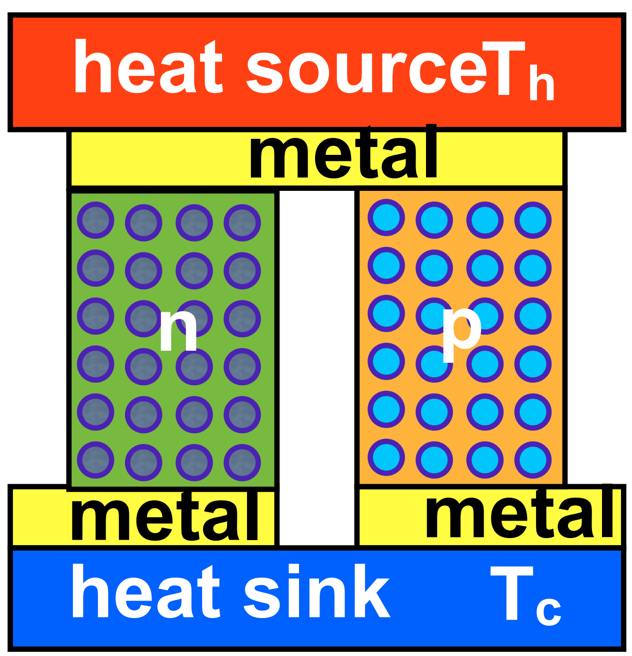
Vertical superlattice



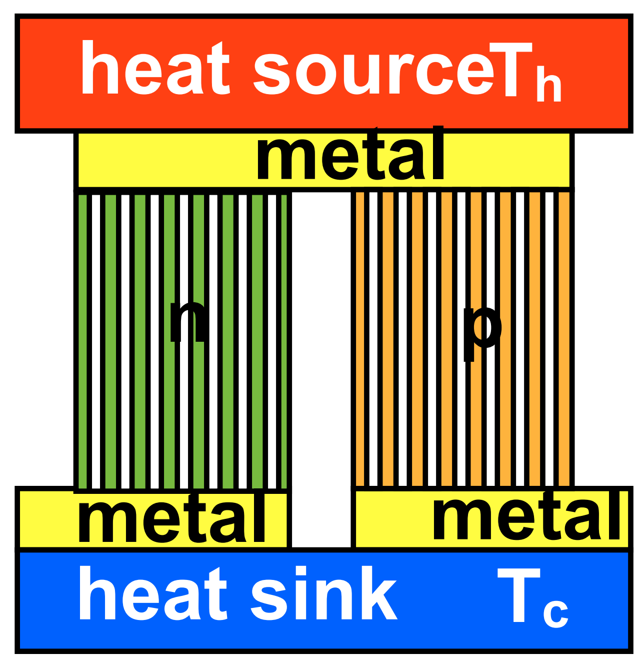


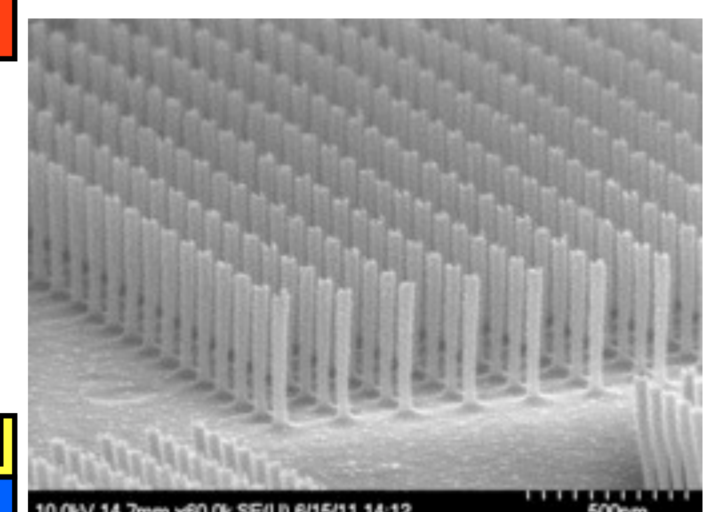


Quantum Dots

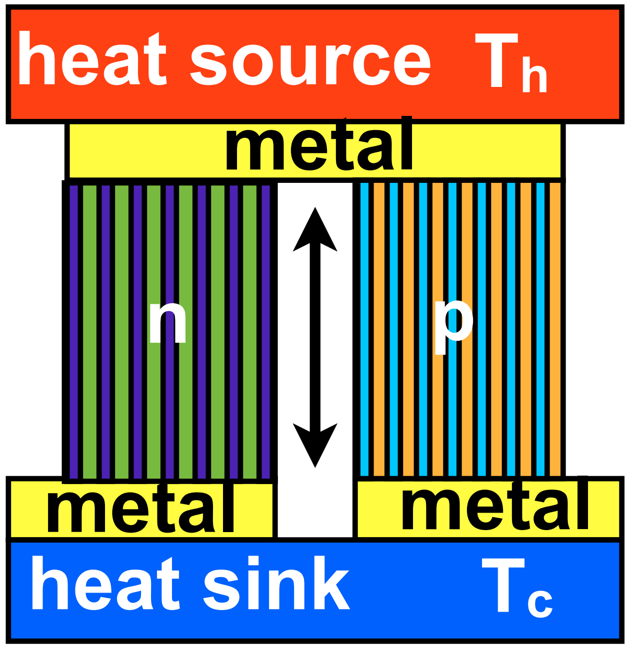


Nanowires





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

Figure of merit

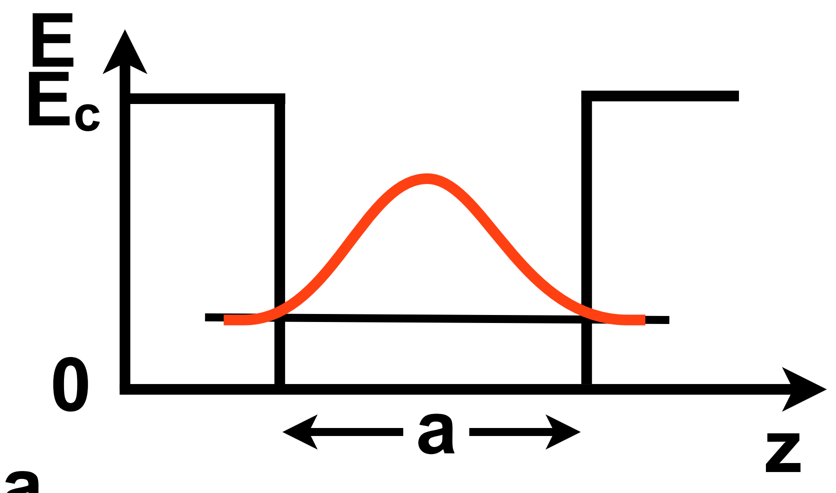
$$\mathrm{ZT} = \frac{\alpha^2\sigma}{\kappa}\mathrm{T}$$

TE Whall and EHC Parker, 1987

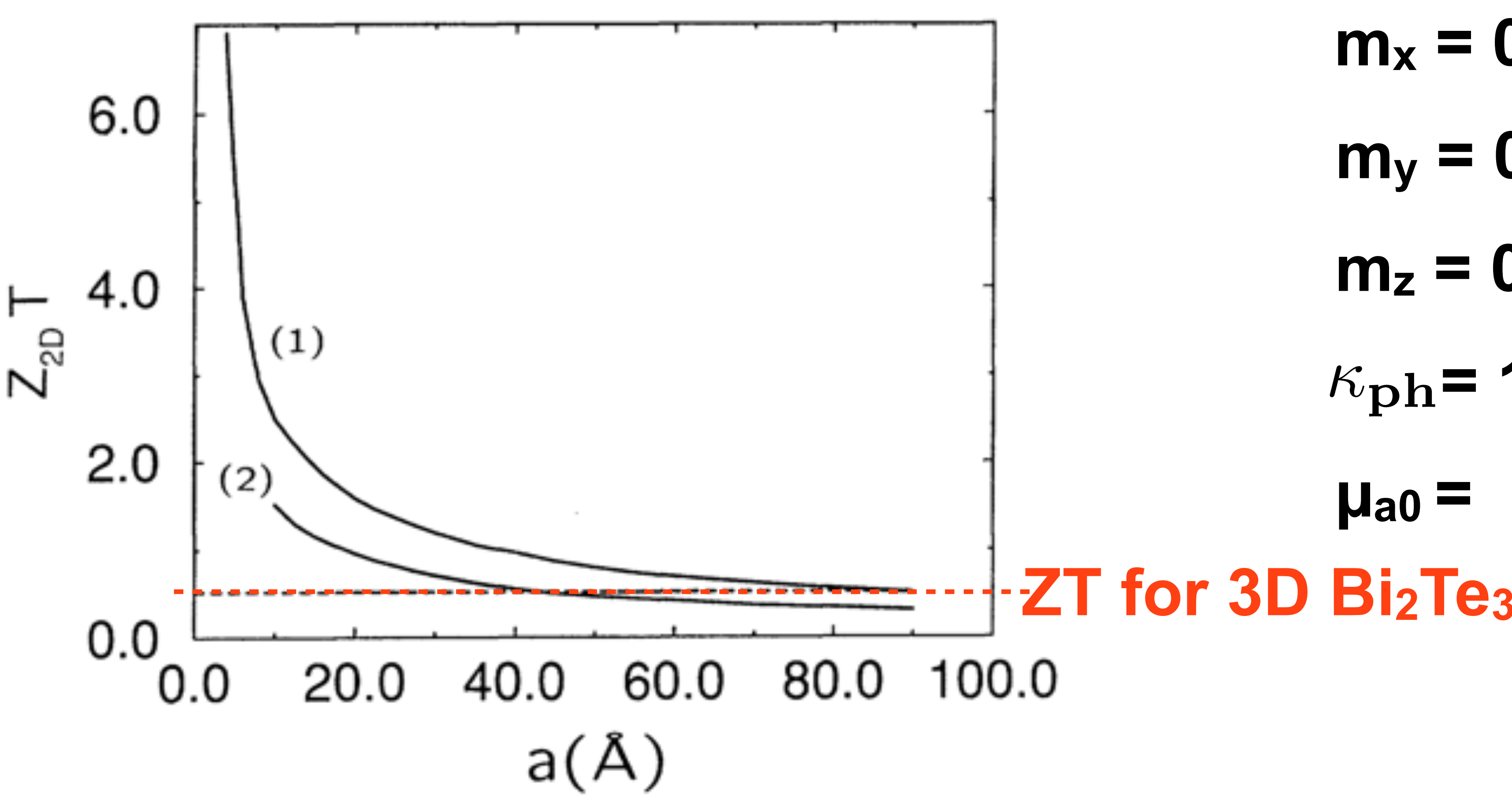
L.D. Hicks and M.S. Dresselhaus, Phys. Rev. B 47, 12737 (1993)

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



$m_x = 0.021\ m_0$

$m_y = 0.081\ m_0$

$m_z = 0.32\ m_0$

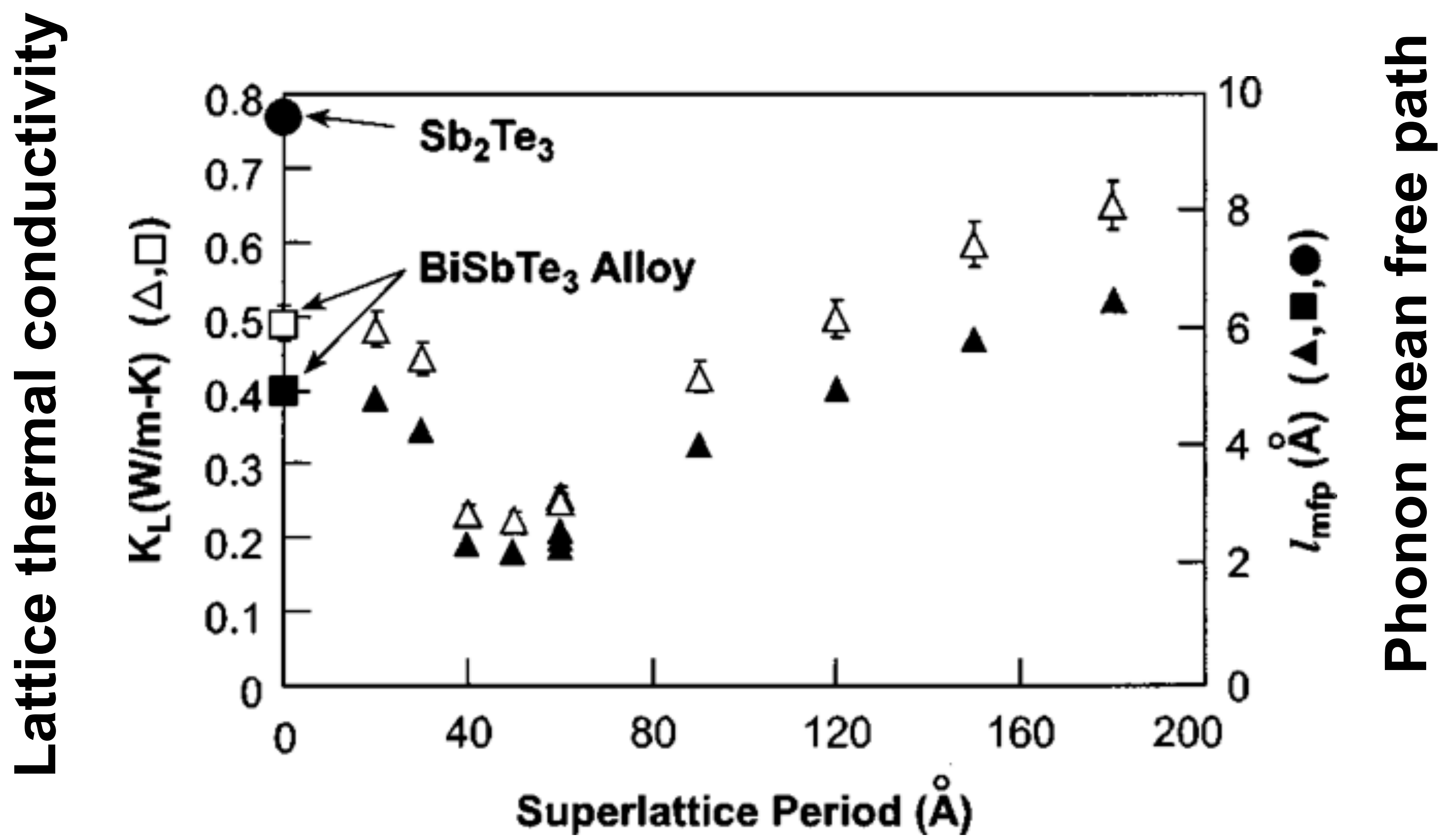
$\kappa_{ph} = 1.5\ Wm^{-1}K^{-1}$

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

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

p-Bi_2Te_3 / Sb_2Te_3 Superlattices

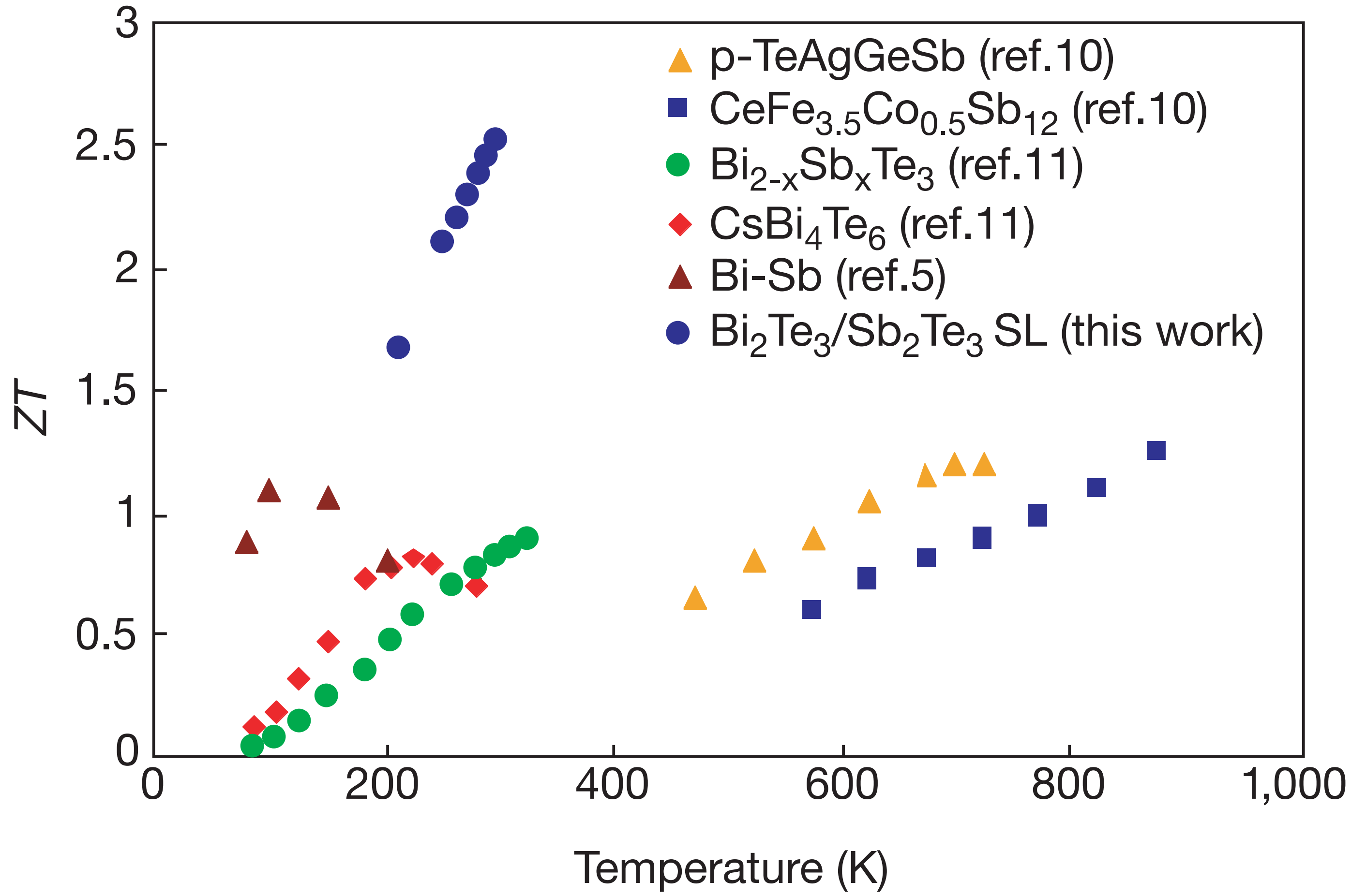
- Bi_2Te_3 κ_{ph} = 1.05 $Wm^{-1}K^{-1}$



- 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



Bulk Bi_2Te_3 ZT ~ 0.8
Superlattice ZT = 2.6

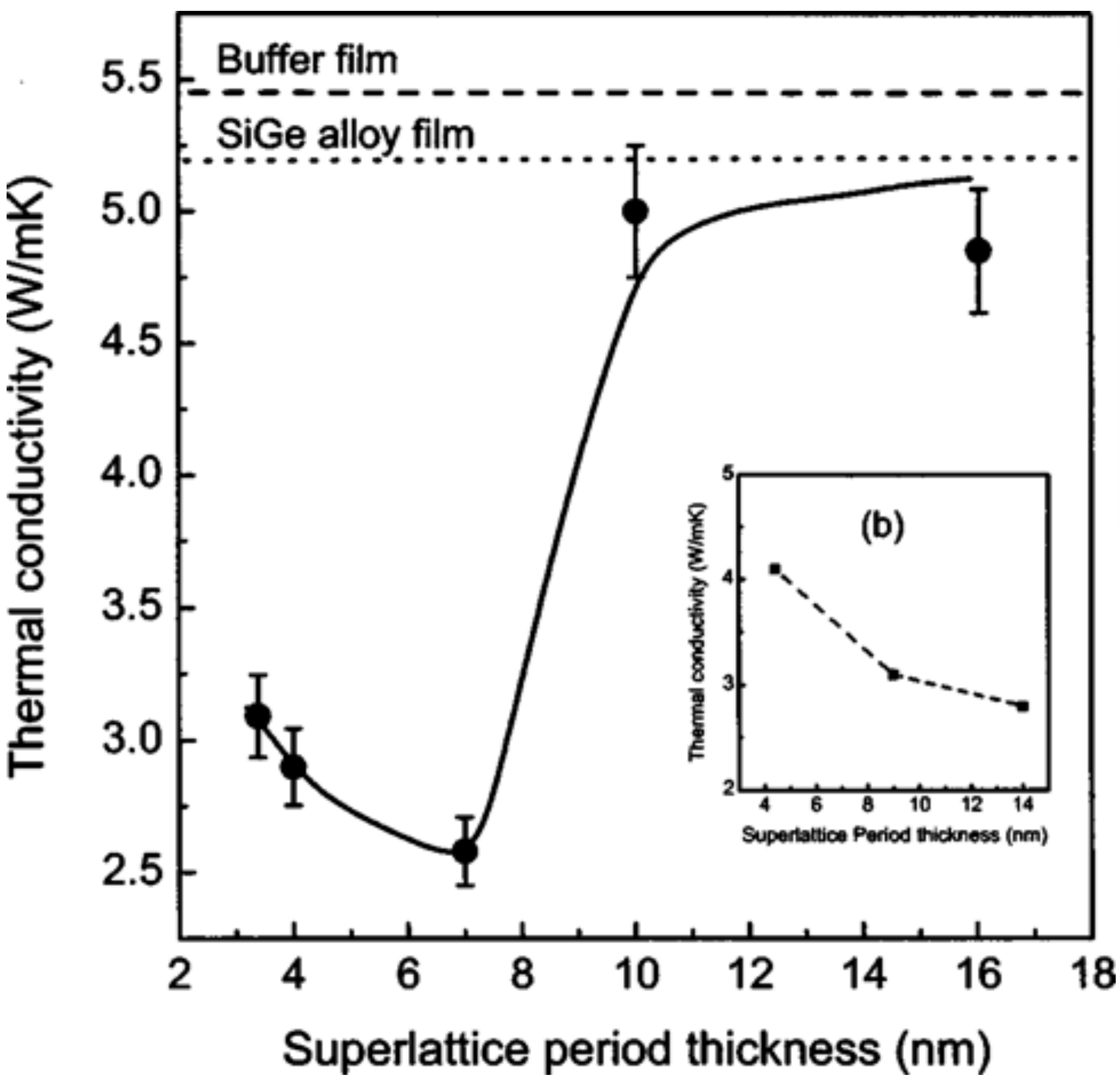
Electrons	Phonons
$\mu = 383\ cm^2V^{-1}s^{-1}$	
l = 11.4 nm	Λ_{ph} = 3 nm
$k_{el}l \sim 7.6$	$k_{ph}\Lambda \sim 0.5$

