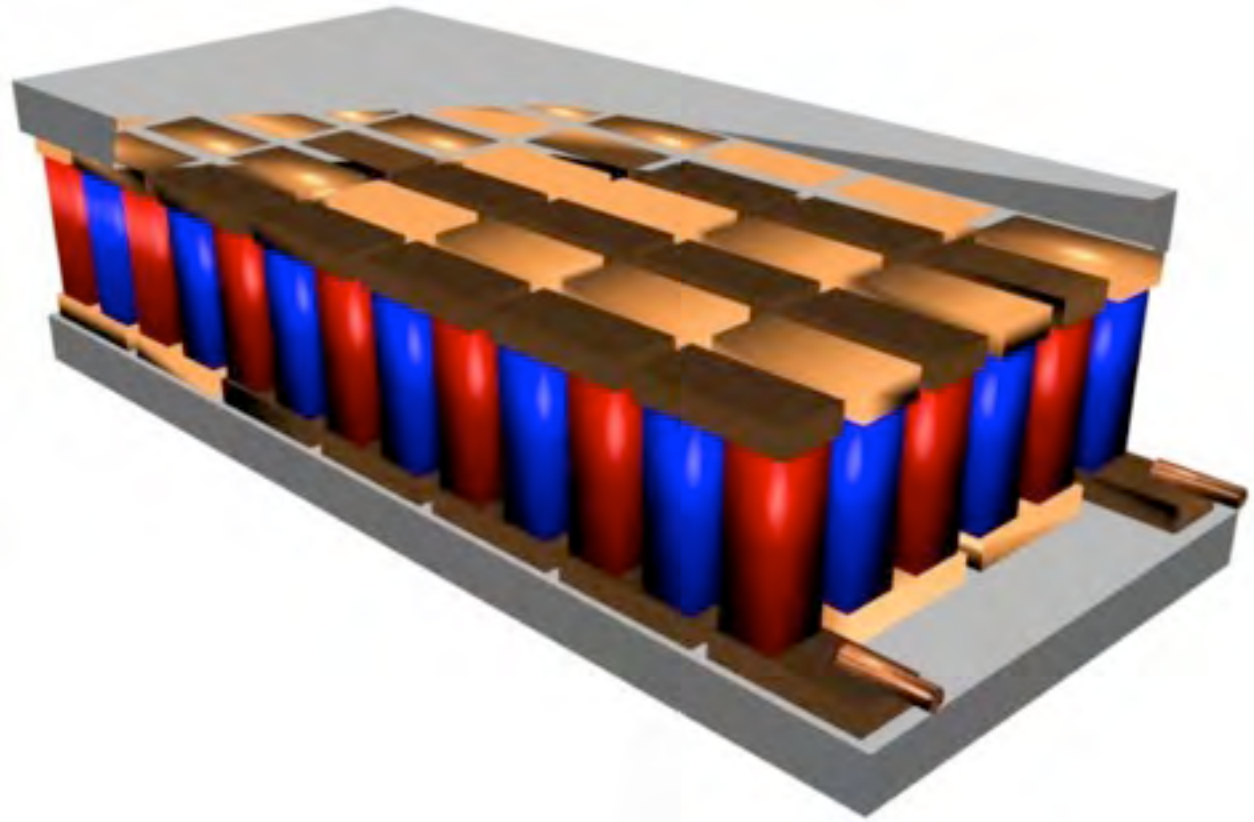
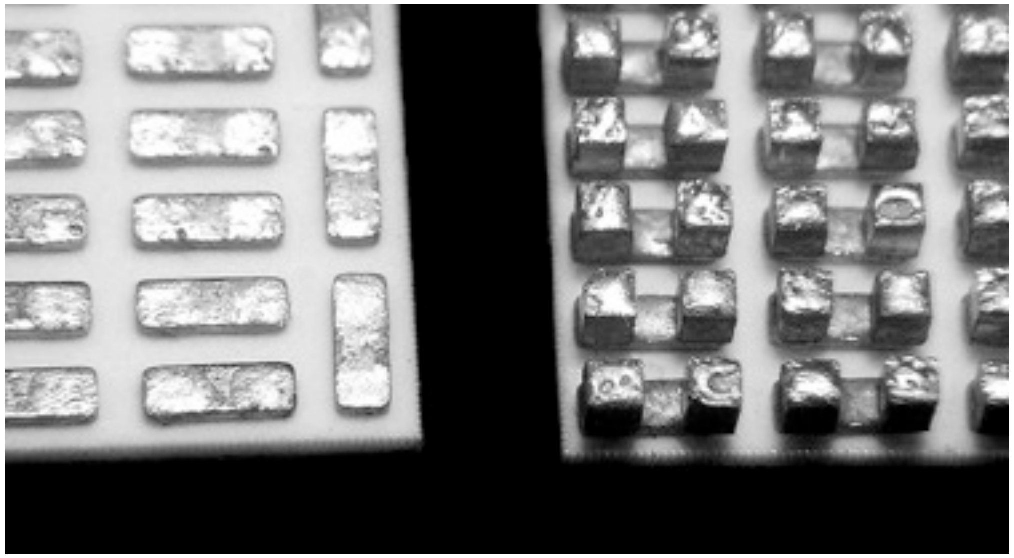
# Thermoelectric Energy Harvesting



**Douglas J. Paul**

**School of Engineering**
**University of Glasgow, U.K.**



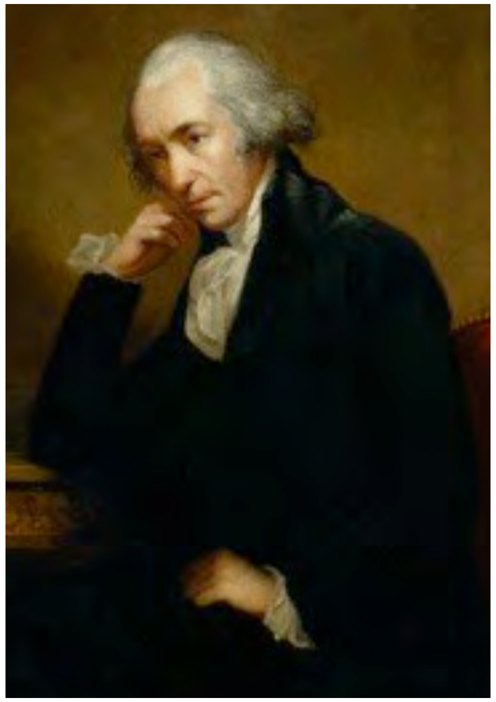
# The University of Glasgow

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

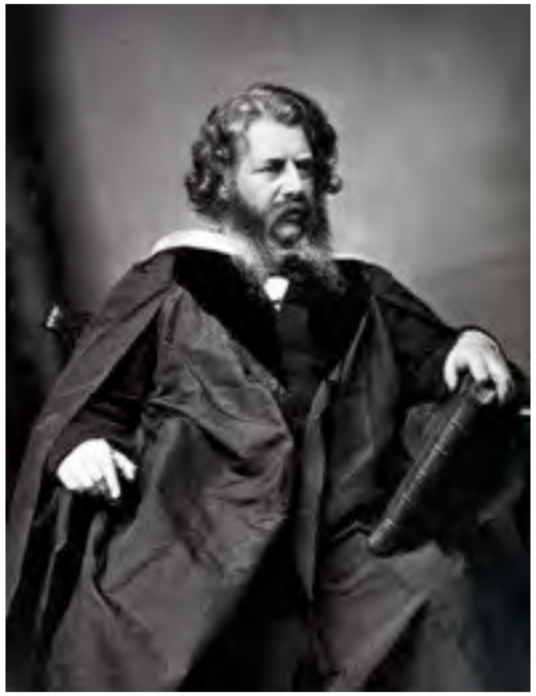
- 400 years in High Street
- Moved to Gilmorehill in 1870
- Neo-gothic buildings by Gilbert Scott

# Famous Glasgow Scholars

William Thomson (Lord Kelvin)



James Watt



William John Macquorn Rankine

Rev Robert Stirling

Rev John Kerr

Joseph Black

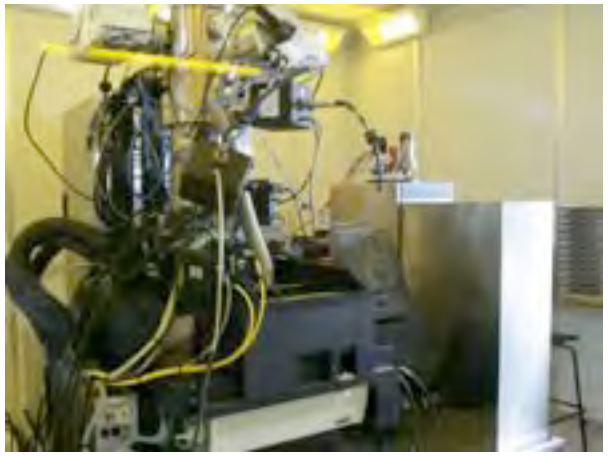
John Logie Baird

Adam Smith

# James Watt Nanofabrication Centre @Glasgow

University of Glasgow

Vistec VB6 & EBPG5



E-beam lithography

Süss MA6 optical & nanoimprint lithography

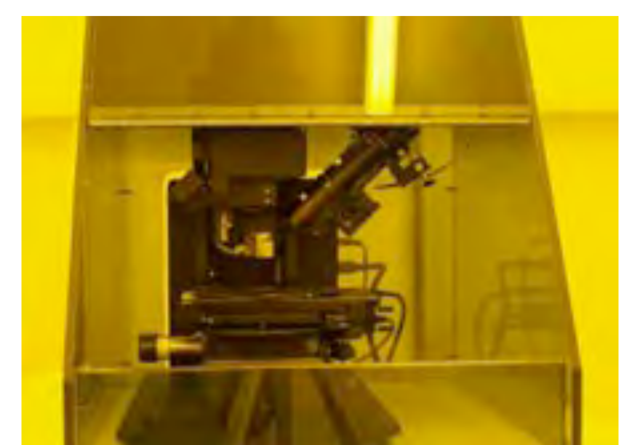
- 750m$^2$ cleanroom - pseudo-industrial operation
- 18 technicians + 5 research technologists (PhD level process engineers)
- Large number of process modules
- Processes include: Si/SiGe/Ge, III-V, II-VI, piezoelectric MMICs, optoelectronics, metamaterials, MEMS
- Commercial access through KNT
- http://www.jwnc.gla.ac.uk

8 RIE / PECVD

3 Metal dep tools

4 SEMs: Hitachi S4700

Veeco: AFMs



# James Watt Nanofabrication Centre @Glasgow

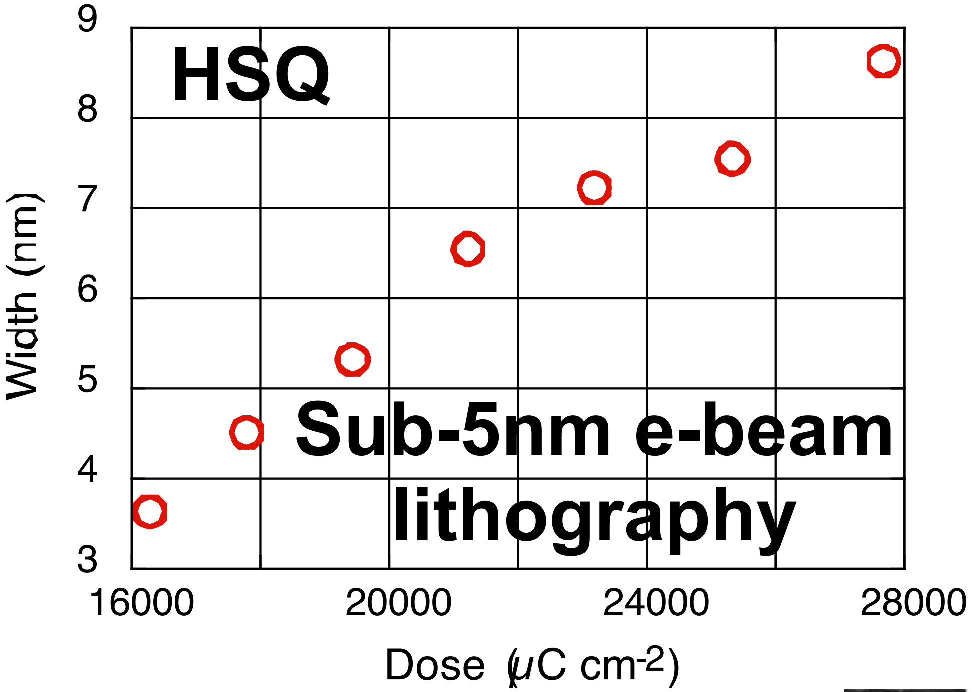
- In School of Engineering
- £53M active research grant portfolio (£14M pa, industry ~£1M)
- 2nd highest cited E&EE Department in UK after Cambridge

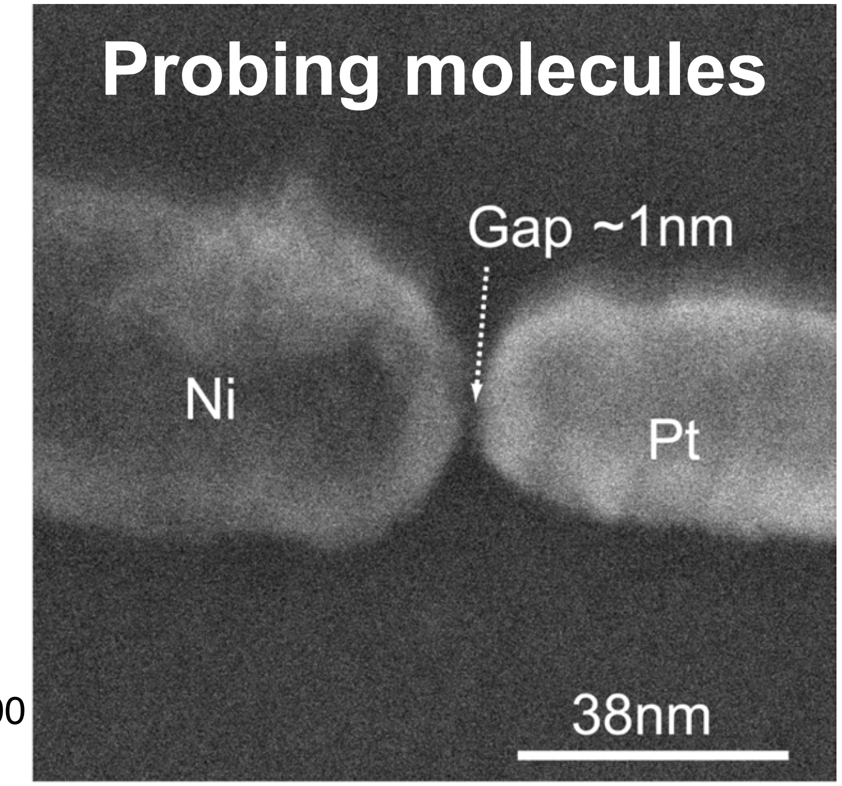
**World Bests:**

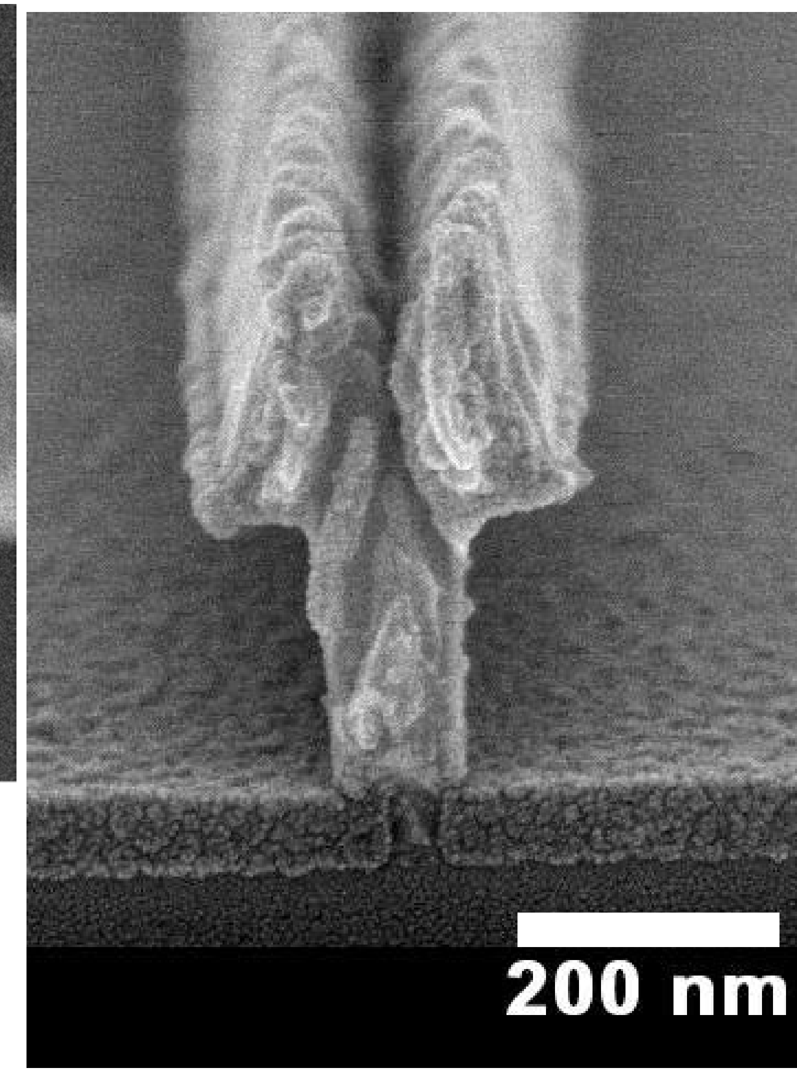
- Smallest electron-beam lithography pattern – 3 nm
- Best layer-to-layer alignment accuracy (0.42 nm rms)
- Smallest diamond transistor (50 nm gate length)
- Lowest loss silicon optical waveguide (< 0.9 dB/cm)
- Fastest mode locked laser (2.1 THz)
- Highest Q silicon nanowire cavity (Q = 177,000)

# JWNC@Glasgow Nanofabrication

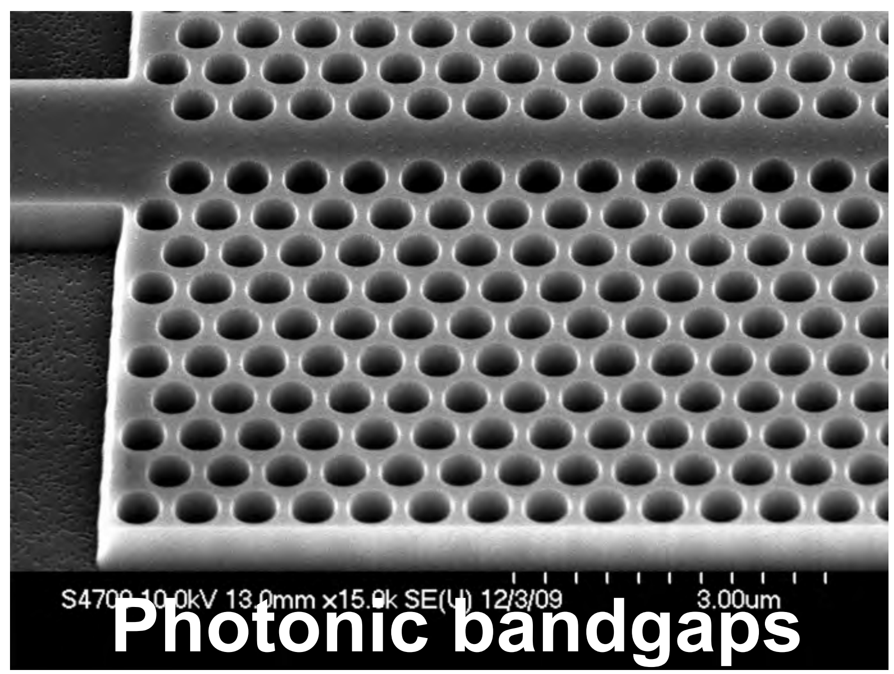
Measured linewidth vs dose



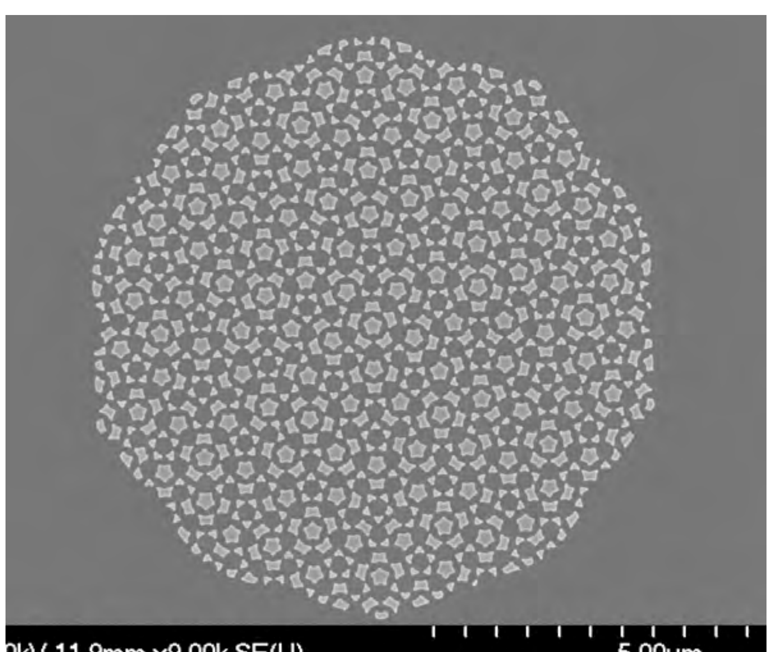



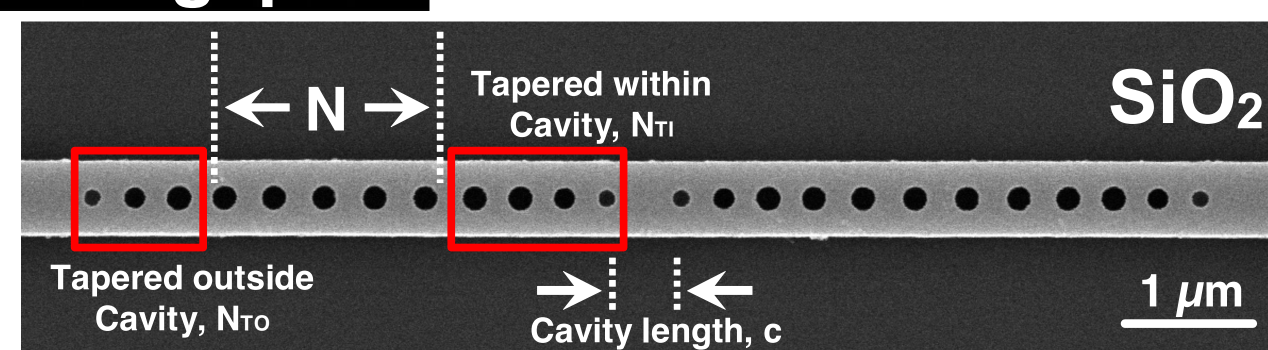

22 nm T-gate HEMTs




Penrose tile:
0.46 nm rms alignment




Si nanowire cavity
Q = 177,000



# 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 / mm-wave electronics, beer! etc...)
- Thermoelectric generators – some industrial energy harvesting

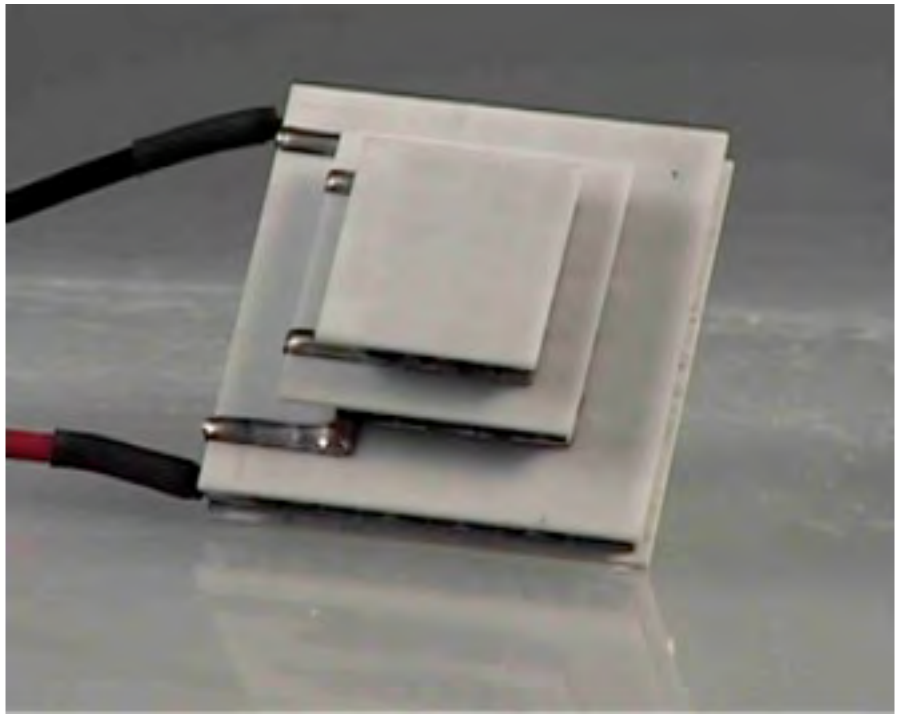
**As renewable energy interest increases, renewed interest in thermoelectrics**

D.J. Paul
School of Engineering
University of Glasgow

# 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
- Most losses result in heat
- Most heat sources are "static"
- Waste heat from many systems could be harvested

home, industry, background



# Background Physics

## Fourier thermal transport

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

## Joule heating

$$Q = I^2 R$$

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

$E_F$ = chemical potential

$V$ = voltage

$A$ = area

$q$ = electron charge

$g(E)$ = density of states

$k_B$ = Boltzmann's constant

$R$ = resistance

$I$ = current ($J = I/A$)

$\kappa$ = thermal conductivity

$\sigma$ = electrical conductivity

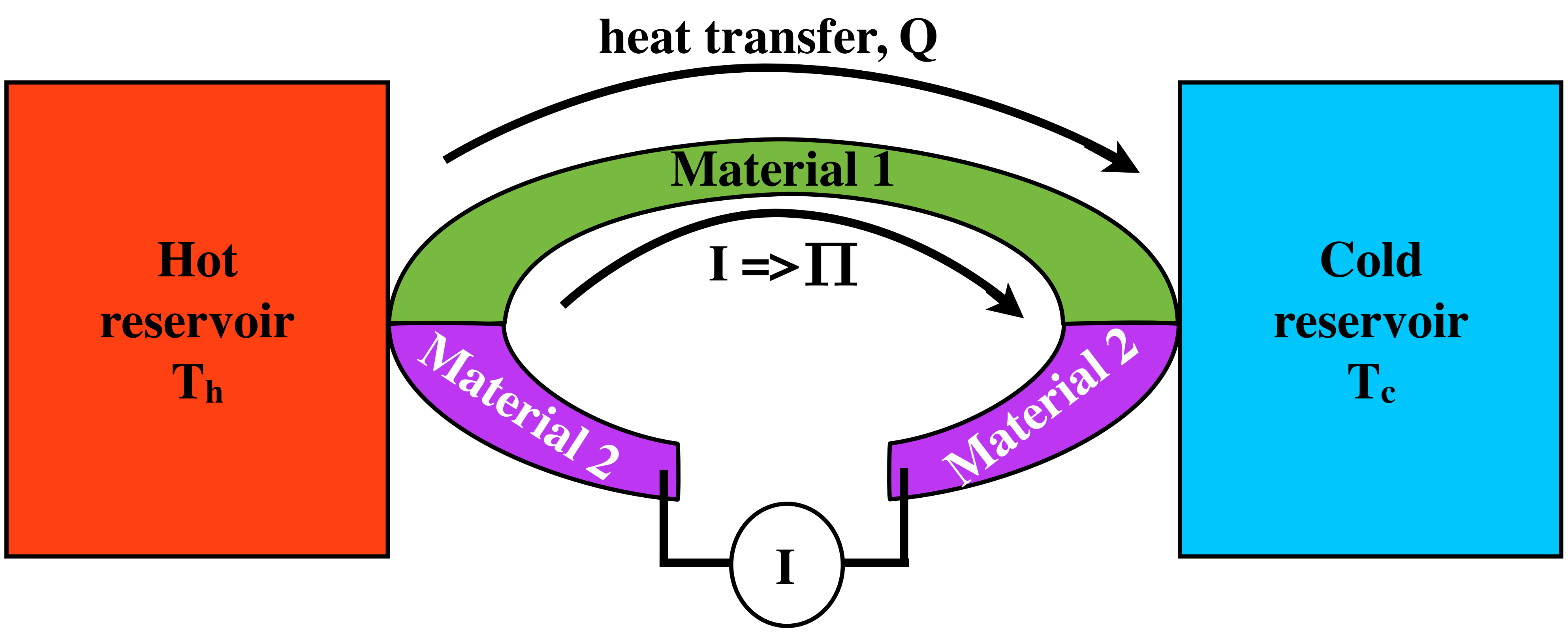
$\alpha$ = Seebeck coefficient

$f(E)$ = Fermi function

$\mu(E)$ = mobility

*D.J. Paul*
*School of Engineering*
University of Glasgow

# The Peltier Effect




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

units: W/A = V

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

# The Peltier Coefficient

- Full derivation uses relaxation time approximation & Boltzmann equation

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

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

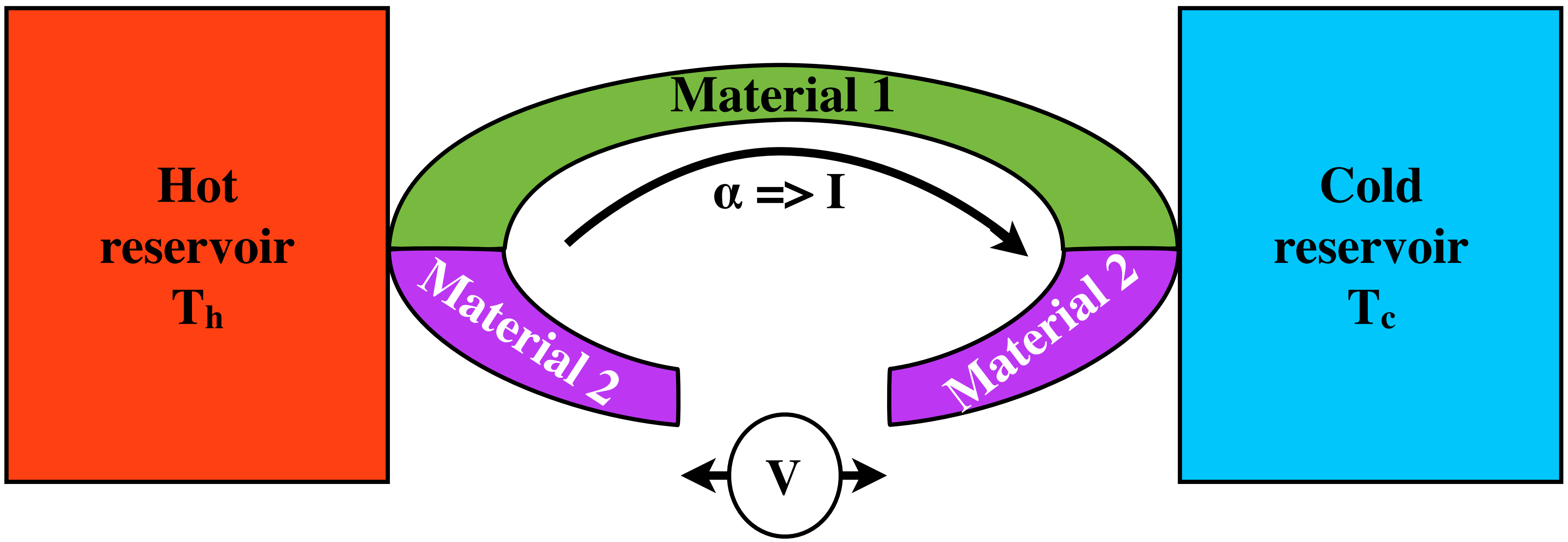
- This derivation works well for high temperatures (> 100 K)