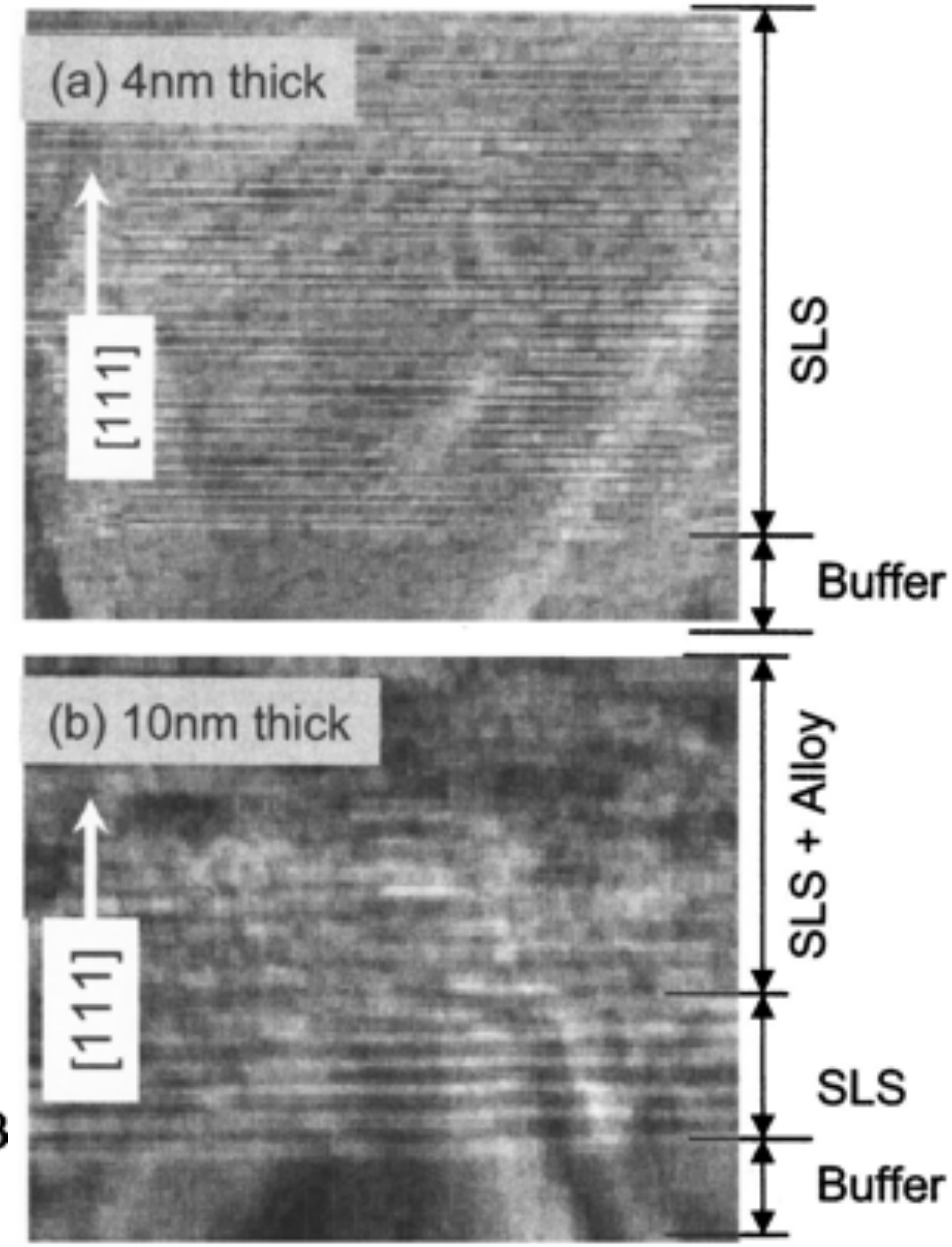
=> Phonon blocking

- **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)

Si/Ge Superlattice Reduced Thermal Conductivity

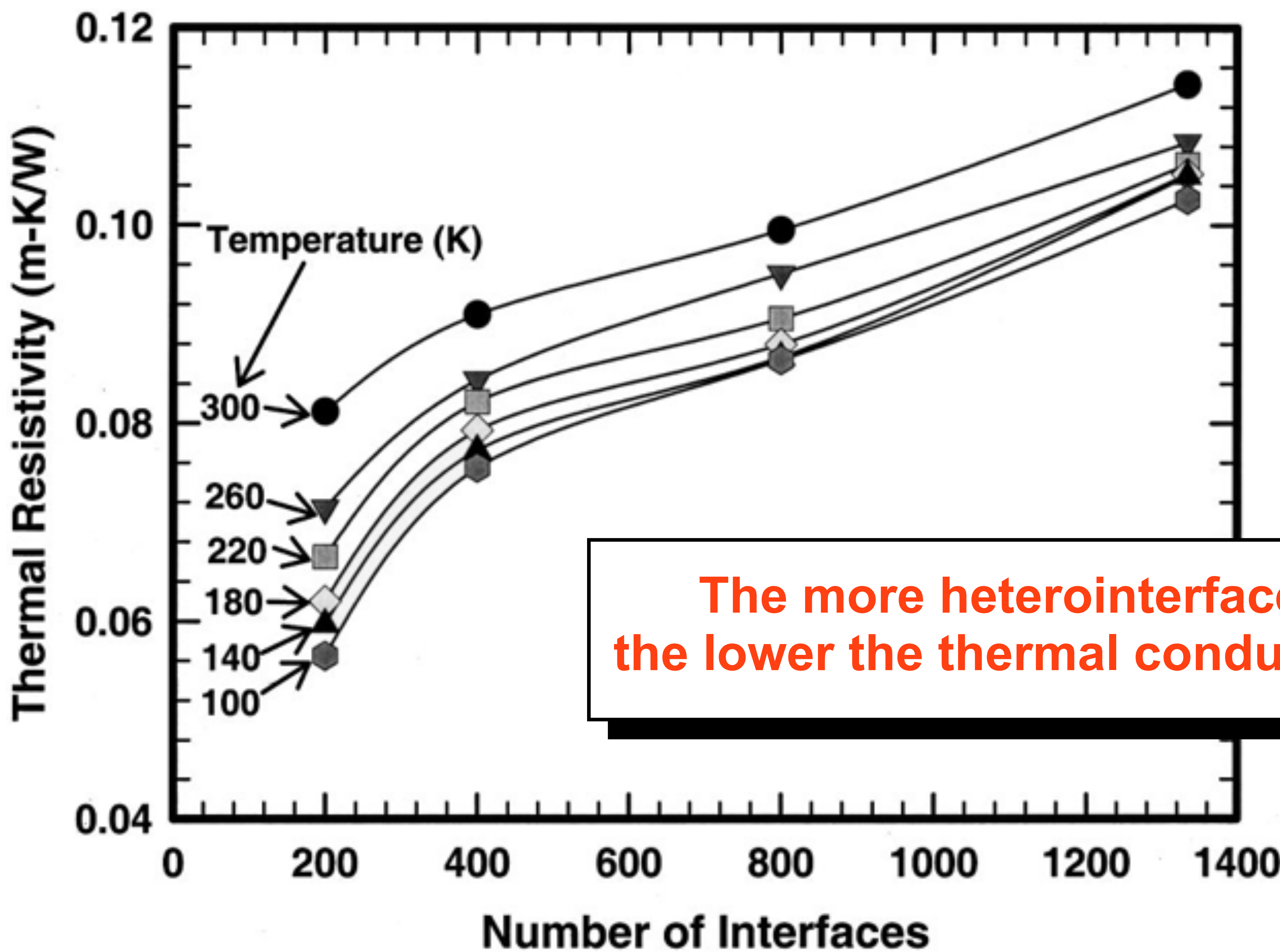




$Si_{0.5}Ge_{0.5}$ buffer

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

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



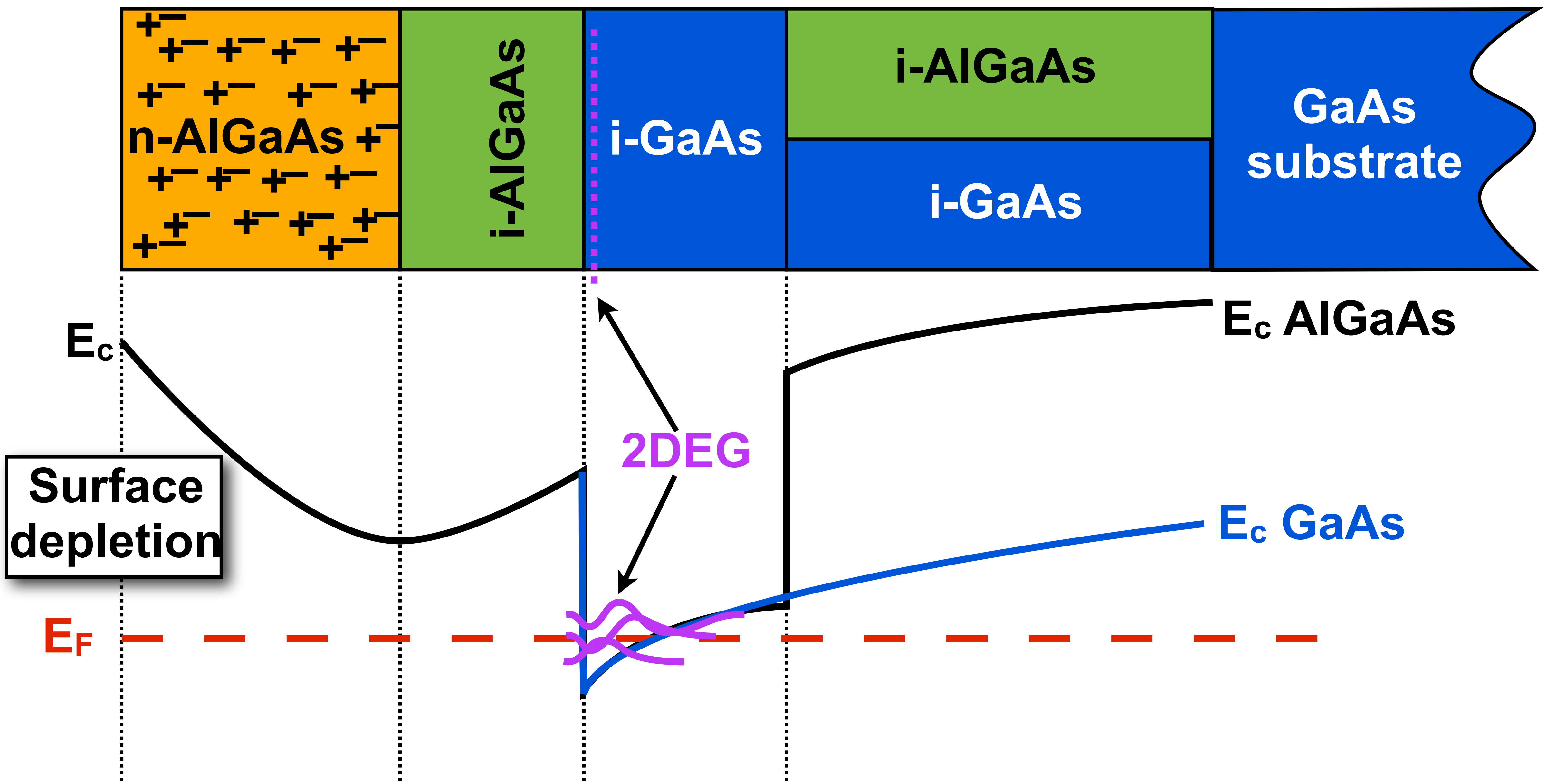
The more heterointerfaces,
the lower the thermal conductivity

- Physically: more heterointerfaces –> more phonon scattering

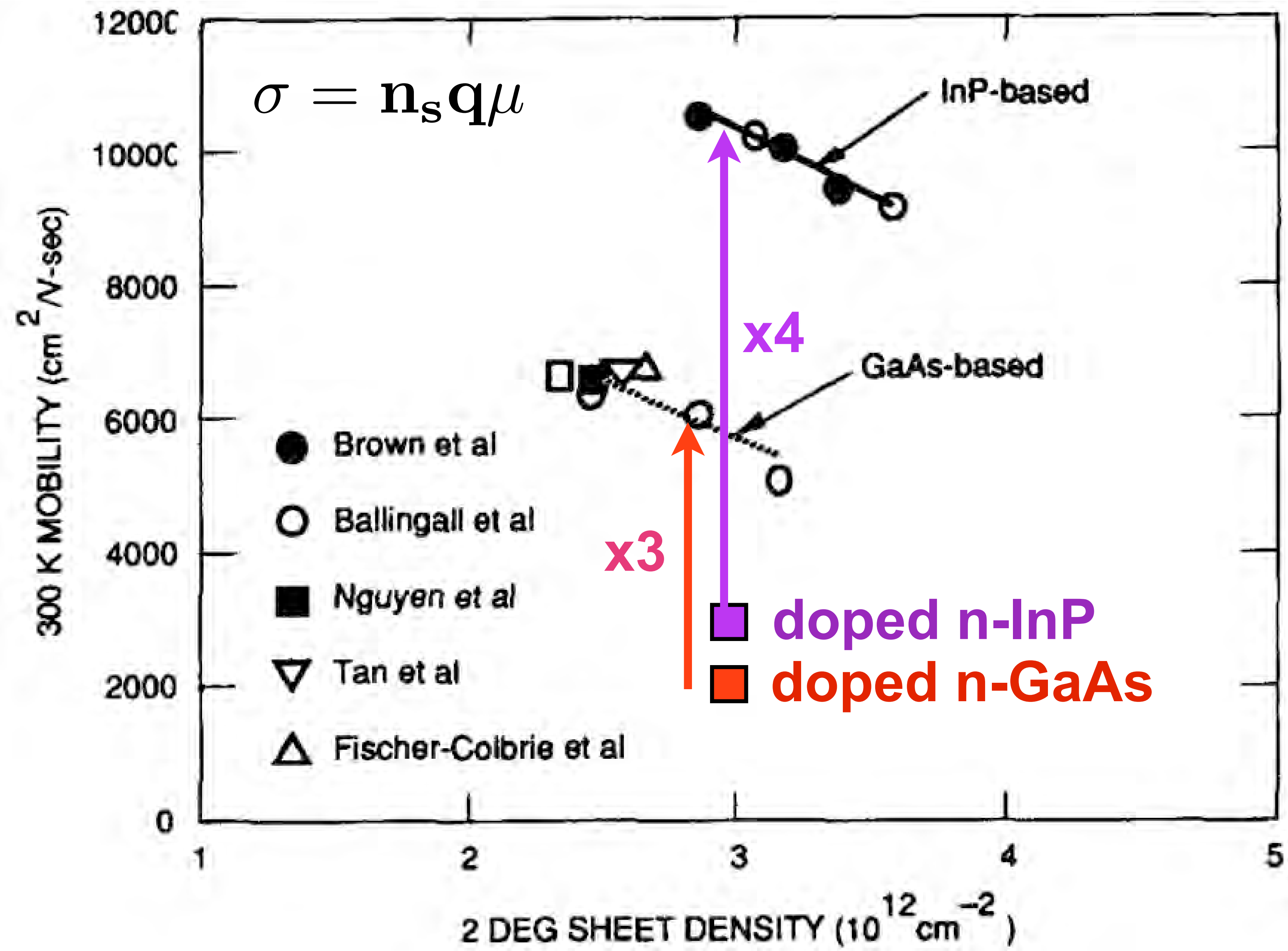
S. Huxtable et al., Appl. Phys. Lett. 80, 1737 (2002)

Modulation-Doping

Concept: Separate the electrons from the dopants which donate them to E_c –> reduce Coulombic scattering –> increase mobility

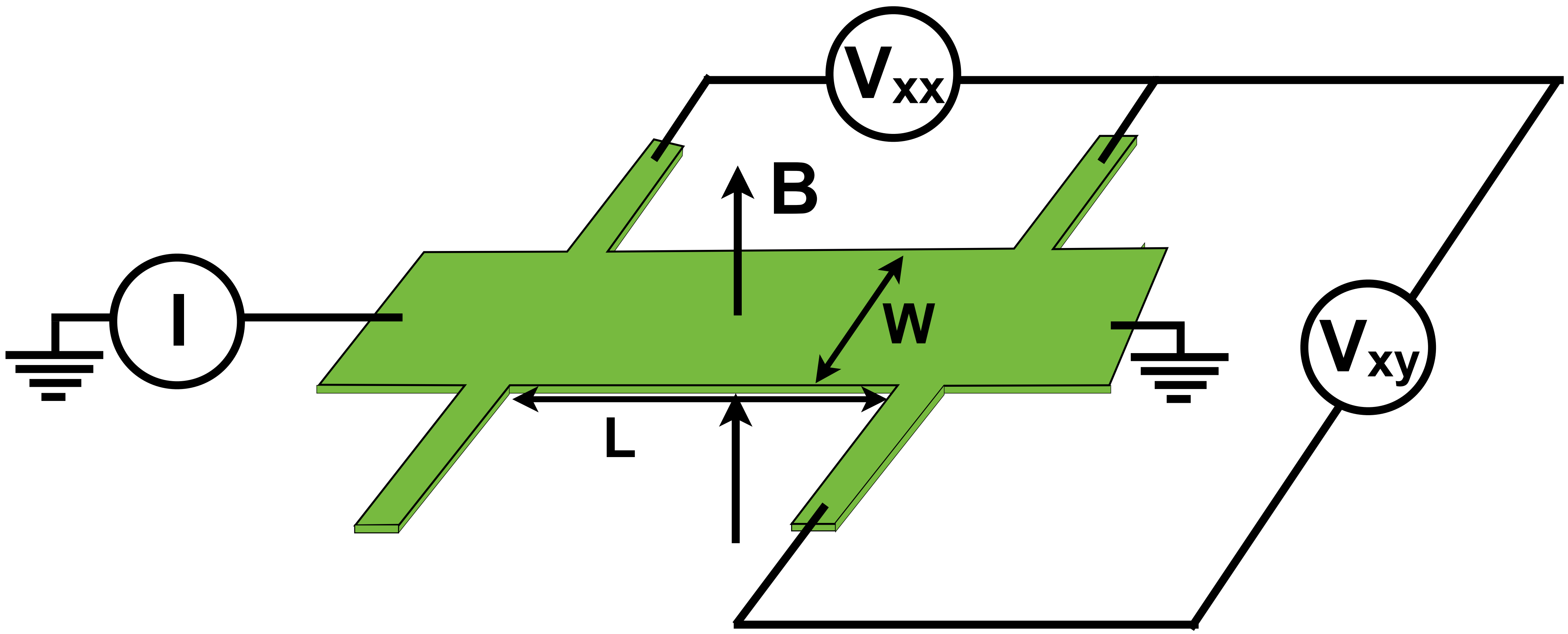


μ in Modulation-Doped Quantum Wells



- **For high densities, 2DEG mobility is significantly higher than bulk material**

Electrical Measurements: Hall Measurements

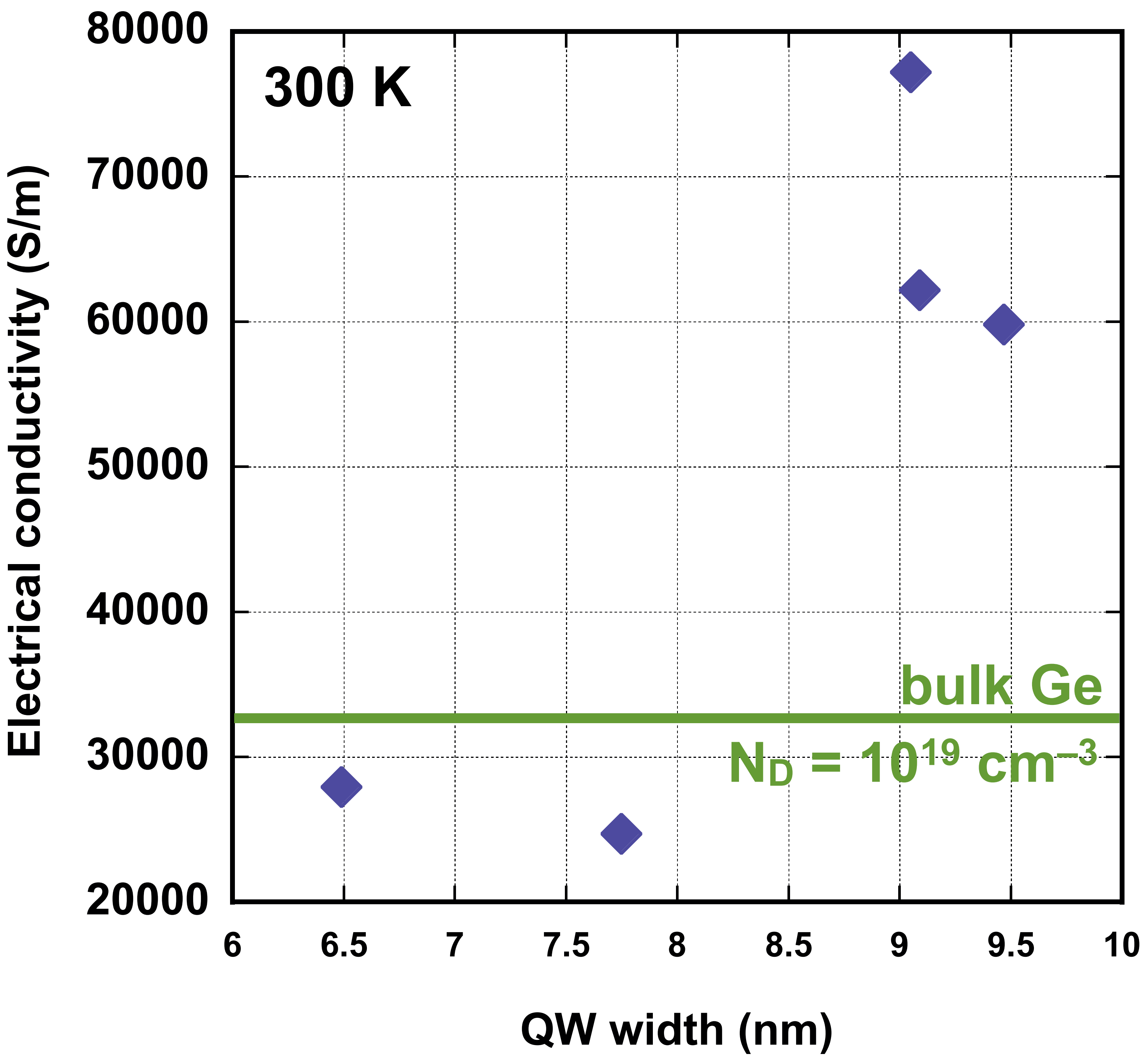


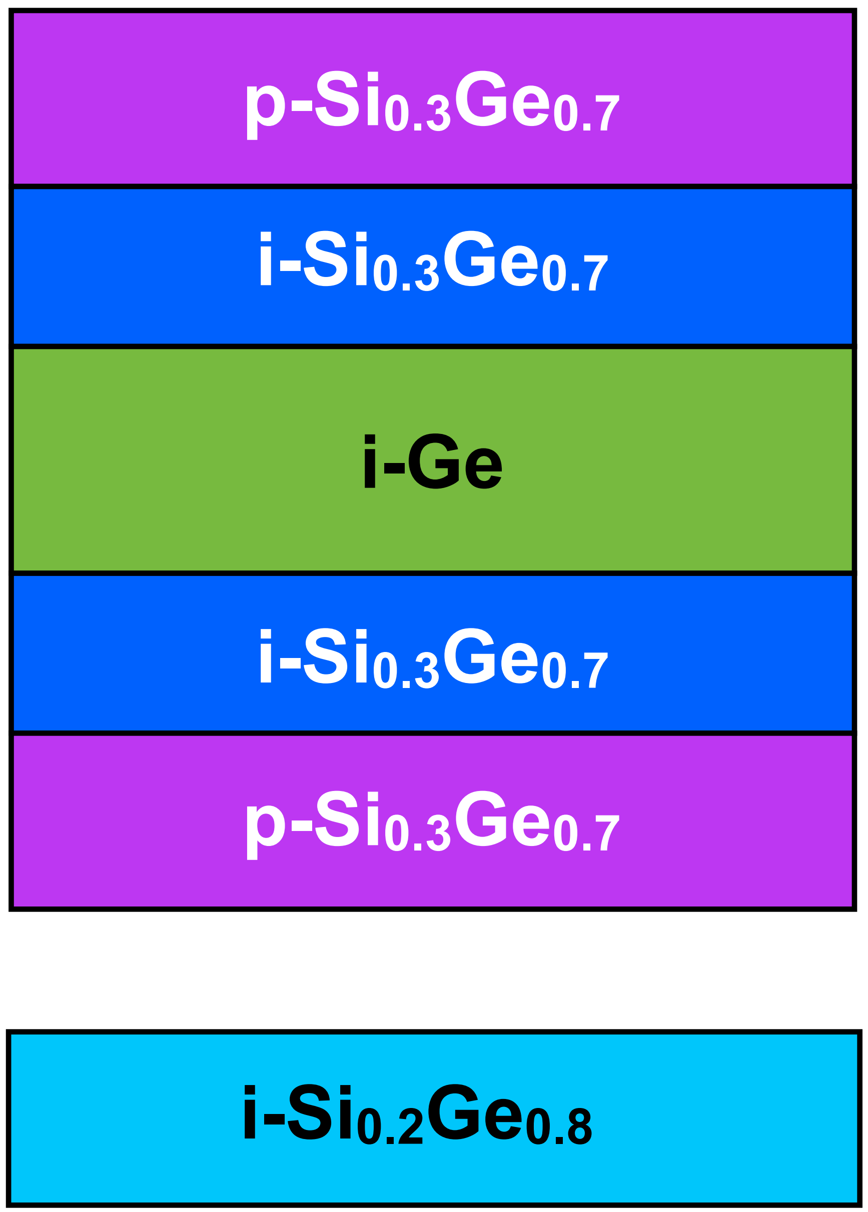
$$\sigma = \frac{\mathbf{IW}}{\mathbf{V_{xx}L}}$$

If L > 3W then Δσ < 10^{-3}

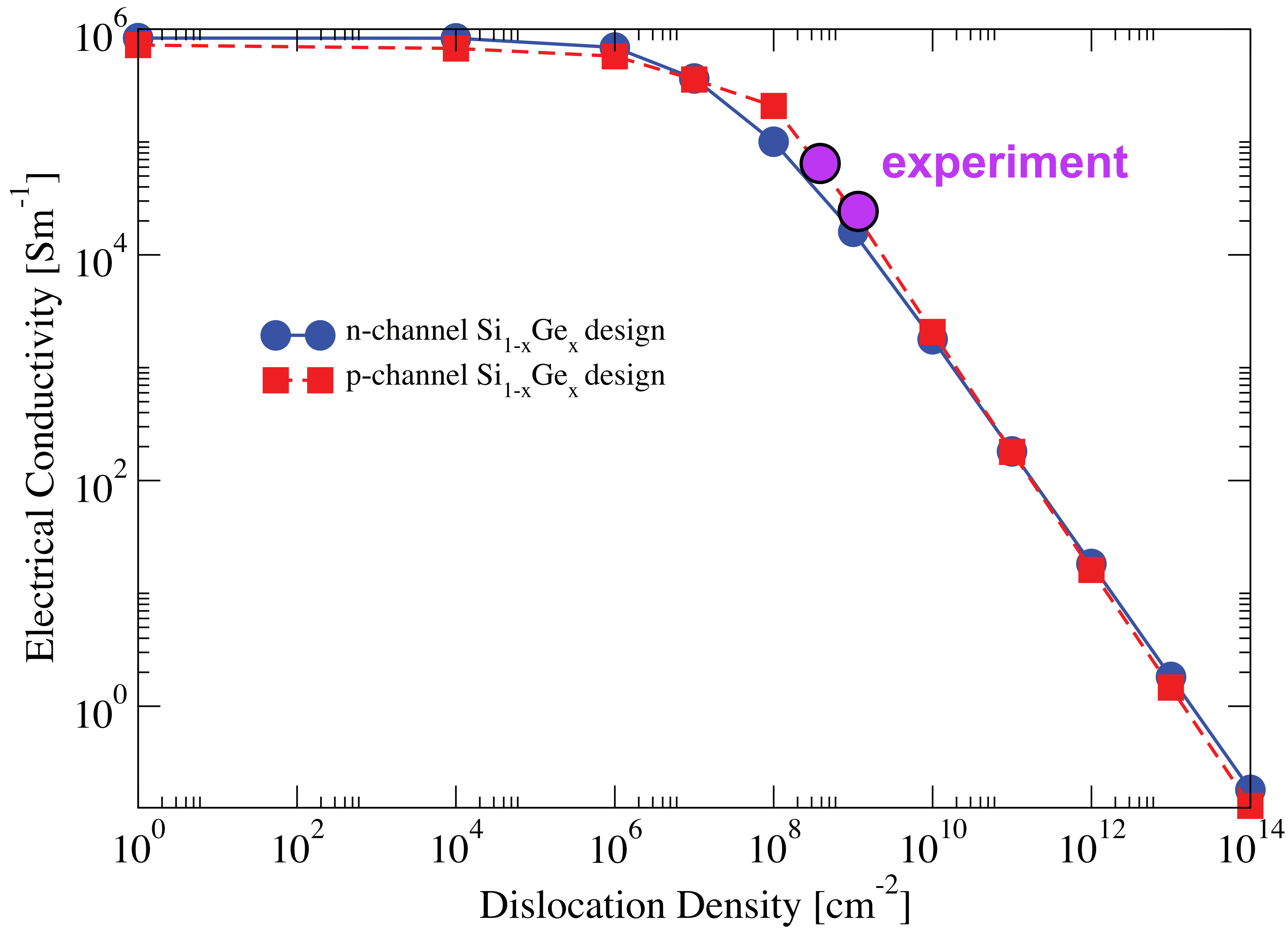
Application of magnetic field, B gives carrier density and mobility through V_{xy} measurement

Electrical Conductivity vs QW Width



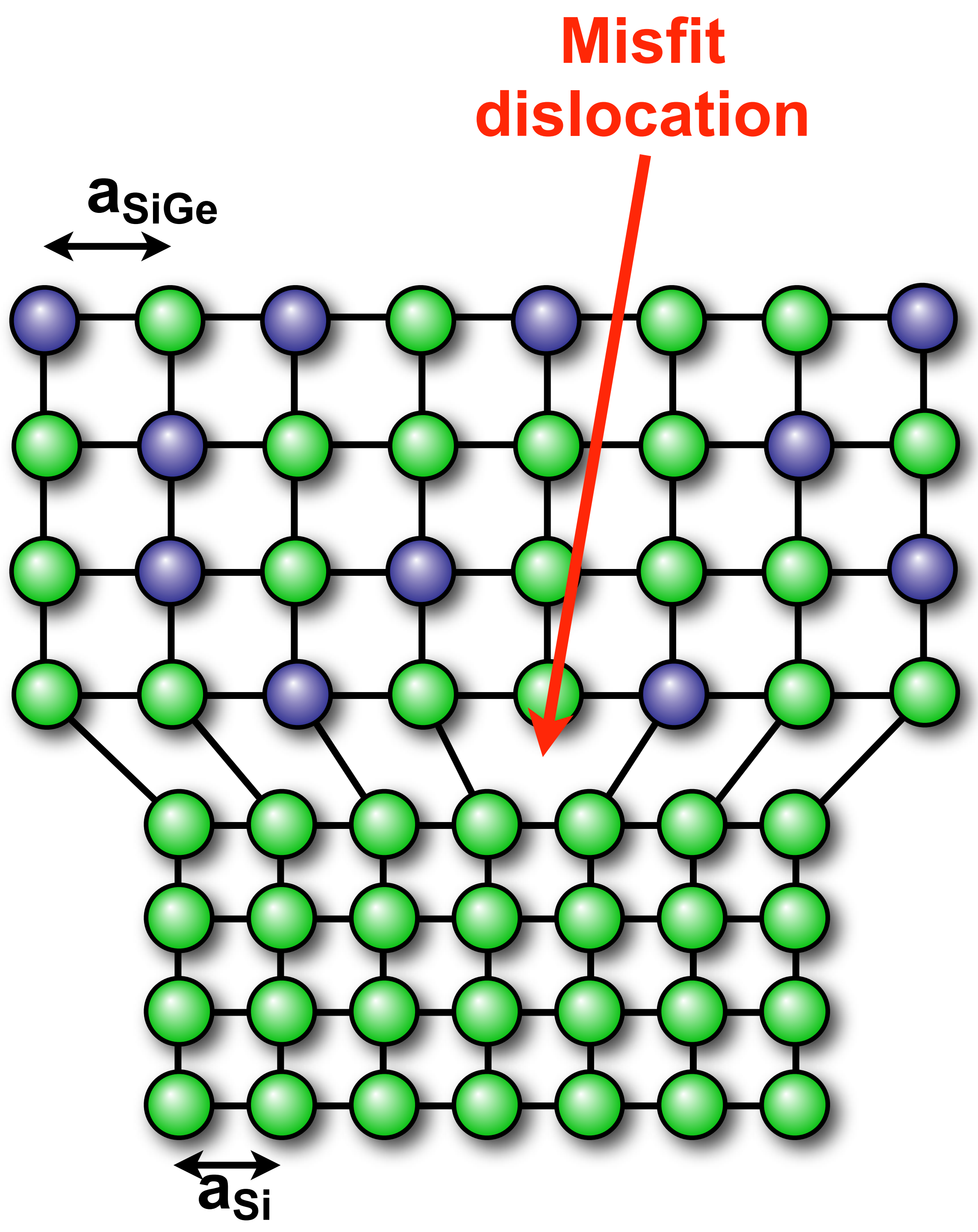


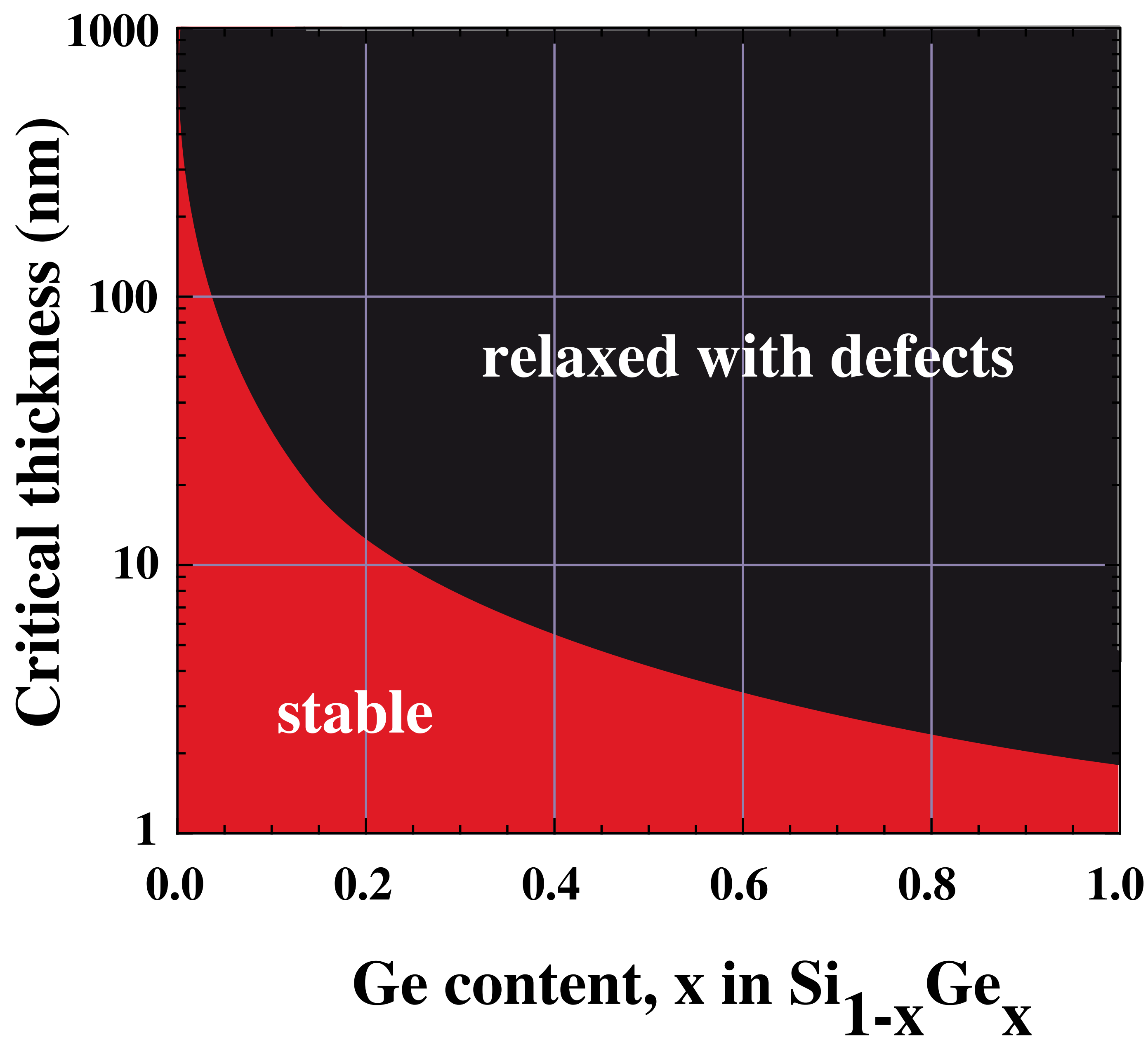
Electrical Conductivity vs Dislocation Density



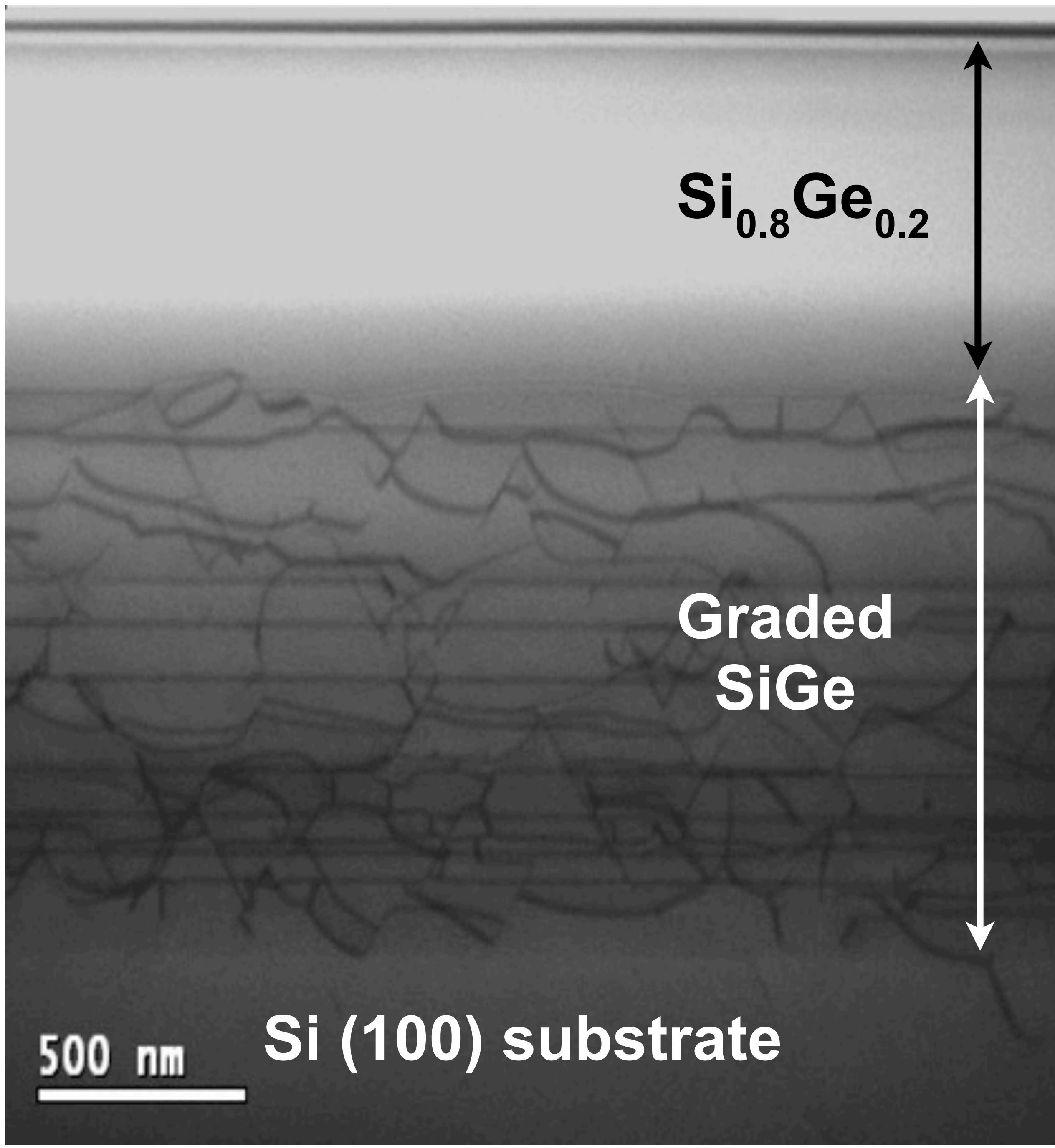
J.R. Watling & D.J. Paul, J. Appl. Phys. 110, 114508 (2011)

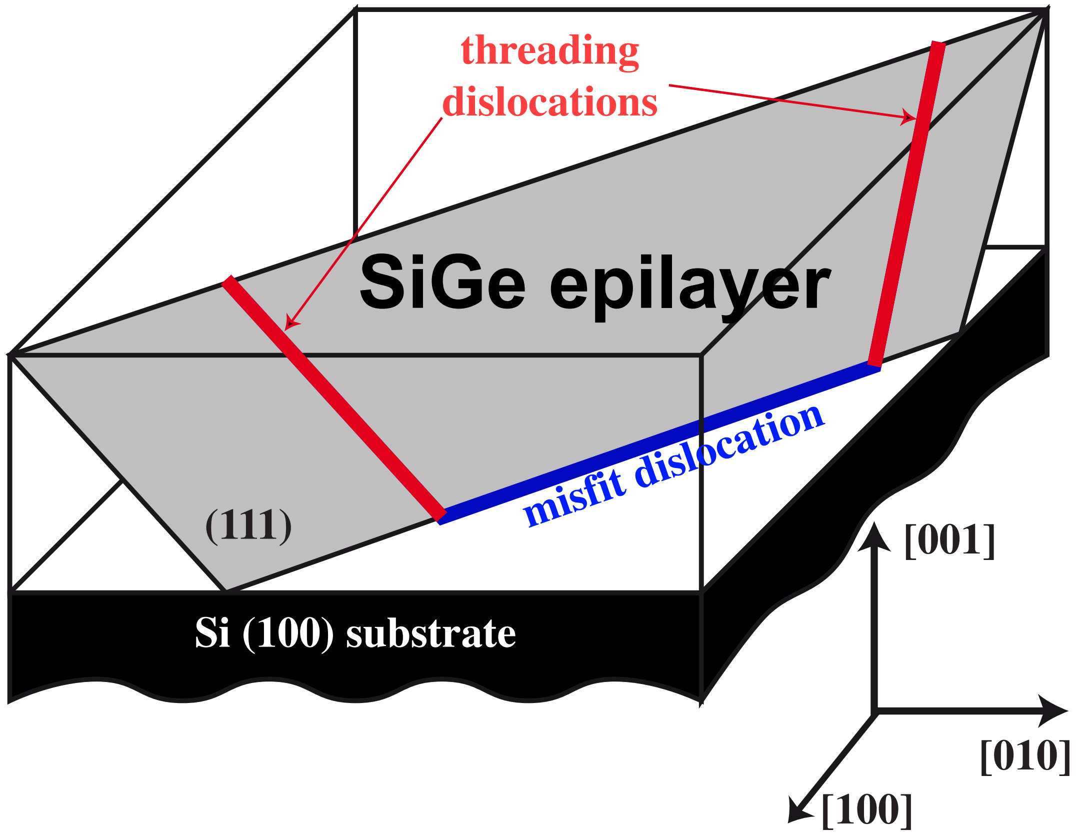
Critical Thickness for Pseudomorphic Layers