- At low temperatures phonon drag effects must be added

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

D.J. Paul
School of Engineering

# The Seebeck Effect




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

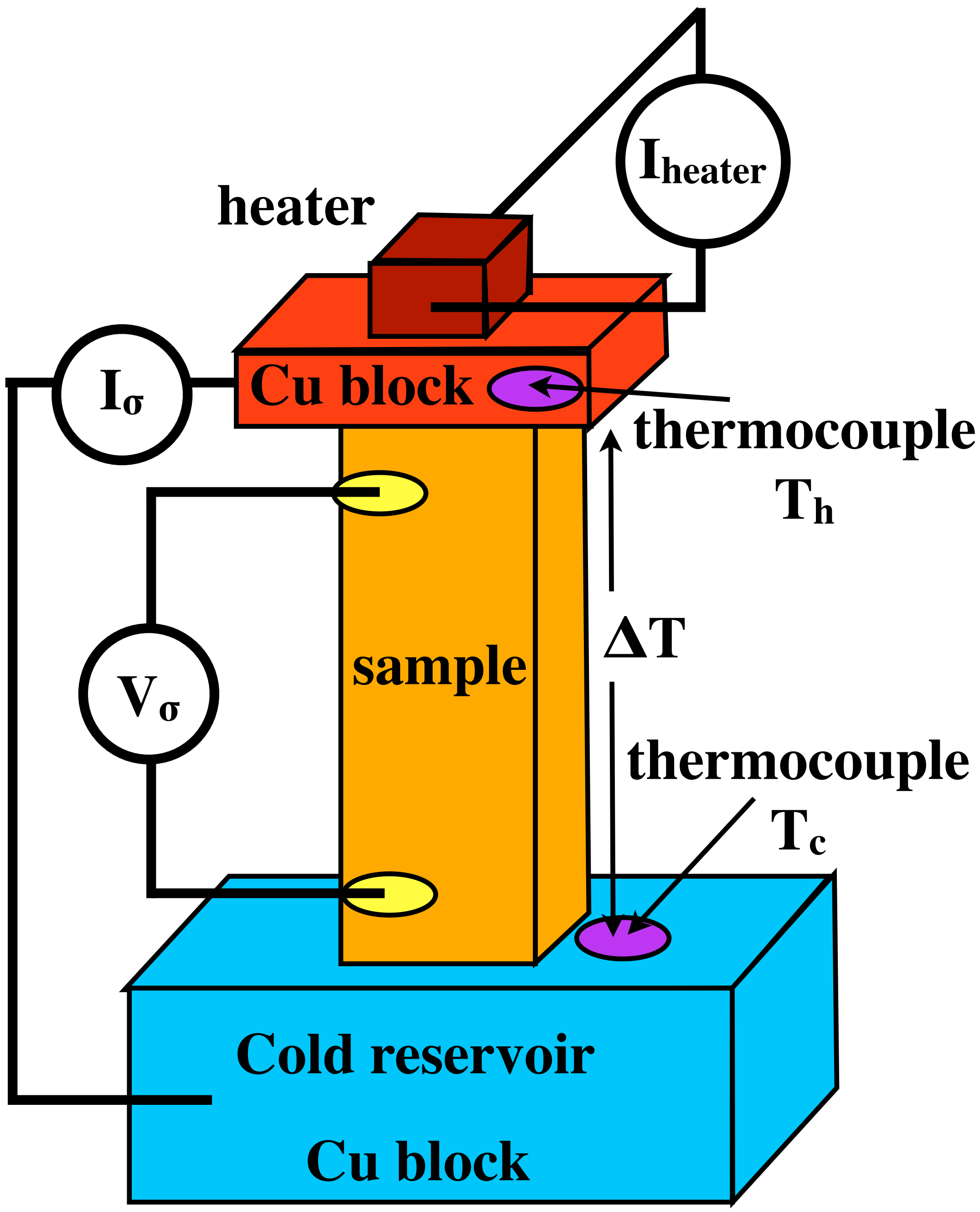
Seebeck coefficient, $\alpha = \frac{dV}{dT}$

units: V/K

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

*D.J. Paul*
*School of Engineering*
University of Glasgow

# Measuring Seebeck Coefficient




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


*D.J. Paul*
*School of Engineering*
University of Glasgow

# The Seebeck Coefficient

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

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

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

**For electrons in the conduction band, $E_c$ of a semiconductor**

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

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

*D.J. Paul*
*School of Engineering*
University of Glasgow

# The Seebeck Coefficient for Metals

- $$f(1-f) = -k_B T \frac{df}{dE}$$
- Expand $g(E)\mu(E)$ in Taylor's series at $E = E_F$
- $$\alpha = -\frac{\pi^2}{3}\frac{k_B}{q}k_B T\left[\frac{d\ln(\mu g)}{dE}\right]E_F$$ (Mott's formula)

  Mott and Jones, 1958
- i.e. Seebeck coefficient depends on the asymmetry of the current contributions above and below $E_F$

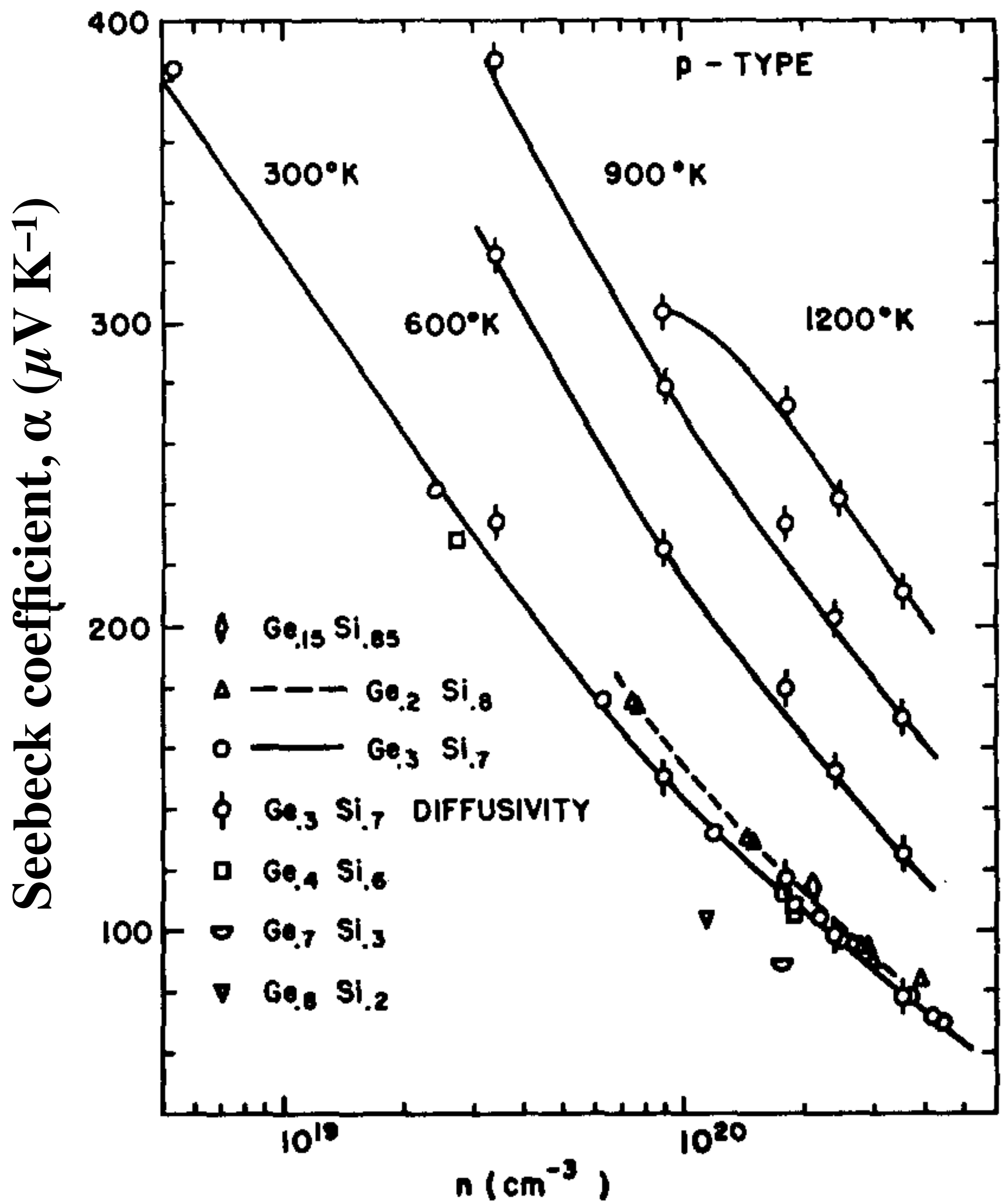
Using the energy-independent scattering approximation:

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

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

D.J. Paul
School of Engineering
University of Glasgow

# Semiconductor Example: SiGe Alloys



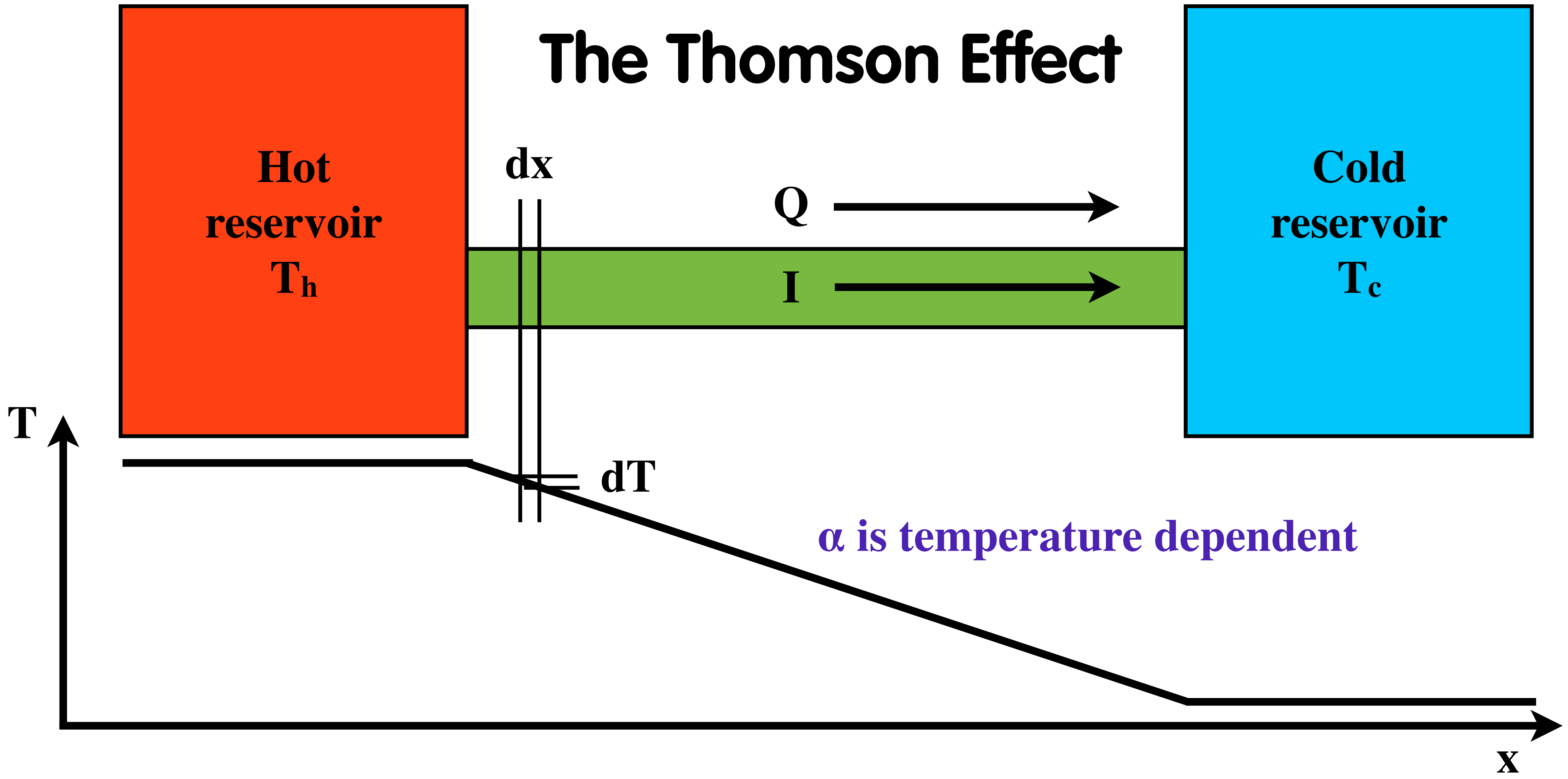

*J.P. Dismukes et al., J. Appl. Phys. 35, 2899 (1964)*

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

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


D.J. Paul
School of Engineering
University of Glasgow

# The Thomson Effect




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

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

units: V/K

# The Kelvin Relationships

- Derived using irreversible thermodynamics

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

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

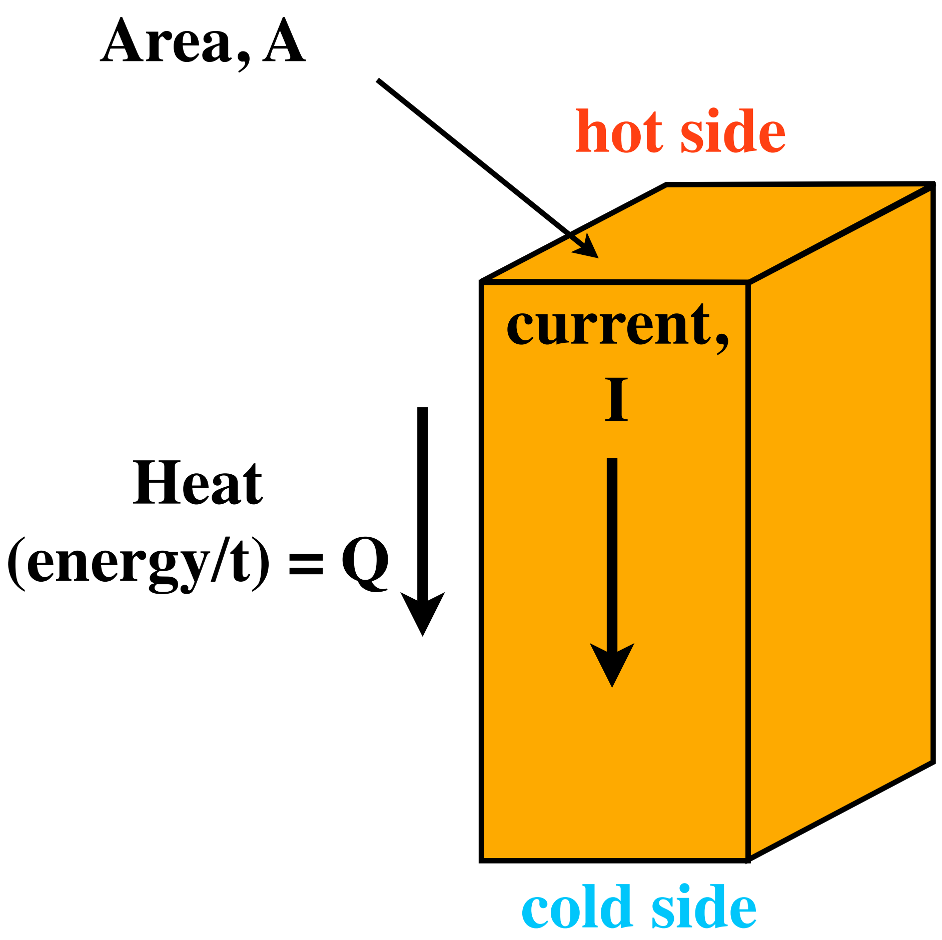
- These relationships hold for all materials
- Seebeck, α is easy to measure experimentally
- Therefore measure α to obtain $\Pi$ and $\beta$

D.J. Paul
School of Engineering

University of Glasgow

# Peltier Effect, Heat Flux and Temperature

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




- Heat flux per unit area =

  ( = Peltier + Fourier )

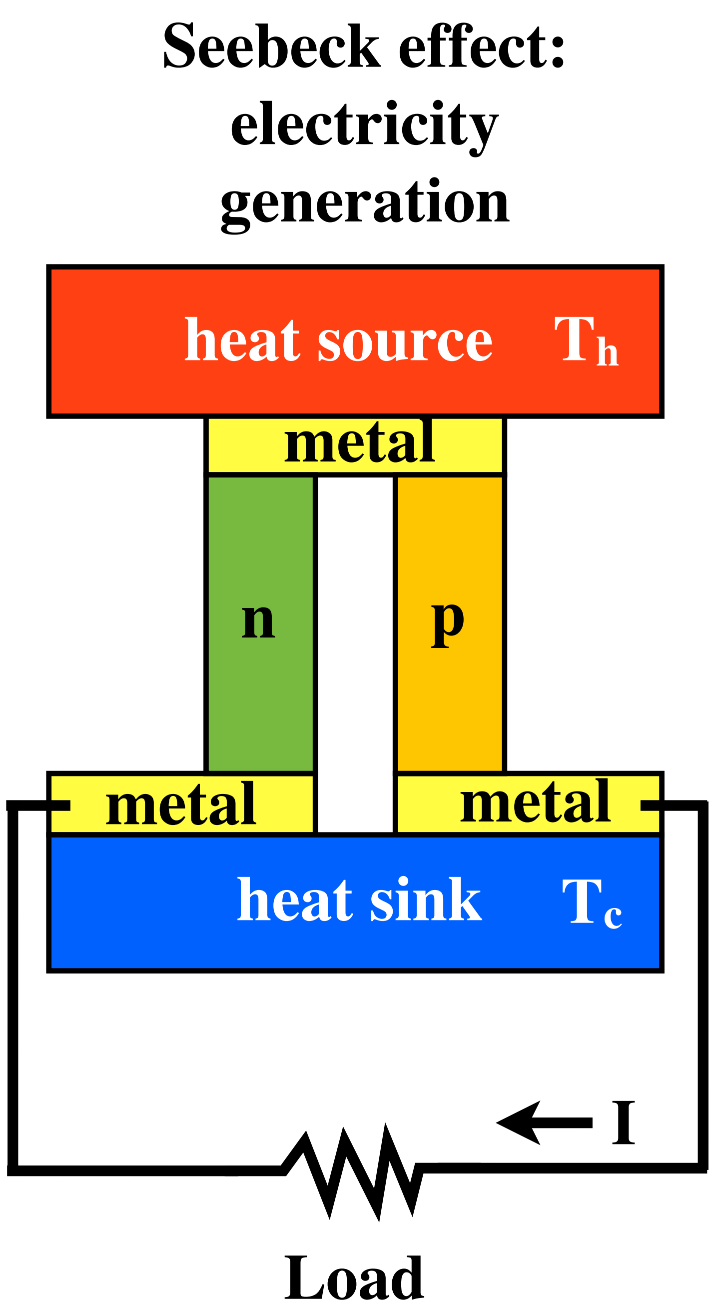
- $$\frac{Q}{A} = \Pi J - \kappa \nabla T$$

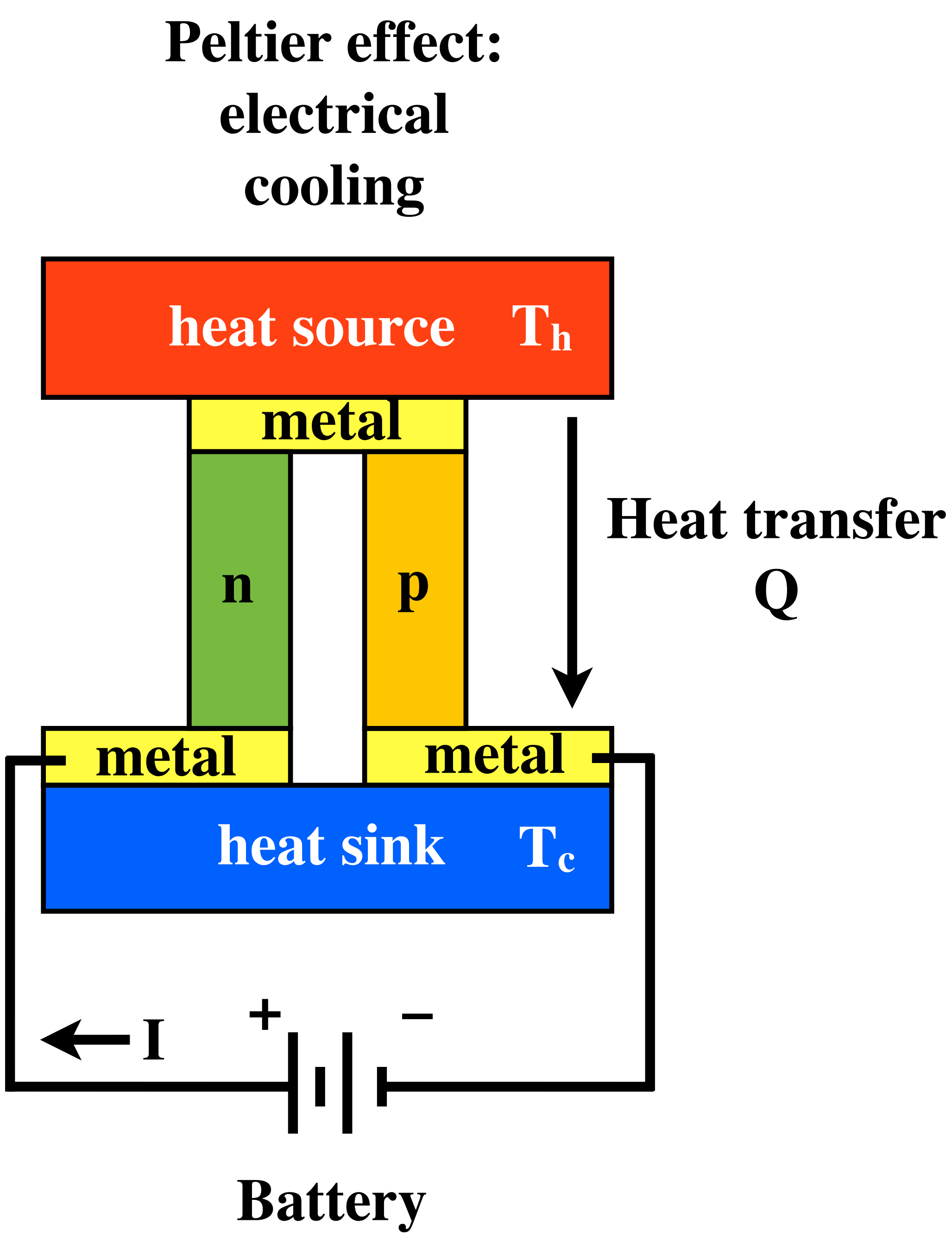
but $\Pi = \alpha T$ and $J = \frac{I}{A}$

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

D.J. Paul
School of Engineering
University of Glasgow

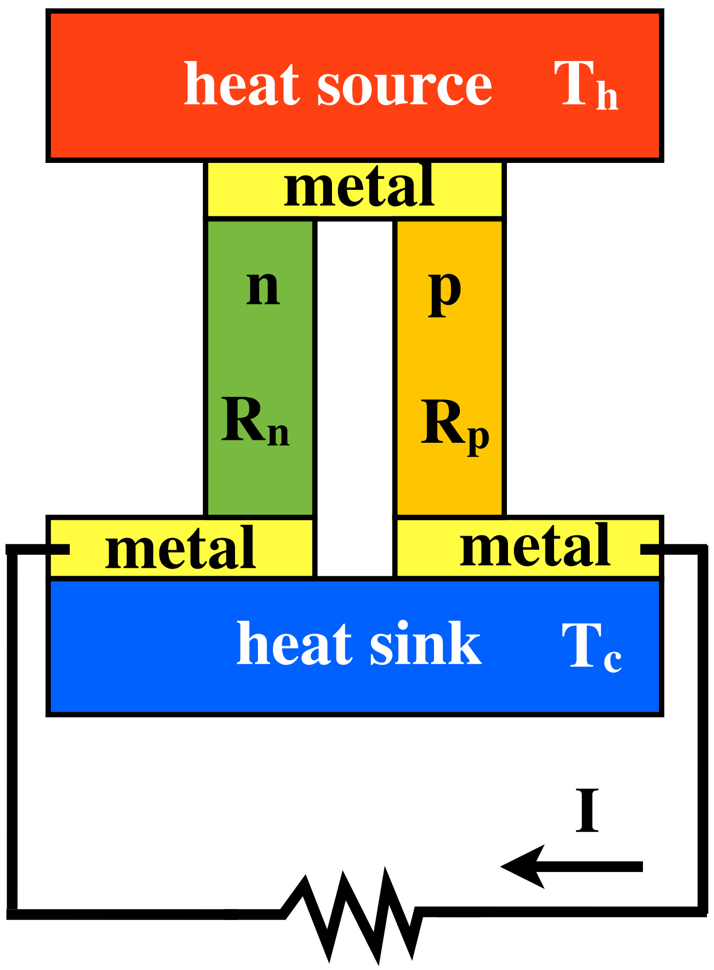
# Semiconductors and Thermoelectrics




*D.J. Paul*
*School of Engineering*
University of Glasgow

# Conversion Efficiency




Load, $R_L$

$R = R_n + R_p$

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

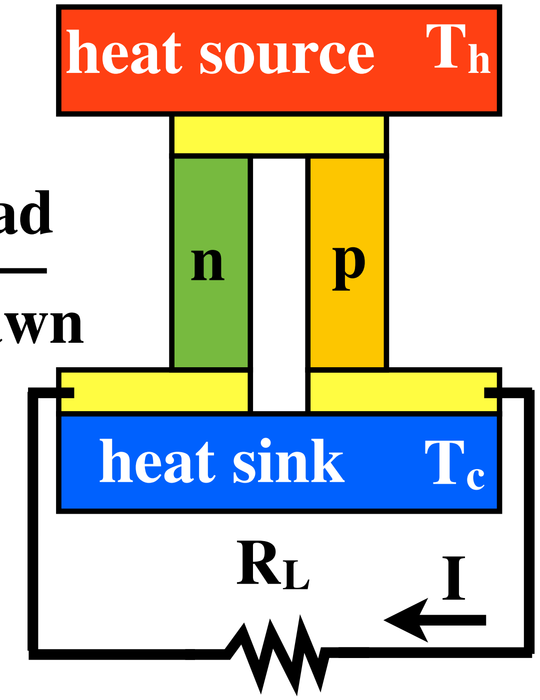
NB half Joule heat returned to hot junction


*D.J. Paul*
*School of Engineering*

University of Glasgow

# Conversion Efficiency

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




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

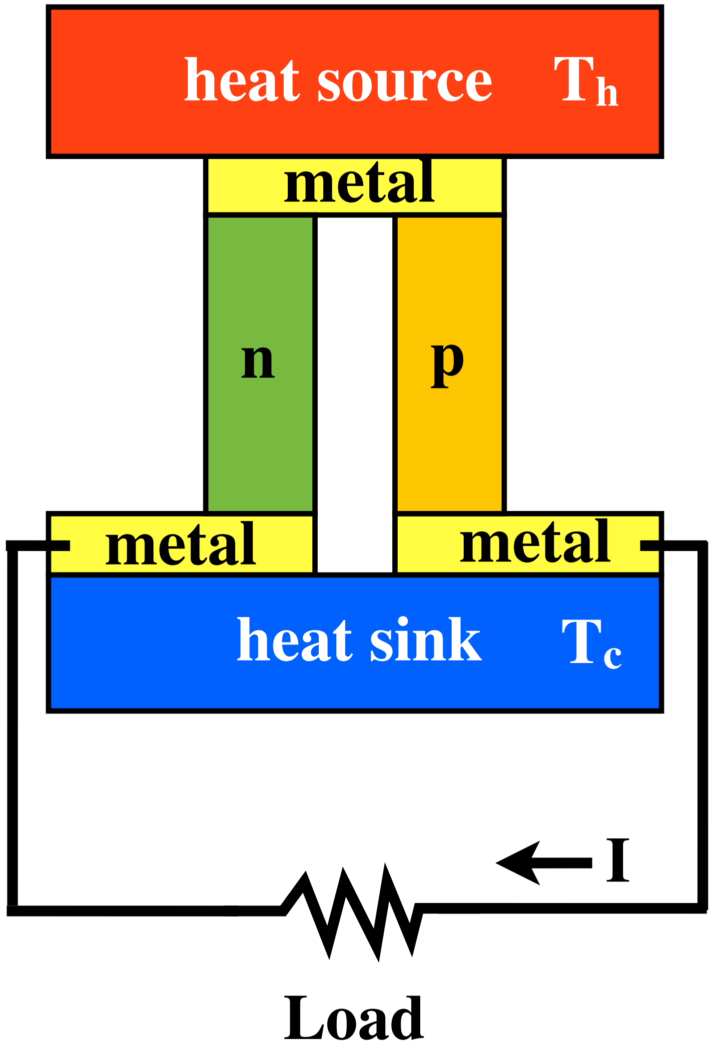
For maximum value $\dfrac{d\eta}{d(\frac{R_L}{R})} = 0$ $\qquad T = \frac{1}{2}(T_h + T_c)$