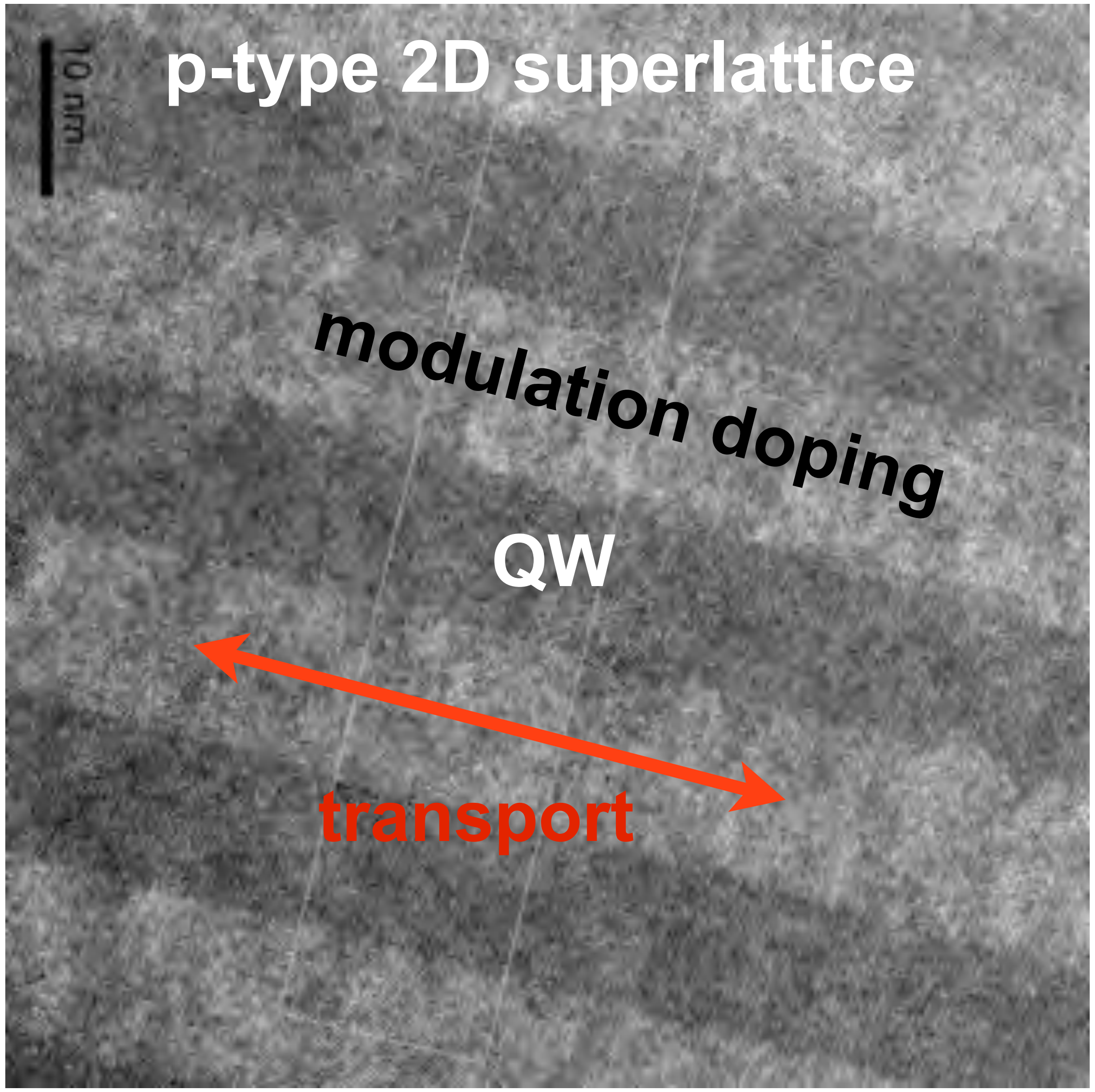


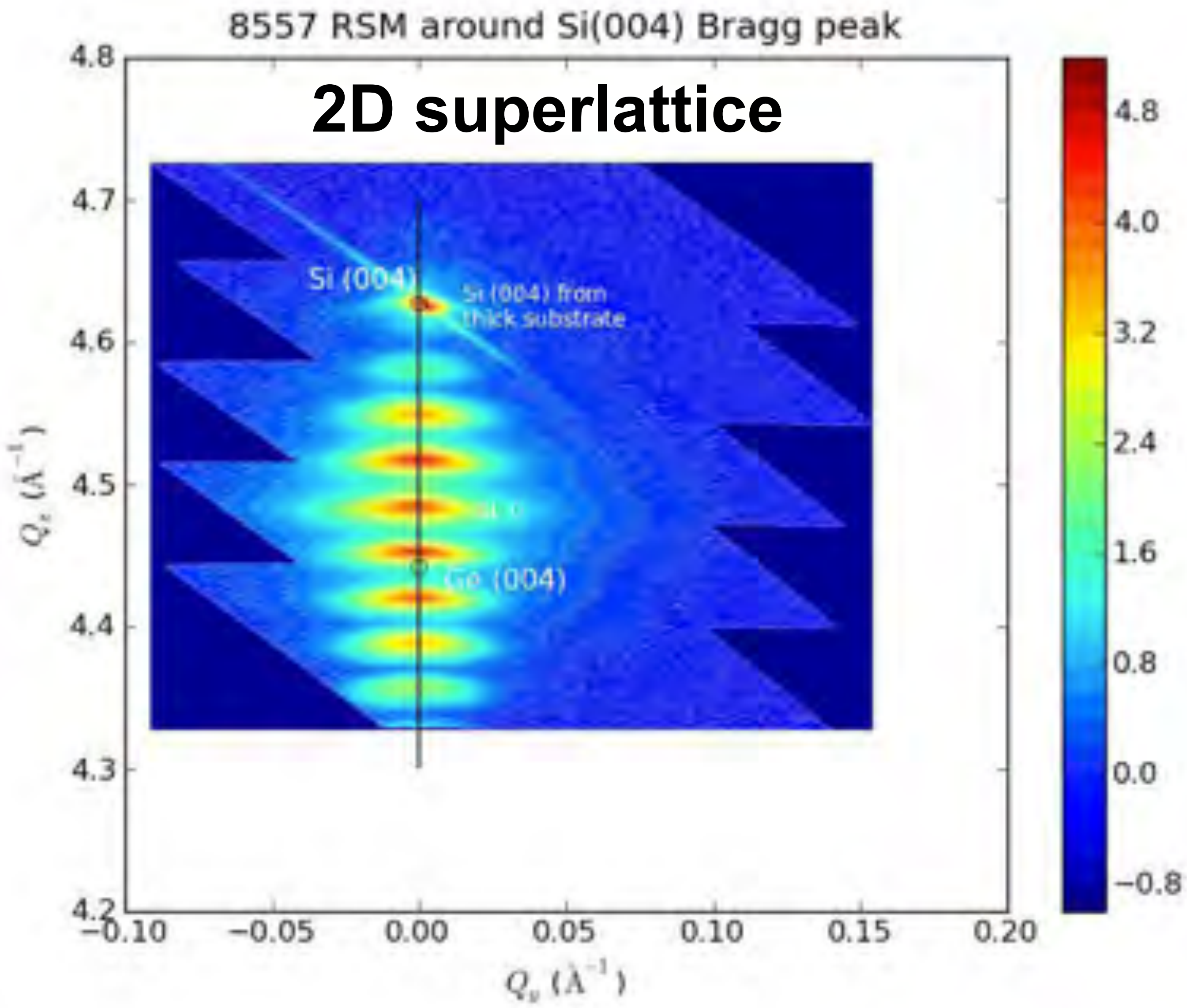
TEM of SiGe Strain Relaxation Buffer





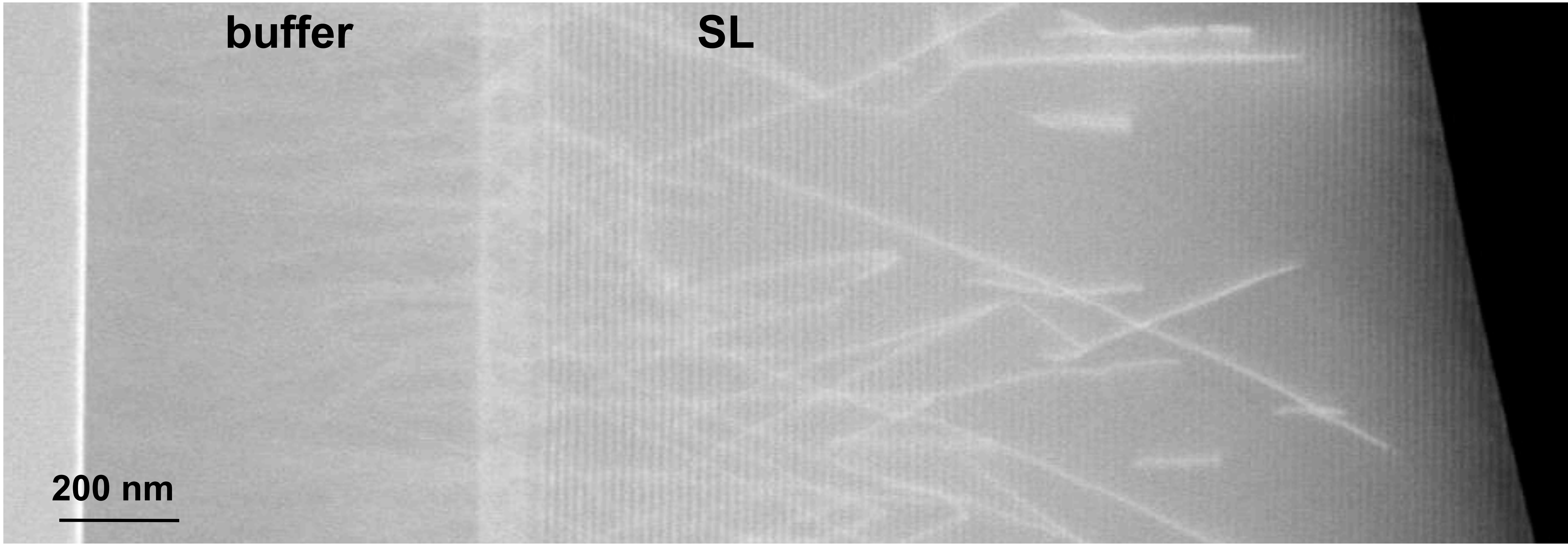
Modulation Doped Si/SiGe





- **TEM & XRD characterisation of first 2D modulation-doped superlattice designs**
- **Threading dislocation densities from 10^8 to 10^9 cm^{-2}**

TEM-characterisation

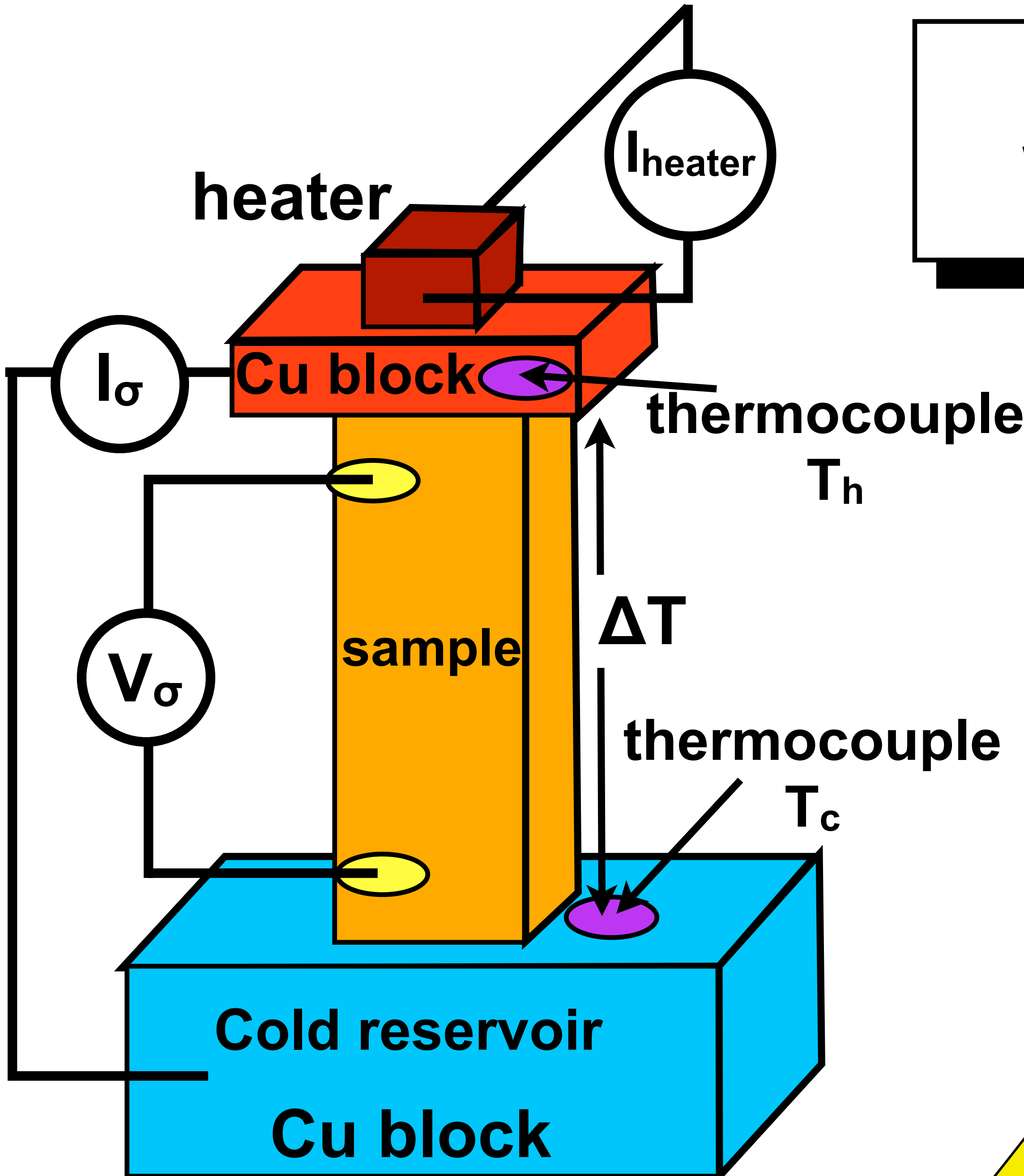


DF STEM:
sample 8569 B6

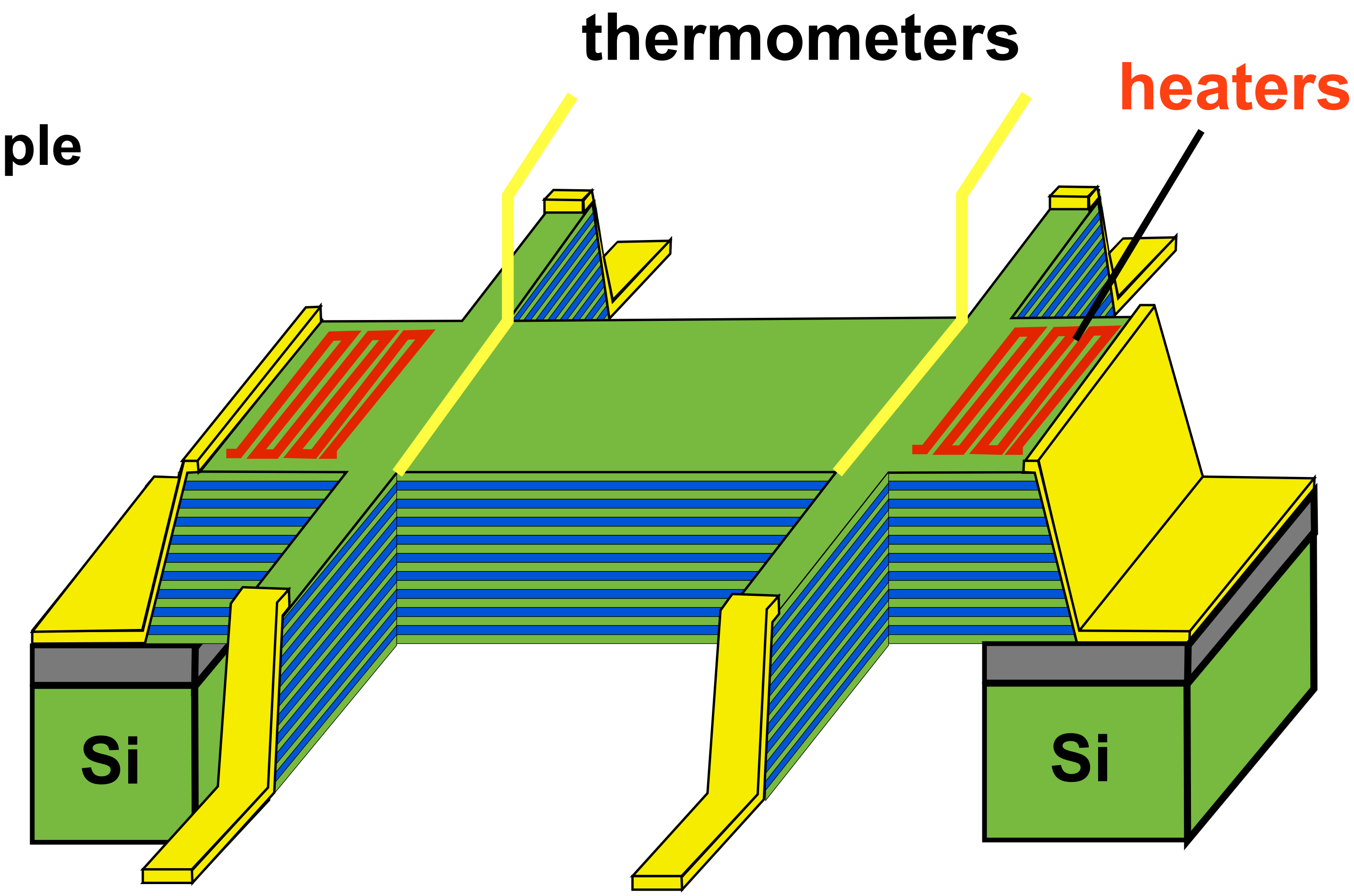
- **Threading dislocations penetrating from the buffer to the superlattice**
- **Intermediate layer not able to stop the dislocations to cross the interface from buffer to SL –> new design**
- **Threading dislocation density ~3x10^9 cm^{-2}**

Measuring Seebeck and Thermal Conductivity

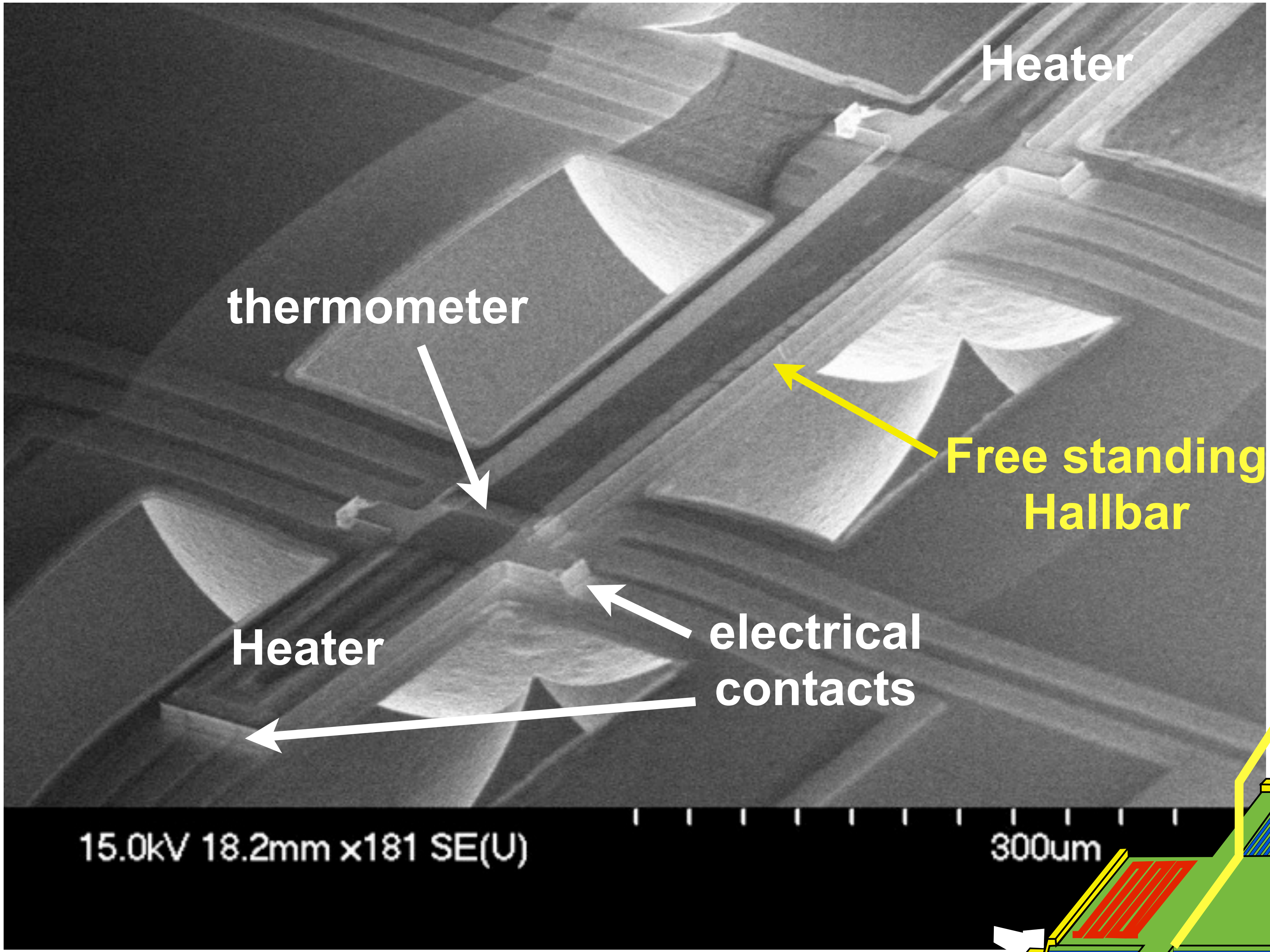
Seebeck coefficient, $\alpha = \frac{\mathbf{dV}}{\mathbf{dT}}$

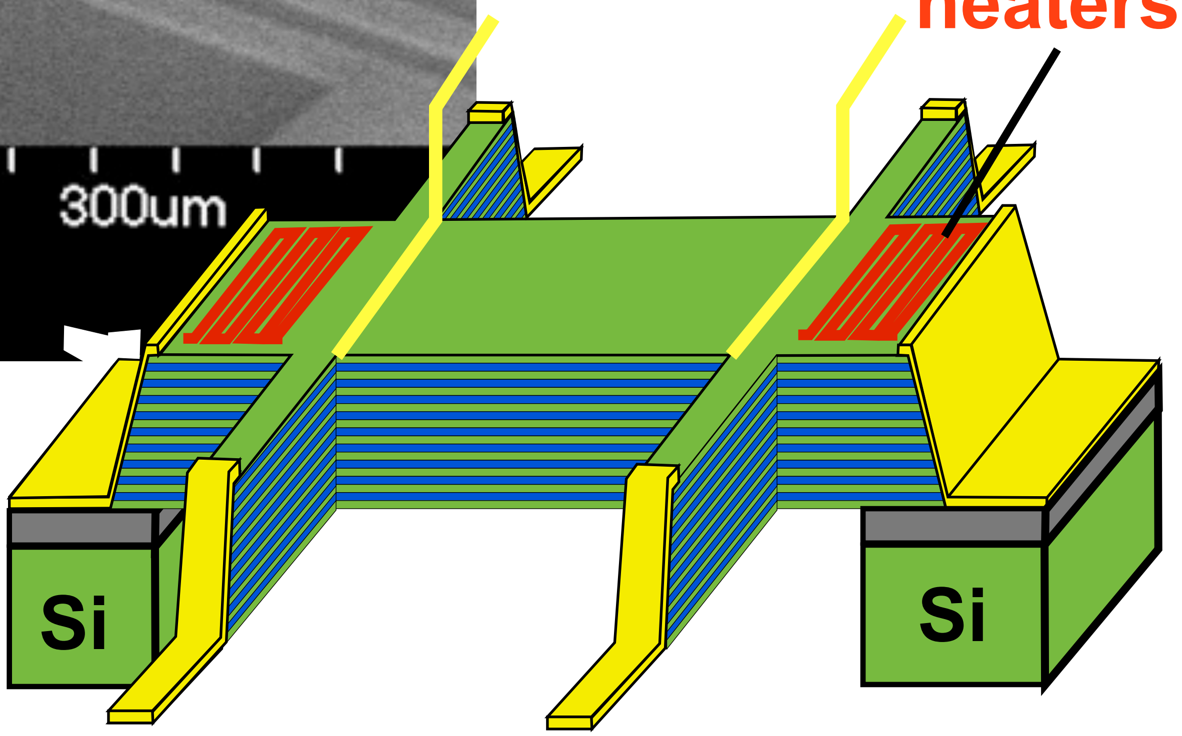


$$\mathbf{Q} = -\kappa \mathbf{A} \frac{\mathbf{T_c} - \mathbf{T_h}}{\mathbf{L}}$$



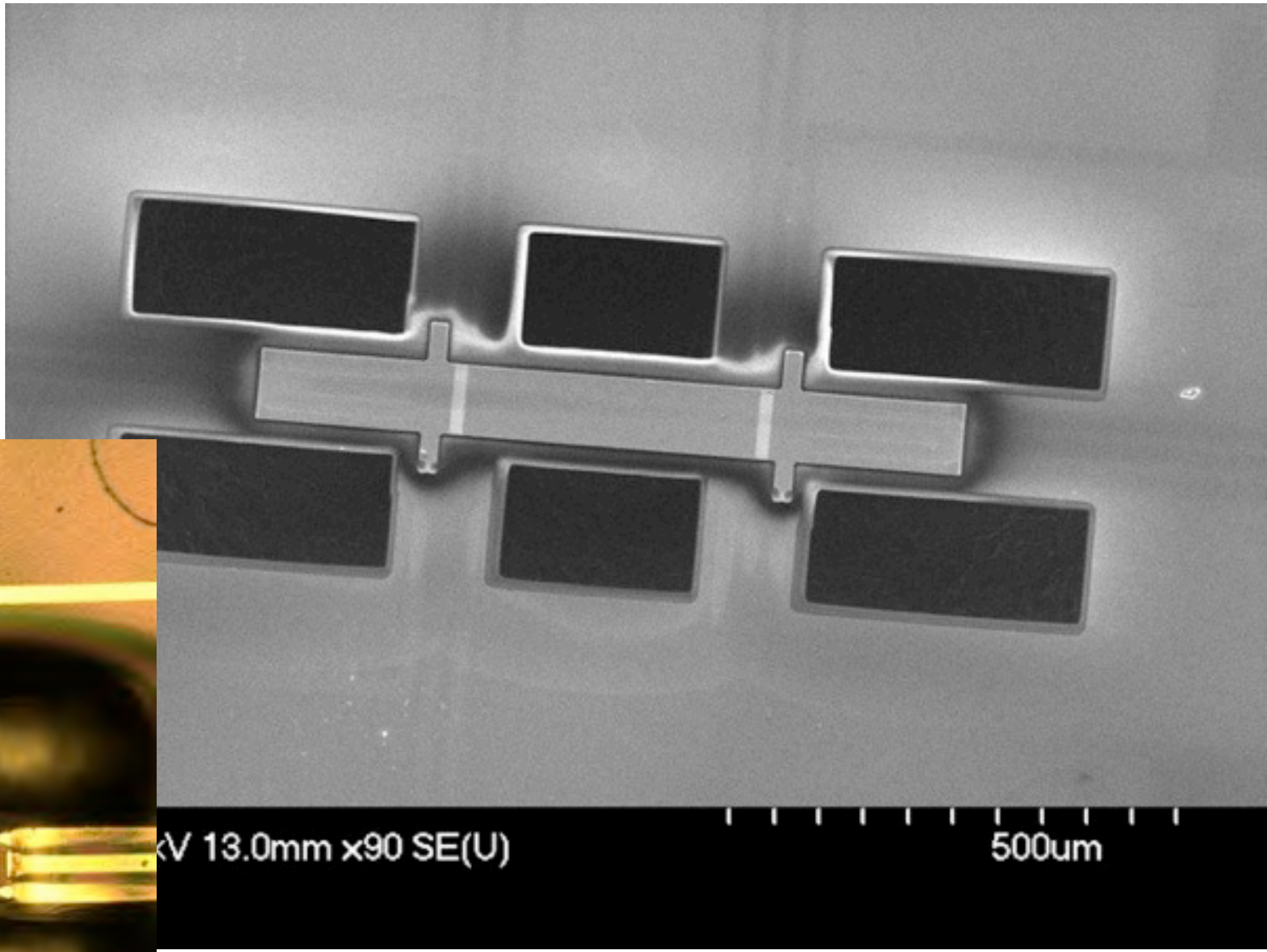
Free Standing Hallbars

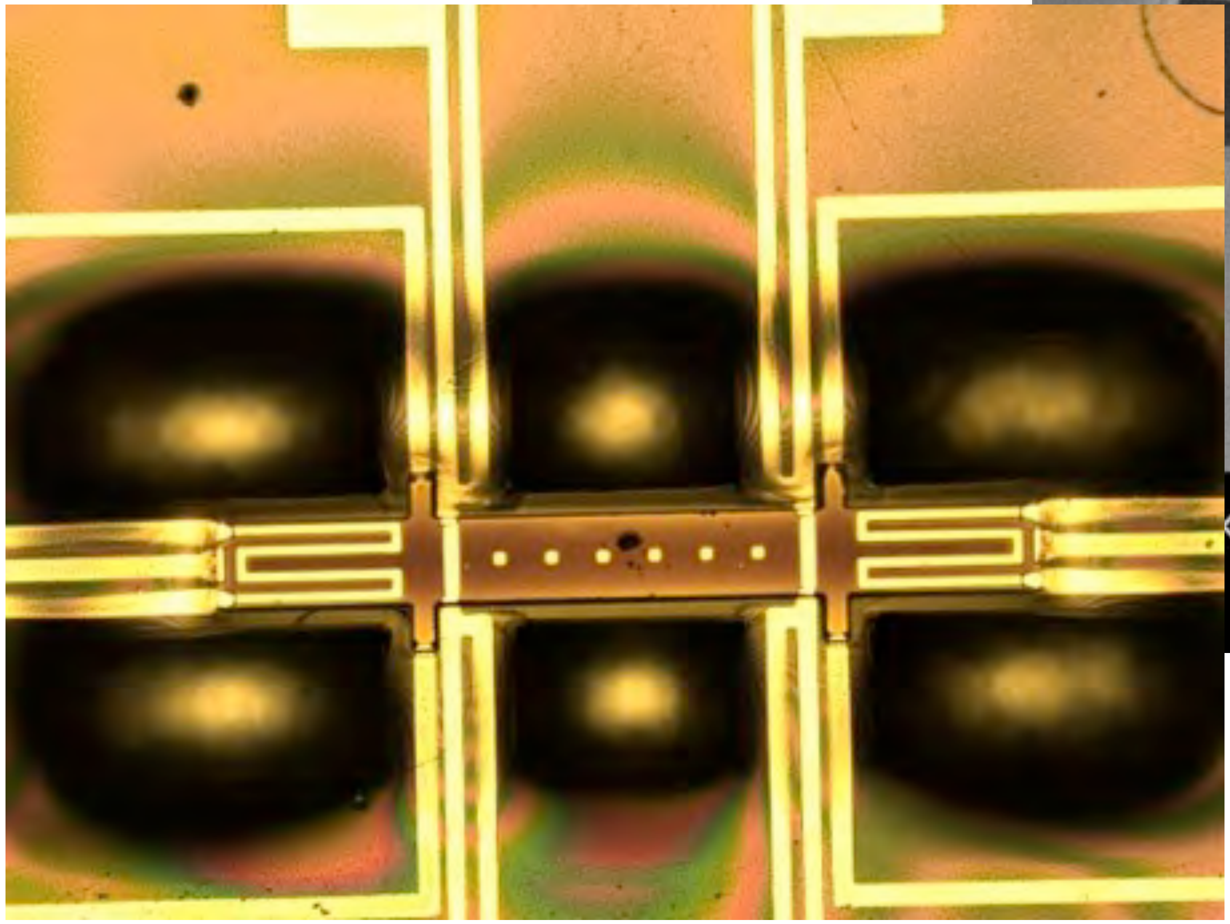




Suspended Hallbar

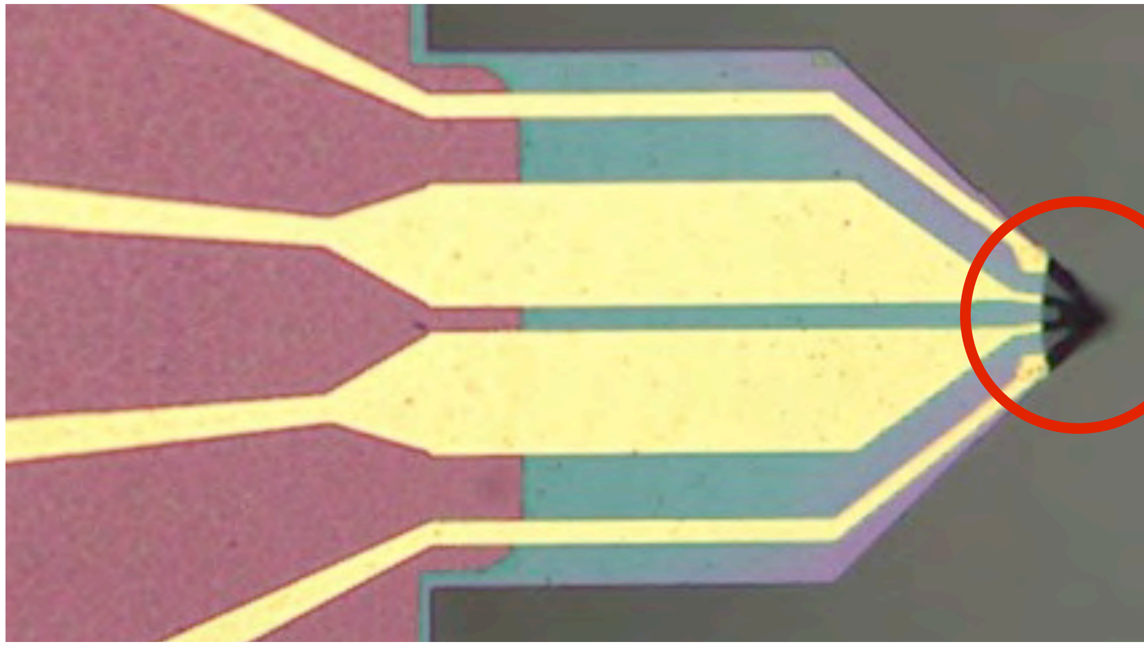
8579 lateral structure suspended membranes

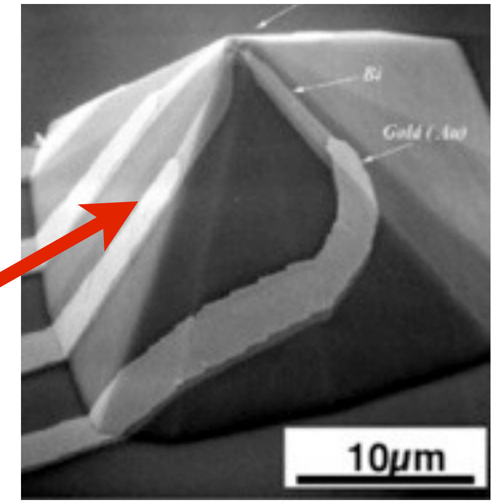


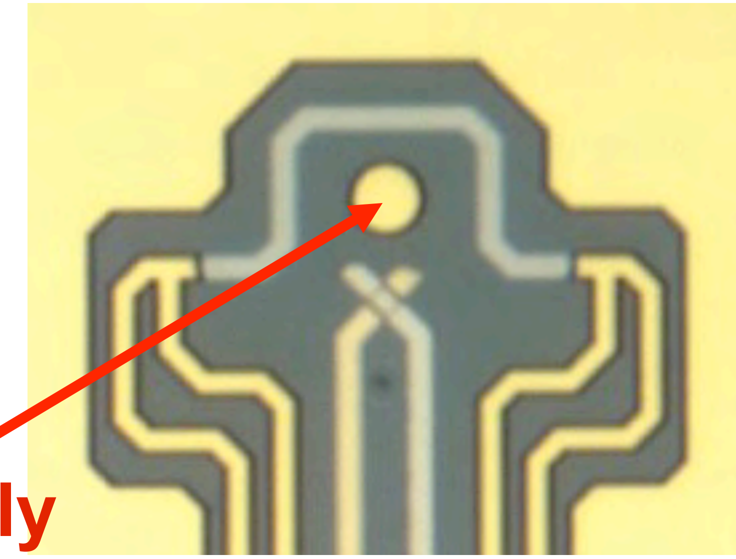


- **High electrical conductivity of σ = 79,000 ± 3000 S/m at 300 K**

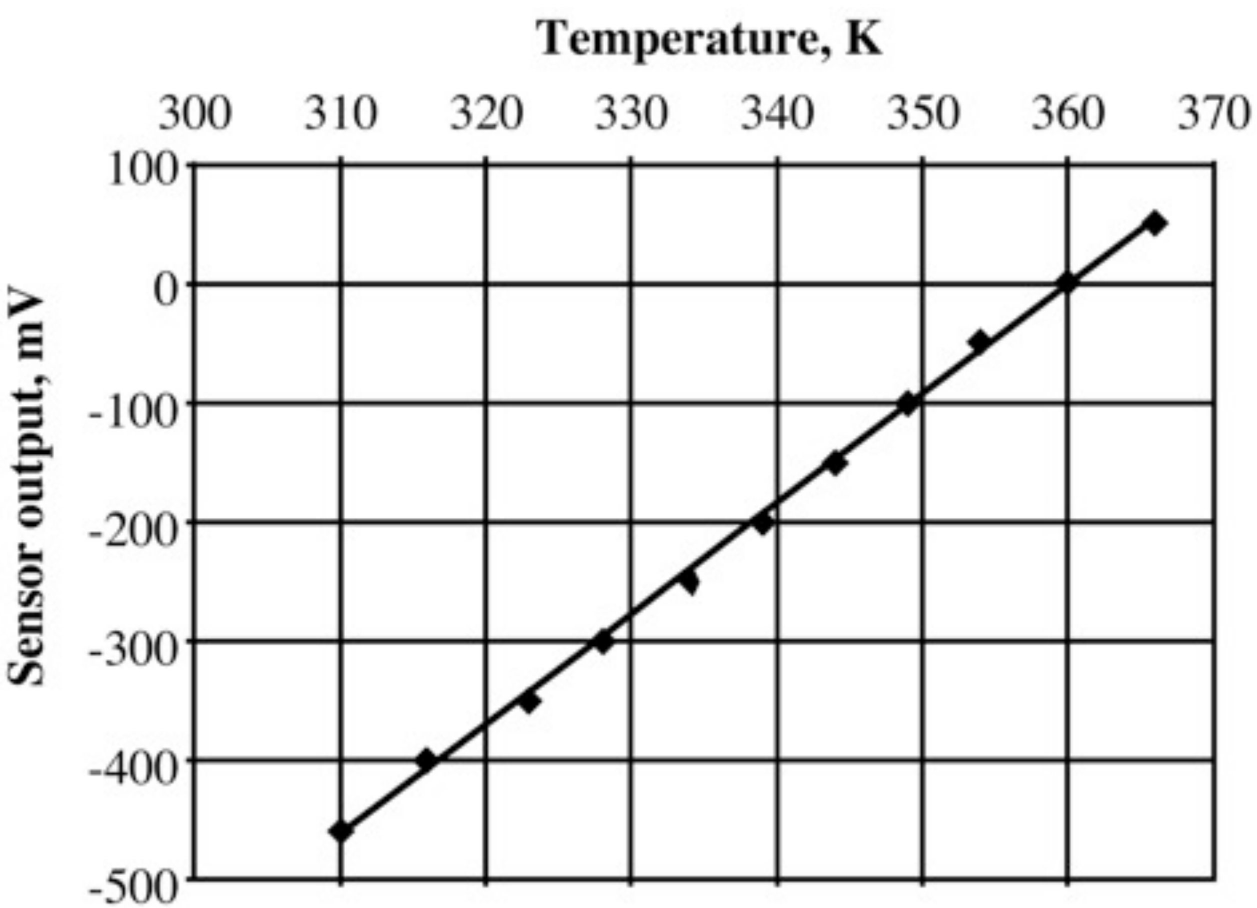
Scanning Thermal Microscopy

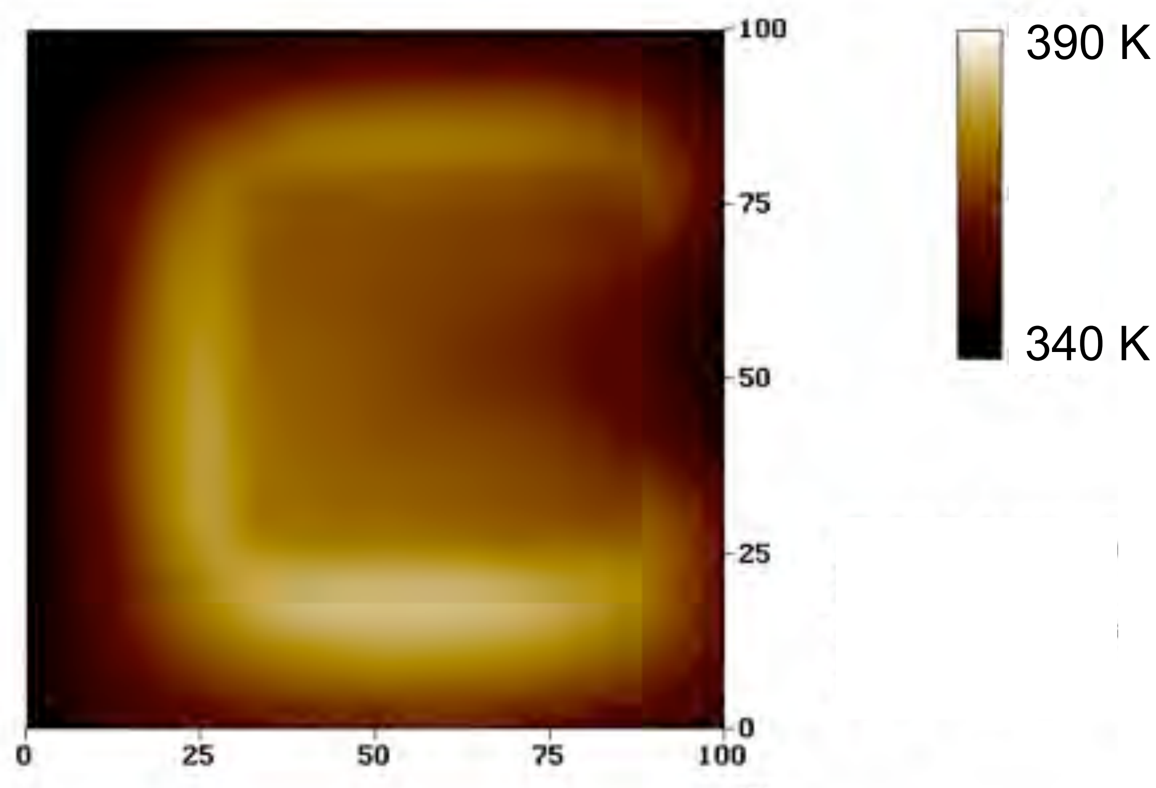






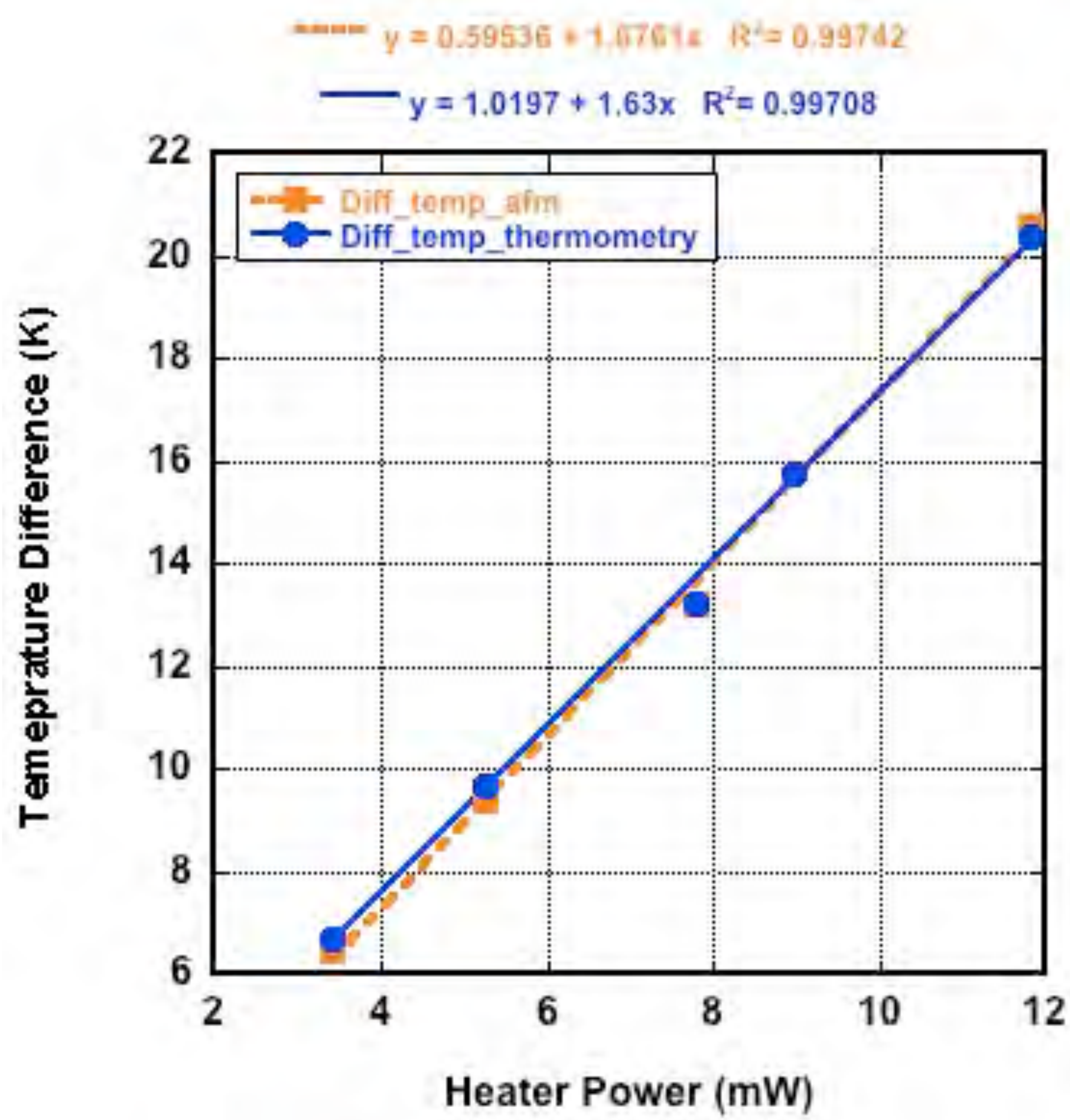
Electrically isolated Au spot: isothermal with resistor

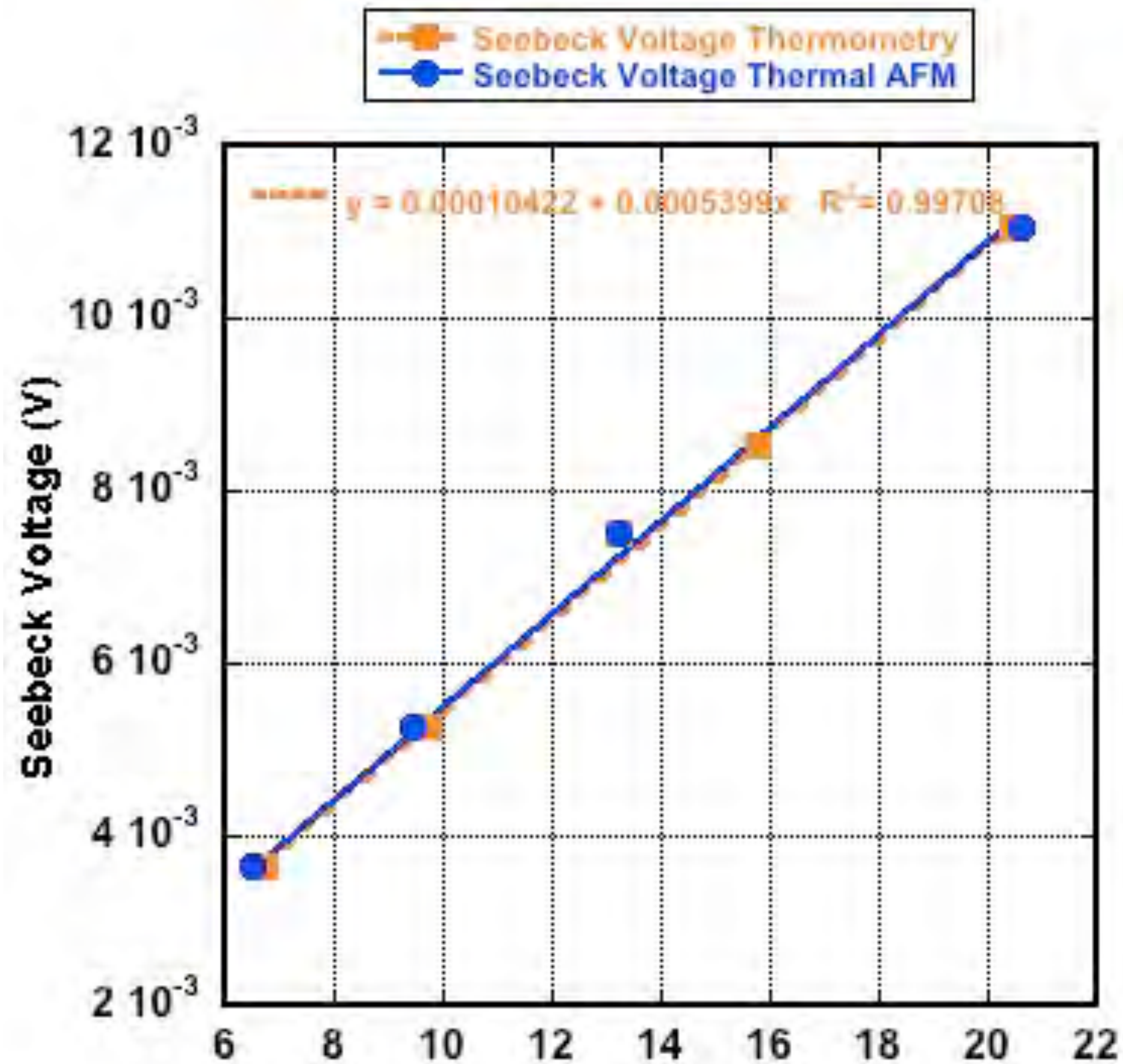




P. S. Dobson, et al., Rev. Sci. Inst. 76, 054901 (2006)

Seebeck Measurements Compared



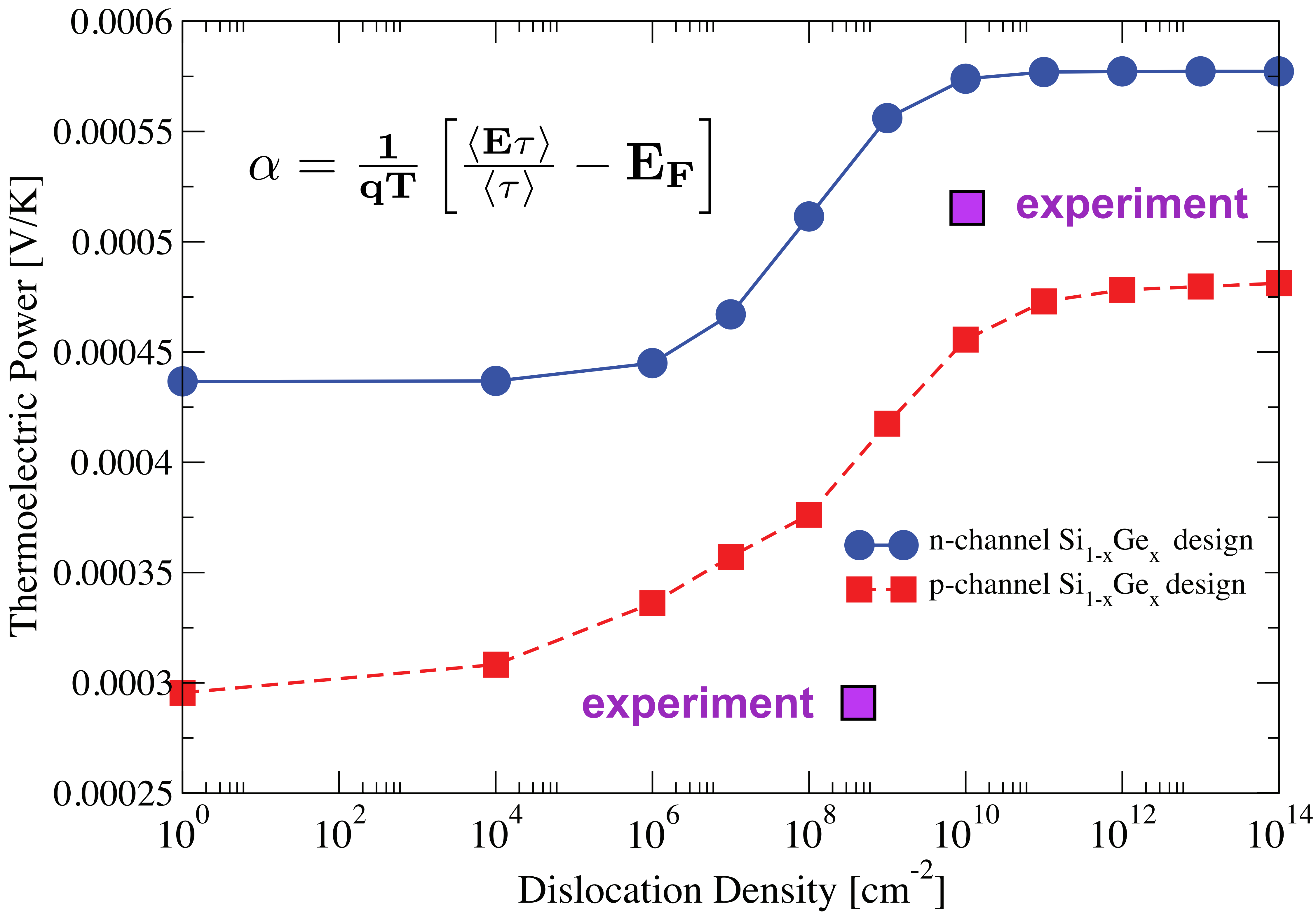


Temperature Difference (K)