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

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

= Carnot x Joule losses and irreversible processes

# Thermoelectric Power Generating Efficiency




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

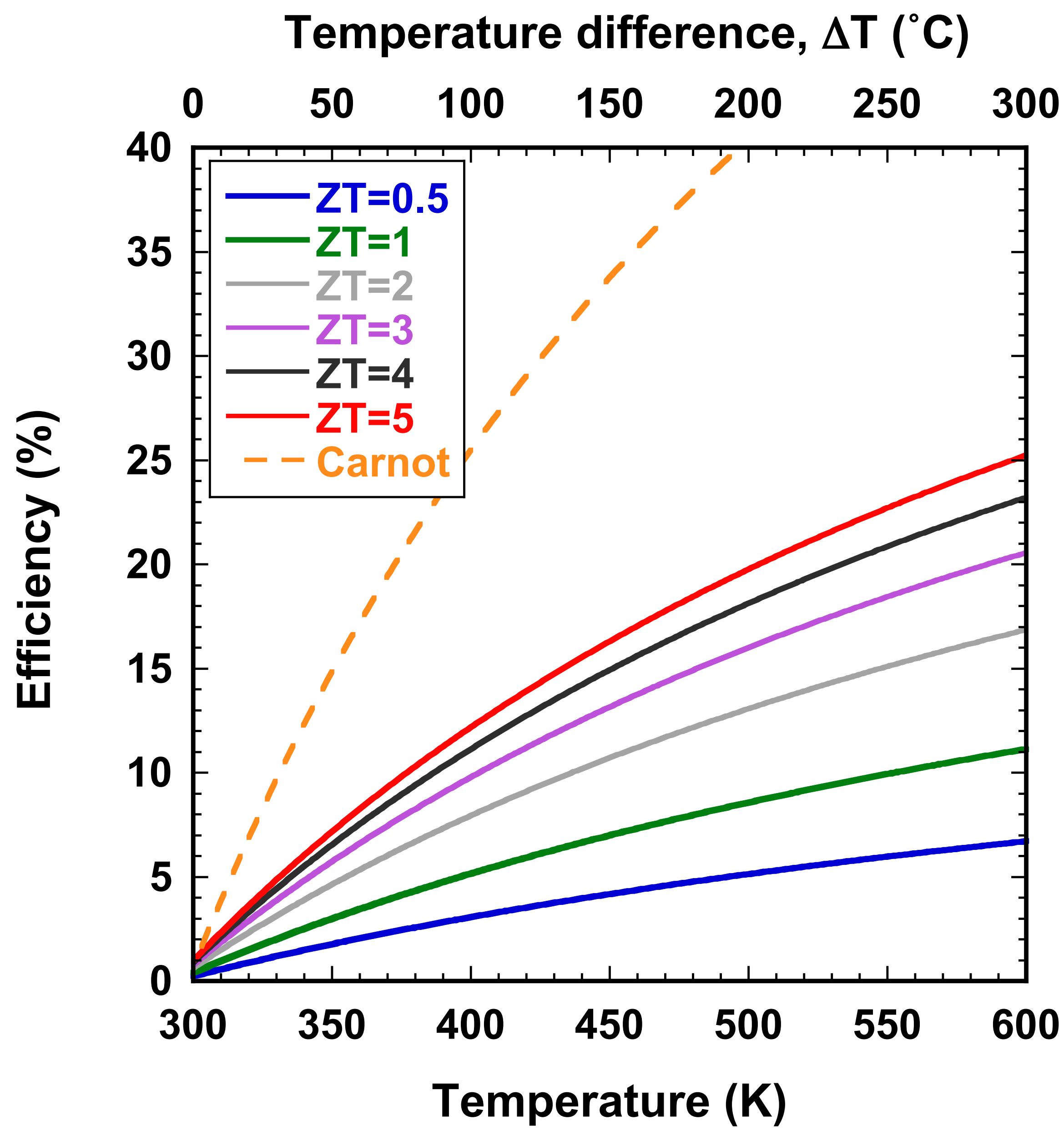


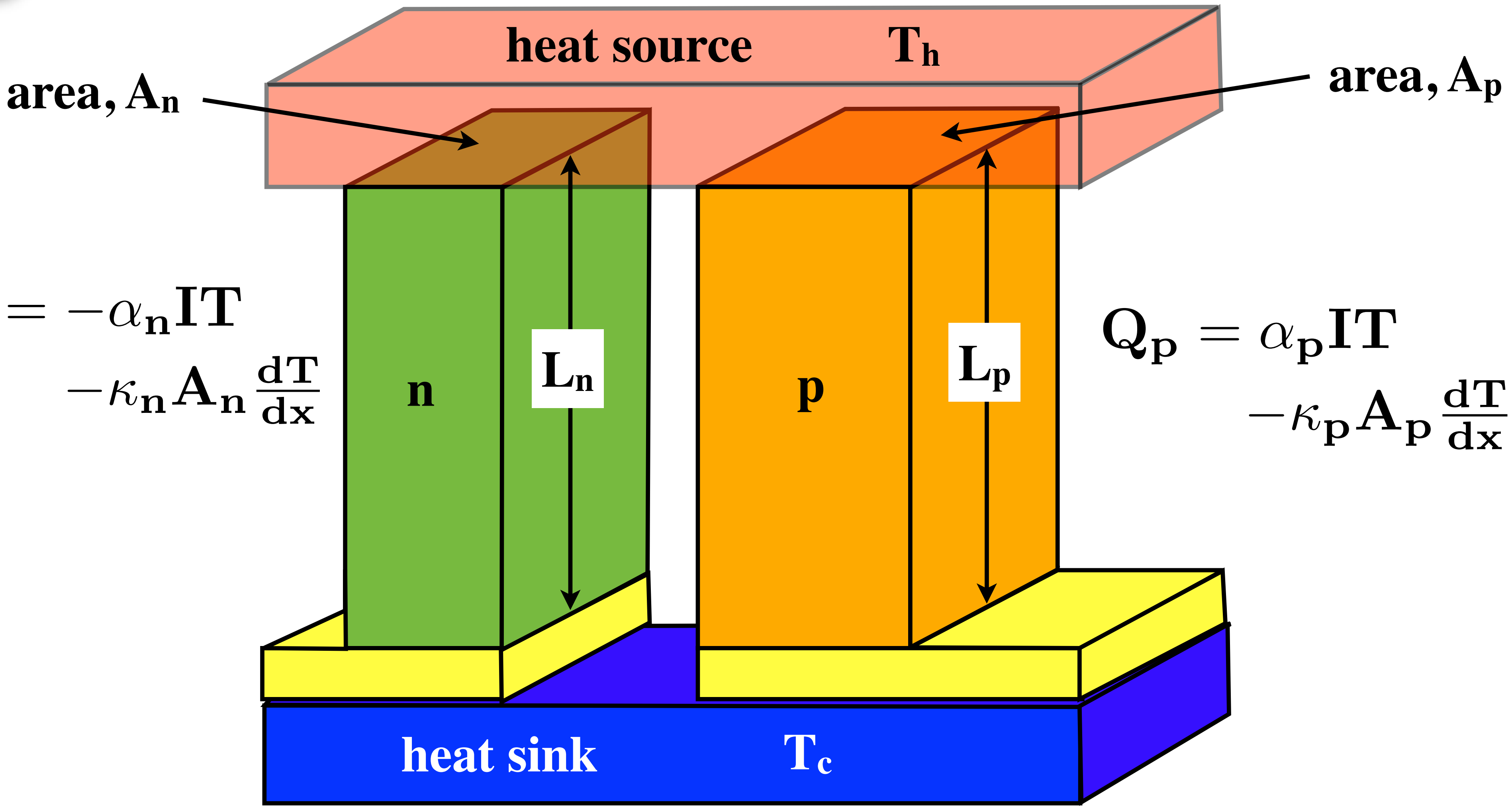

**Figure of merit**

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

*D.J. Paul*
*School of Engineering*
University of Glasgow

# Heat Transfer in Thermoelectric Element

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




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

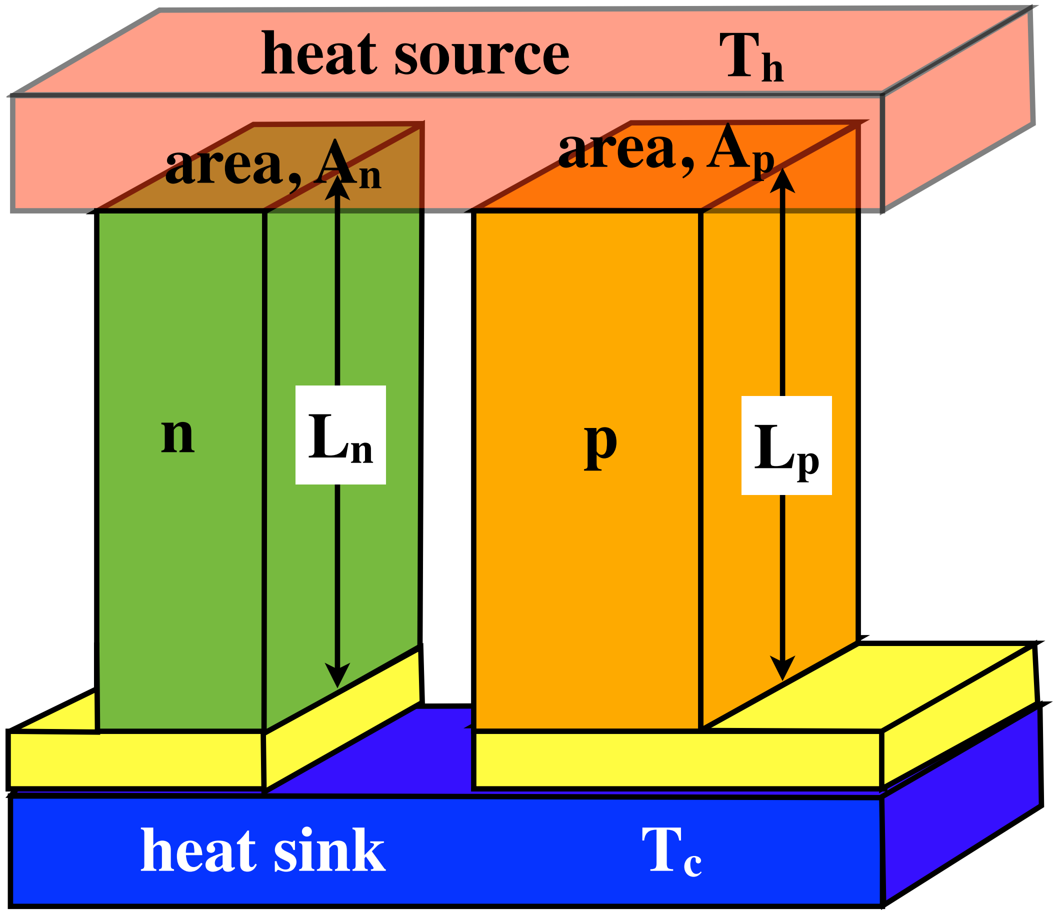
$$Q_p = \alpha_p I T - \kappa_p A_p \frac{dT}{dx}$$

- Z for a couple depends on relative dimensions

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

*D.J. Paul*
*School of Engineering*
University of Glasgow

# Maximising ZT for an Unbalanced Couple




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

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

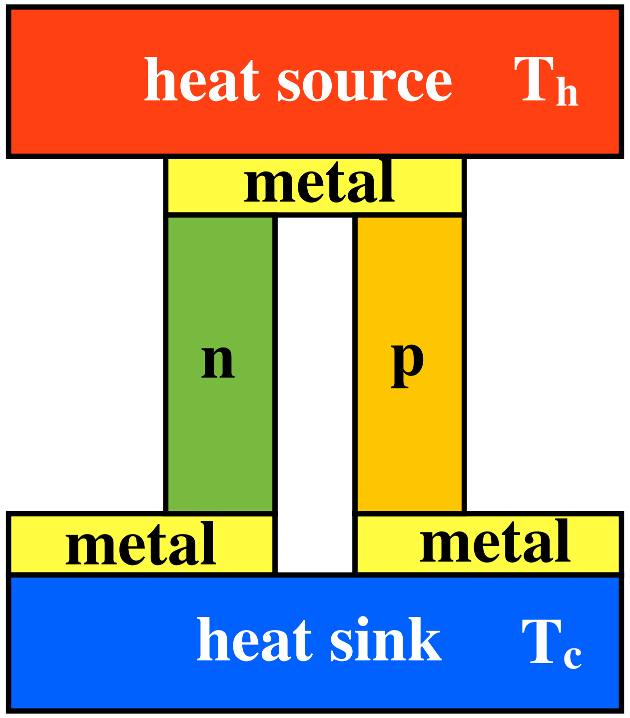
- We need good ZT for both n- and p-type semiconductors

D.J. Paul
School of Engineering
University of Glasgow

# Maximum Temperature Drop

- As the system has thermal conductivity $\kappa$ a maximum $\Delta T$ which can be sustained across a module is limited due to heat transport

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

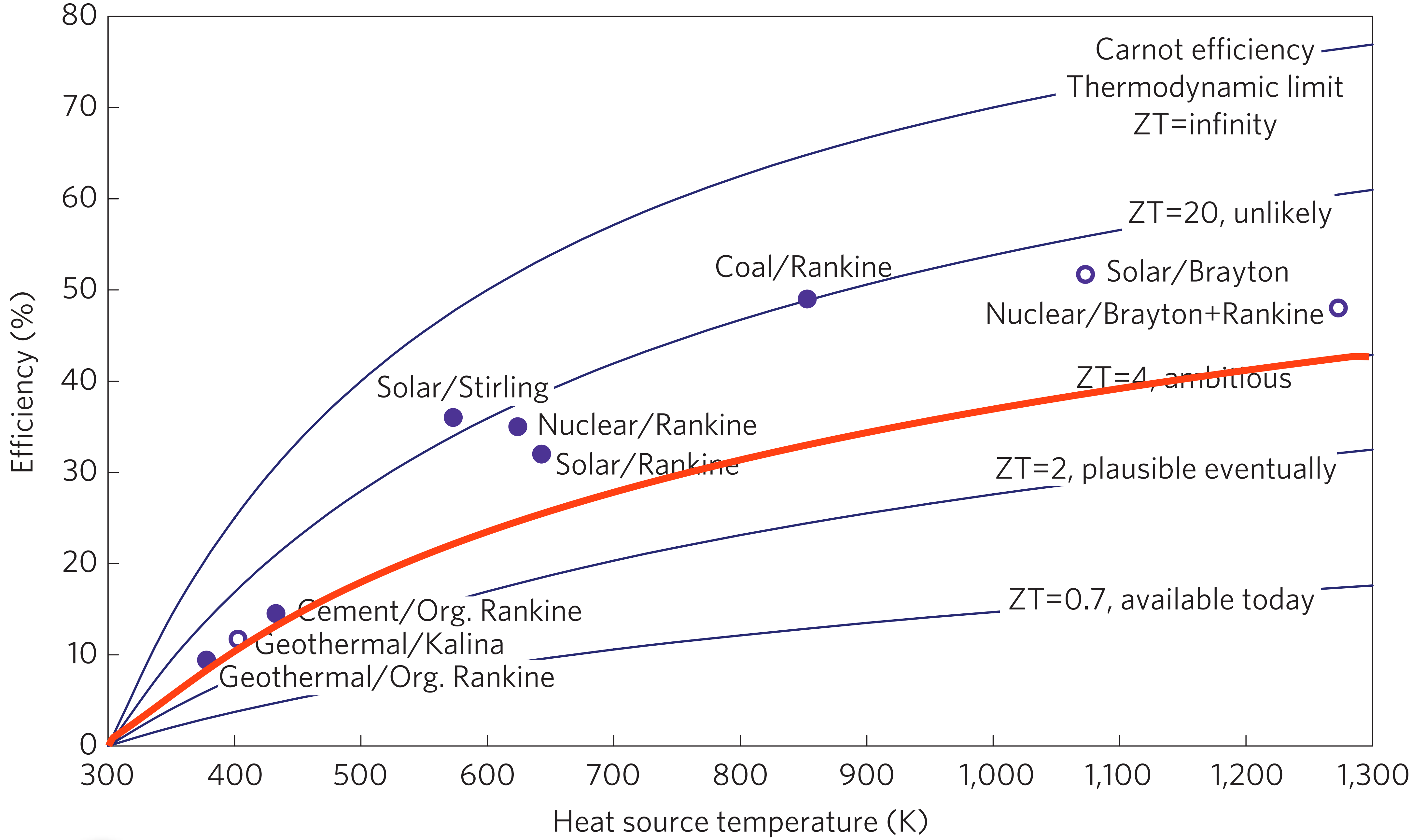



- The efficiency cannot be increased indefinitely by increasing $T_h$

- The thermal conductivity also limits maximum $\Delta T$ in Peltier coolers

- Higher $\Delta T_{max}$ requires better Z materials

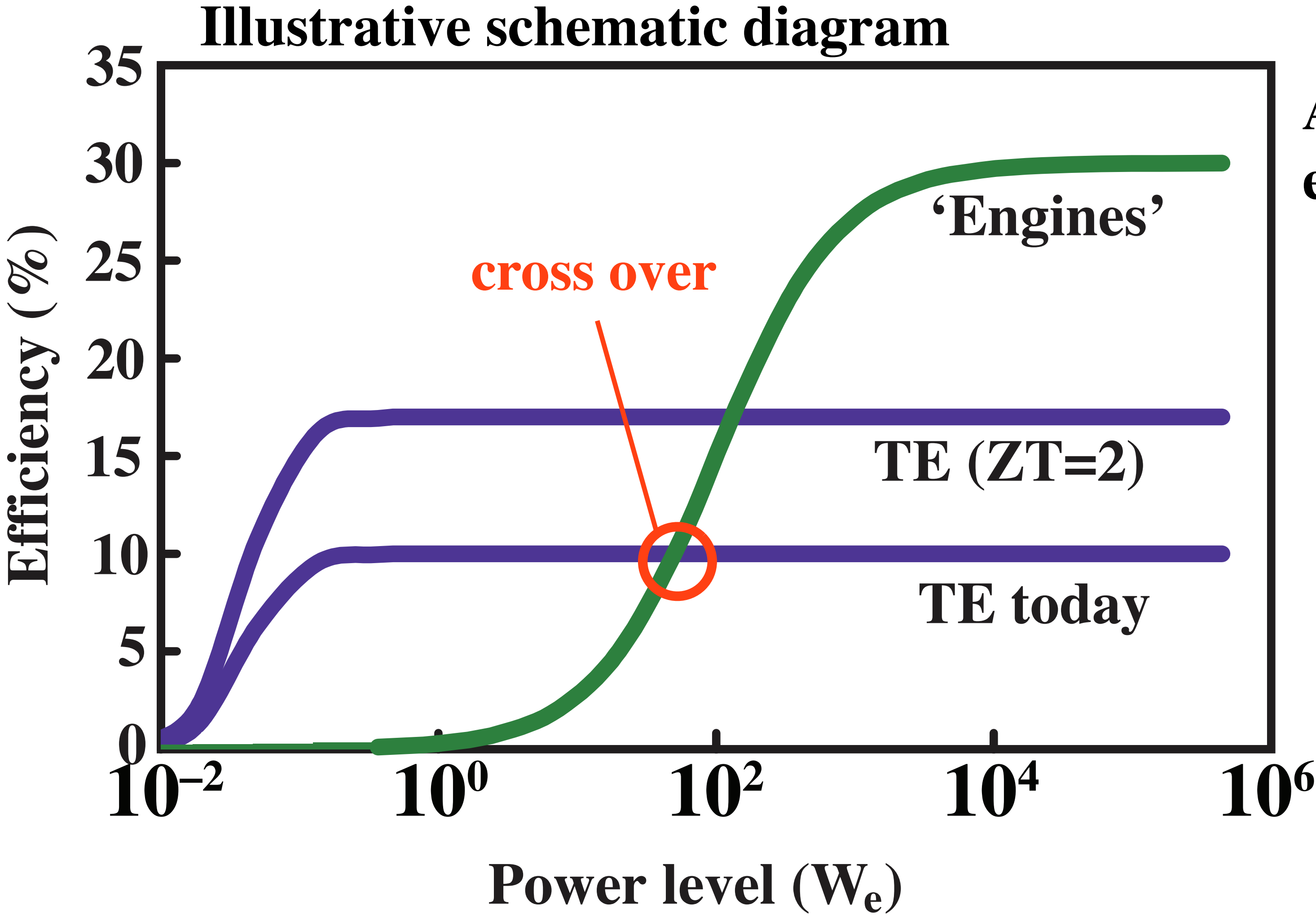
# Thermodynamic Efficiency: The Competition




- **ZT of 4 start to become seriously competitive**

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

# Power Generation From Macro to Micro




At large scale, thermodynamic engines more efficient than TE

ZT average for both n and p over all temperature range

Diagram assumes high T

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

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

# Thermal Conductivity of Bulk Materials

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

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

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

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

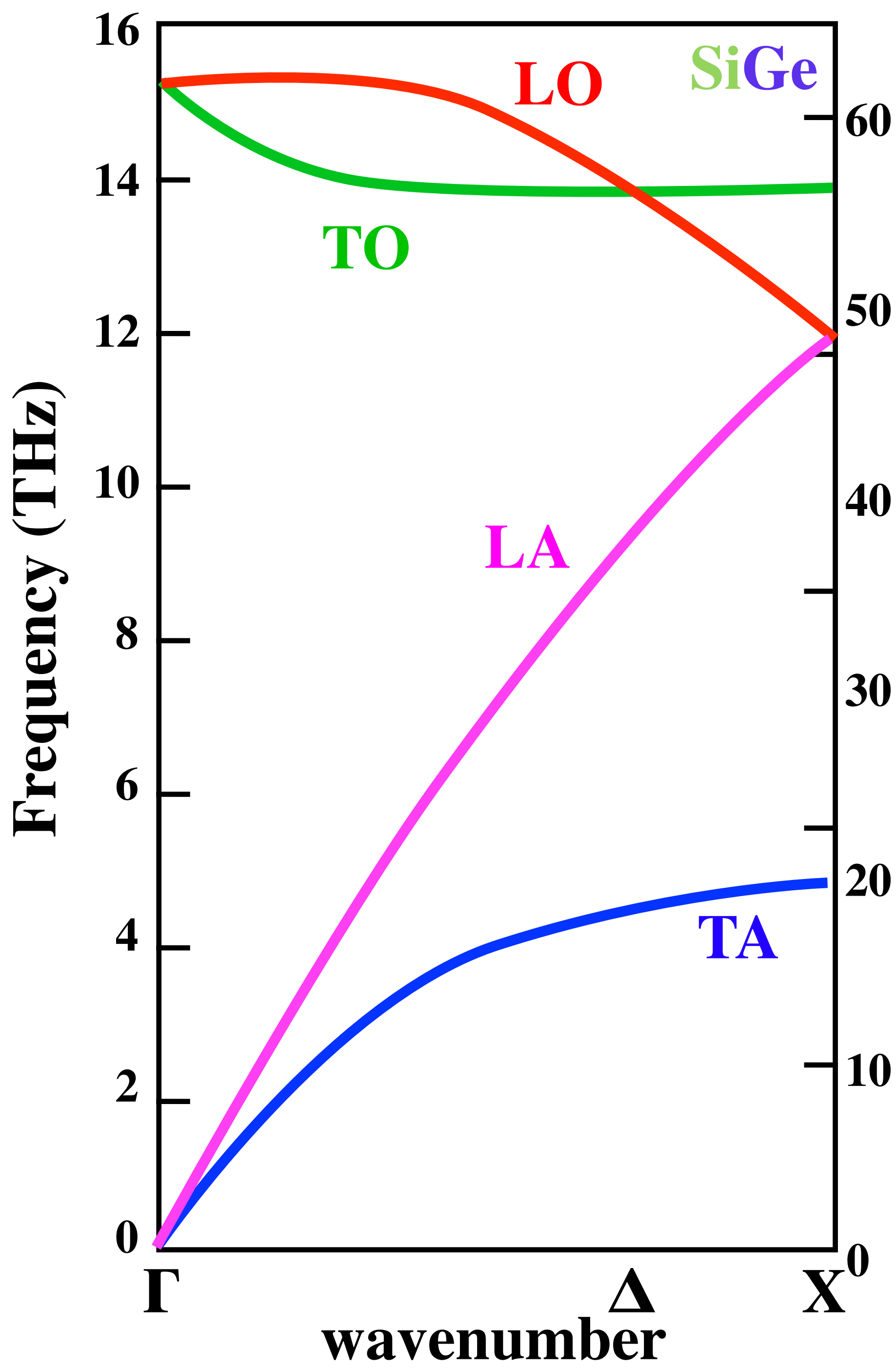
- For high carrier densities in semiconductors (degenerate) $\kappa_{\mathbf{el}} \gg \kappa_{\mathbf{ph}}$

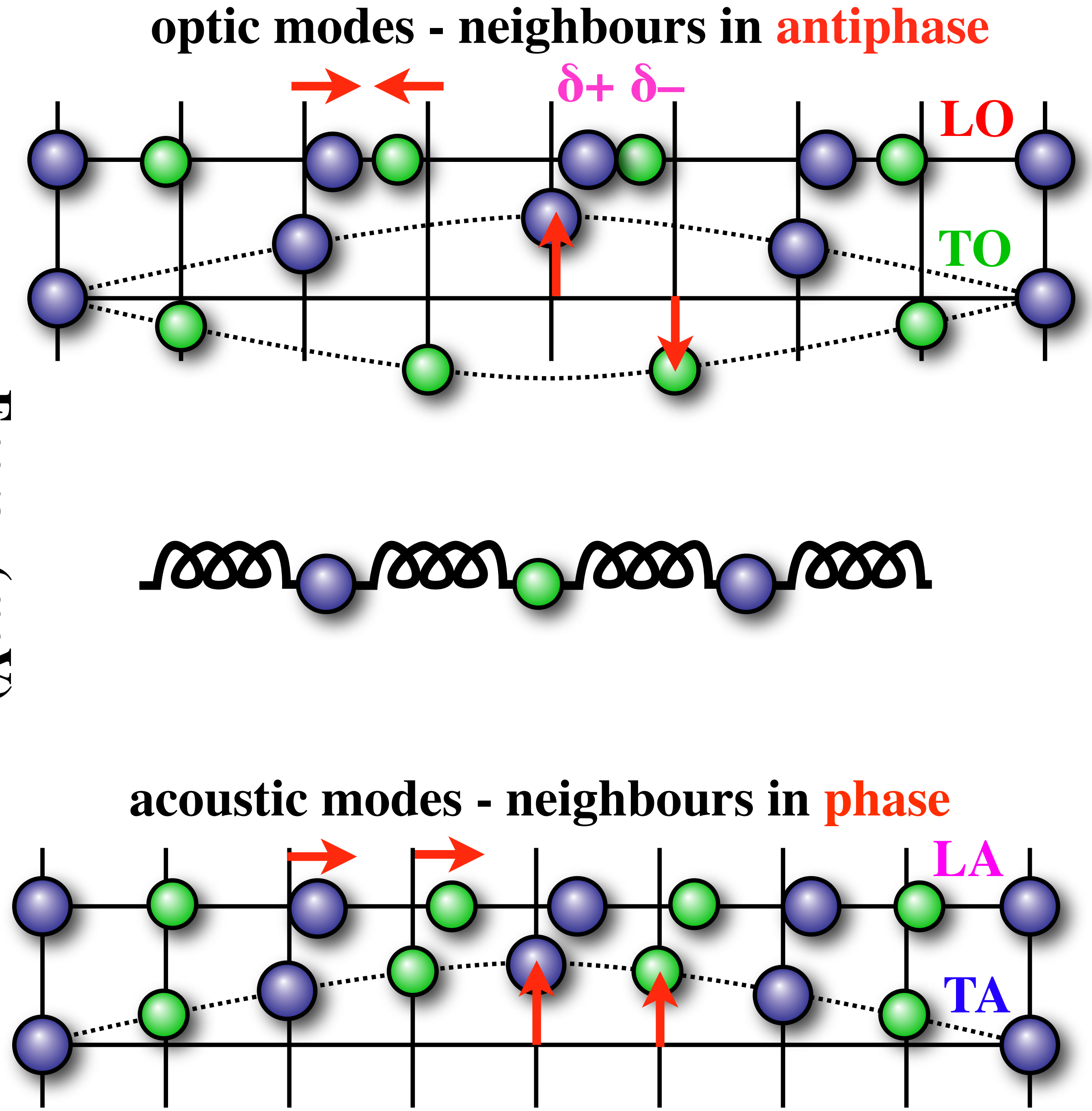
- Good thermoelectric materials should ideally have $\kappa_{\mathbf{el}} \ll \kappa_{\mathbf{ph}}$

i.e. electrical and thermal conductivities are largely decoupled

D.J. Paul
School of Engineering
University of Glasgow

# Phonons: Lattice Vibration Heat Transfer



# Wiedemann-Franz Law

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

# Wiedemann-Franz Law for Metals

- In metals, the thermal conductivity is dominated by $\kappa_{\mathrm{el}}$

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

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

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

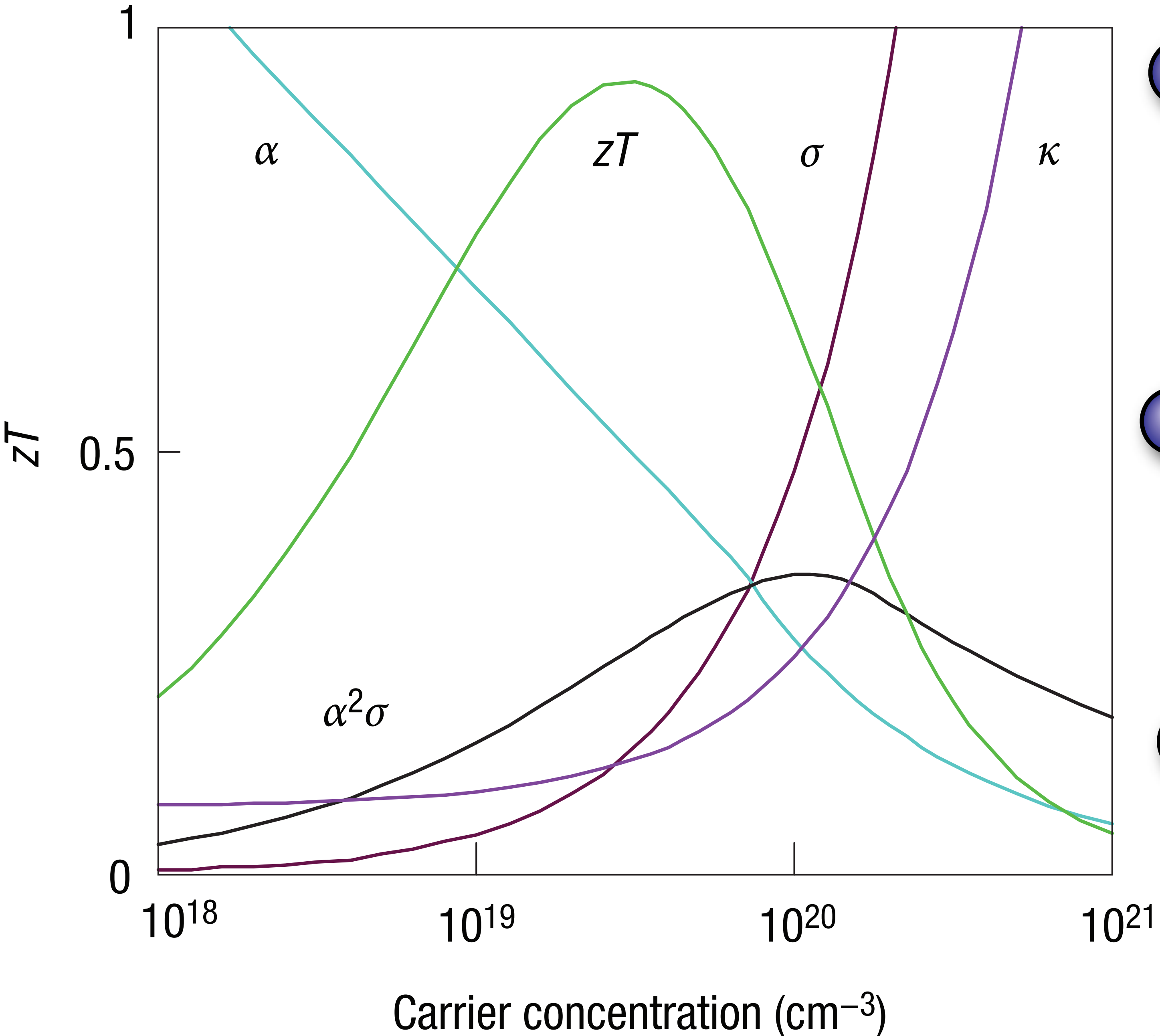
for $\kappa_{\mathrm{el}} \gg \kappa_{\mathrm{ph}}$