$\alpha = 540 \pm 2\ \mu V / K$ at 300 K

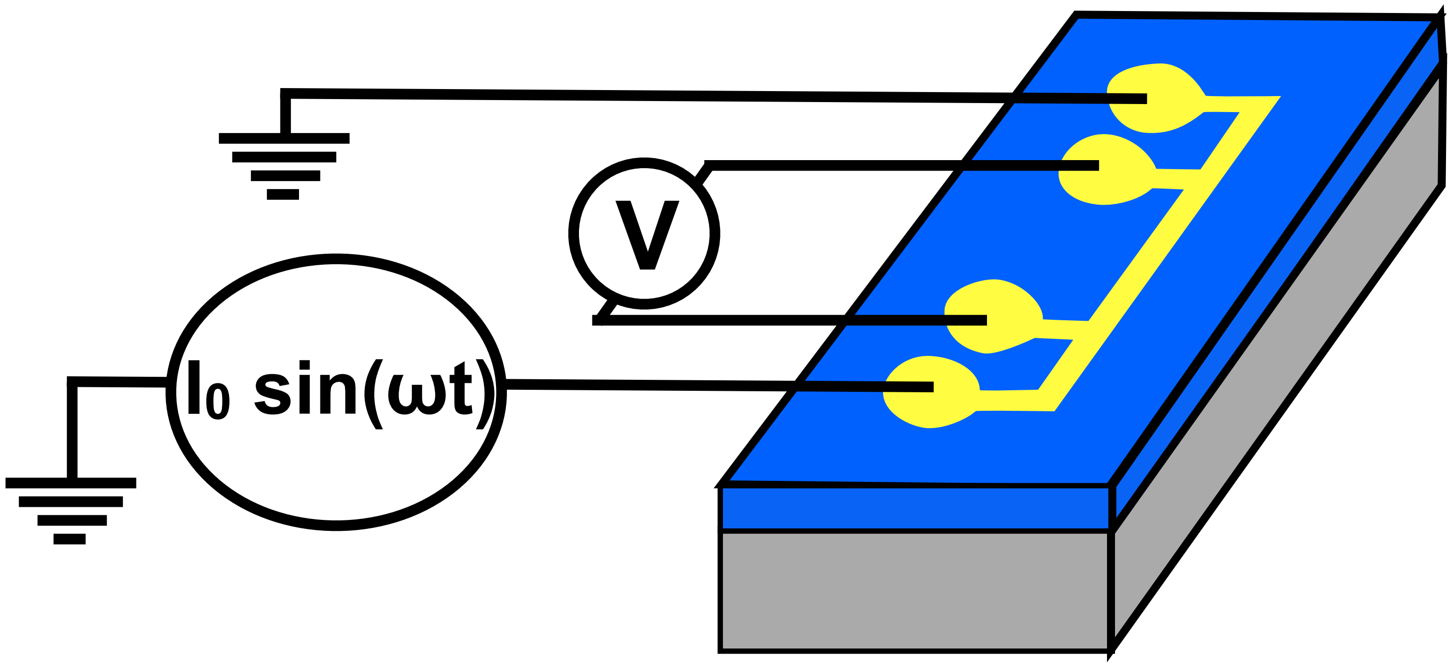
Calibrated thermometers and thermal AFM agree within 0.1%

Seebeck Coefficient versus Dislocation Density



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

3ω Thermal Conductivity Measurements



I ~ ω

T ~ I^2 ~ 2ω

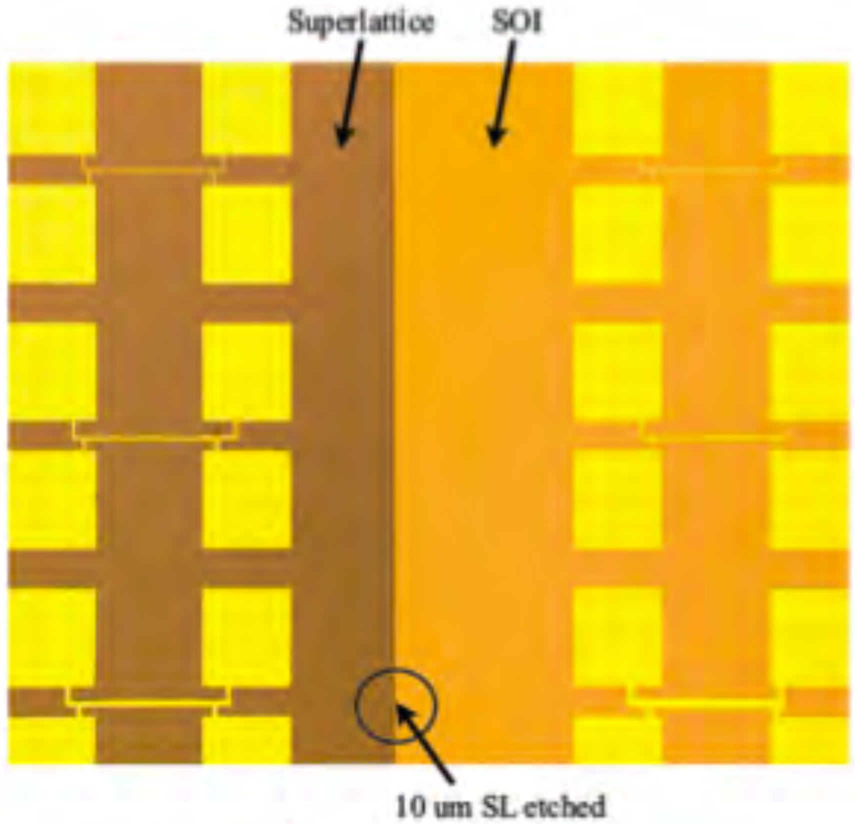
R ~ T ~ 2ω

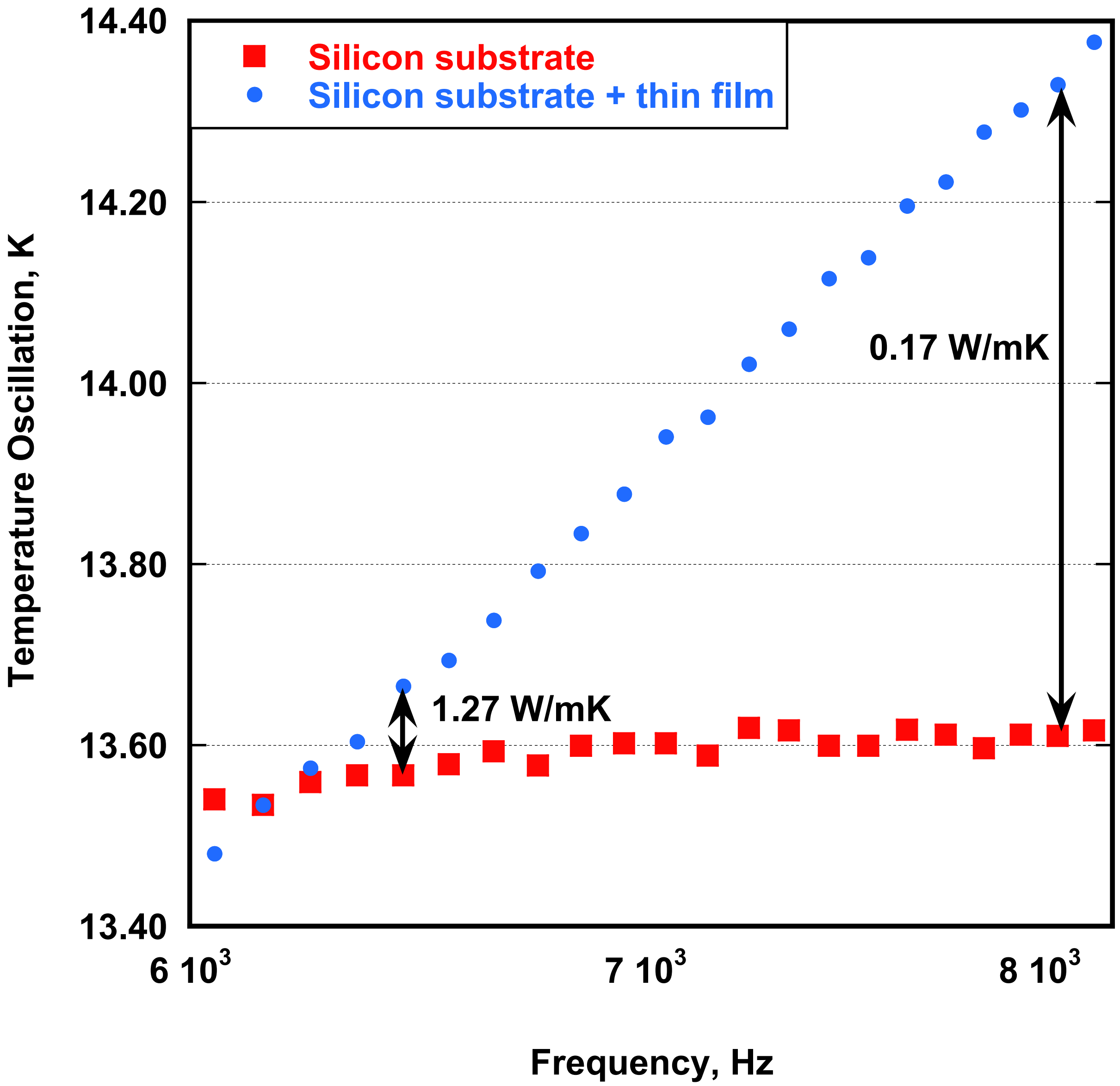
V = IR ~ 3ω

- **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

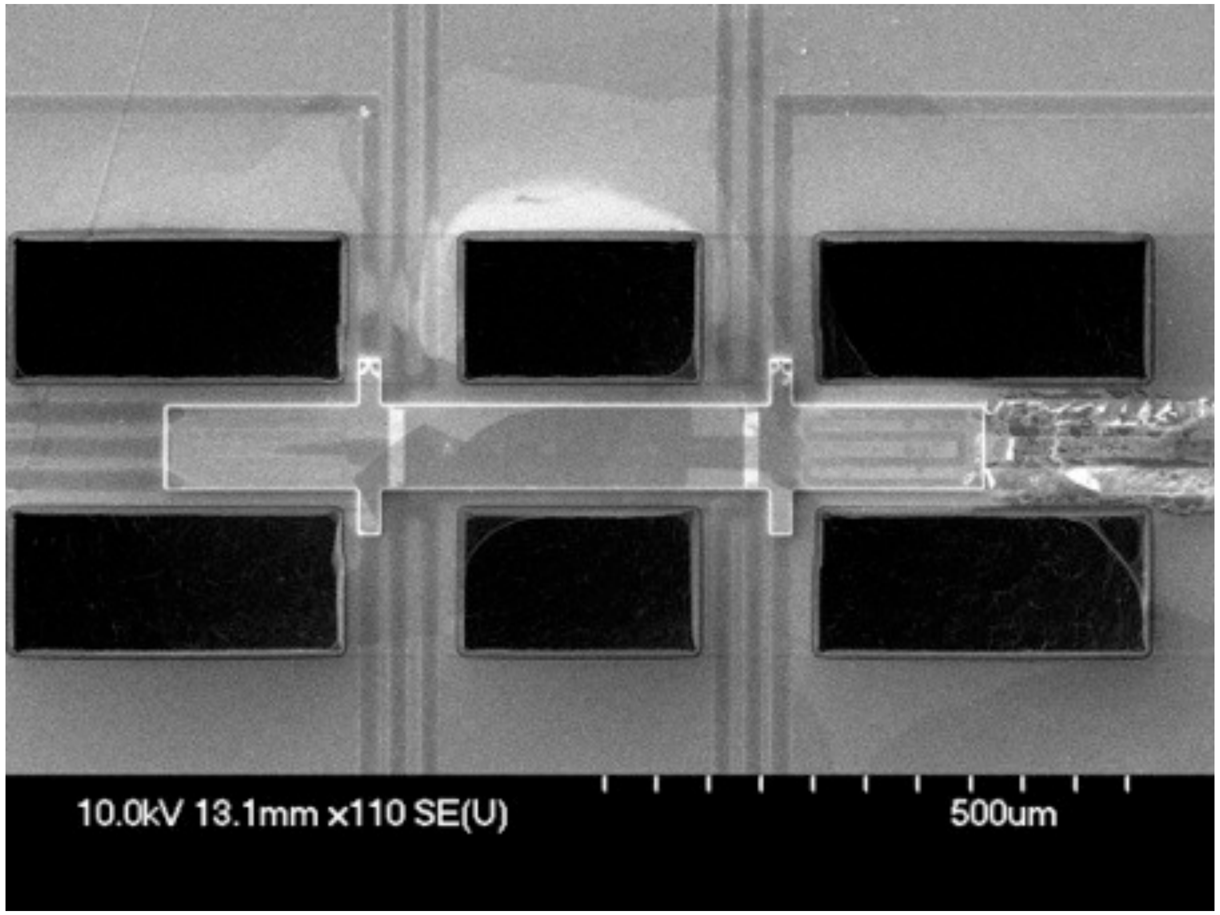




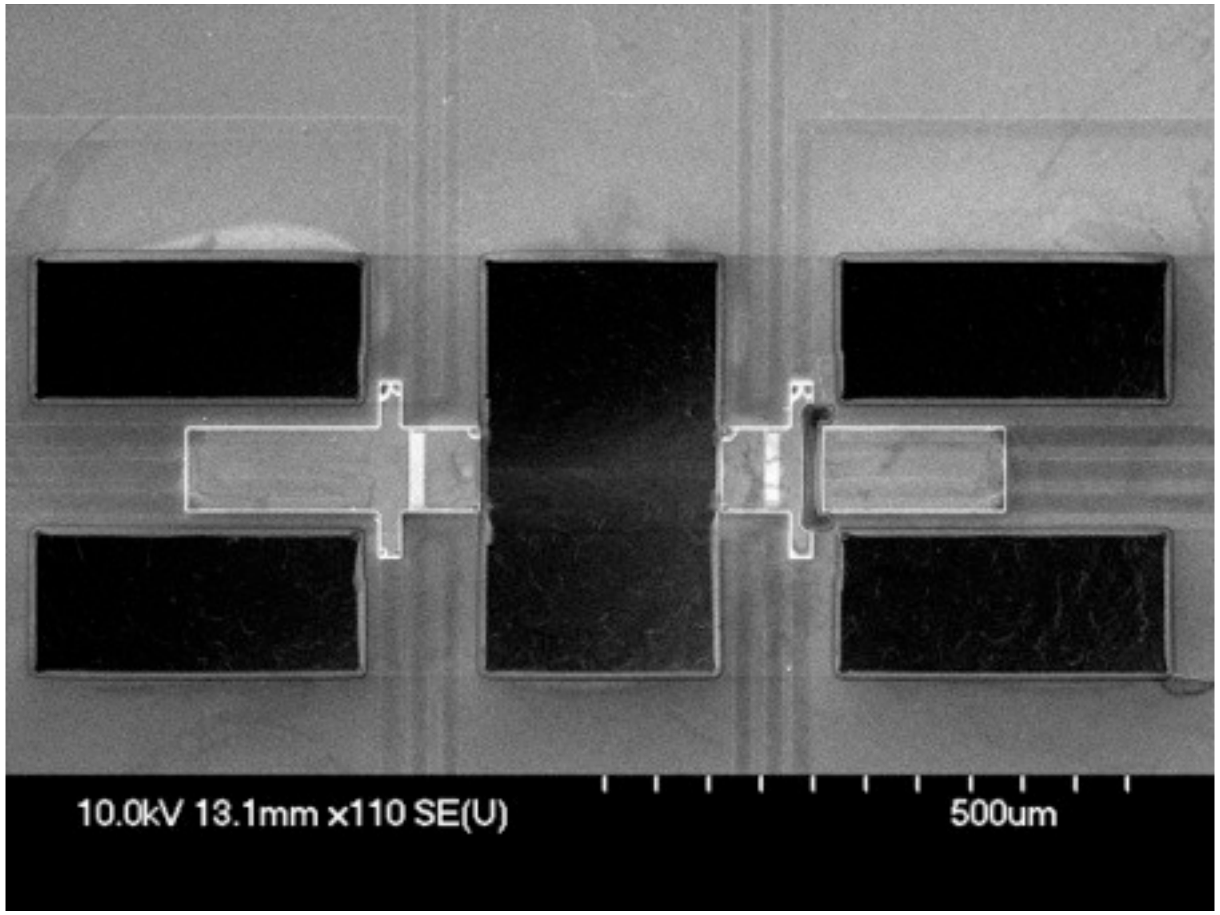
- α = 280 μV/K
- σ = 79,000 S/m
- κ = 0.17 W/mK
- => ZT = 10.9 !!
- BUT is the 3ω technique valid for superlattices?
- NO: lines should be parallel

Heat Flux Measurement

Hall Bar system

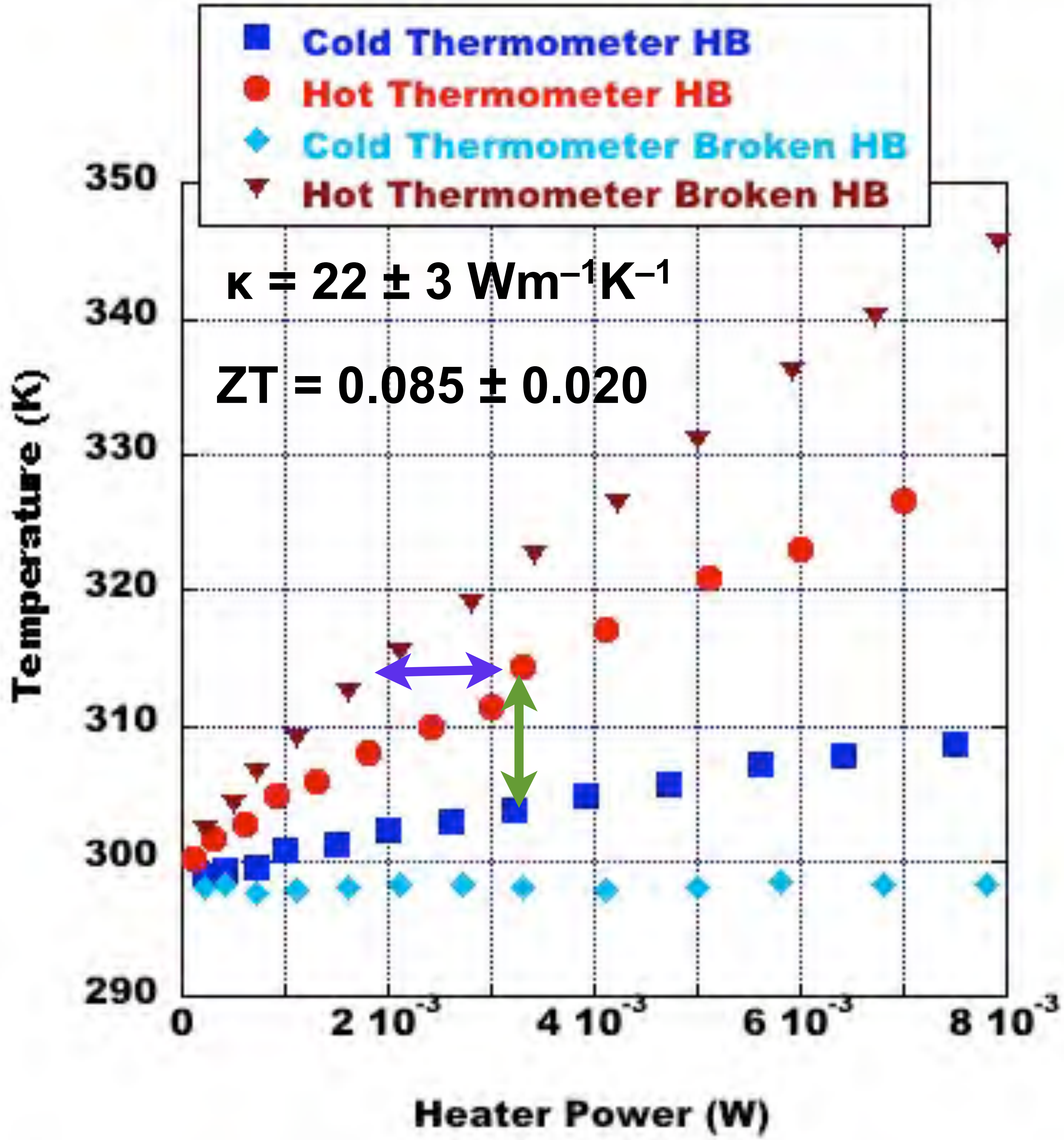


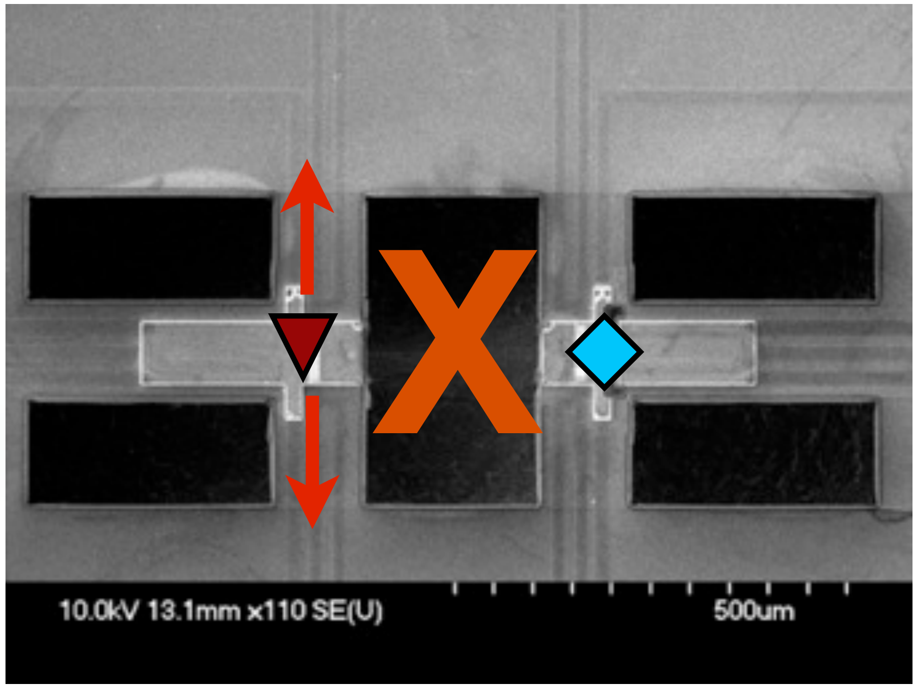
Broken Hall Bar system

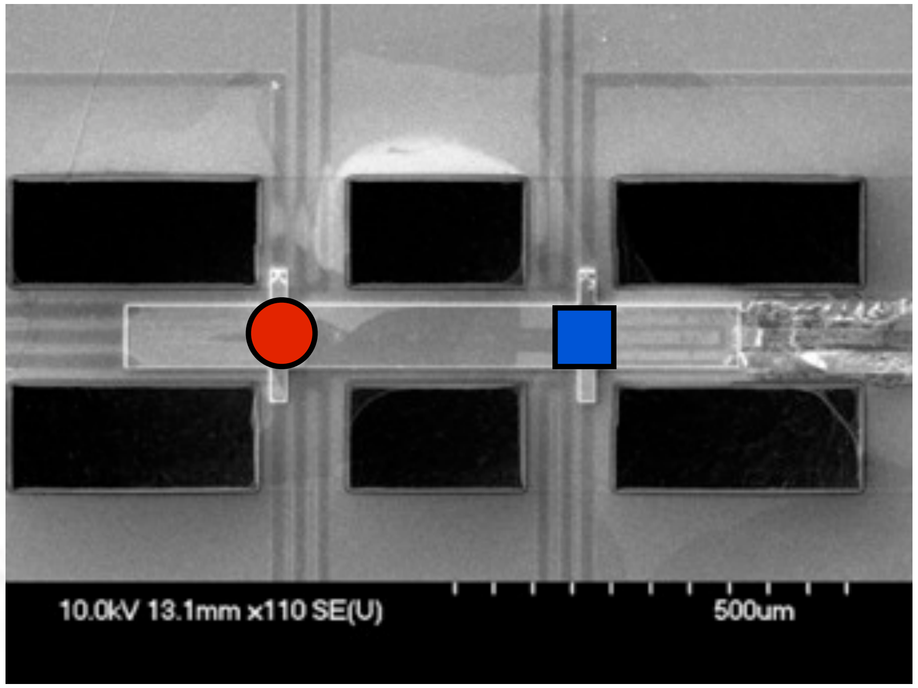


- Eliminate the contribution of spurious path along supporting arms
- Brake the heat conduction along to Hallbar to evaluate heat flux between the thermometers
- SiO_2, Si, SiGe supporting structure taken in account numerically
- Thermal AFM measurements to confirm results