**Exceptions:**

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

*D.J. Paul*
*School of Engineering*
University of Glasgow

# $Bi_2Te_3$ ZT Optimisation Through Doping

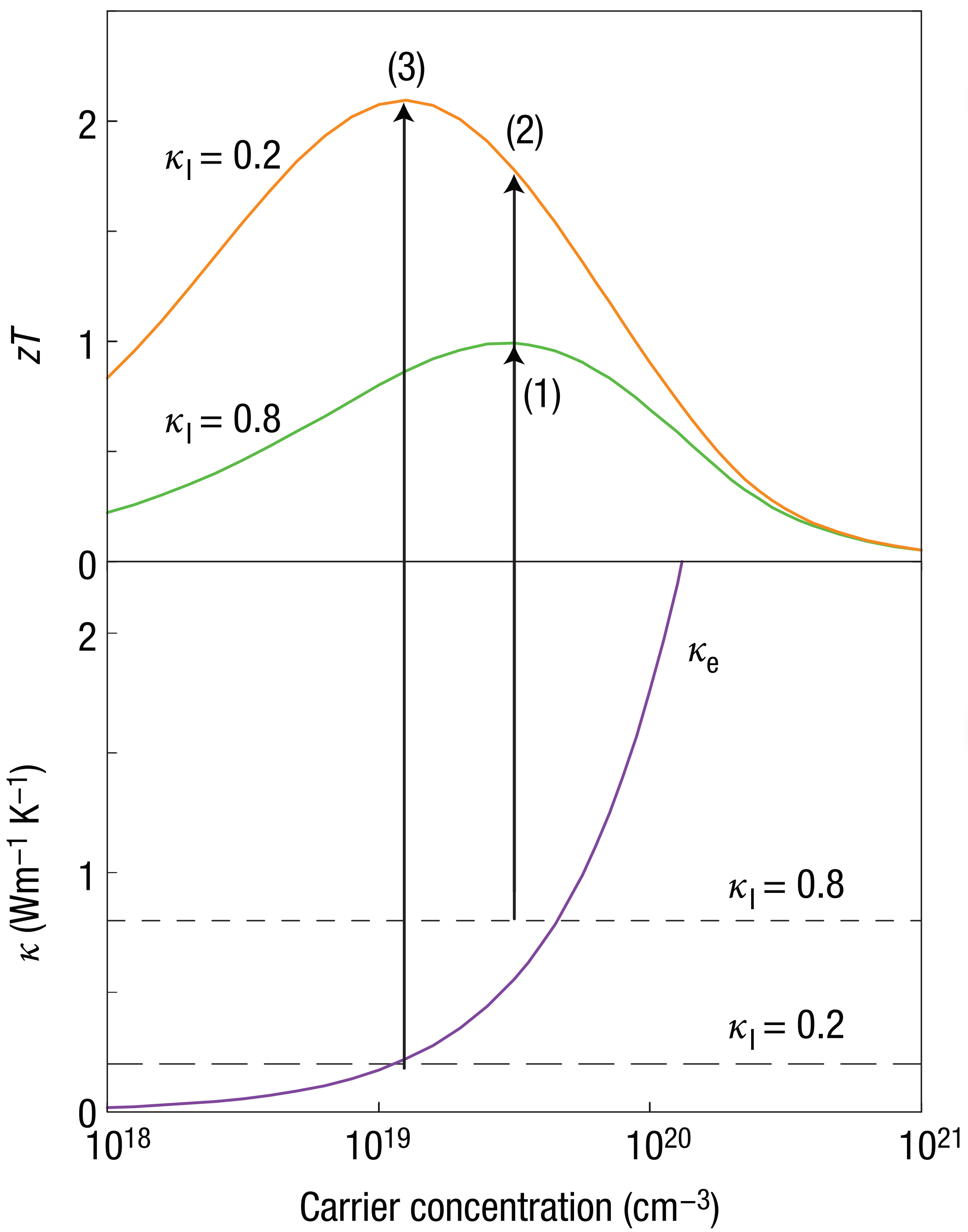



- Maximum ZT requires compromises with α, σ & κ
- Limited by Wiedemann-Franz Law
- Maximum ZT ~ 1 at ~100 ˚C

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


D.J. Paul
School of Engineering
University of Glasgow

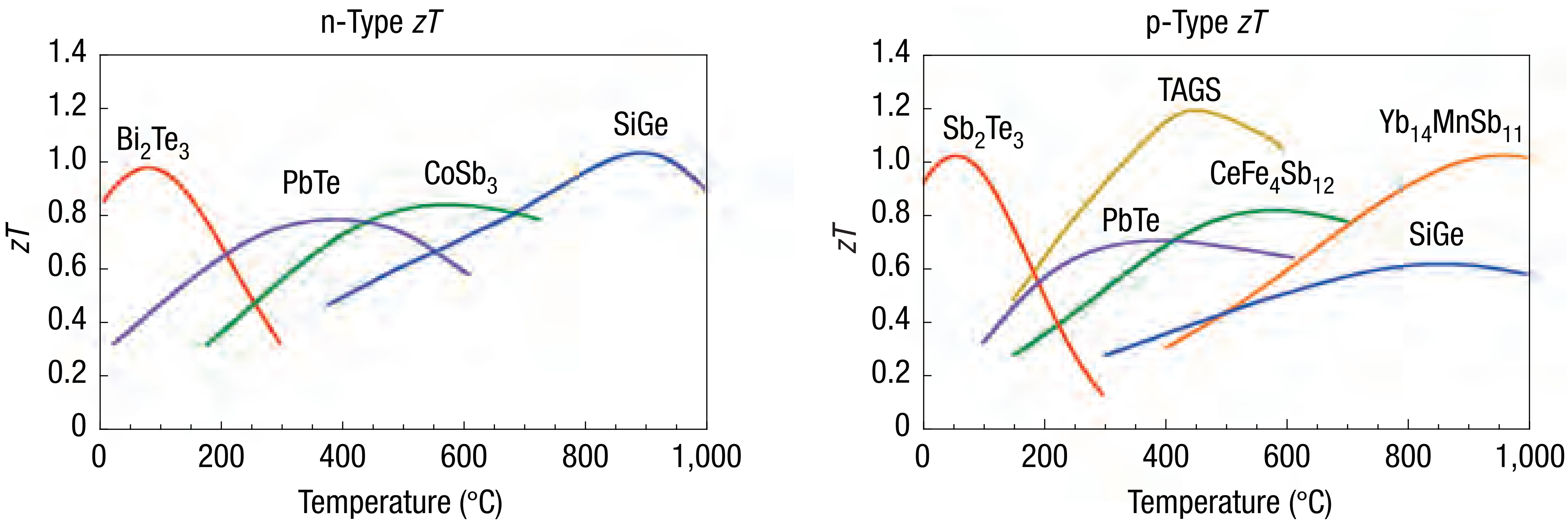
# Optimising ZT in Bulk by Reducing $\kappa_{\mathbf{ph}}$




- **Example for $Bi_2Te_3$ where $\kappa_{\mathbf{ph}}$ is theoretically reduced by x 4**
- **Polycrystalline or defects can be used to reduce $\kappa_{\mathbf{ph}}$ faster than σ**
- $$\mathbf{ZT} = \frac{\alpha^{\mathbf{2}}}{\mathbf{L}(\mathbf{1}+\frac{\kappa_{\mathbf{ph}}}{\kappa_{\mathbf{el}}})}$$
- **"Phonon glasses" search to improve ZT**

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

# Bulk Thermoelectric Materials Performance

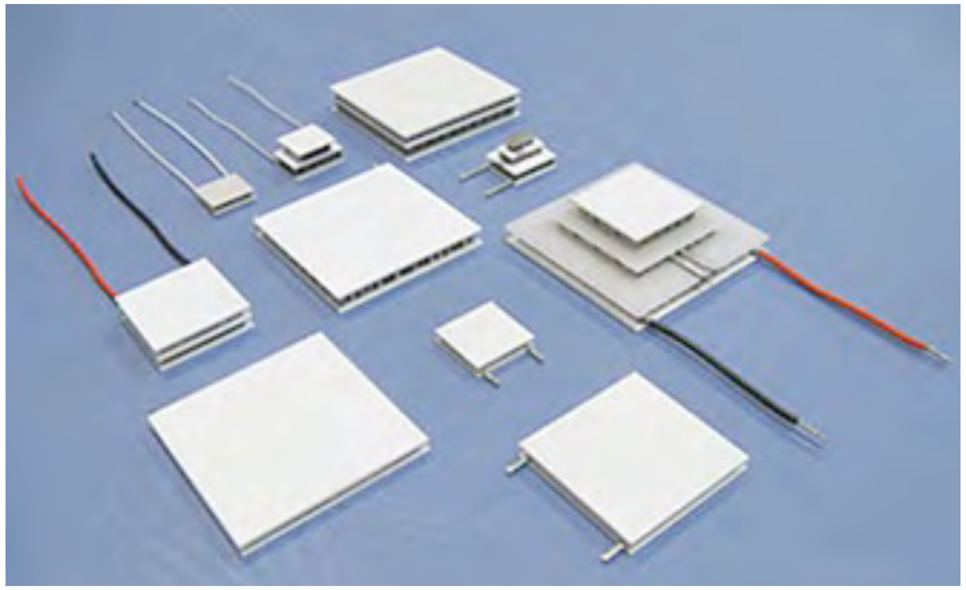



*Nature Materials 7, 105 (2008)*

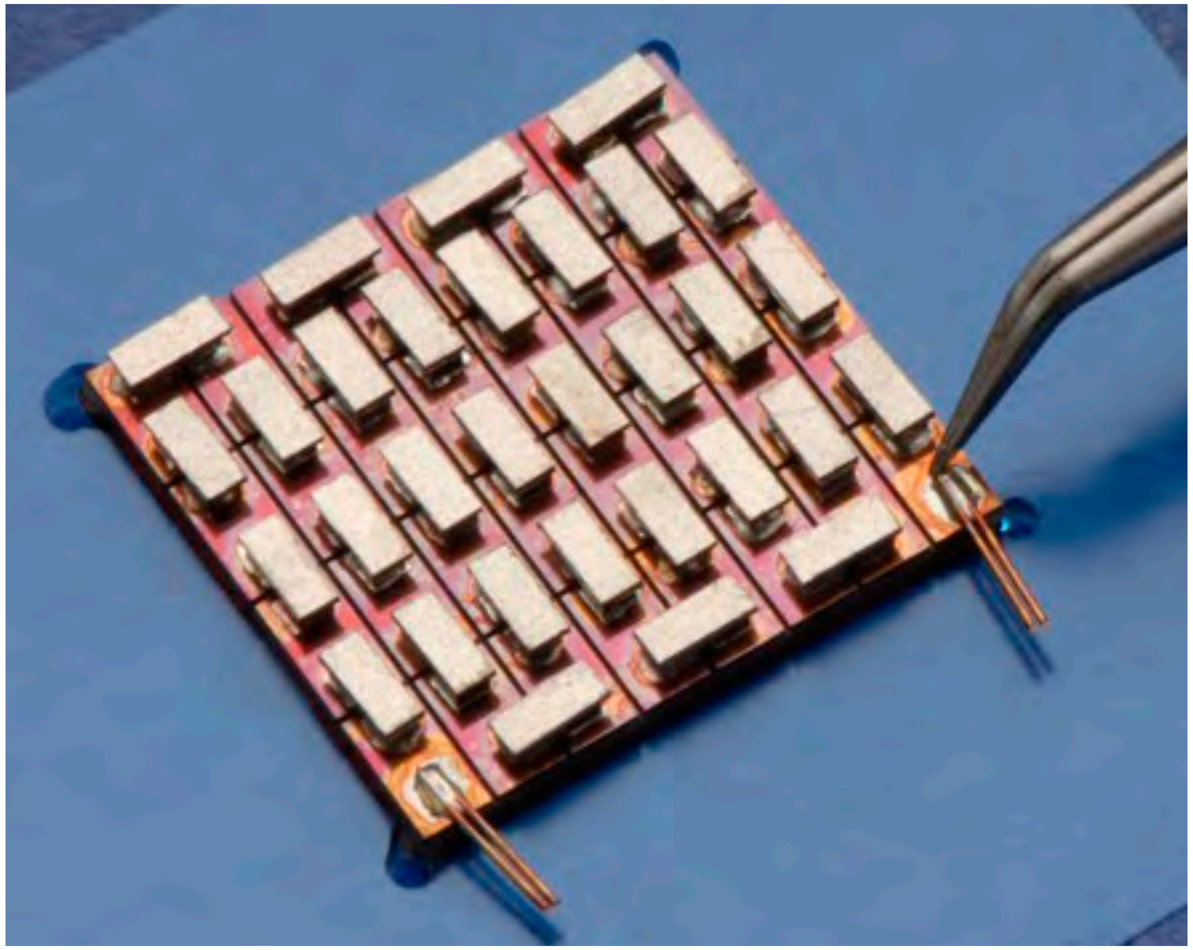
- **Bulk n-$Bi_2Te_3$ and p-$Sb_2Te_3$ used in most commercial Peltier coolers**
- **Bulk $Si_{1-x}Ge_x$ (x~0.2 to 0.3) used for high temperature satellite applications**

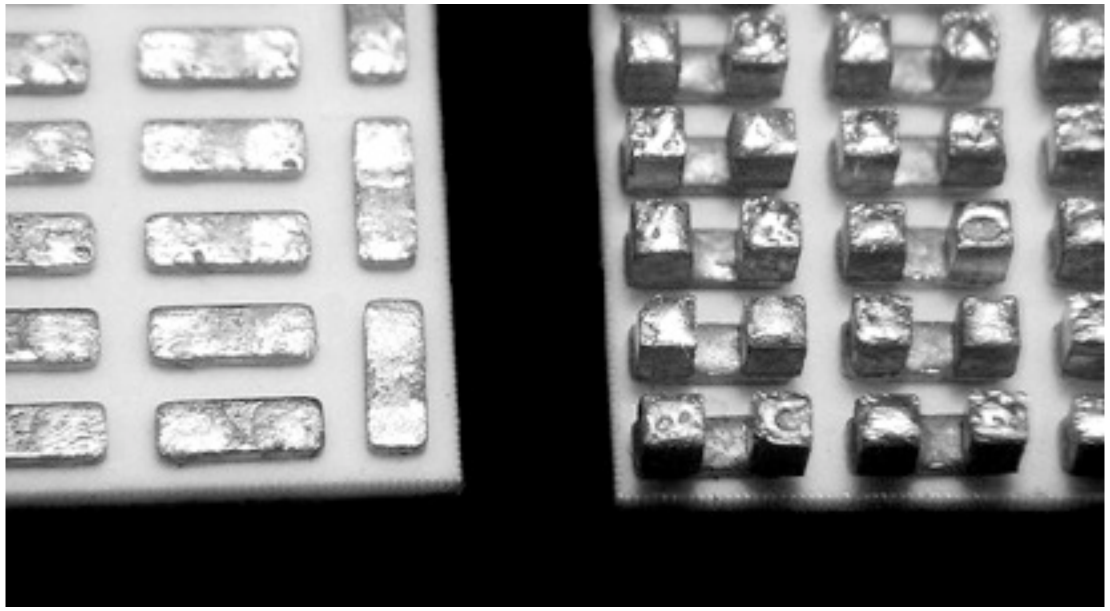
*D.J. Paul*
*School of Engineering*
University of Glasgow

# Thermoelectric Generators / Peltier Coolers



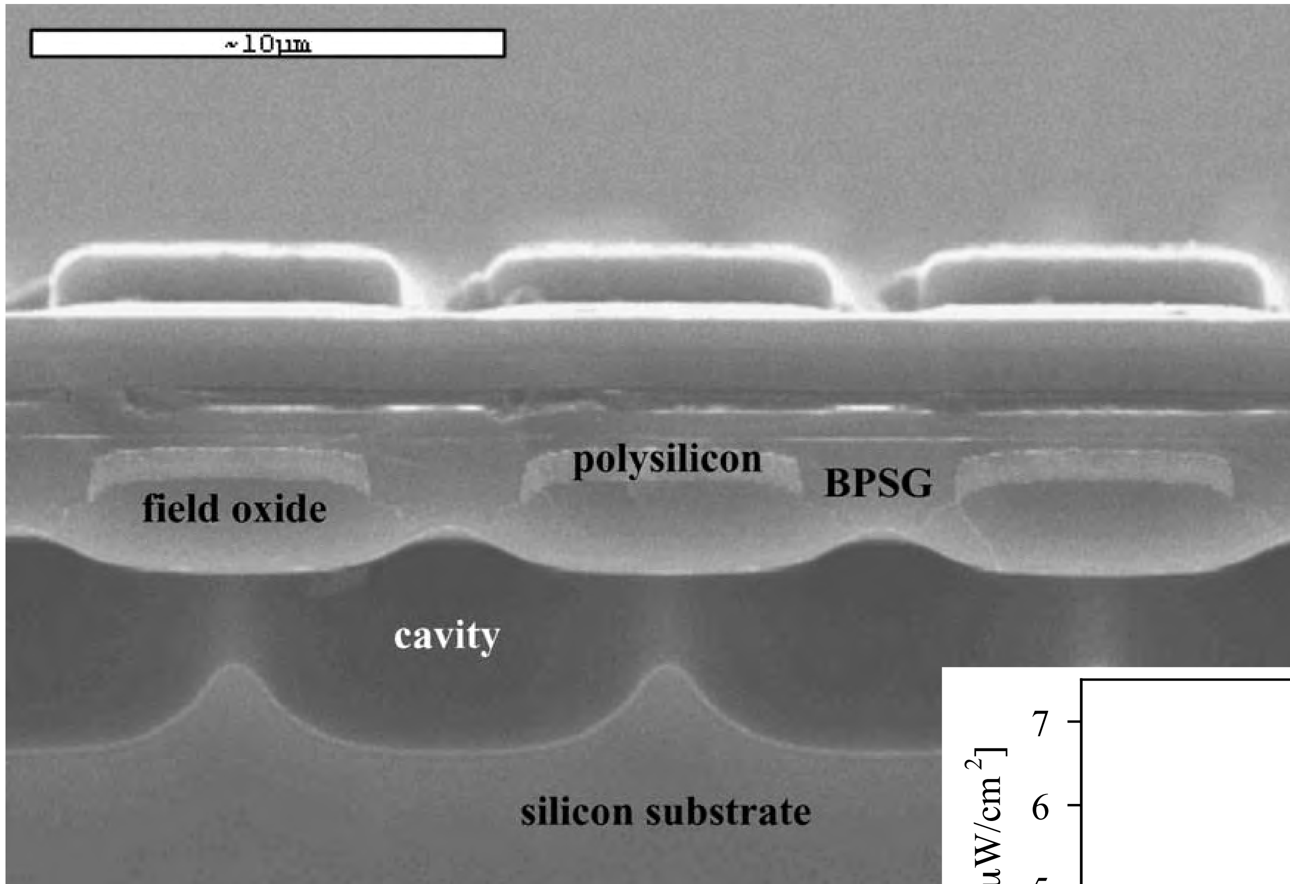
Bulk n-$Bi_2Te_3$ and p-$Sb_2Te_3$ devices



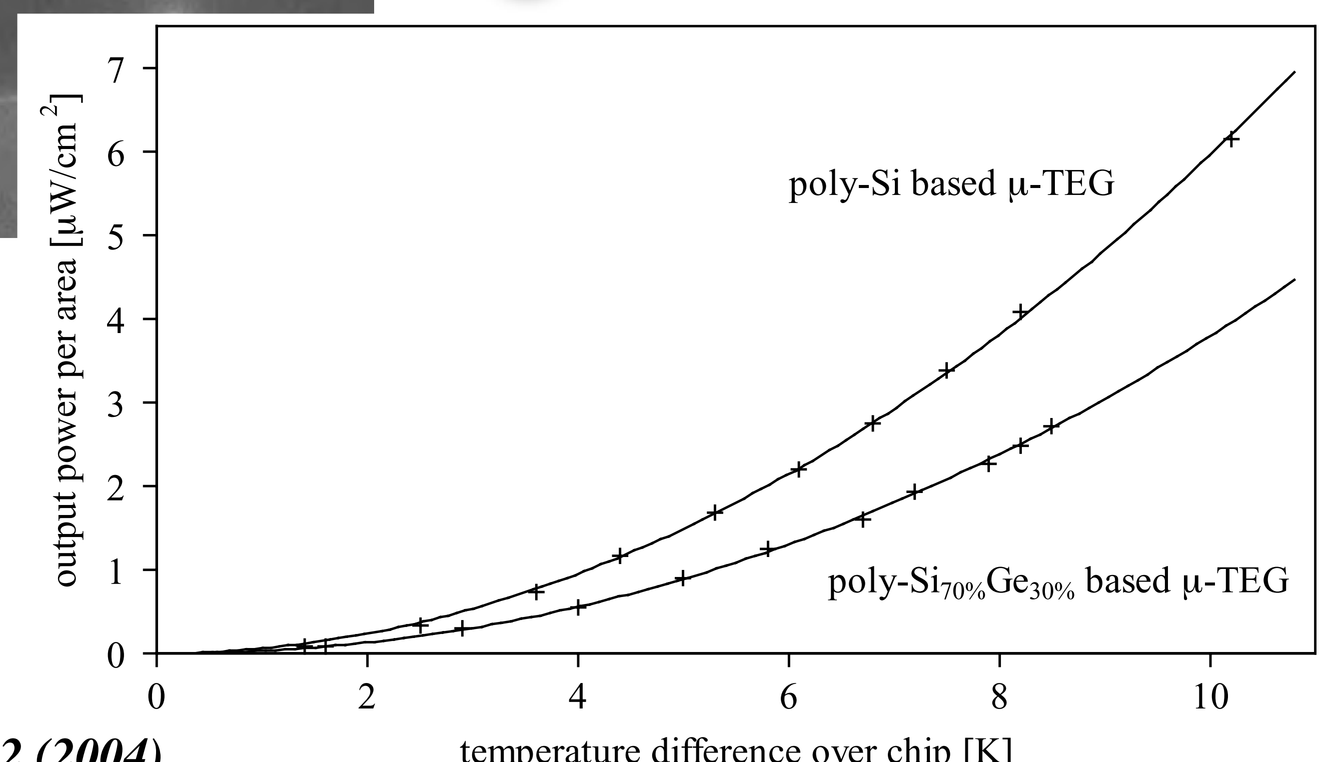


*D.J. Paul*
*School of Engineering*
University of Glasgow

# Small Scale Microfabricated Energy Harvesting



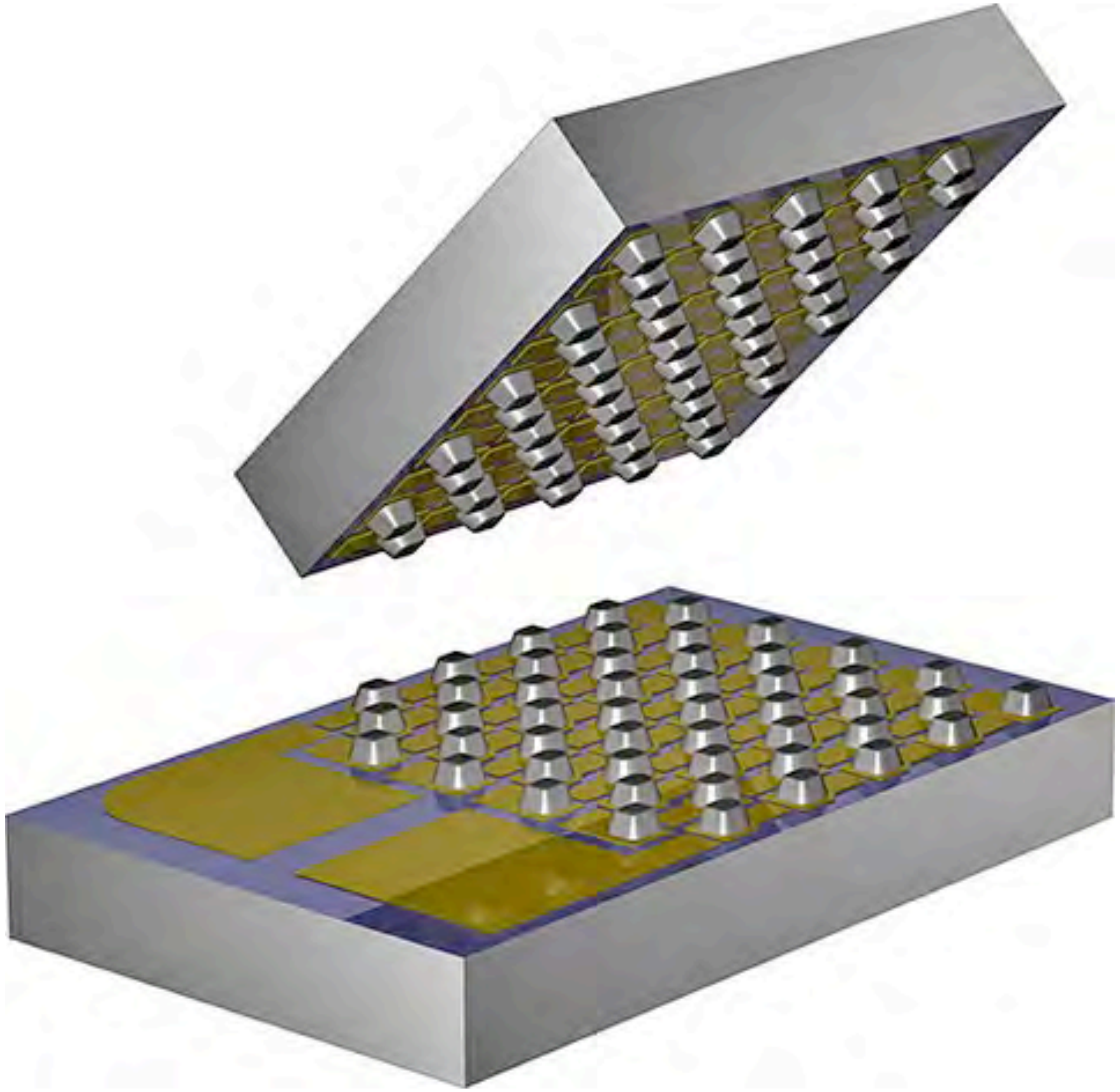

- Si process: poly-Si
- $\alpha_{n+p} = 160\ \mu V/K$
- $\varkappa = 31.4\ Wm^{-1}K^{-1}$
- $\varrho = 1.5\ m\Omega\text{-cm}$

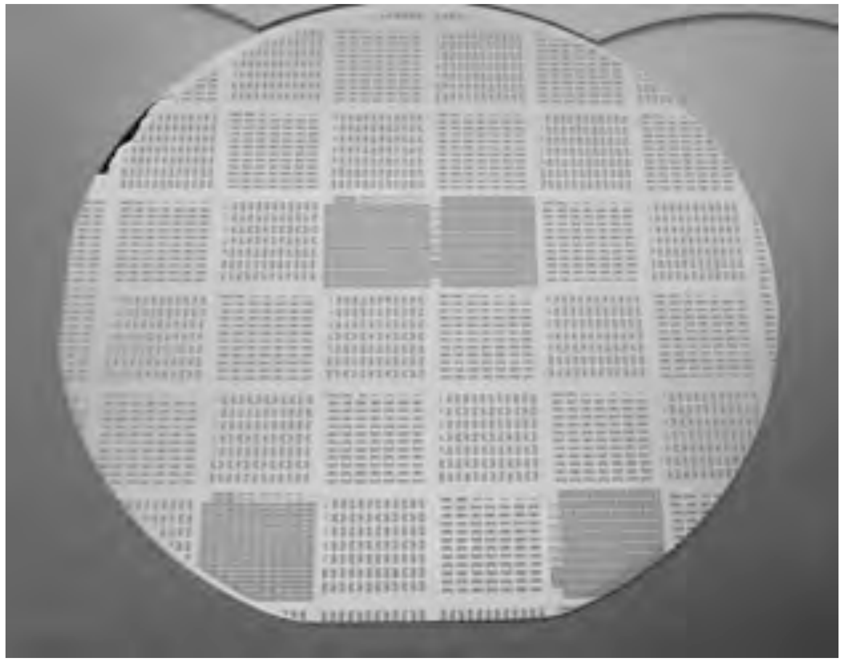


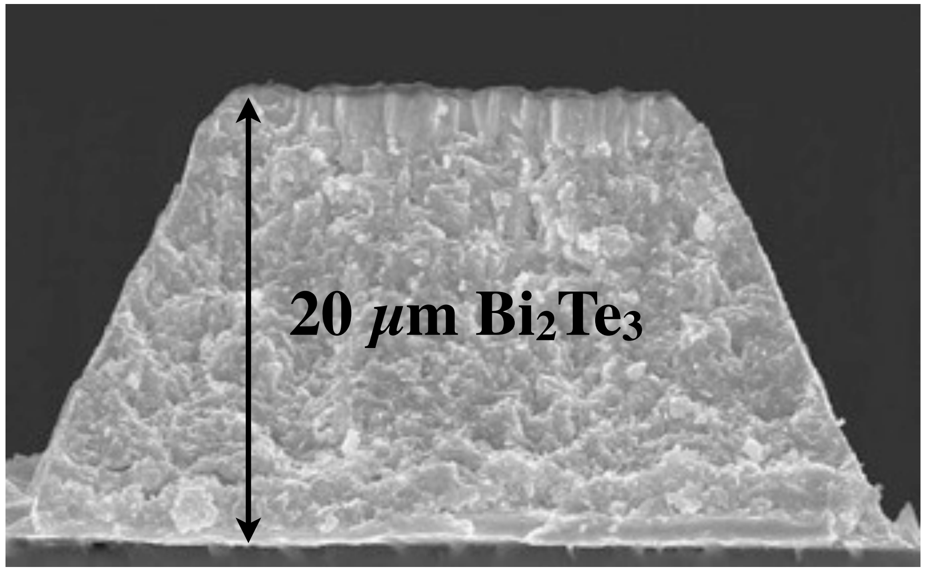

**$\Delta T = 5$ K –> 5 V and 1 $\mu$W**

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

# Micropelt: Microfabricated $Bi_2Te_3$ Technology







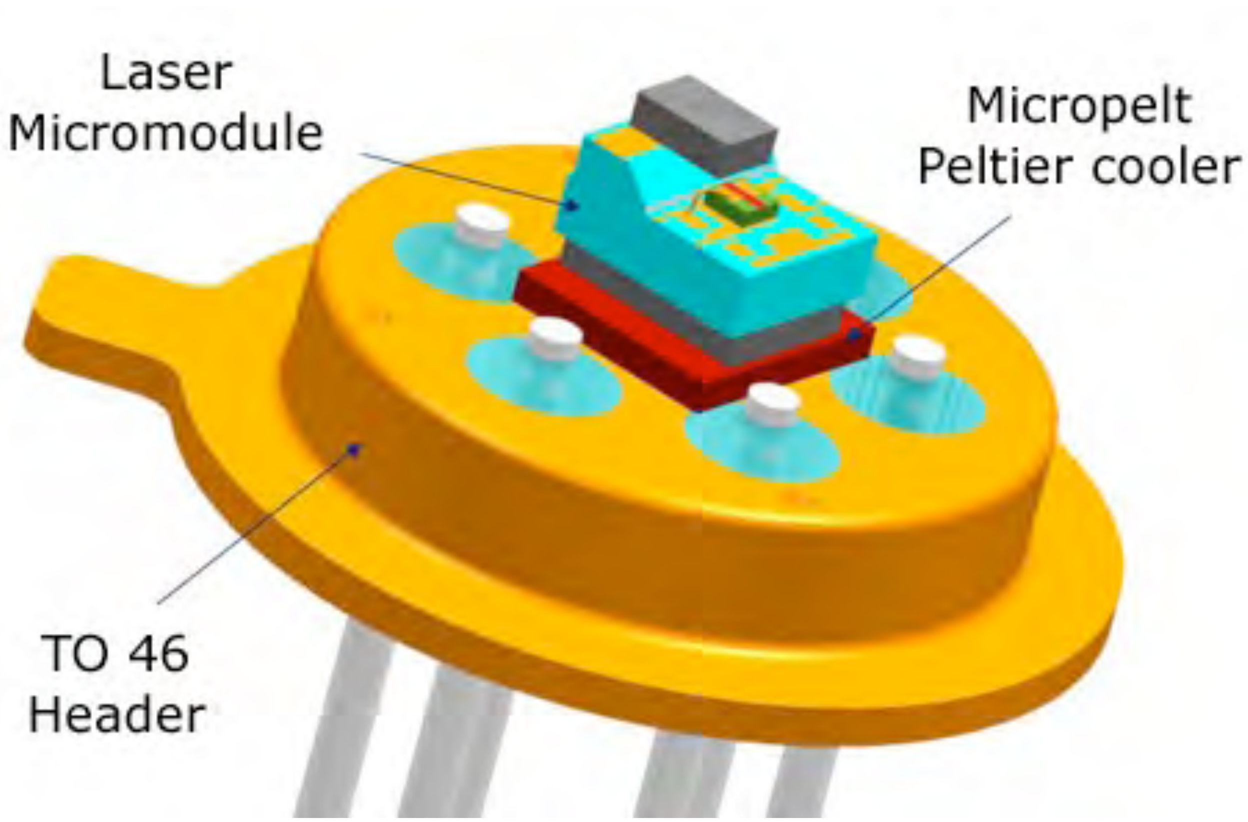

http://www.micropelt.com/

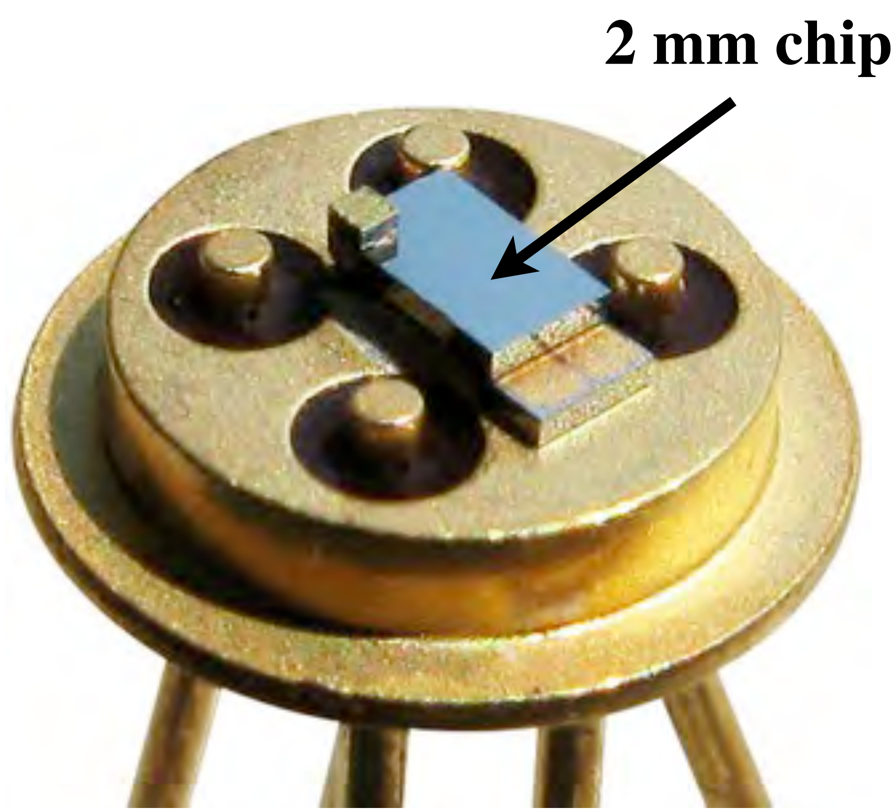

*D.J. Paul*
*School of Engineering*

University of Glasgow

# Micropelt Peltier Coolers for Lasers

- Microfabricated $Bi_2Te_3$ thermoelectric devices



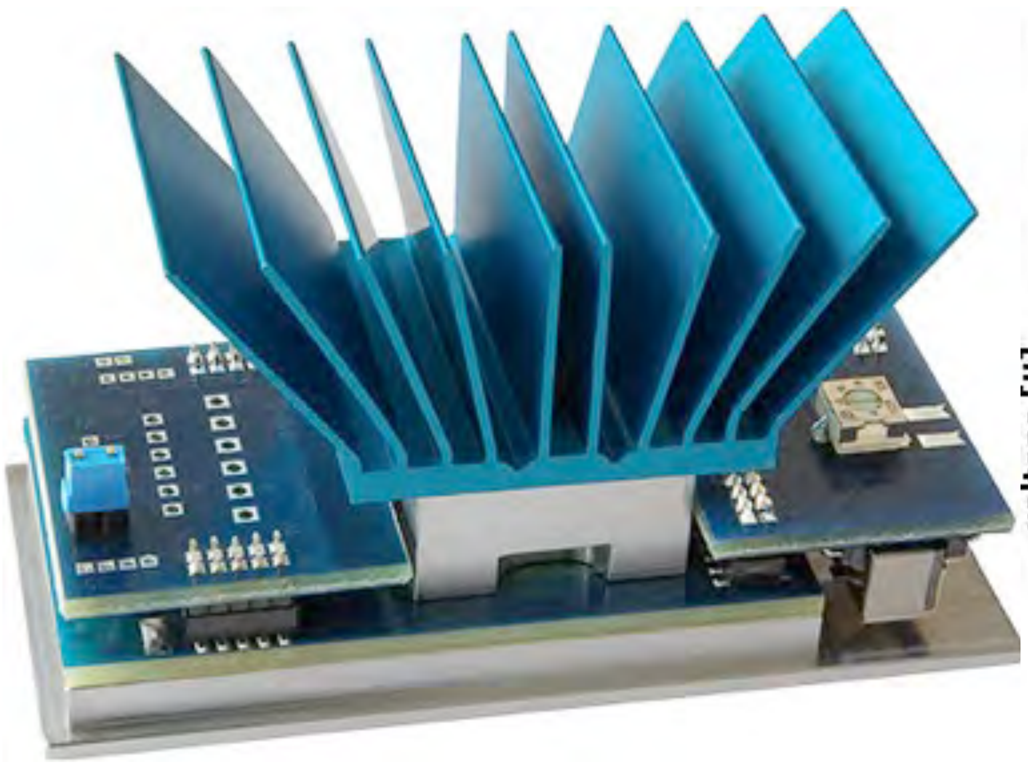




*http://www.micropelt.com/*

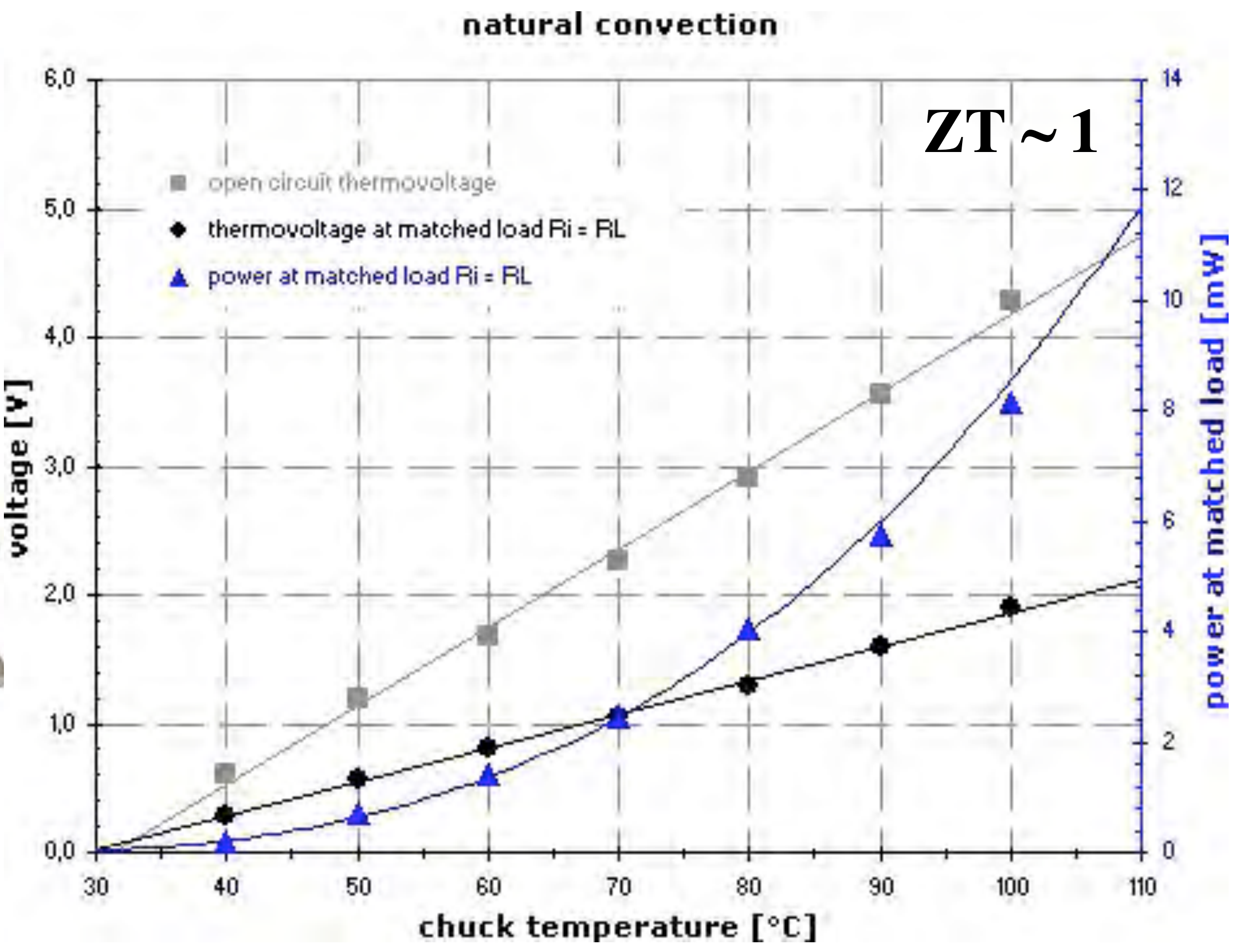
***D.J. Paul***
***School of Engineering***

University of Glasgow

# Micropelt $Bi_2Te_3$ Thermoelectric Energy Harvester



3.4 mm x 3.4 mm
thermoelectric chip




*http://www.micropelt.com/*

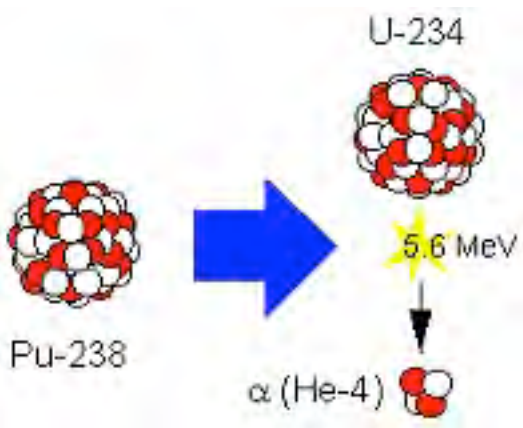
# Present Thermoelectric Energy Harvesting

- VW and BMW announced TE on exhaust in 2008: 24 $Bi_2Te_3$ modules
- 600 W under motorway driving –> 30% of car's electrical requirement
- 5% reduction in fuel consumption through removing alternator

*D.J. Paul*
*School of Engineering*
University of Glasgow

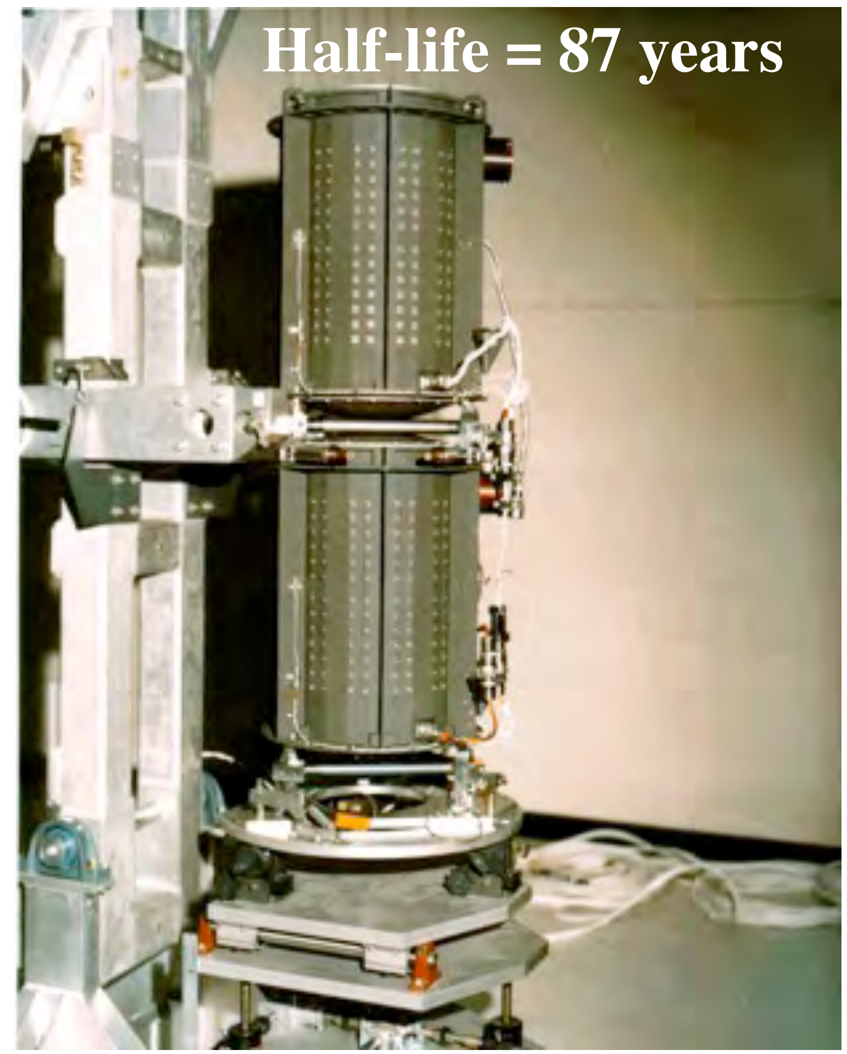
# NASA Radioisotope Thermoelectric Generator

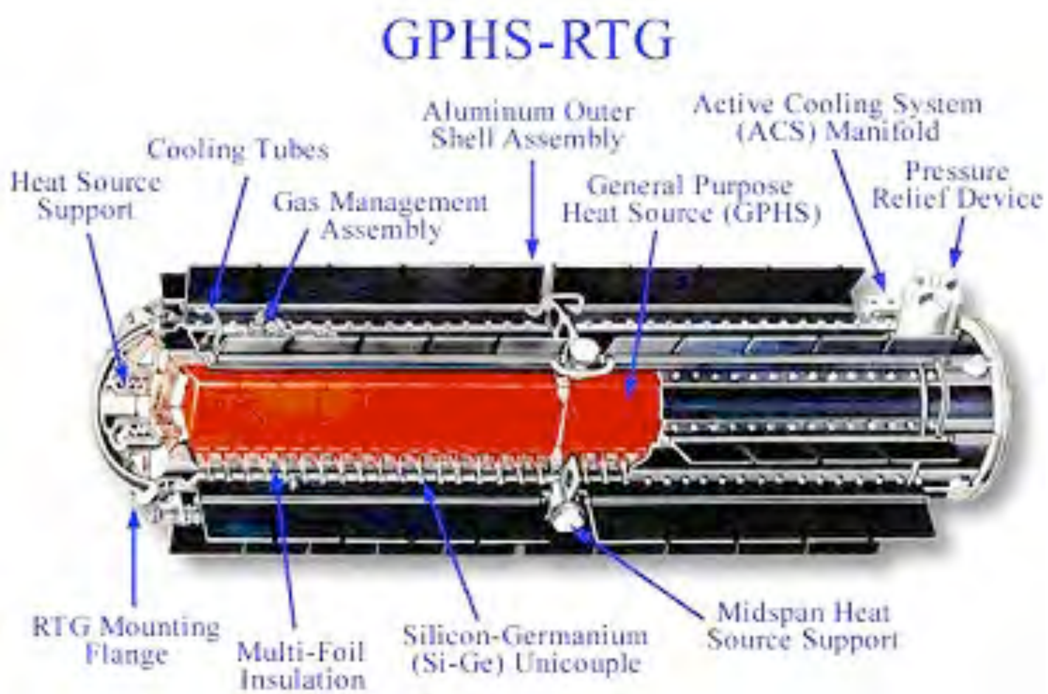
**Radioisotope heater –> thermoelectric generator –> electricity**





**Voyager – $Pu^{238}$**



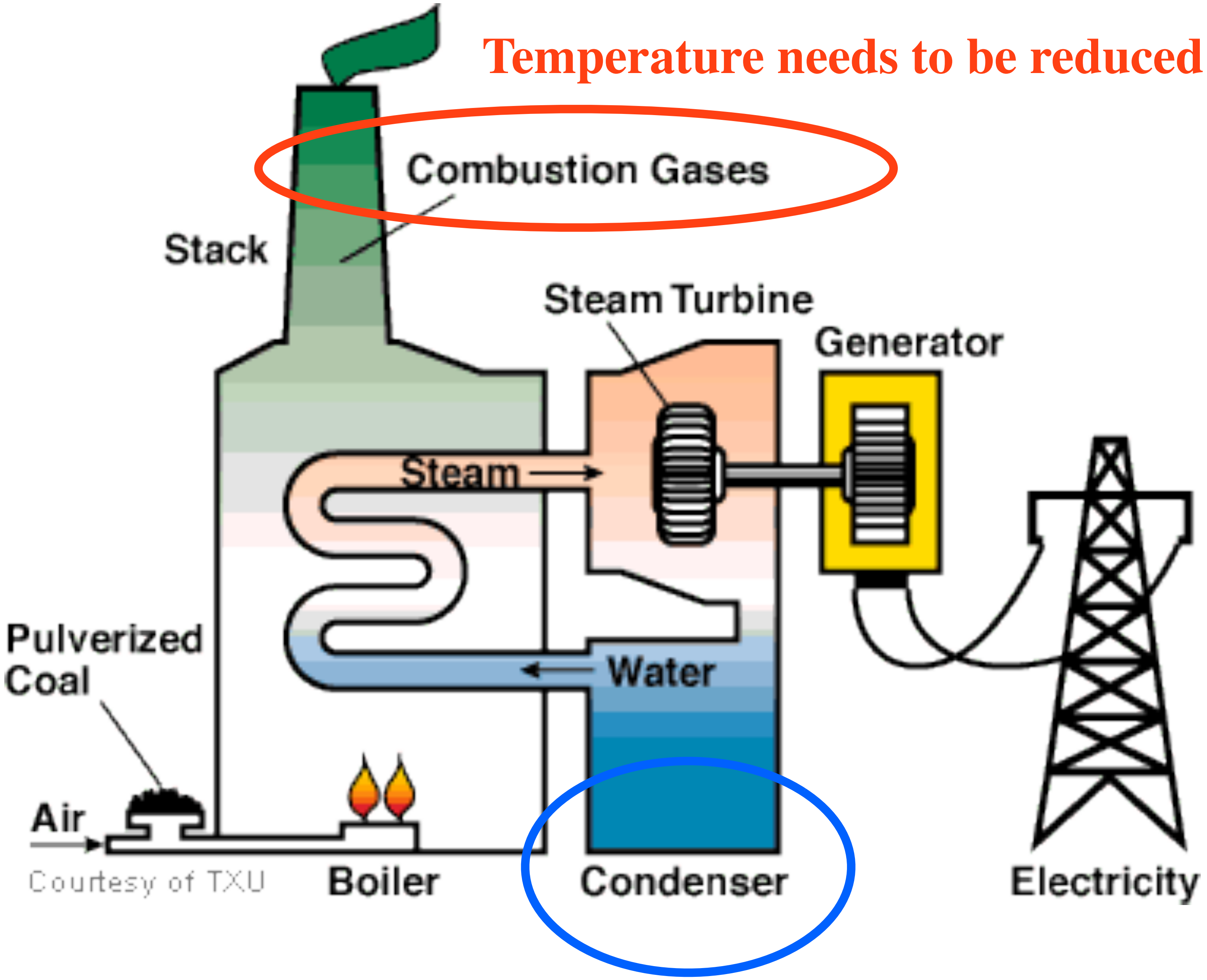



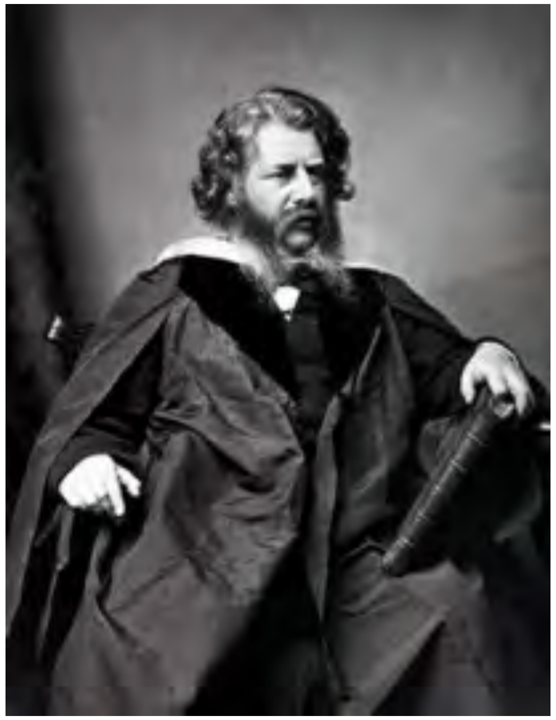

- **470 W @ 30 V on launch, after 33 years power =** $470 \times 2^{-\frac{33}{87}}$ **= 361 W**

*D.J. Paul*
*School of Engineering*
University of Glasgow

# Energy Conversion: Electricity: The Rankine Cycle

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



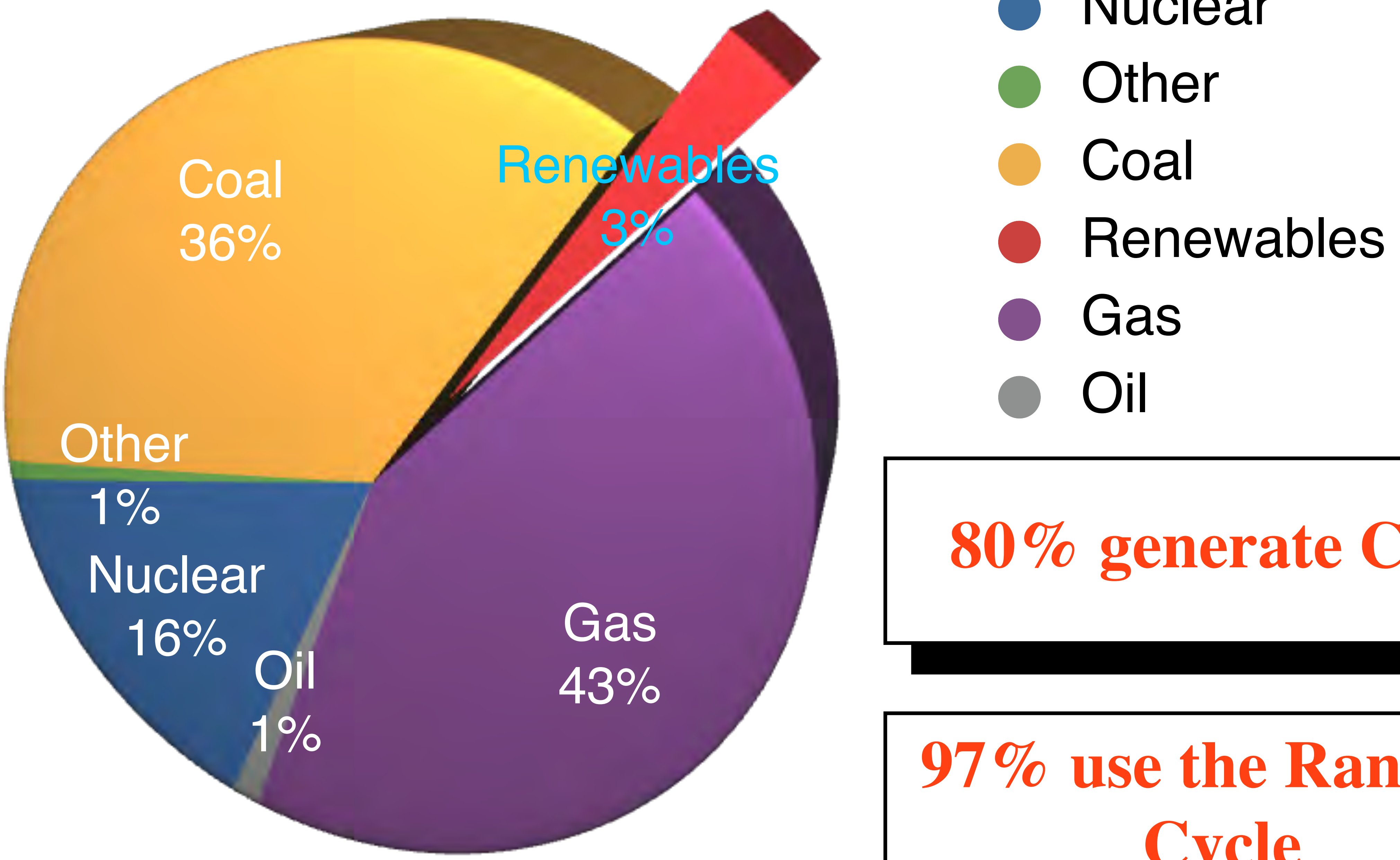



Cooling towers –> throw heat away –> added losses

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


D.J. Paul
School of Engineering

# U.K. Electricity Generation 2007




**80% generate $CO_2$**

**97% use the Rankine Cycle**

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

# Main Strategies for Optimising ZT

**Reducing thermal conductivity faster than electrical conductivity:**

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

**Low-dimensional structures:**

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

**Energy filtering:**

enhance

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

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

**Carrier Pocket Engineering – strain & band structure engineering**

*D.J. Paul*
*School of Engineering*
University of Glasgow

# Length Scales: Mean Free Paths

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

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

3D phonon mean free path

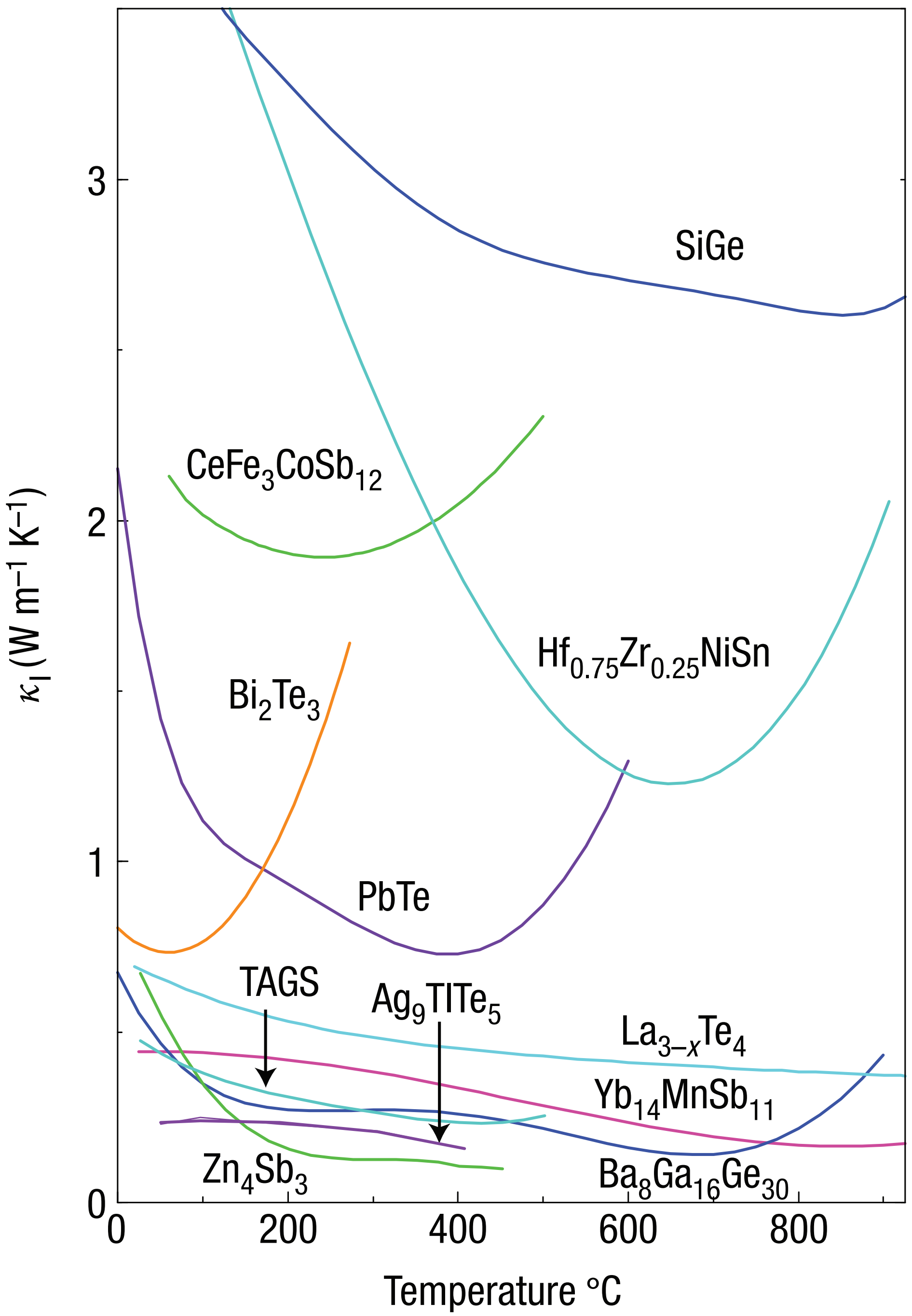
$$\Lambda_{ph} = \frac{3\kappa_{ph}}{C_v \langle v_t \rangle \rho}$$