Thermal Conductivity Measurement

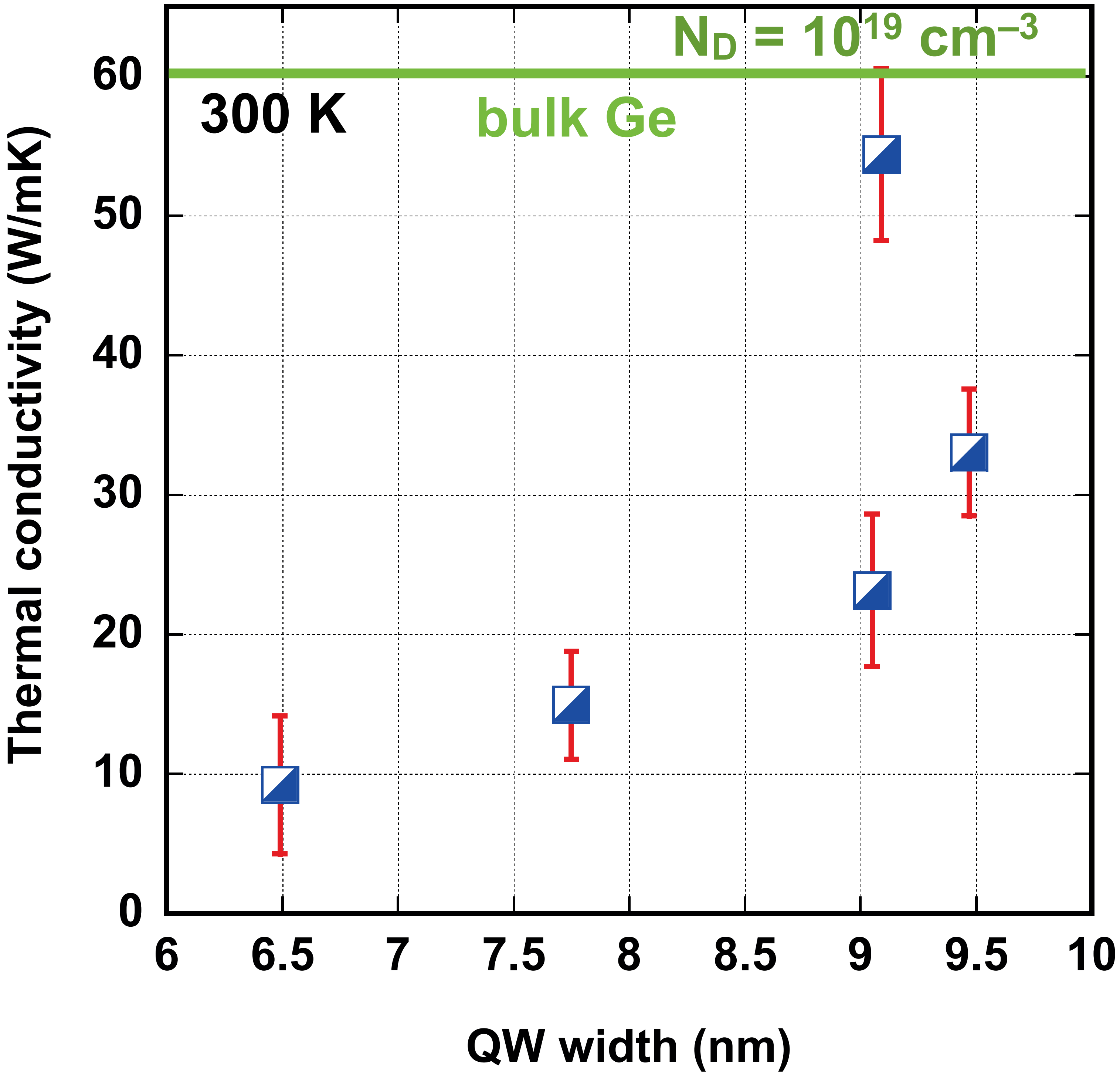


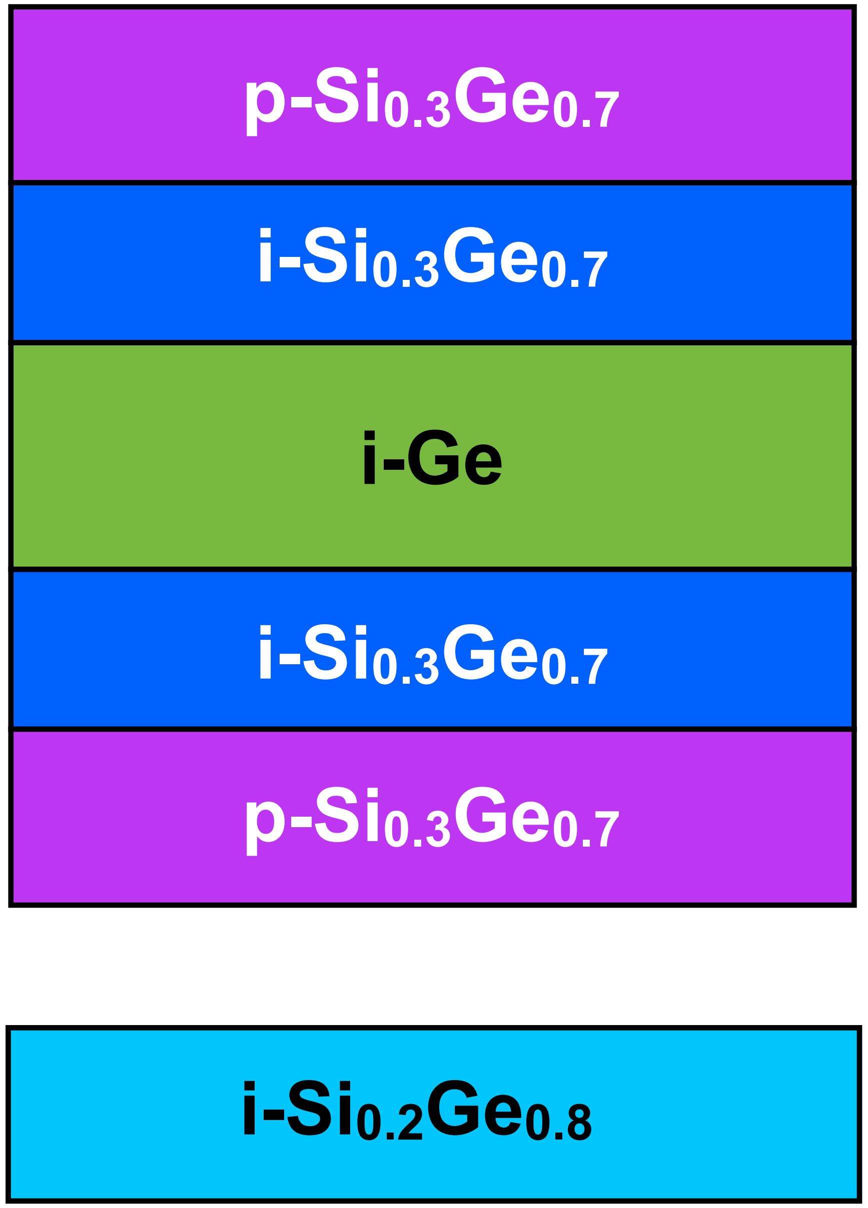




Evaluation of the heat flux that is physically transported in the structure

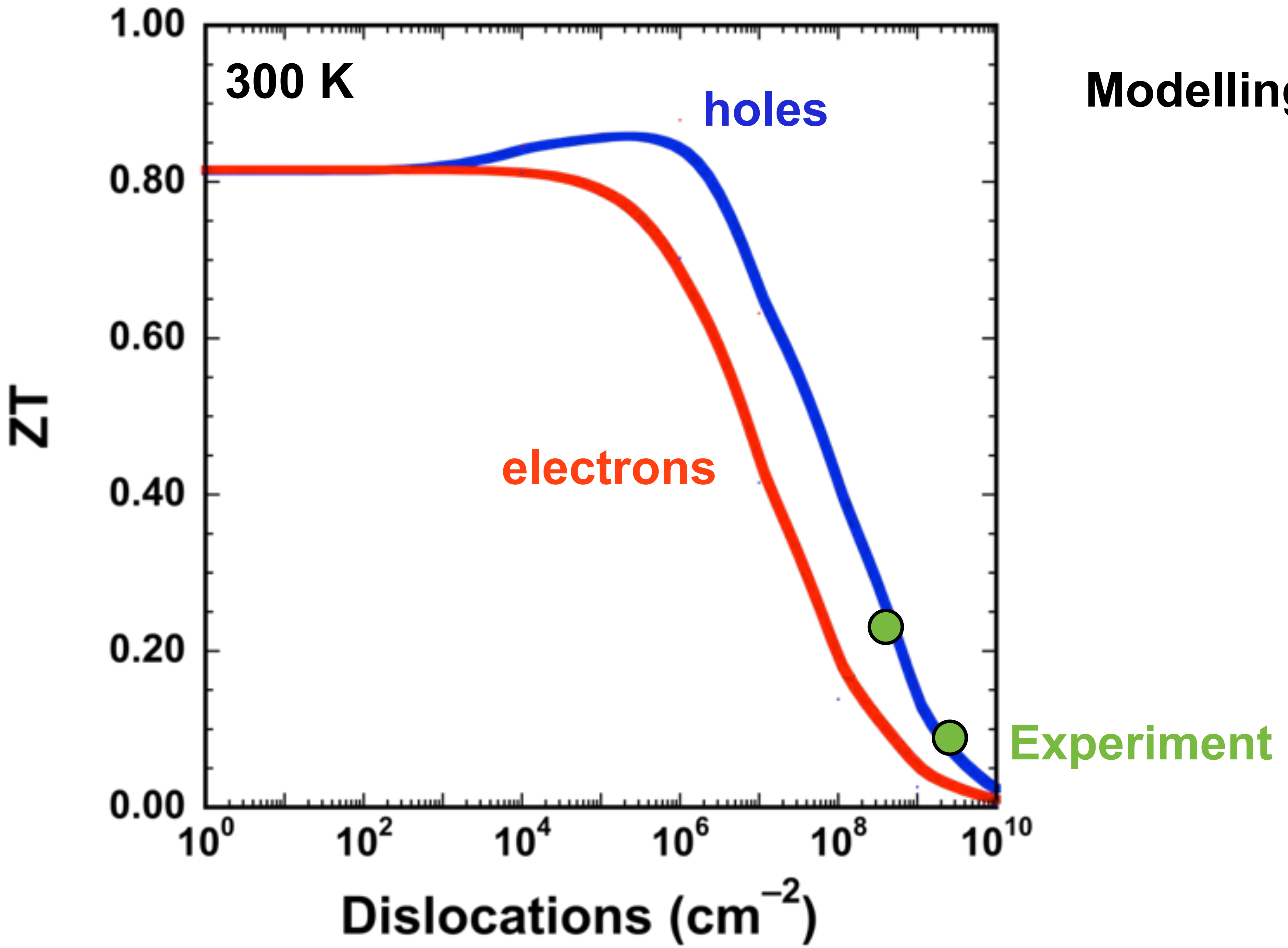
Thermal Conductivity vs QW Width





- Additional phonon scattering as QW width reduces

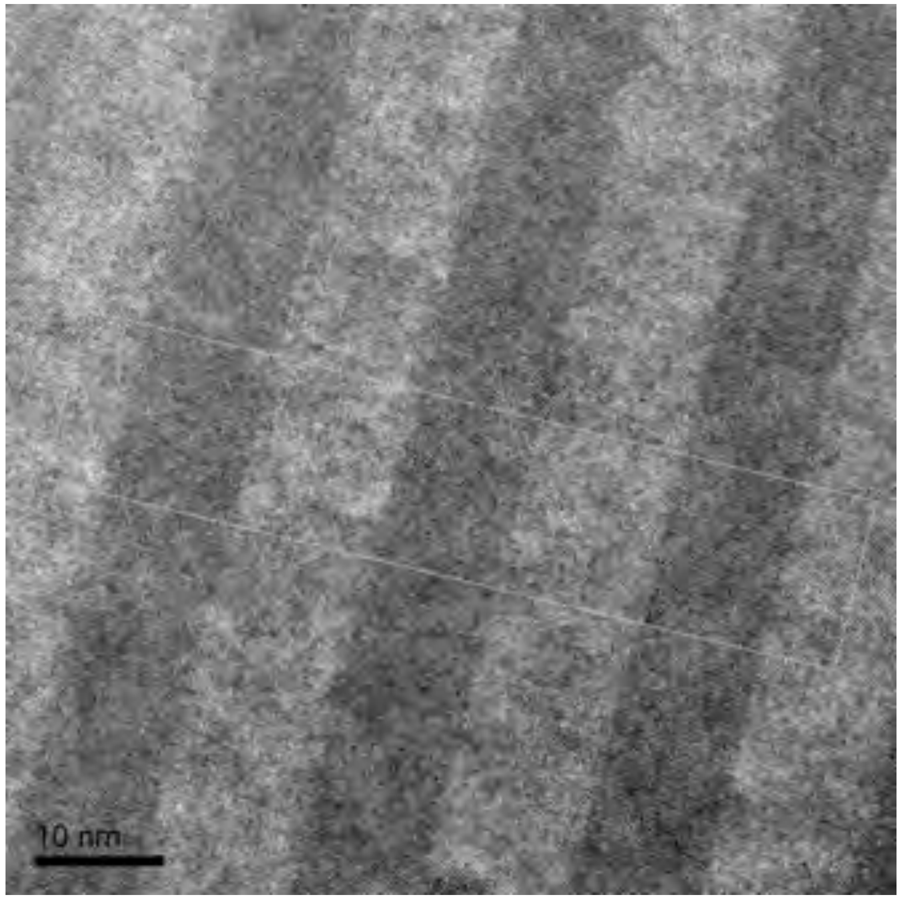
Experiment versus Theory



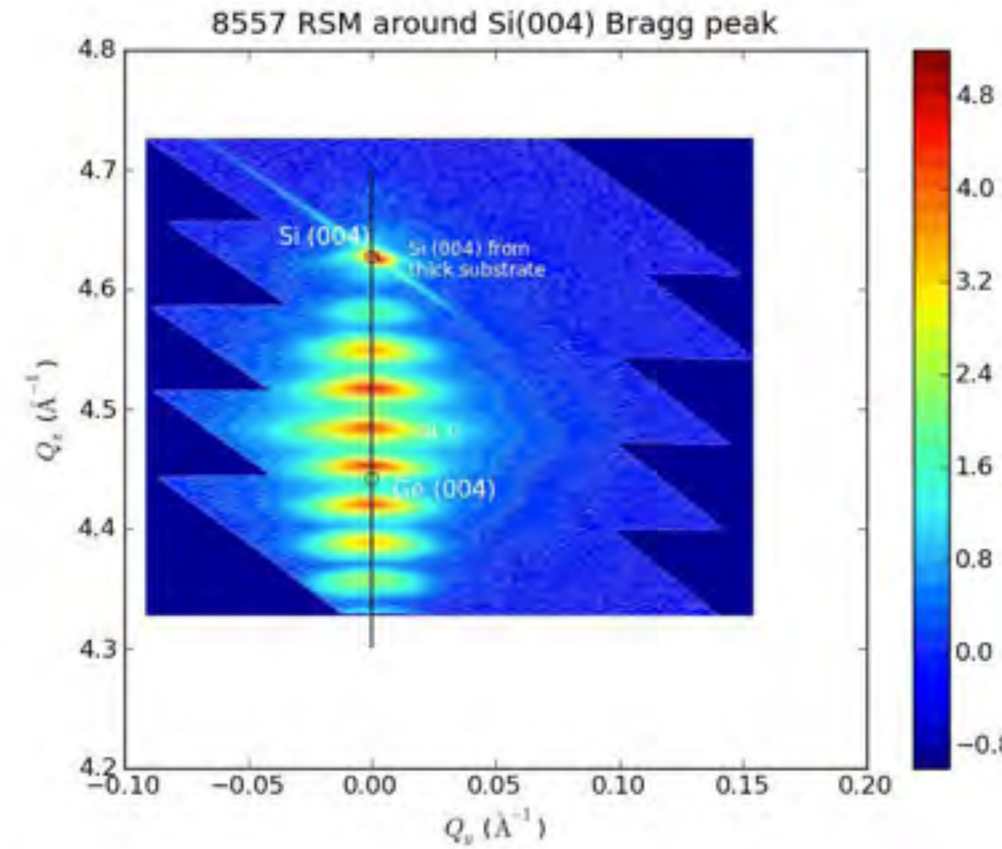
Modelling for 9 nm QW

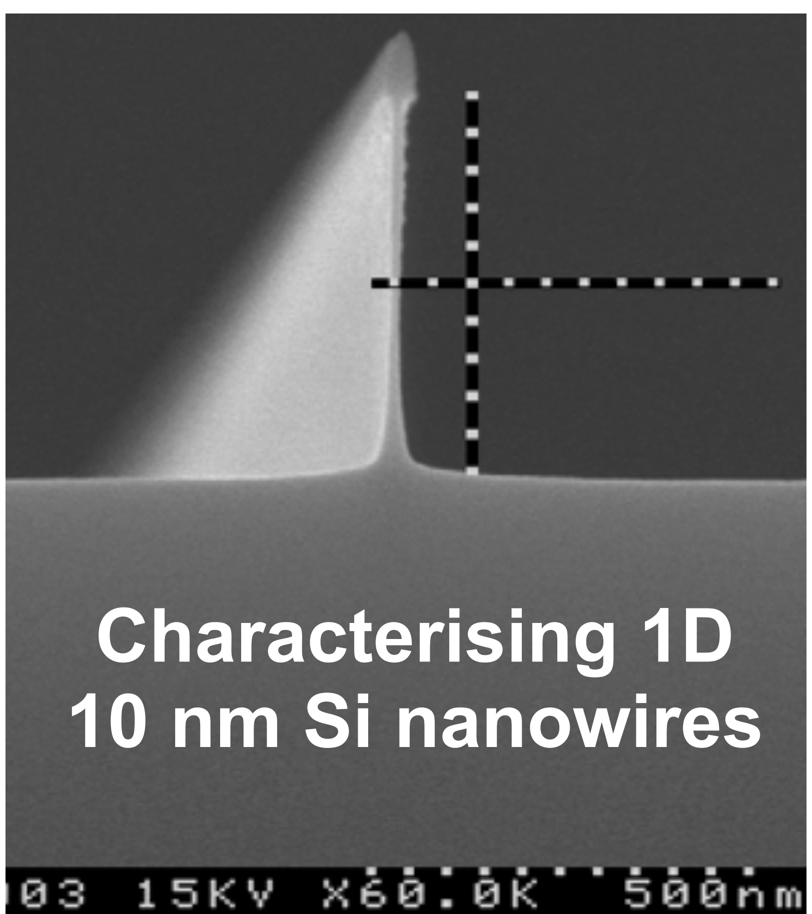
J.R. Watling & D.J. Paul, J. Appl. Phys. 110, 114508 (2011)