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

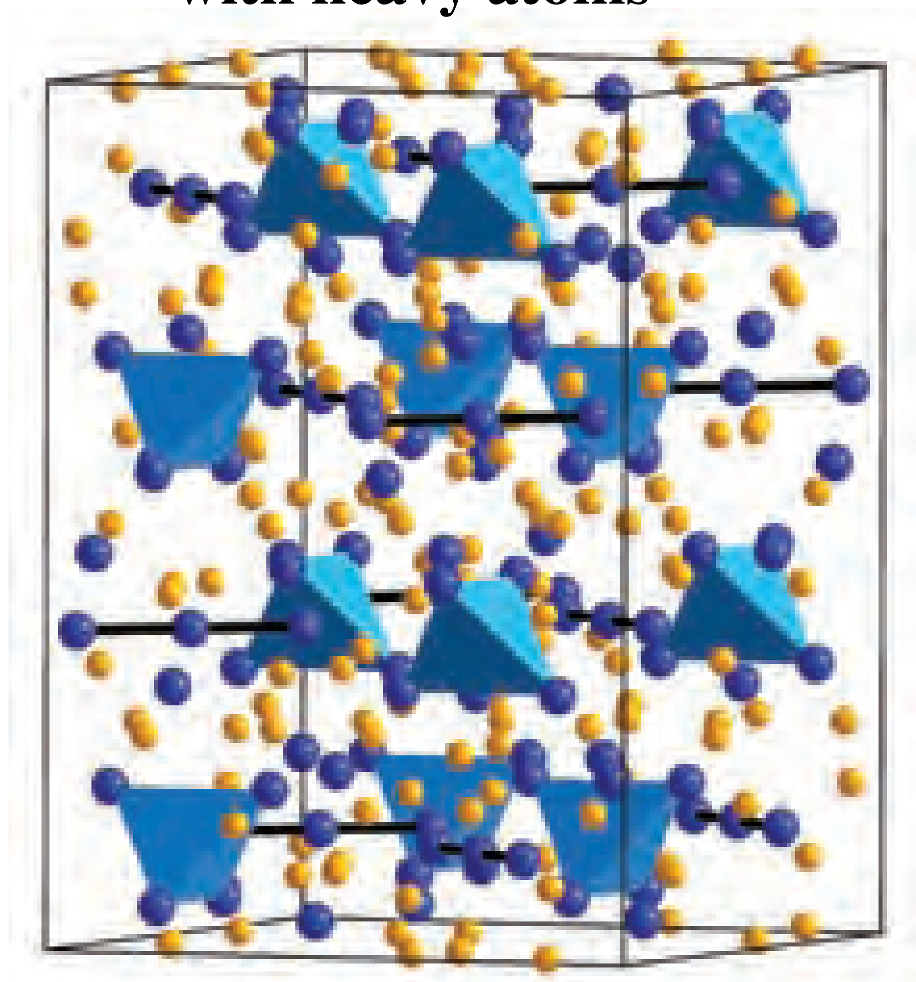
- A structure may be 2D or 3D for electrons but 1 D for phonons (or vice versa!)


*D.J. Paul*
*School of Engineering*
University of Glasgow

# Complex Crystal Structures: Reducing $\kappa_{\mathrm{ph}}$




**Skutterudite structure: filling voids with heavy atoms**

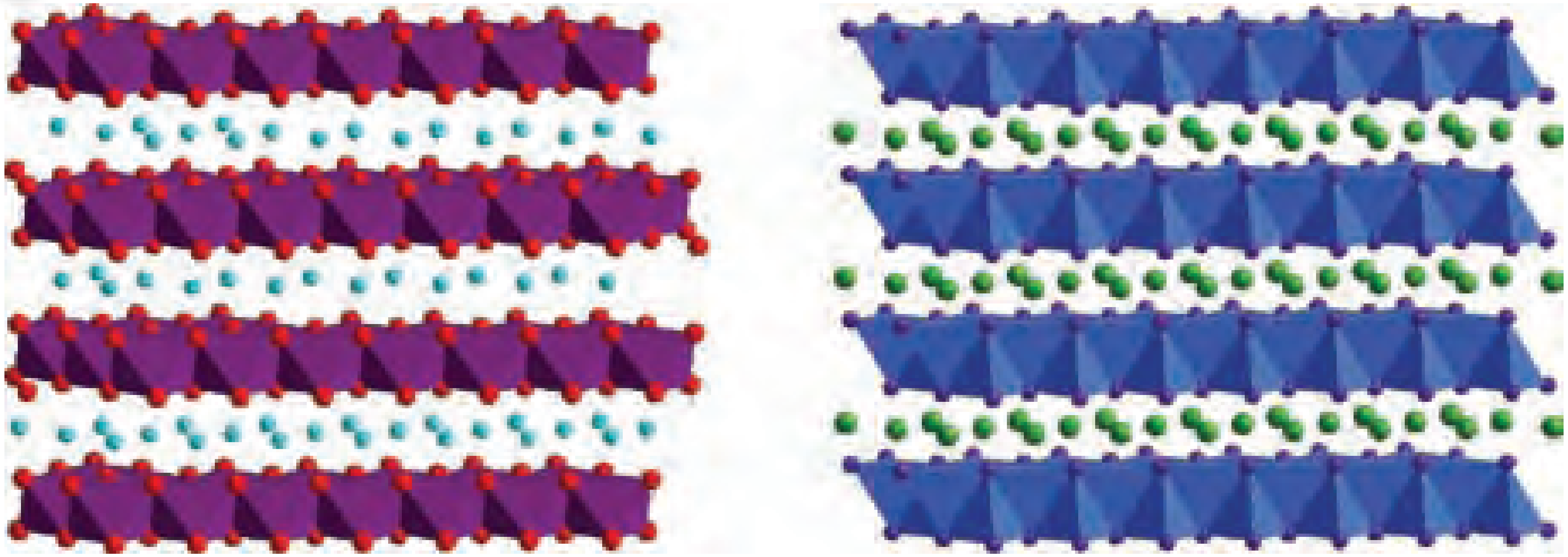


**p-$Yb_{14}MnSb_{11}$ – ZT ~ 1 @ 900 ˚C**

*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



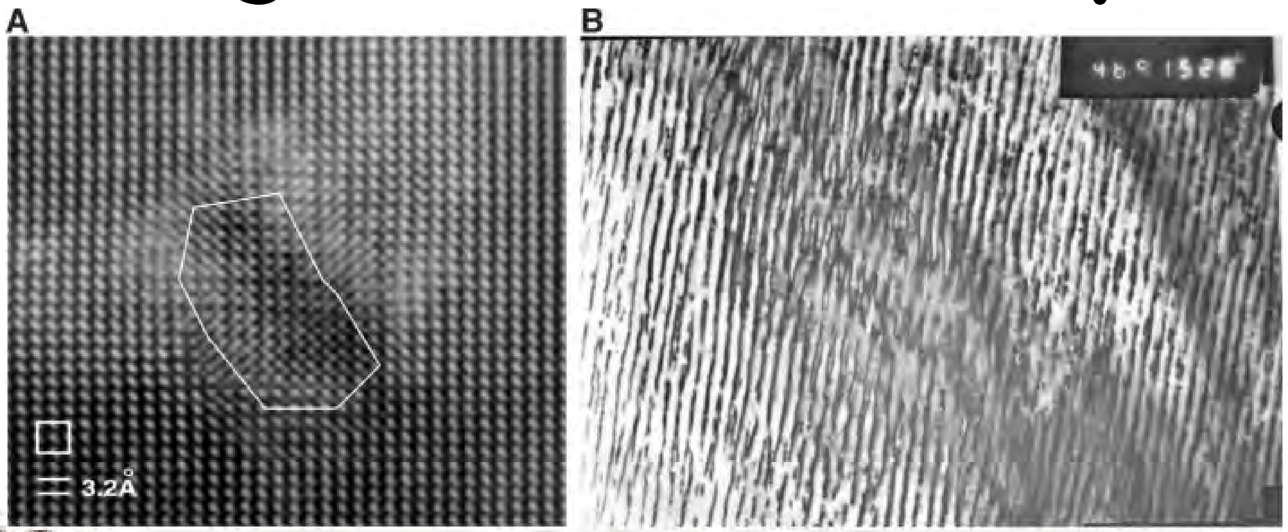
$Na_xCoO_2$ $Ca_xYb_{1-x}Zn_2Sb_2$

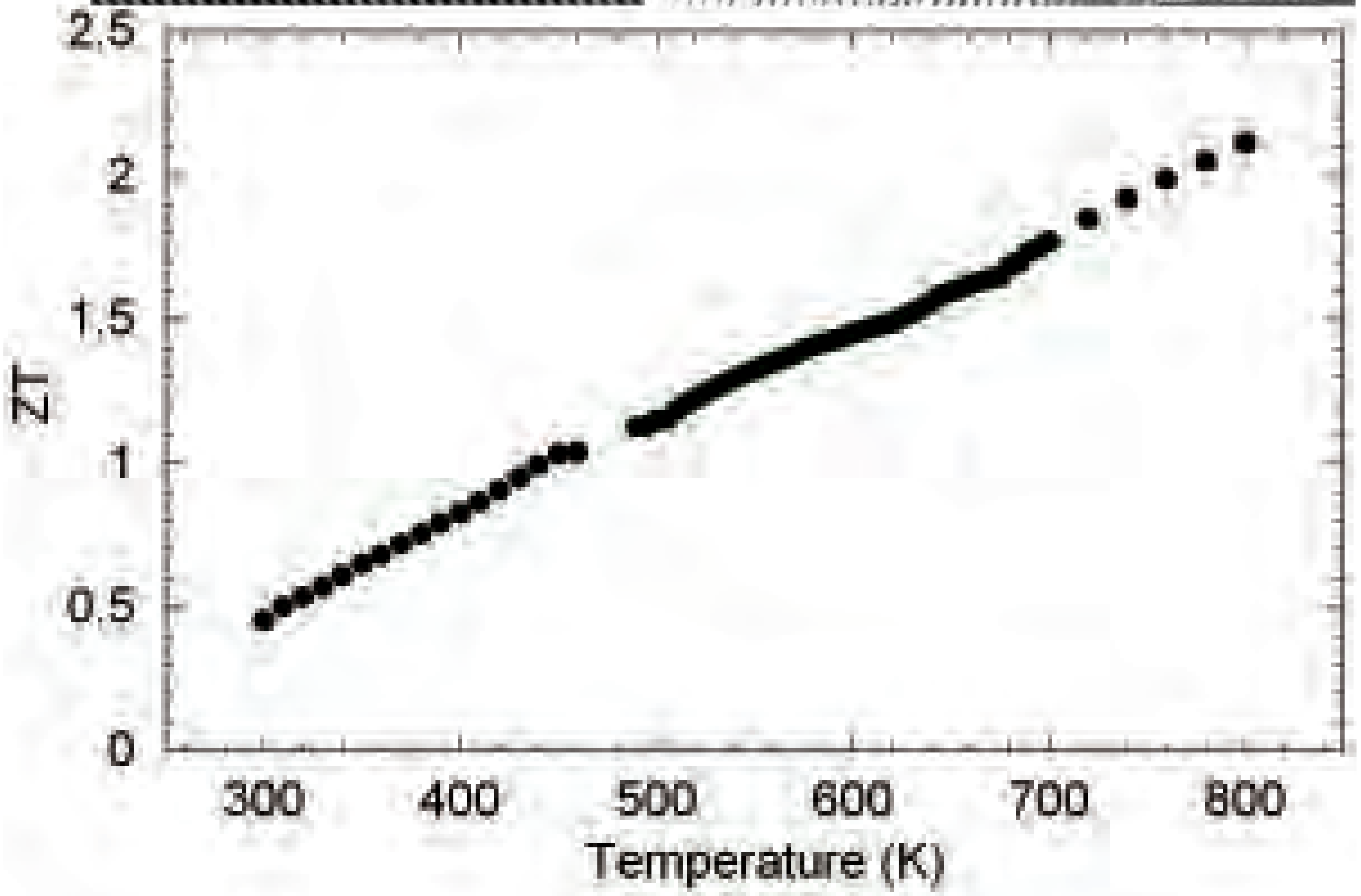
- Only small improvements to ZT observed

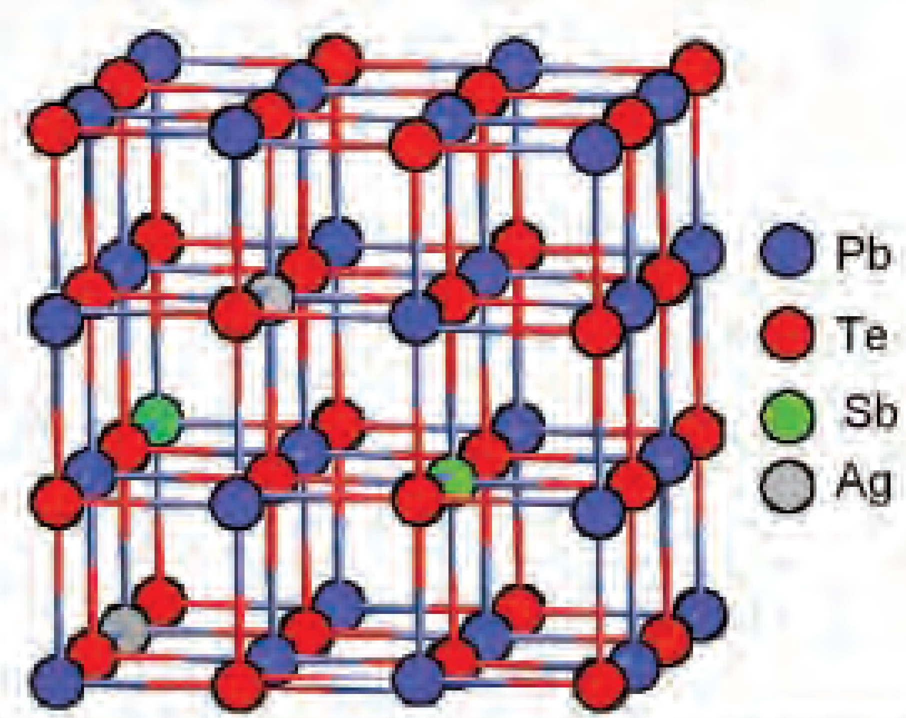
*G.J. Snyder et al., Nat. Mat. 7, 105 (2008)*

D.J. Paul
School of Engineering
University of Glasgow

# AgPb$_{18}$SbTe20 – Nanoparticle Scattering?



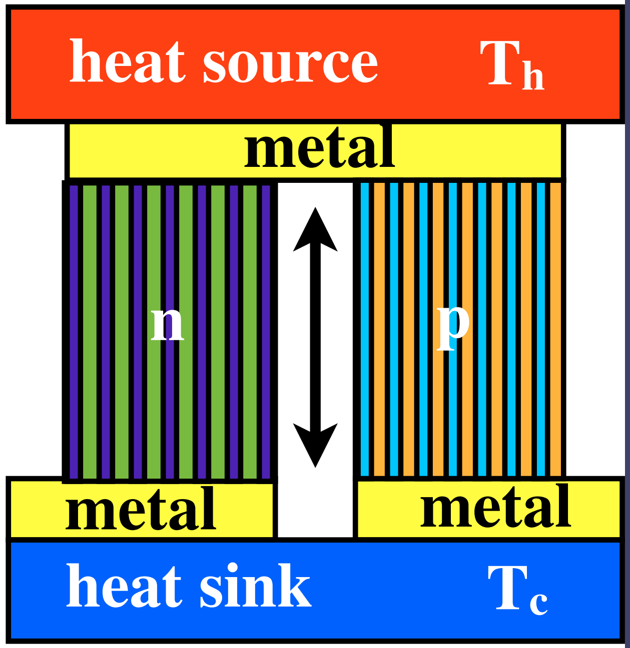




$\alpha$ = –335 $\mu$VK$^{-1}$
$\sigma$ = 30,000 S/m
$\kappa$ = 1.1 Wm$^{-1}$K$^{-1}$
at 700 K

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

D.J. Paul
School of Engineering
University of Glasgow

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

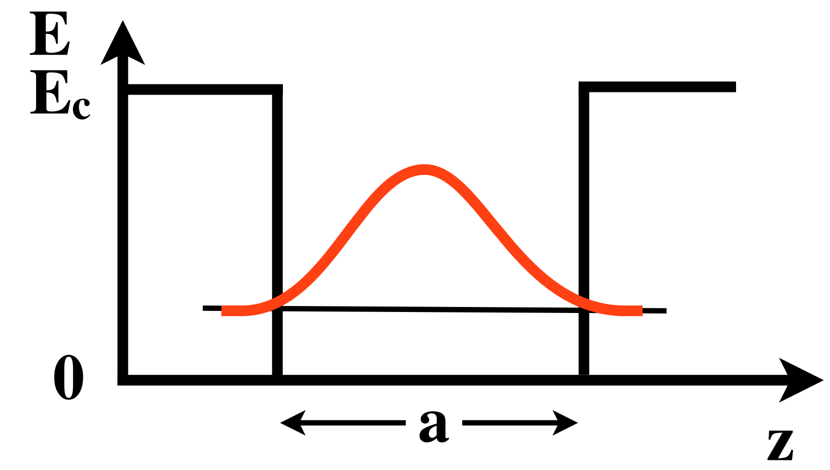
**Figure of merit**

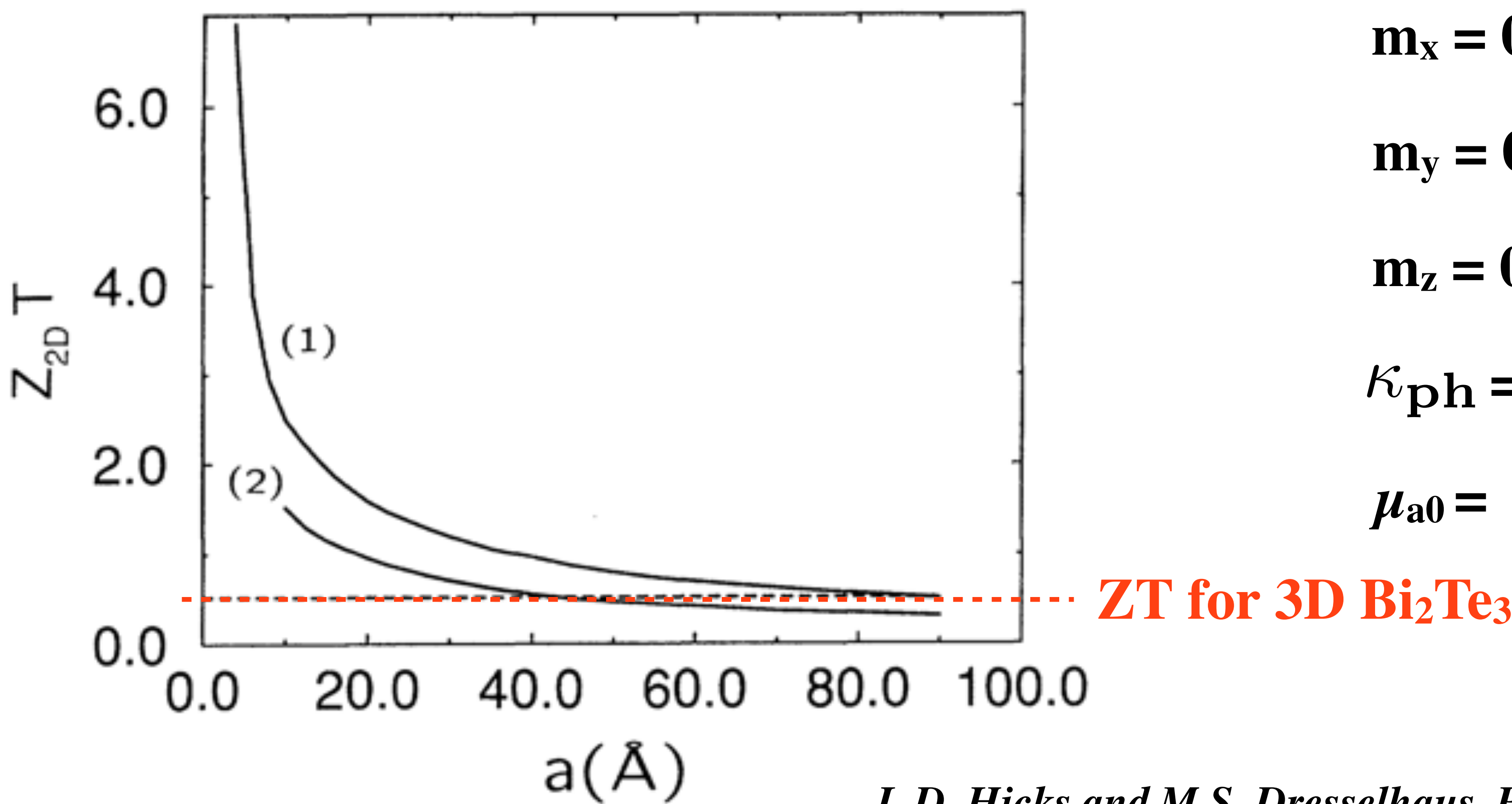
$$ZT = \frac{\alpha^2 \sigma}{\kappa} T$$

*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




$m_x = 0.021\ m_0$

$m_y = 0.081\ m_0$

$m_z = 0.32\ m_0$

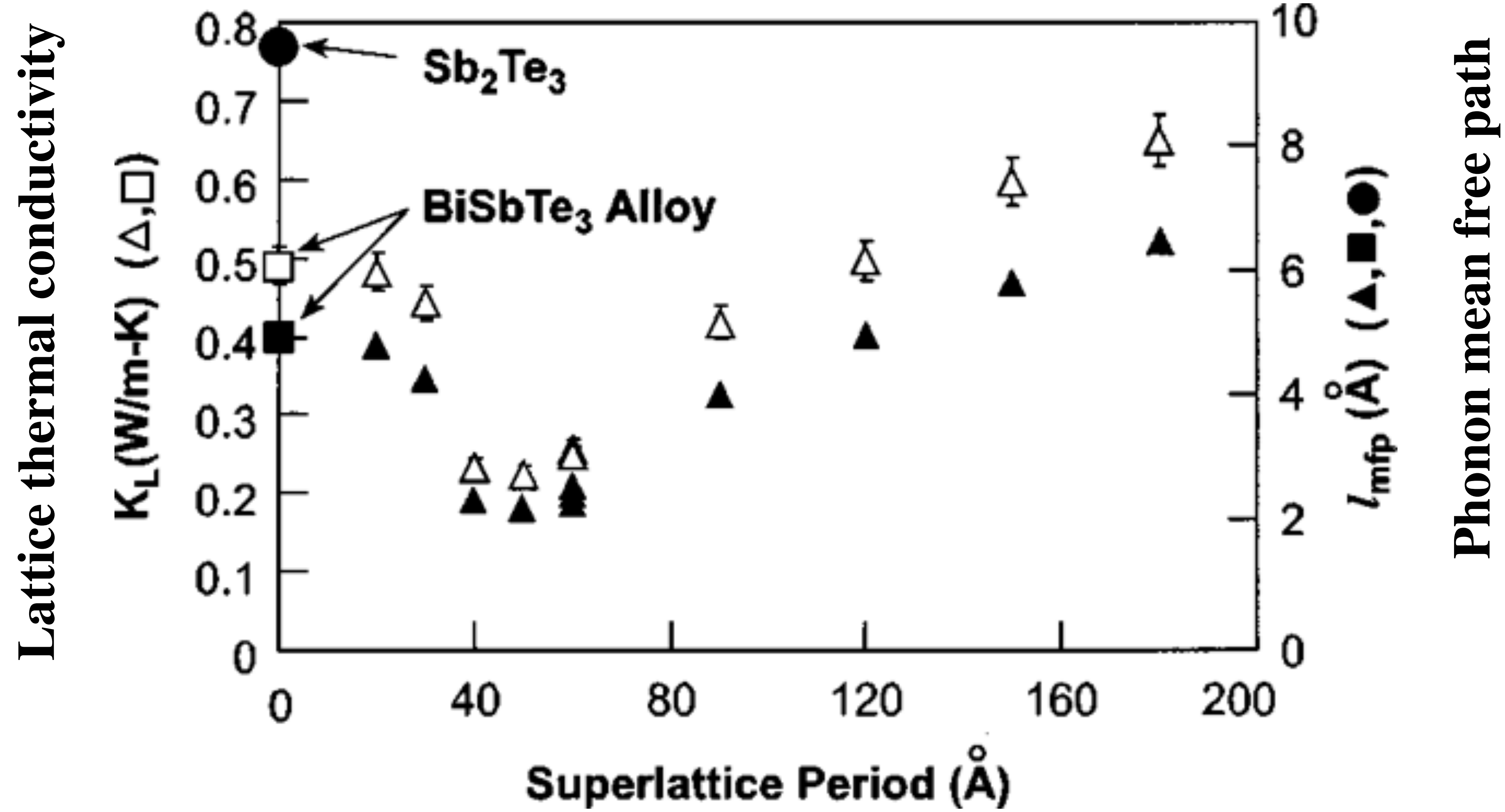
$\kappa_{ph} = 1.5\ Wm^{-1}K^{-1}$

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

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

# p-$Bi_2Te_3$ / $Sb_2Te_3$ Superlattices

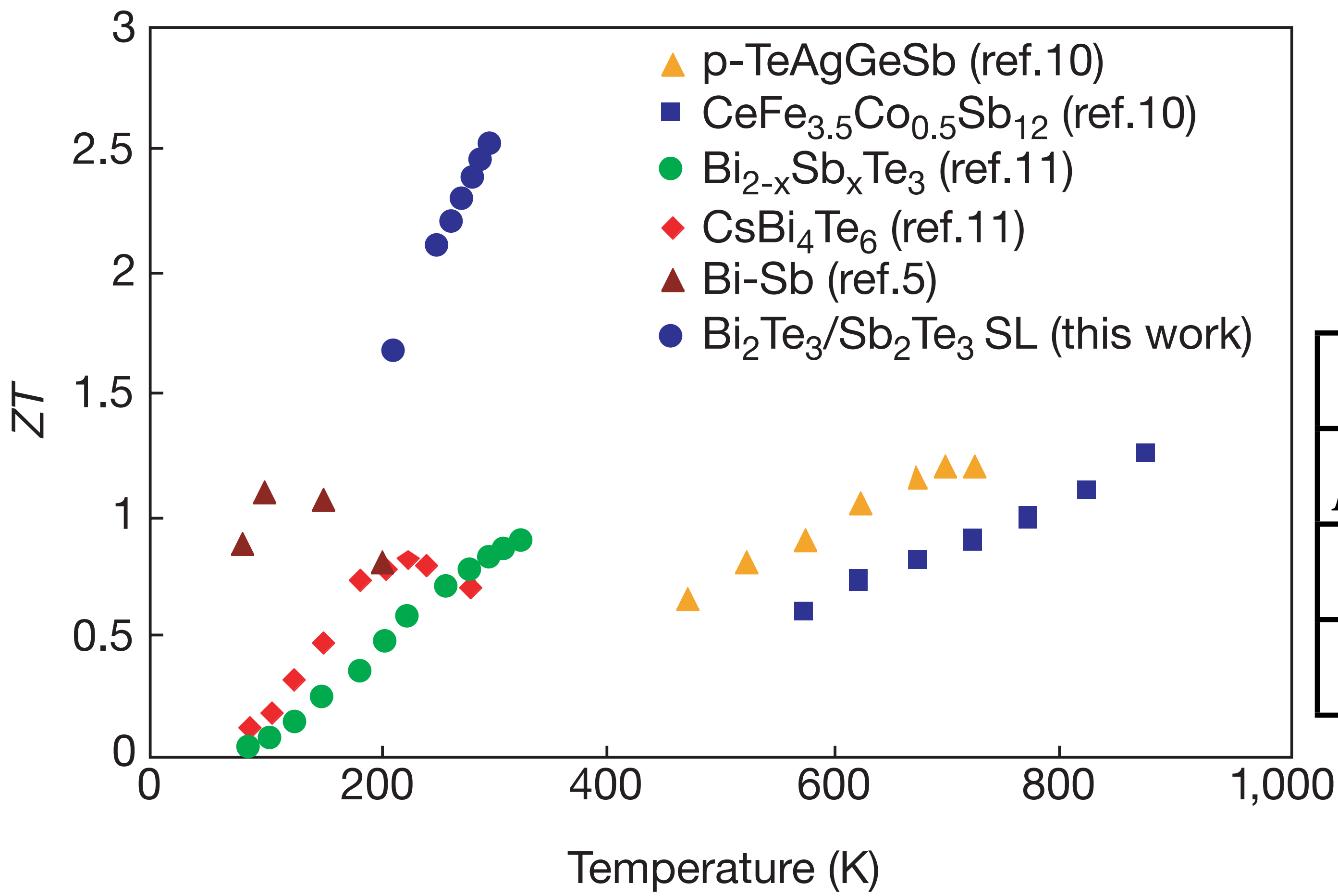
- $Bi_2Te_3$ $\kappa_{ph}$ = 1.05 $Wm^{-1}K^{-1}$




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

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

# p-$Bi_2Te_3$ / $Sb_2Te_3$ Superlattices




**Bulk $Bi_2Te_3$ ZT ~ 1.0**

**Superlattice ZT = 2.6**

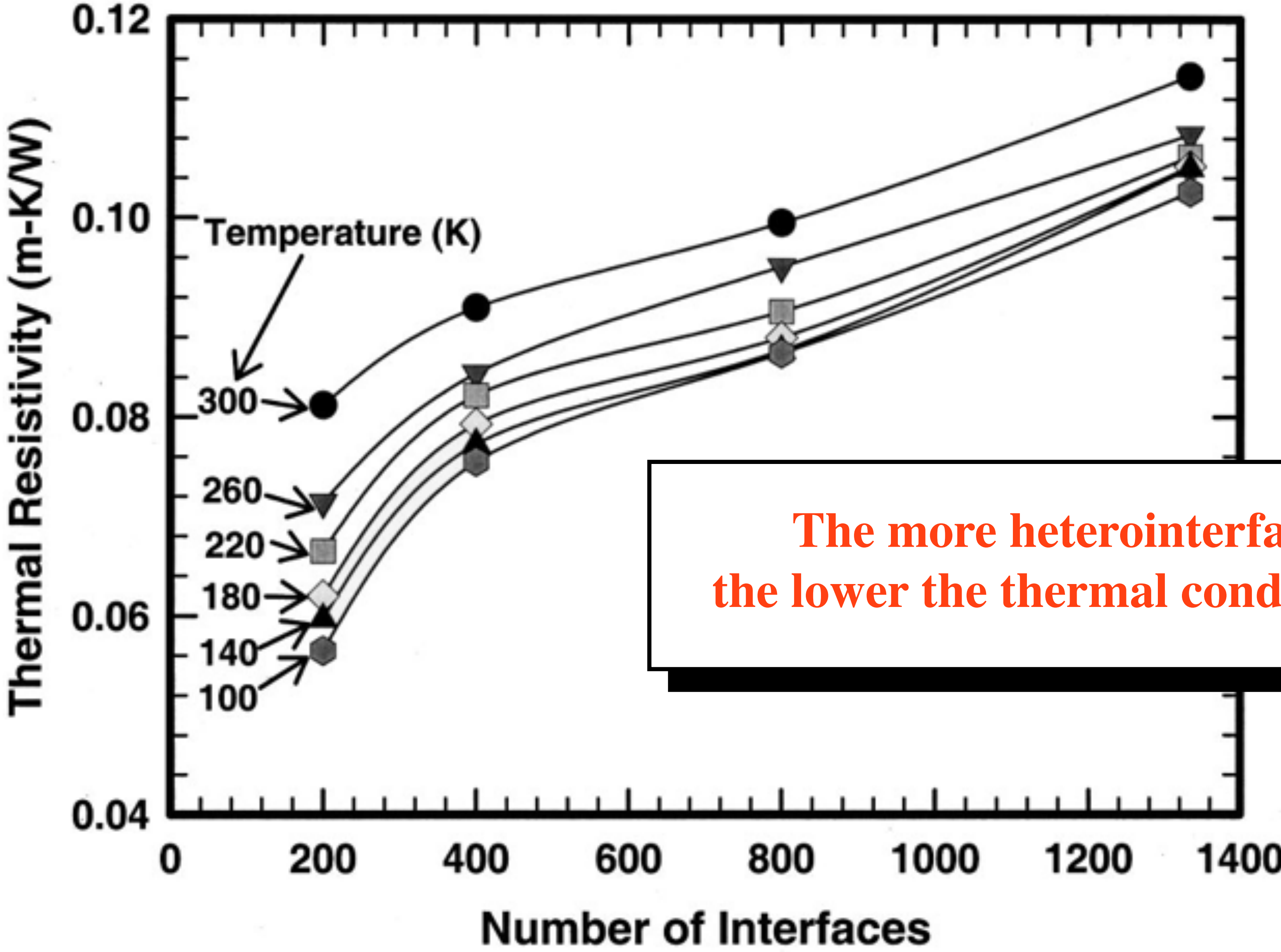
| Electrons | Phonons |
|---|---|
| $\mu$=383 cm$^2$V$^{-1}$s$^{-1}$ | |
| $\ell$ = 11.4 nm | $\Lambda_{ph}$ = 3 nm |
| $k_{el}\ell$ ~ 7.6 | $k_{ph}\Lambda$ ~ 0.5 |

**=> Phonon blocking**

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

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

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

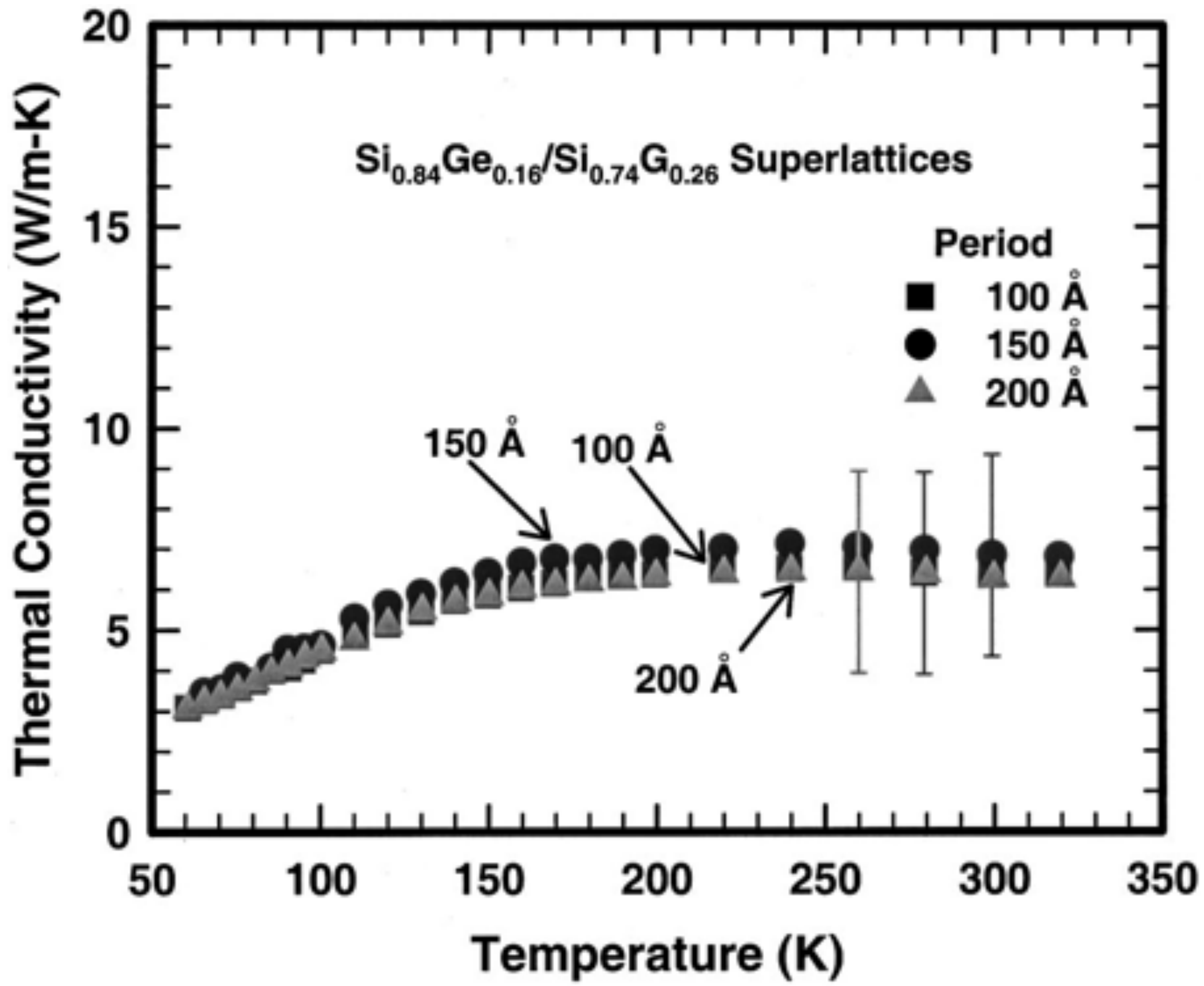



**The more heterointerfaces, the lower the thermal conductivity**

- **Physically: more heterointerfaces –> more phonon scattering**

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

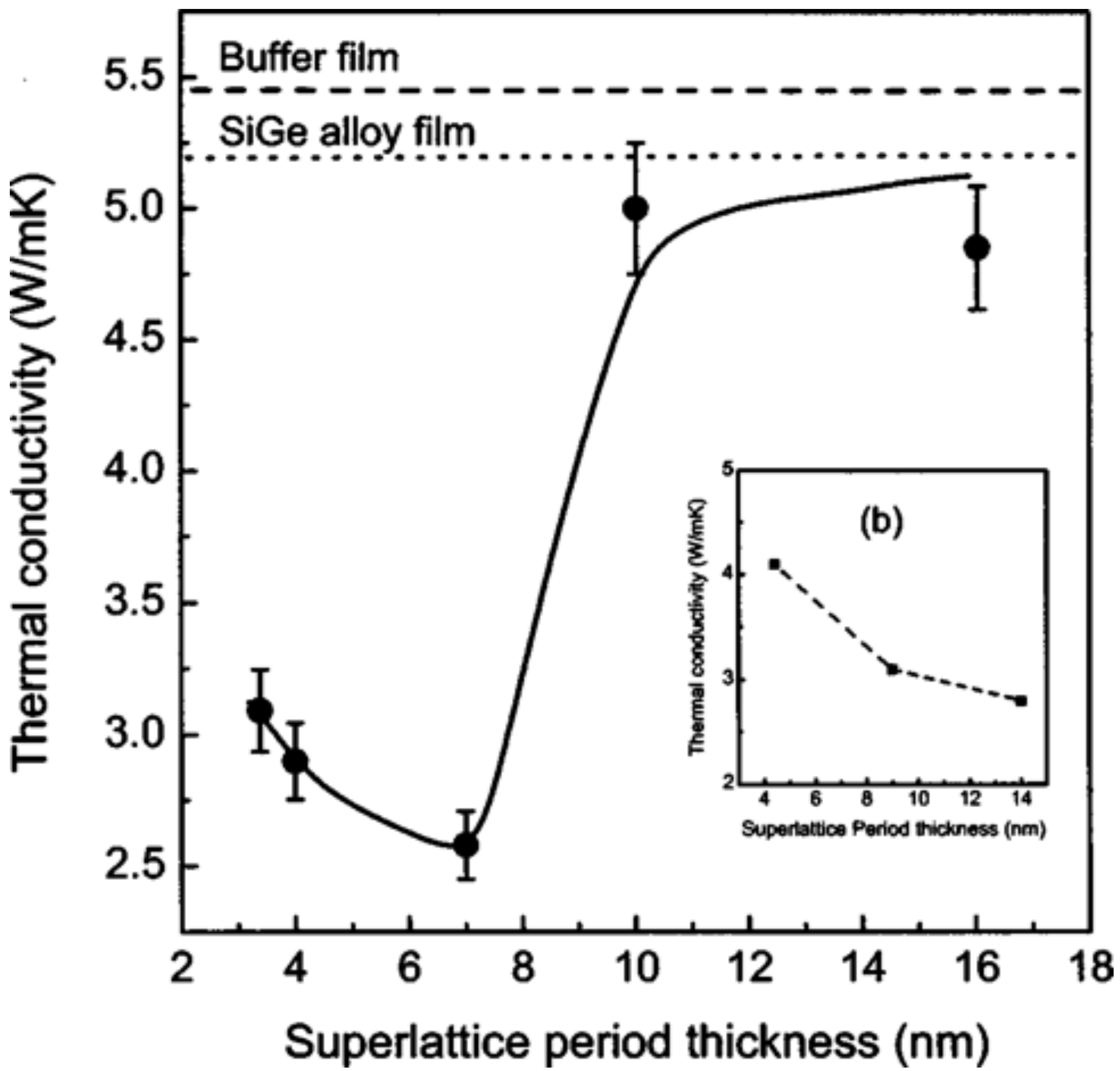
# $Si_{0.84}Ge_{0.16}$ / $Si_{0.74}Ge_{0.26}$ Superlattices

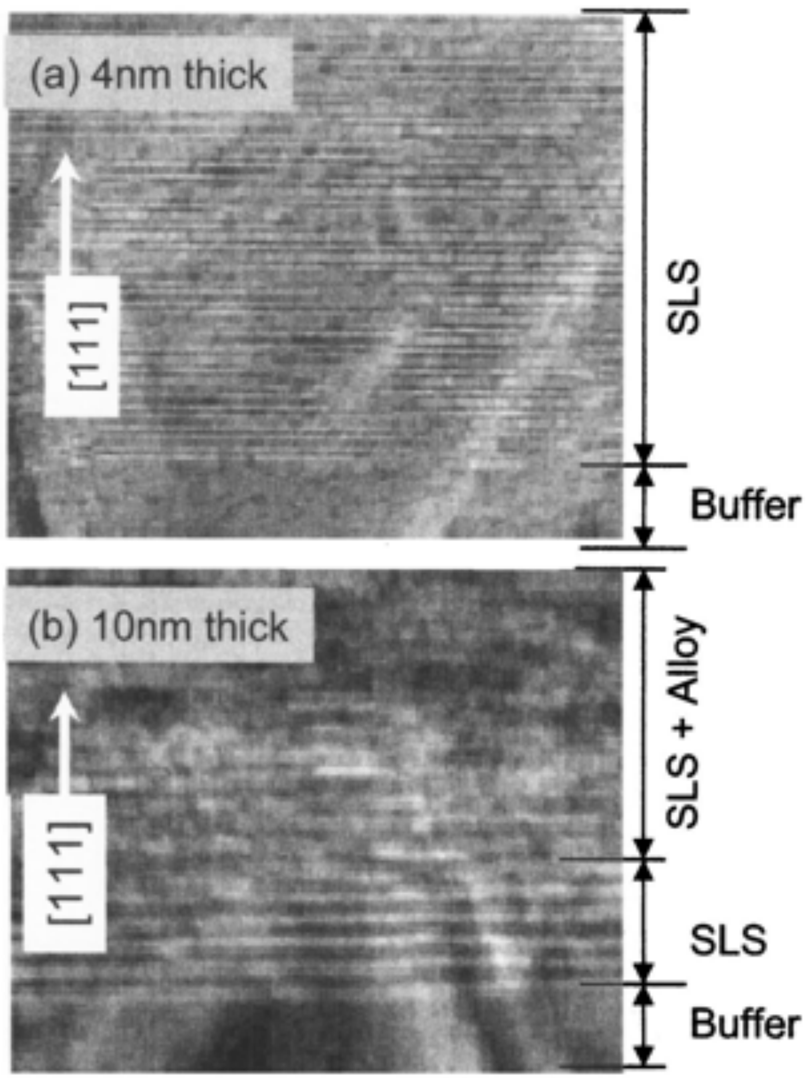



- $Si_{1-x}Ge_x$ is a random alloy
- No effect of superlattice with x =0.16 and x = 0.26
- Results the same as the average alloy Ge content
- A significant atomic mass difference is required

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

# Si/Ge Superlattice Reduced Thermal Conductivity



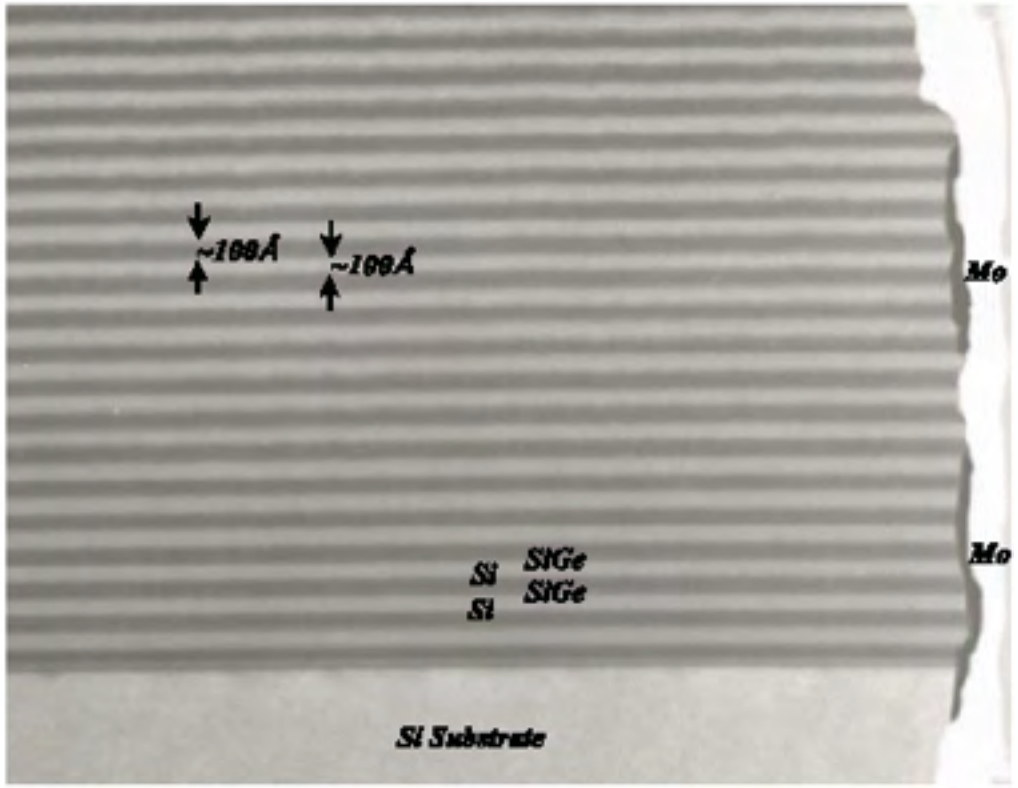




$Si_{0.5}Ge_{0.5}$ buffer

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

*D.J. Paul*
*School of Engineering*
University of Glasgow

# Hi-Z n-Si/SiGe and p-B4C/B9C Superlattice



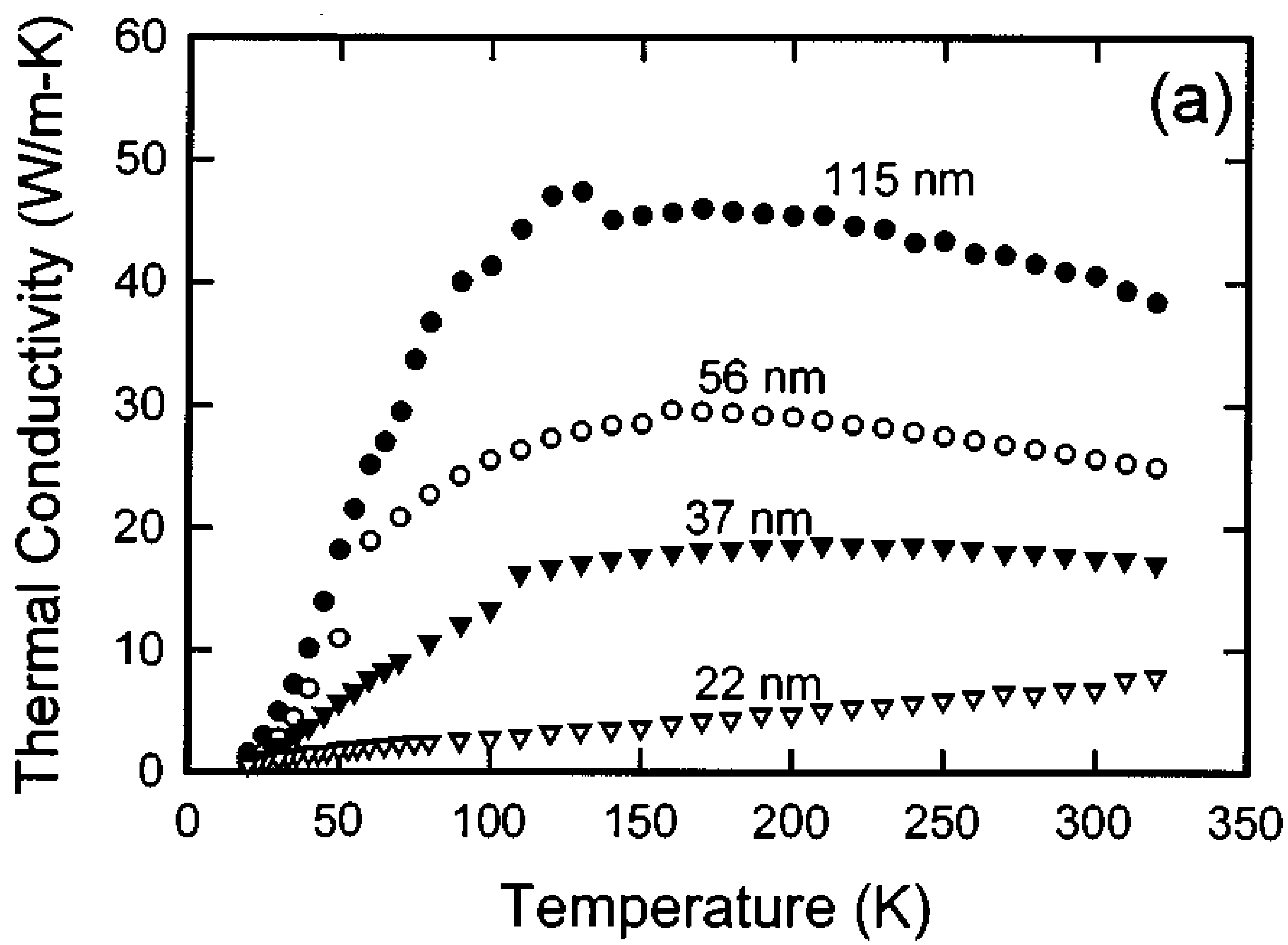

10 $\mu$m n-Si / $Si_{0.8}Ge_{0.2}$ superlattice

- $\alpha = -1260\ \mu VK^{-1}$
- $\sigma = 95{,}200\ 1/(\Omega\text{-m})$
- $\kappa = 14.6\ Wm^{-1}K^{-1}$
- ZT = 3.1 at 300 K

- p-B4C/B9C superlattice with ZT = 4.0
- Claim of NIST and UCSD confirming measurements
- Insufficient data in paper to check if true result
- 15% TE module demonstrated with $\Delta T = 200\ ^{\circ}C \Rightarrow ZT_{module} \sim 3$

*S. Ghamaty & N.B. Elsner, Int. Symp. Nano-Thermoelectrics, June 11-12 (2007) Osaka, Japan*

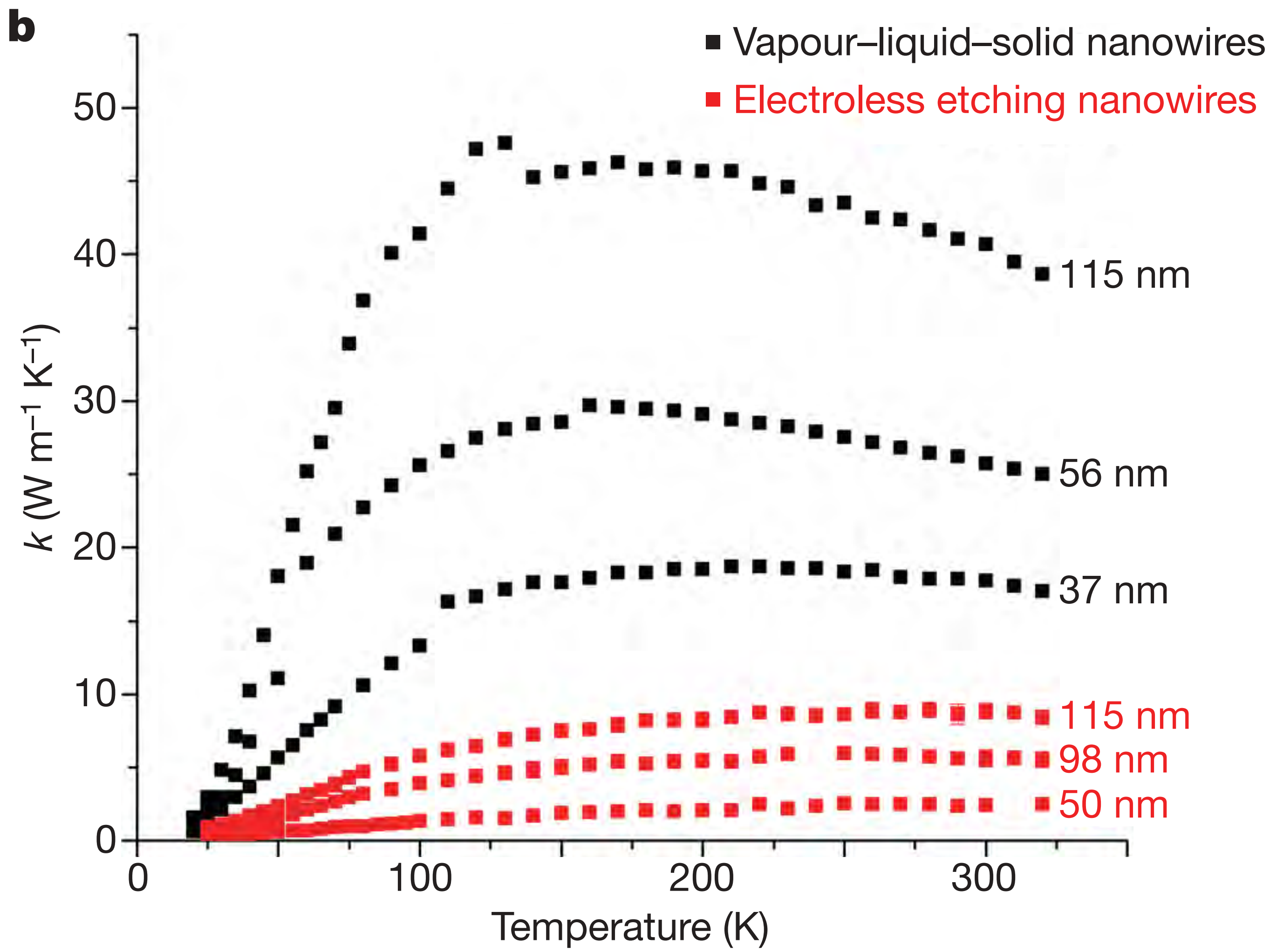
# Thermal Conductivity of Silicon Nanowires




- For bulk Si
  $\kappa \sim 149\ \mathrm{Wm^{-1}K^{-1}}$ at 300 K
- For bulk Si
  $$\Lambda_{\mathrm{ph}} = \frac{3\kappa_{\mathrm{ph}}}{\mathrm{C_v}\langle \mathrm{v_t}\rangle \rho}$$
  ~ 300 nm
- Phonon scattering at boundaries increases for smaller dia. wires