2D, 1D and 0D structures

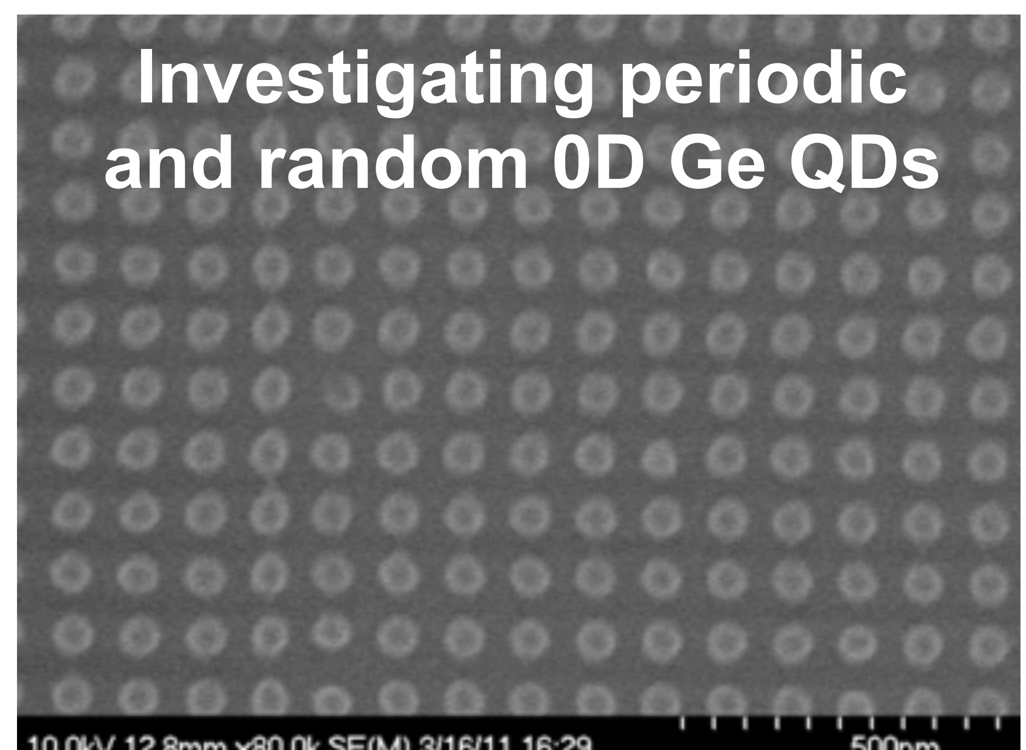


TEM & XRD characterisation of 2D superlattice designs



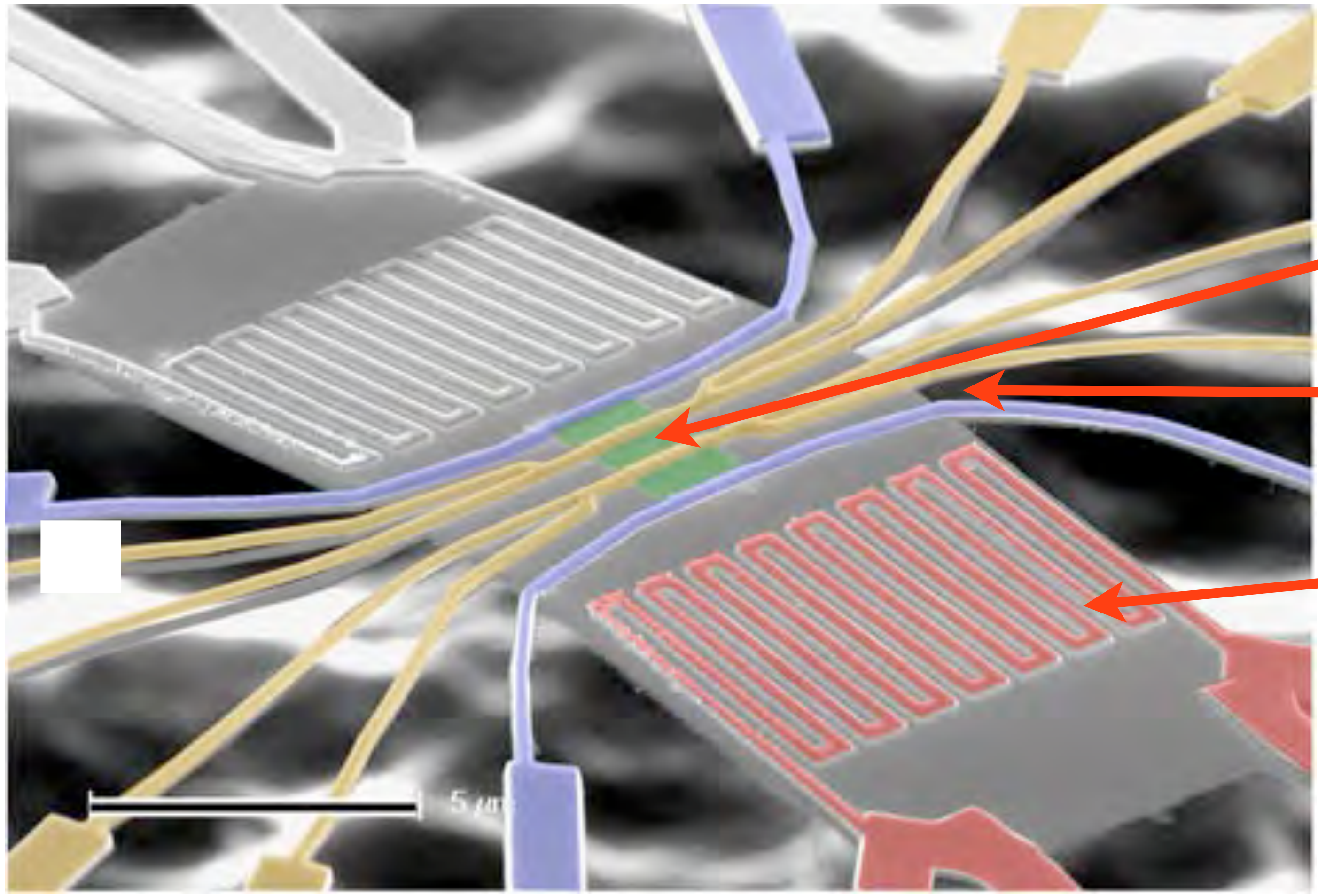


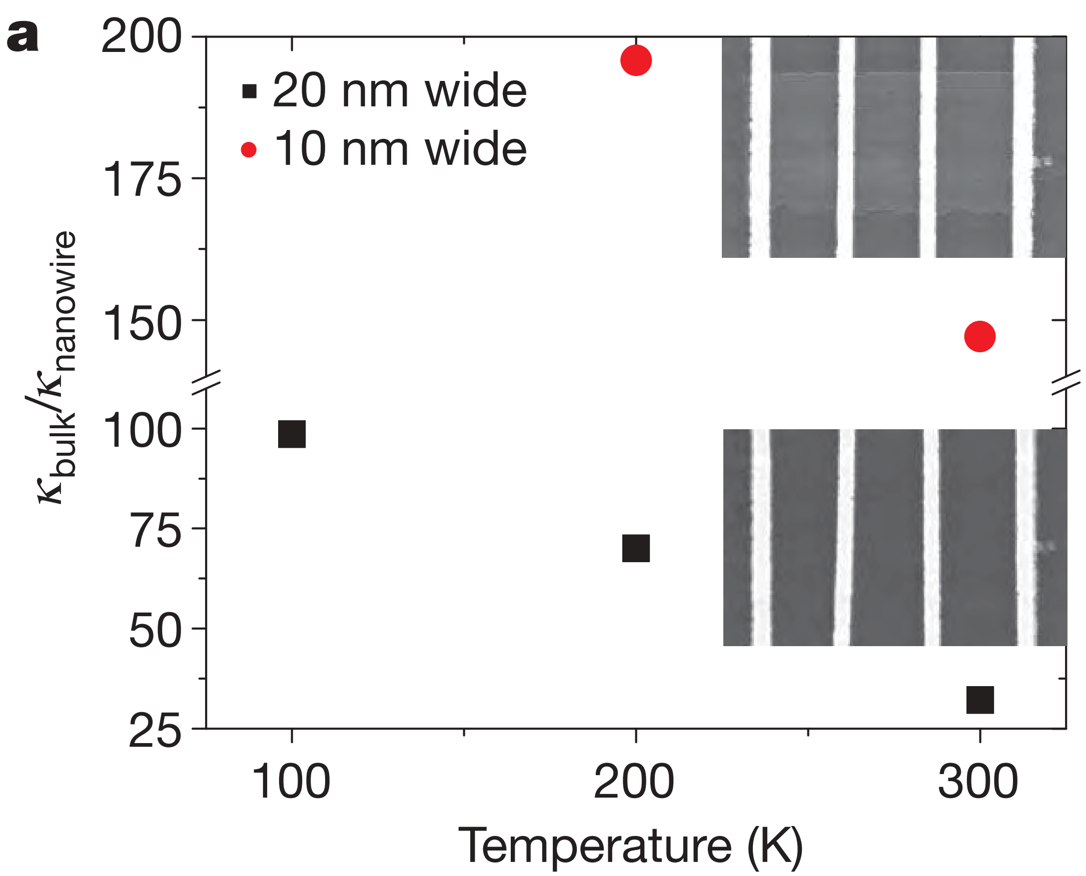
Characterising 1D 10 nm Si nanowires



Investigating periodic and random 0D Ge QDs

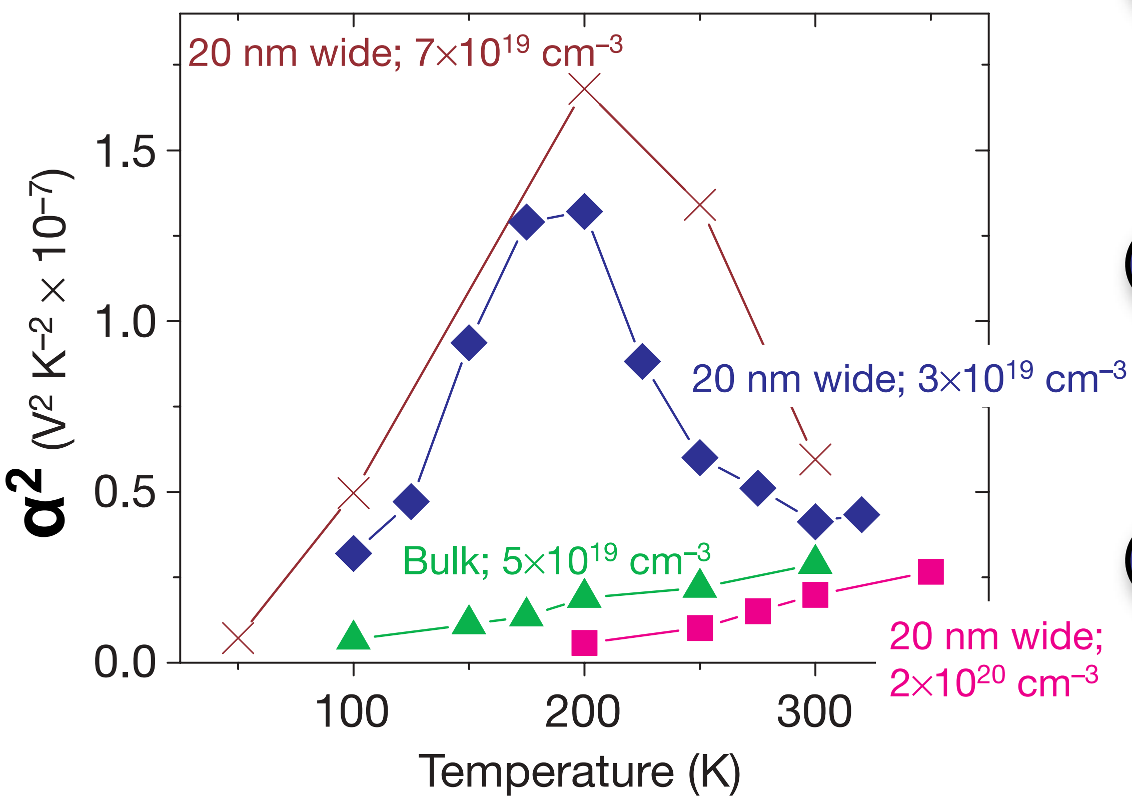
1D Nanowires

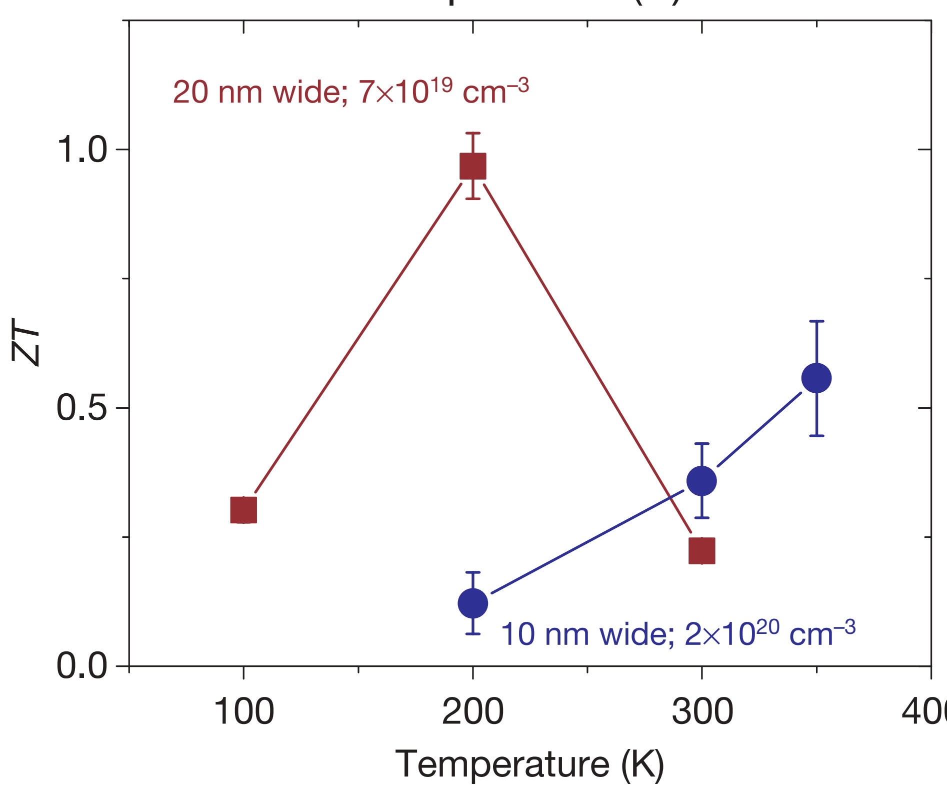




A.I. Boukai et al., Nature 451, 168 (2007)

1D Silicon Nanowires

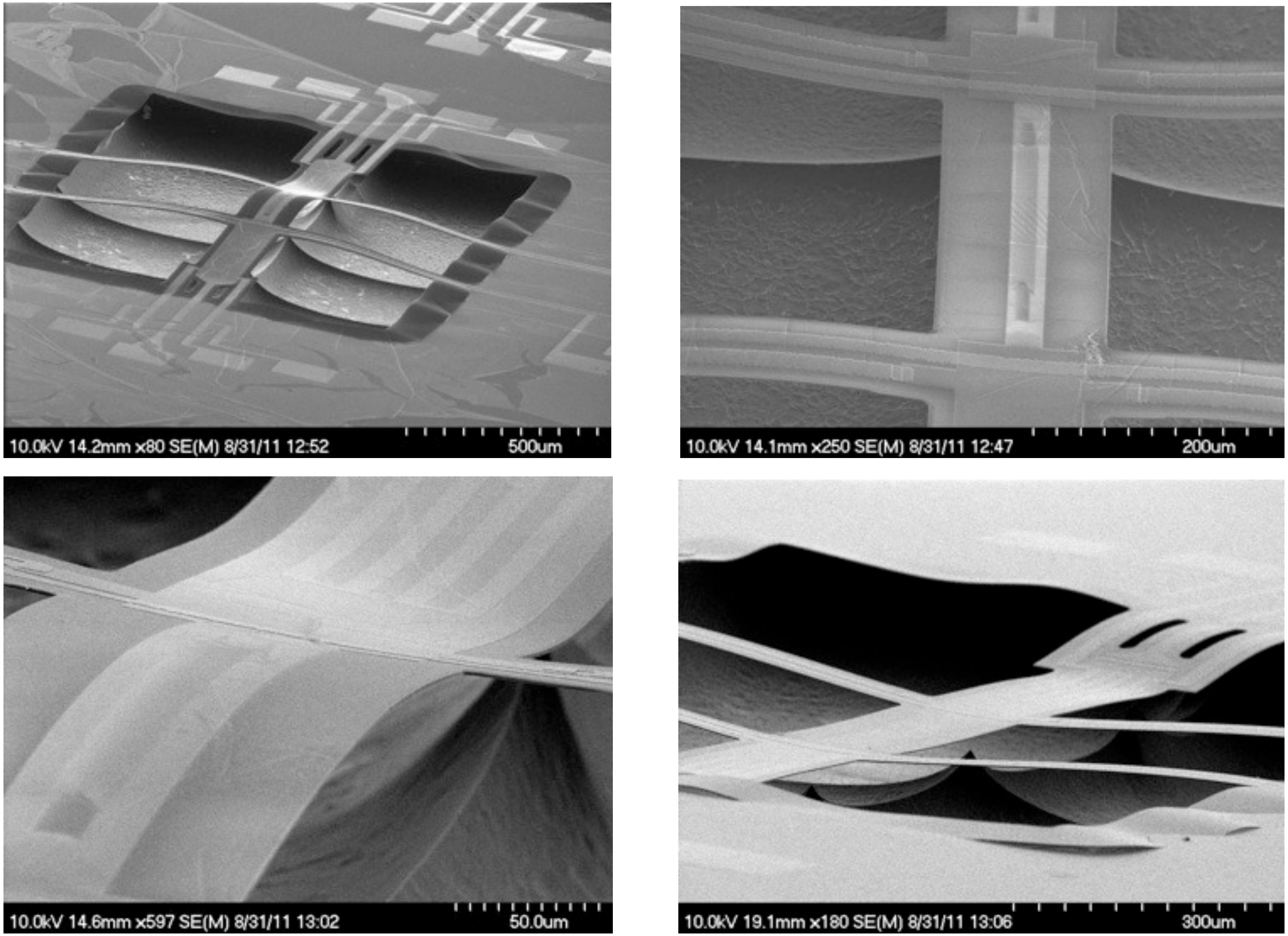




- **Higher α from the higher DOS, g(E)**
- **α increased by ~ 2**
- **κ reduced by factor ~150**
- **ZT increased by factor 600**
- **Thermal conductivity reduced more than electrical conductivity**
- **Fill factor / generation density low**

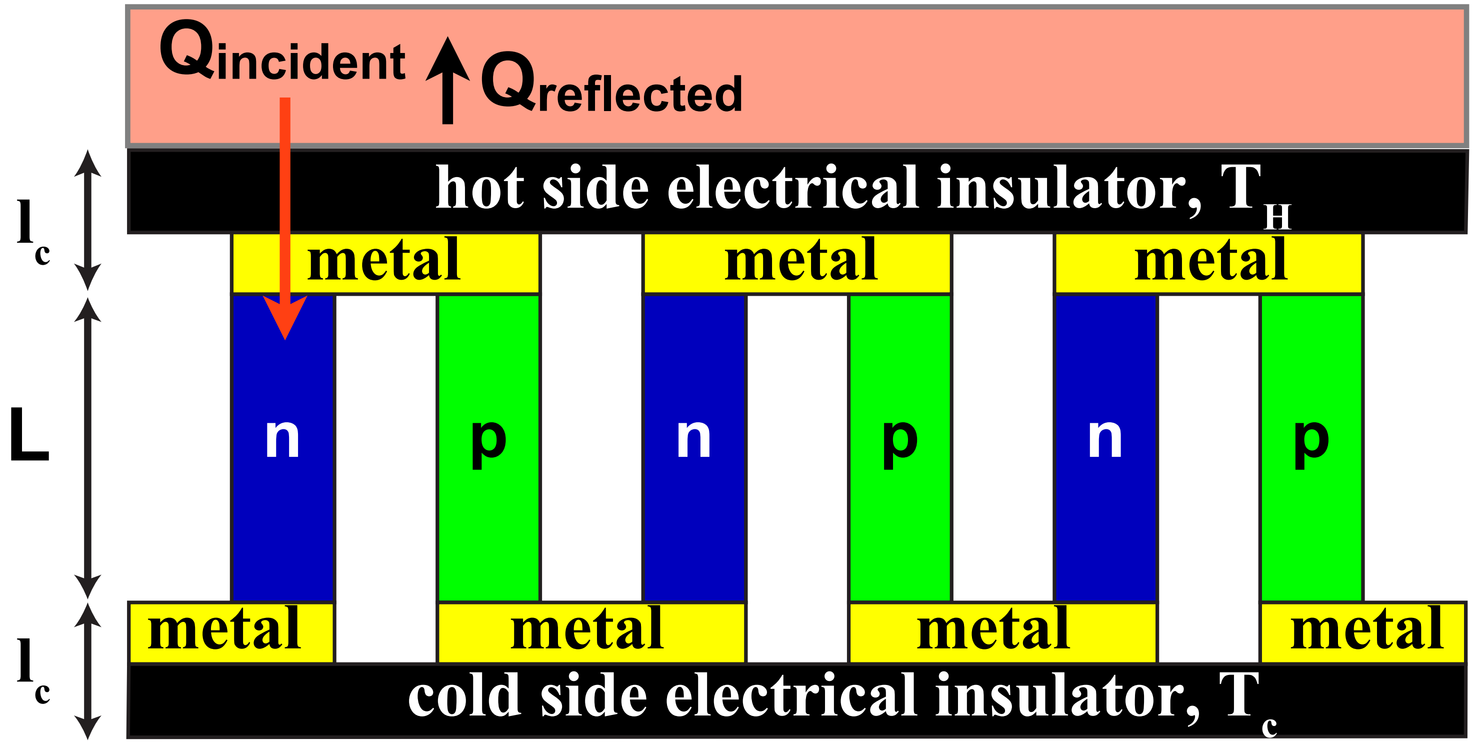
A.I. Boukai et al., Nature 451, 168 (2007)

Free Standing 1D Nanowires



- **With heaters, electrical contacts and thermometers**

Maximum Output Power



A = module leg area

L = module leg length

N = number of modules

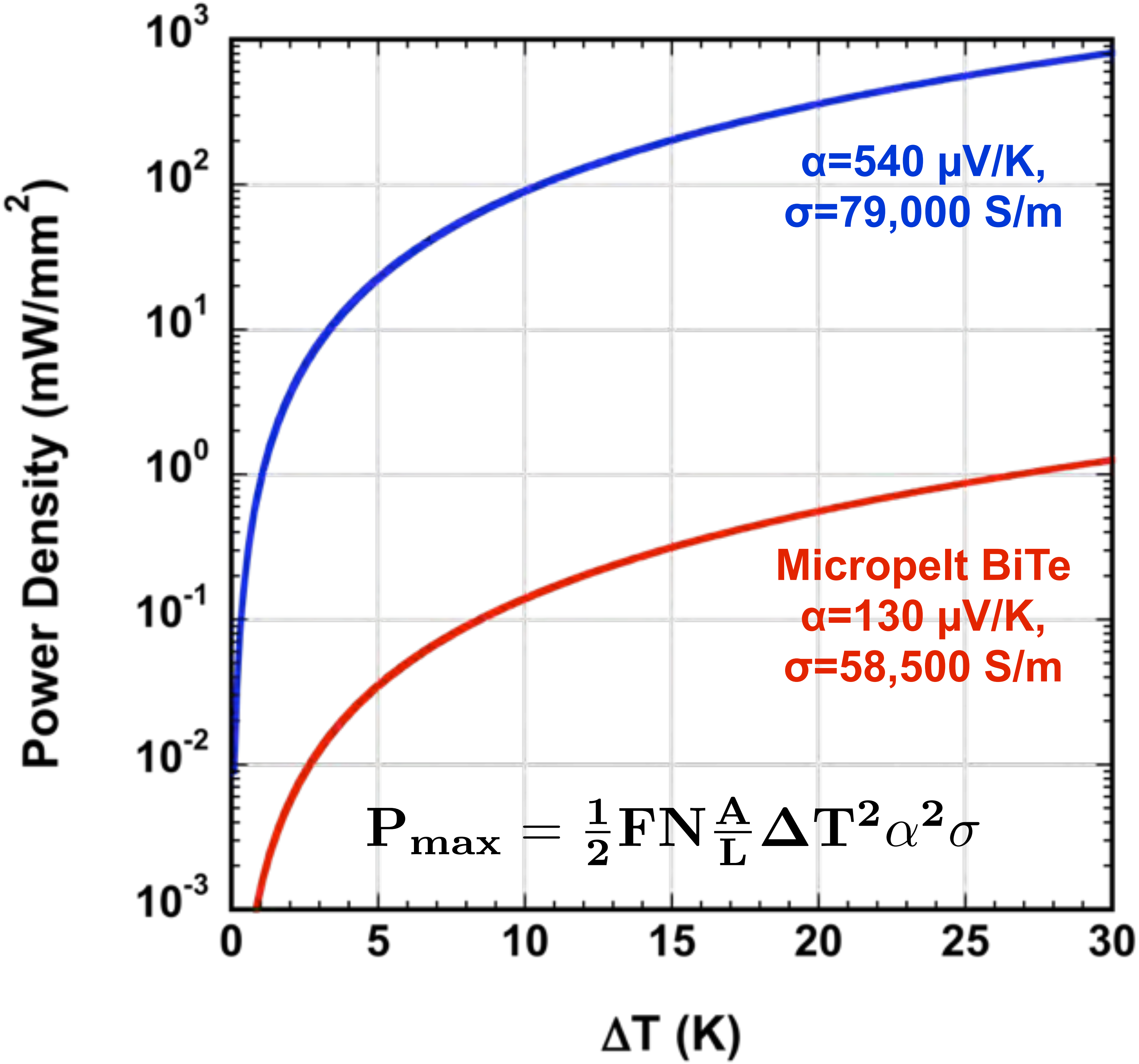
- F = fabrication factor = perfect system – $R_{contact}$ – R_{series} – Lost heat

- Practical systems: both electrical and thermal impedance matching is required

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

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

Power Density Estimates



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

Micropelt MPG-D751

n-BiTe / p-SbTe

N legs = 540

A = 35 μm x 35 μm

Leg L = 40 μm

F = 0.95

Delivered into load = 400 Ω

NB Heat sinking and impedance matching key for maximum power

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)

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