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

# Thermal Conductivity of 1D Silicon Nanowires




**Red data from nanowires with rough boundaries**

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

  **~ 300 nm**

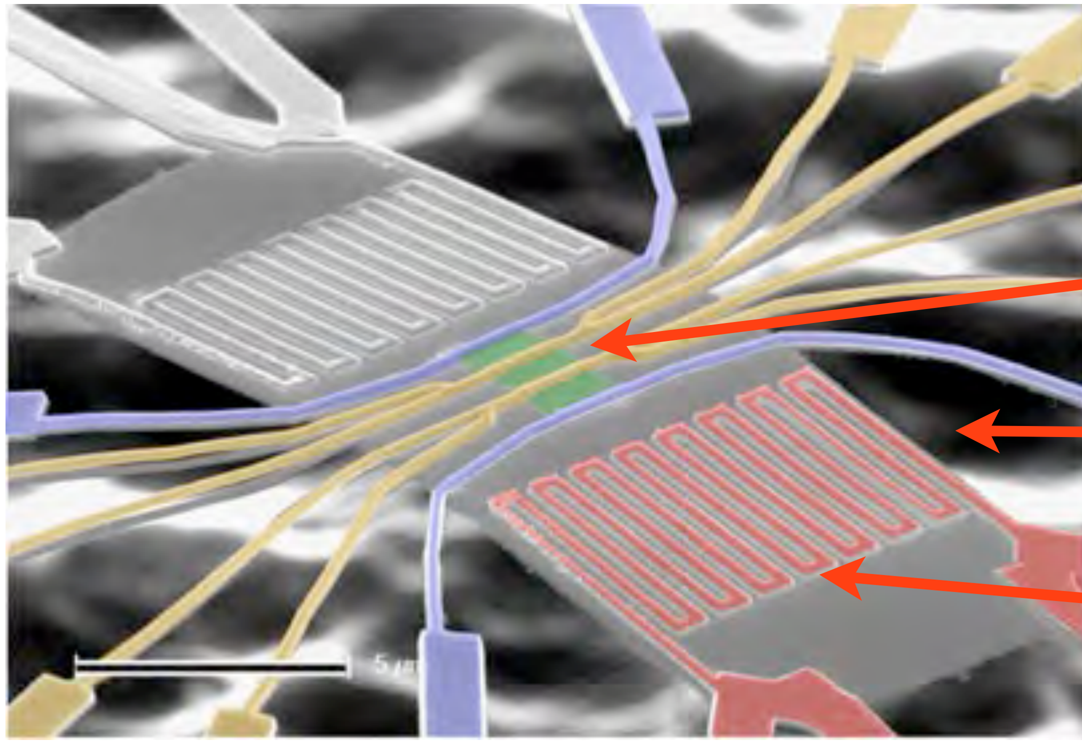
- $\ell$ **= 110 nm**

- **Phonon scattering >> electron scattering**

- **reduces faster than σ**

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

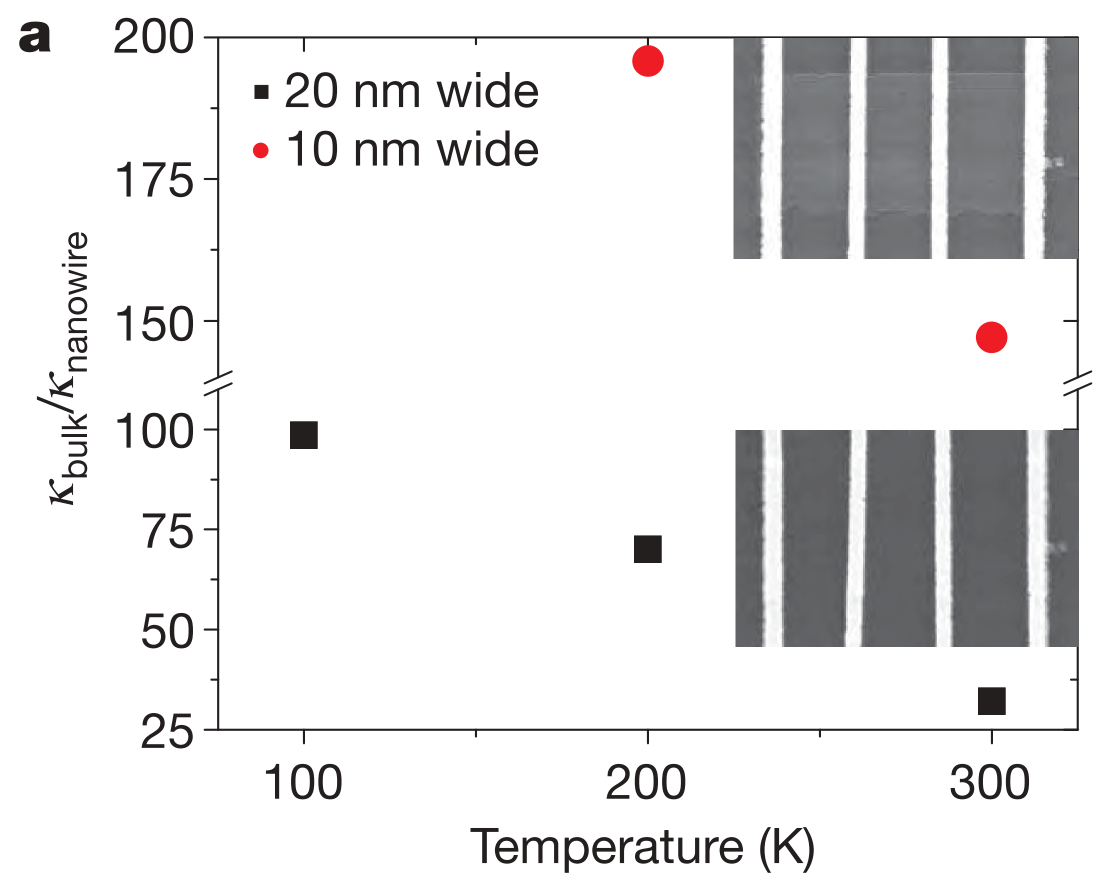
# 1D Nanowires



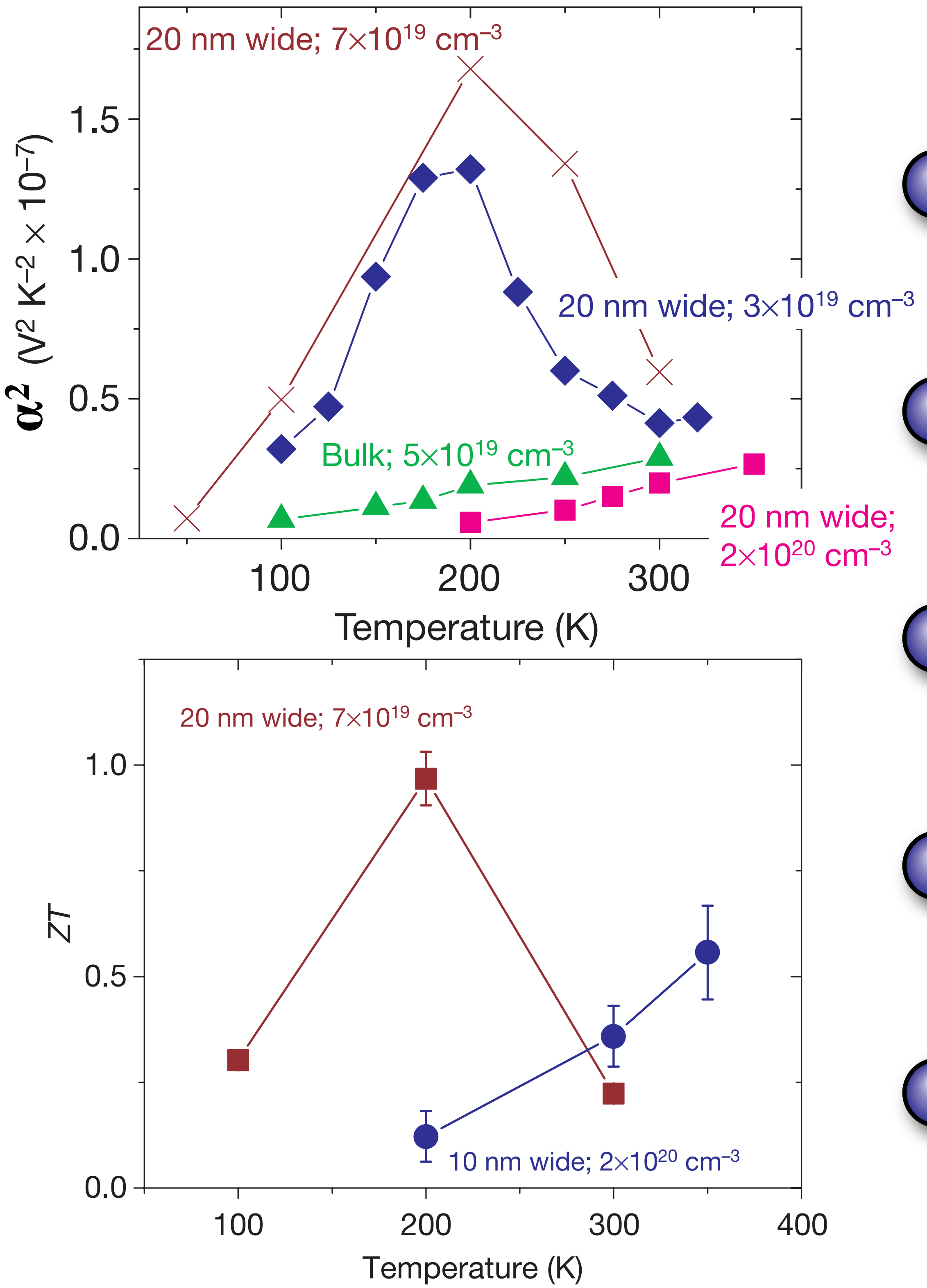
**4 terminal Si nanowires**

**Substrate removed by etching**

**Heaters**




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



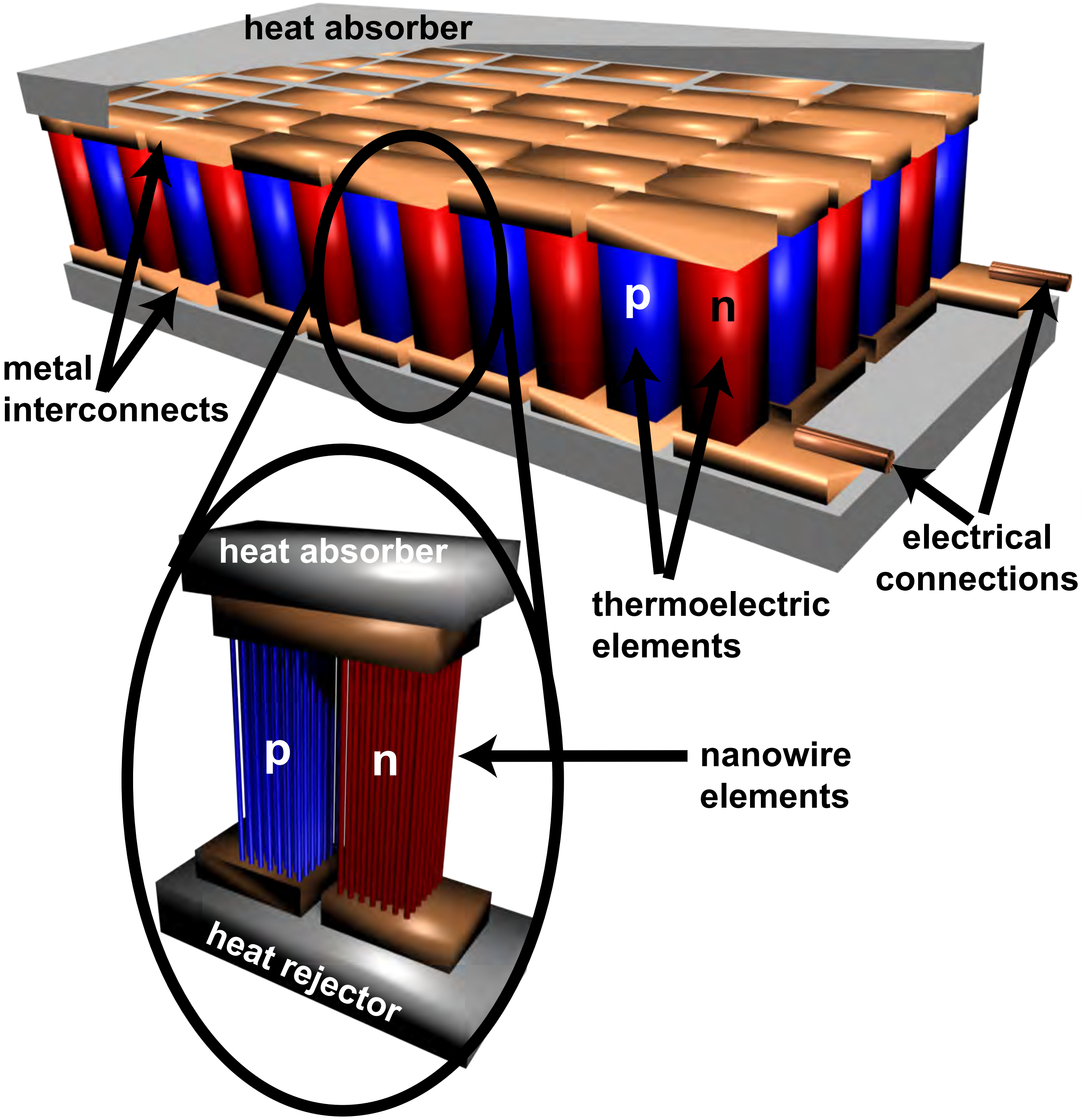

# 1D Silicon Nanowires

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

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

D.J. Paul
School of Engineering

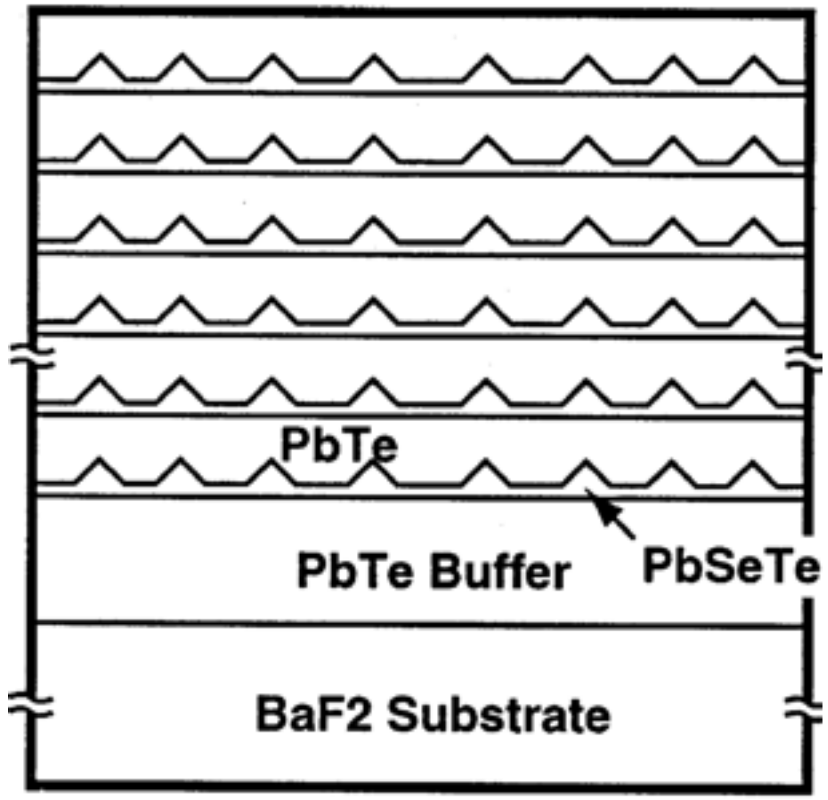
# For Module Require Vertical Nanowires

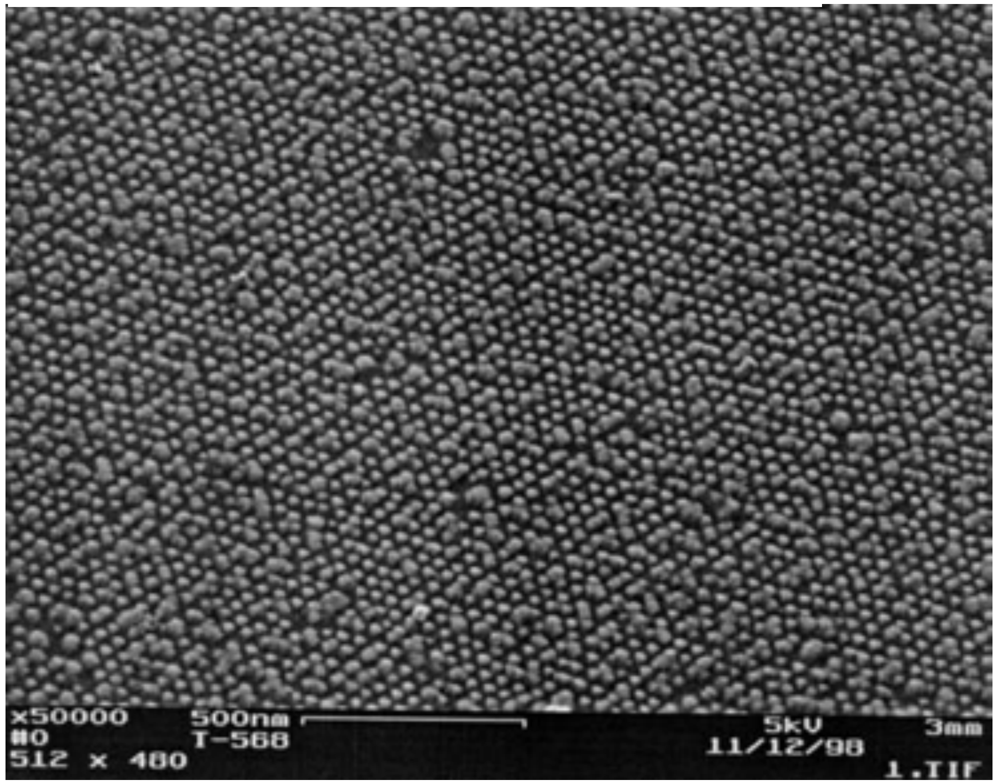


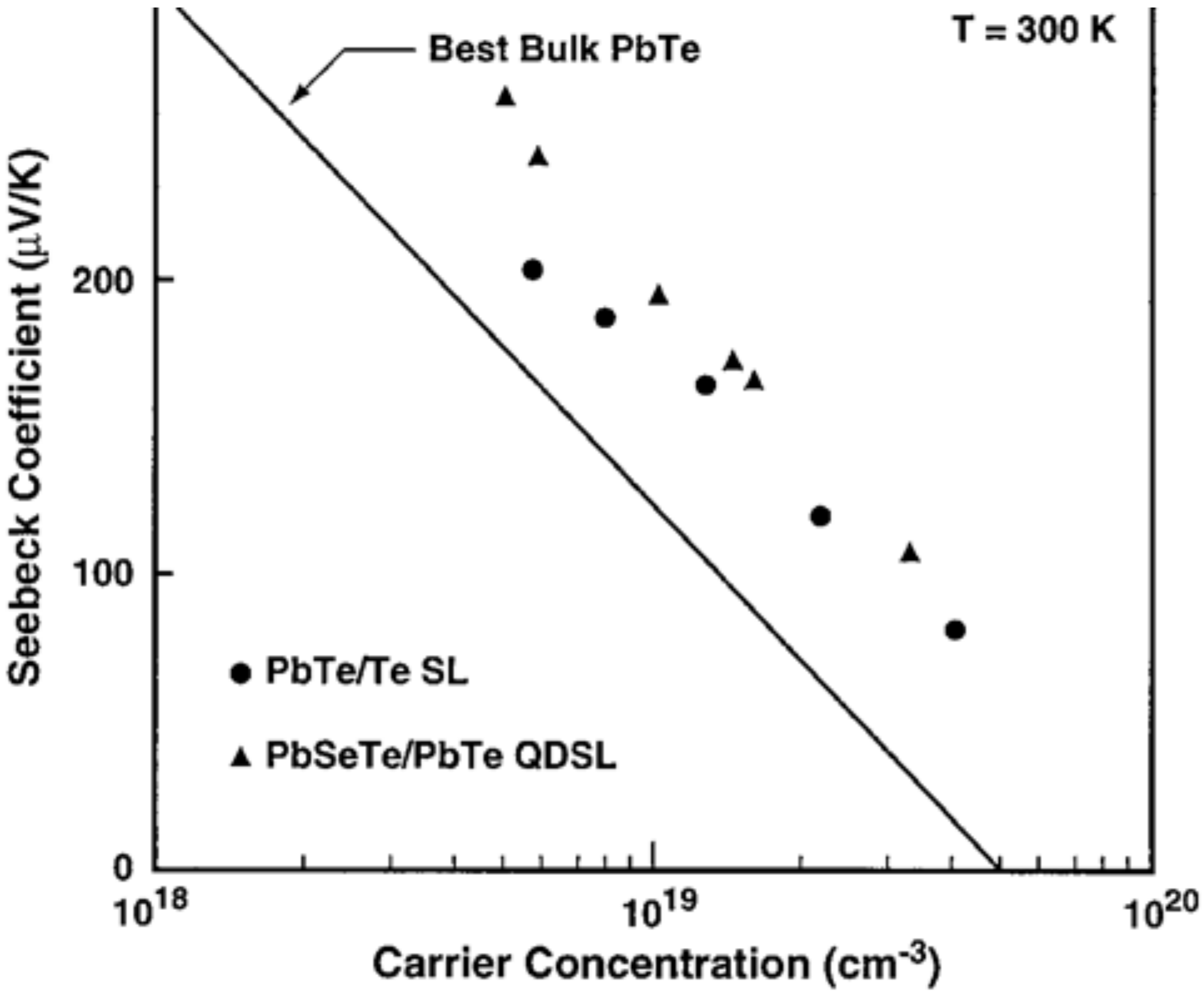

- 20nm vertical Si nanowires >> 5 $\mu$m height required
- High aspect ratio nanowires difficult to etch
- Also difficult to grow

D.J. Paul
School of Engineering

# 0D Quantum Dots



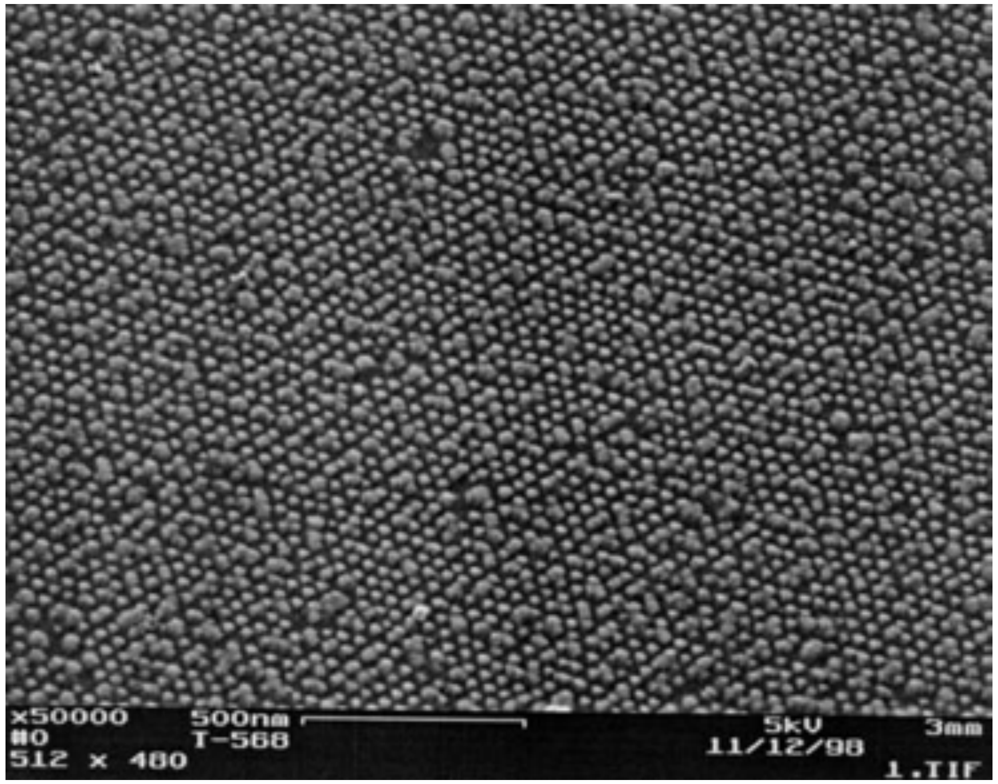



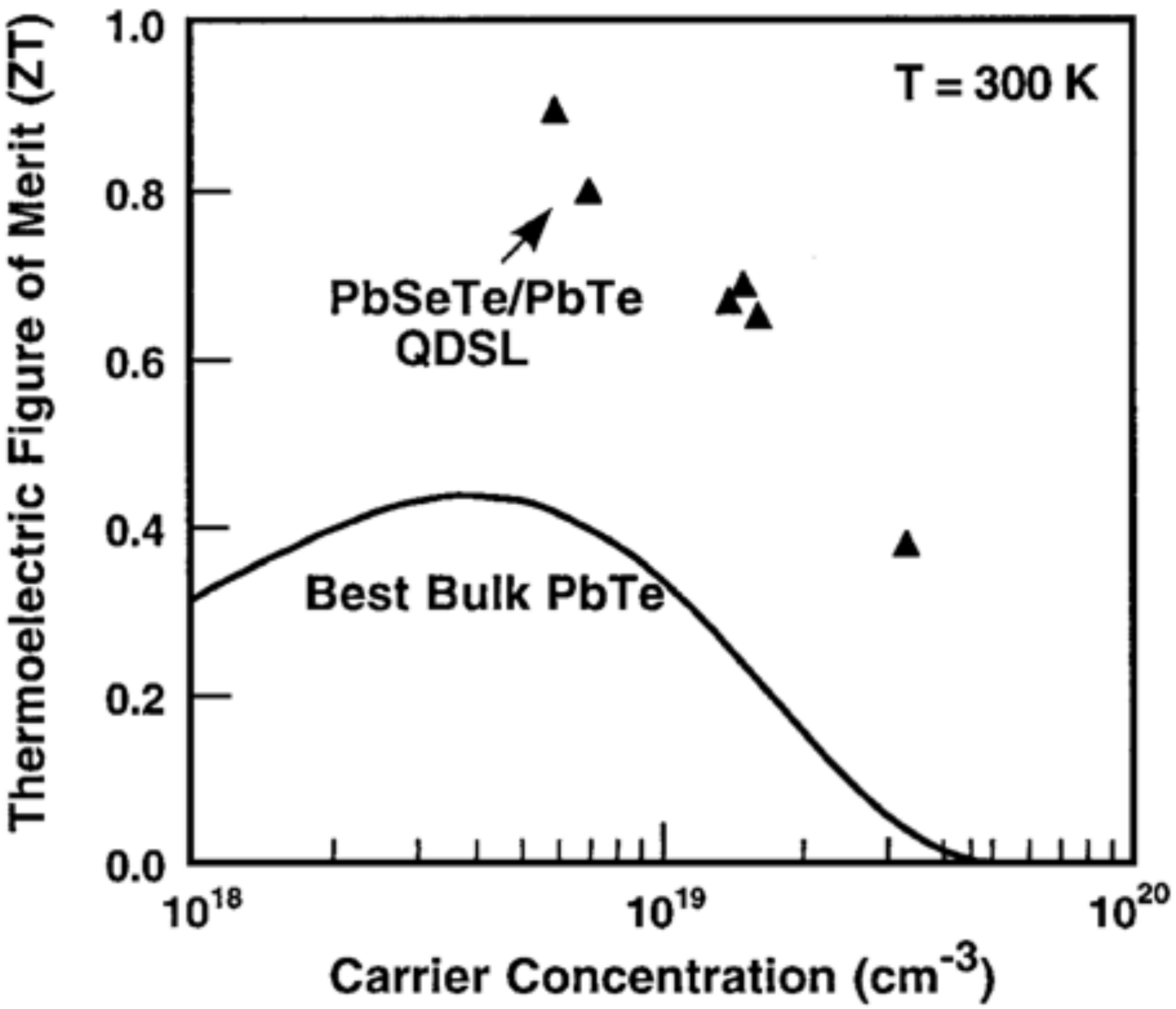

- **Seebeck α: bulk < superlattice < QD**

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

D.J. Paul
School of Engineering
University of Glasgow

# 0D Quantum Dots

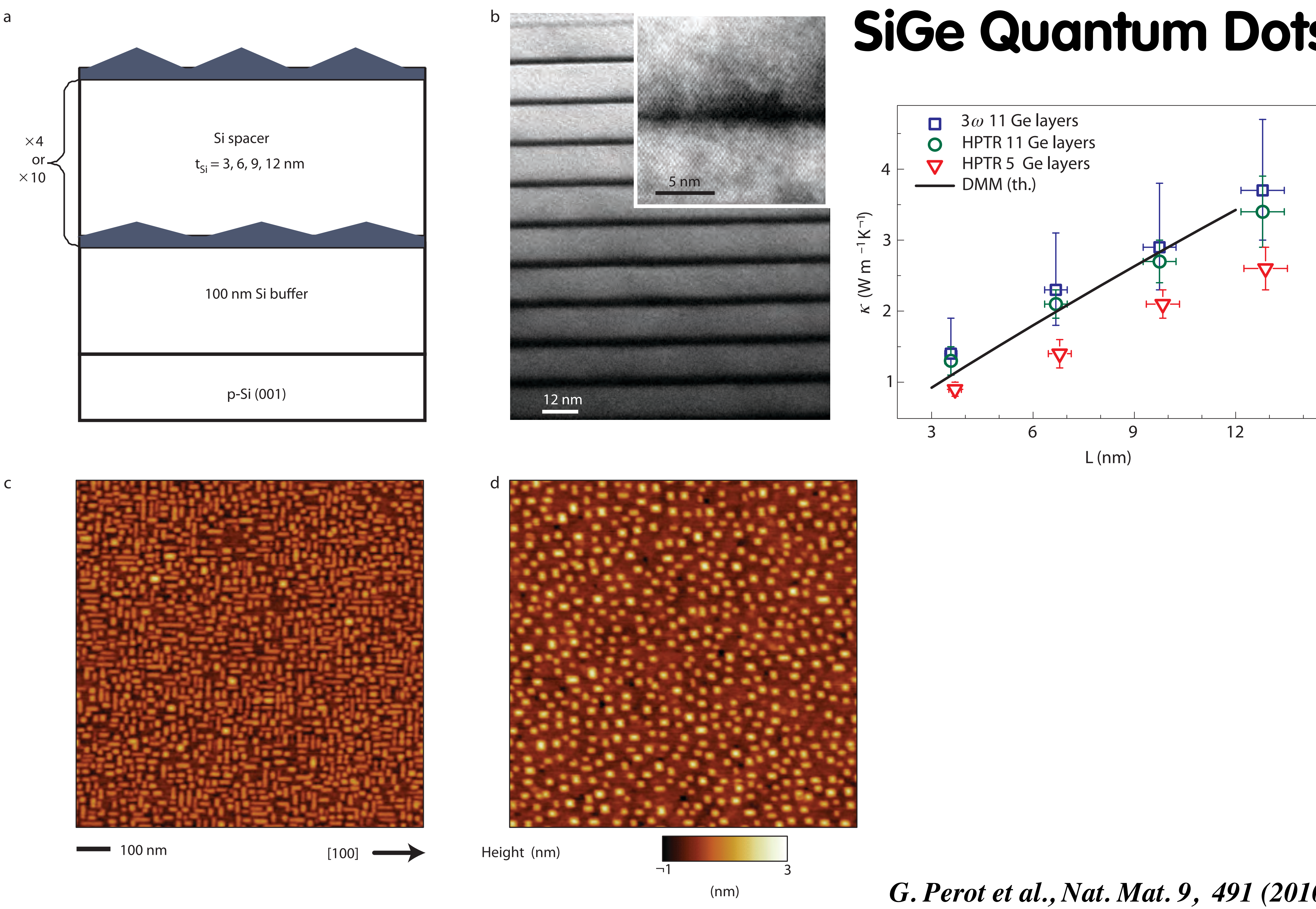



- **Thermal conductivity reduced more than electrical conductivity**

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

# SiGe Quantum Dots




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

**D.J. Paul**
**School of Engineering**
University of Glasgow

# Nanoparticle Engineering

**Advantages:**

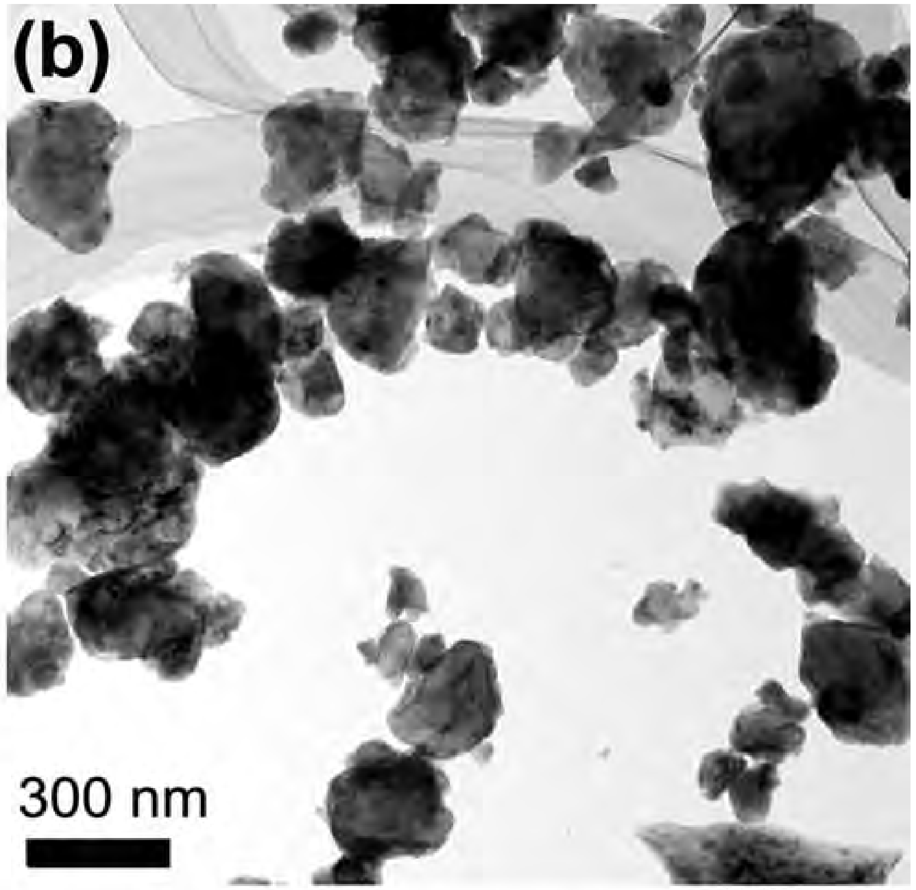
- **Potentially cheap, mass manufacturable technology**
- **Periodic structures not required to reduce thermal conductivity**
- **In SiGe material, particles below 50 nm demonstrate improved ZT**

**Disadvantages:**

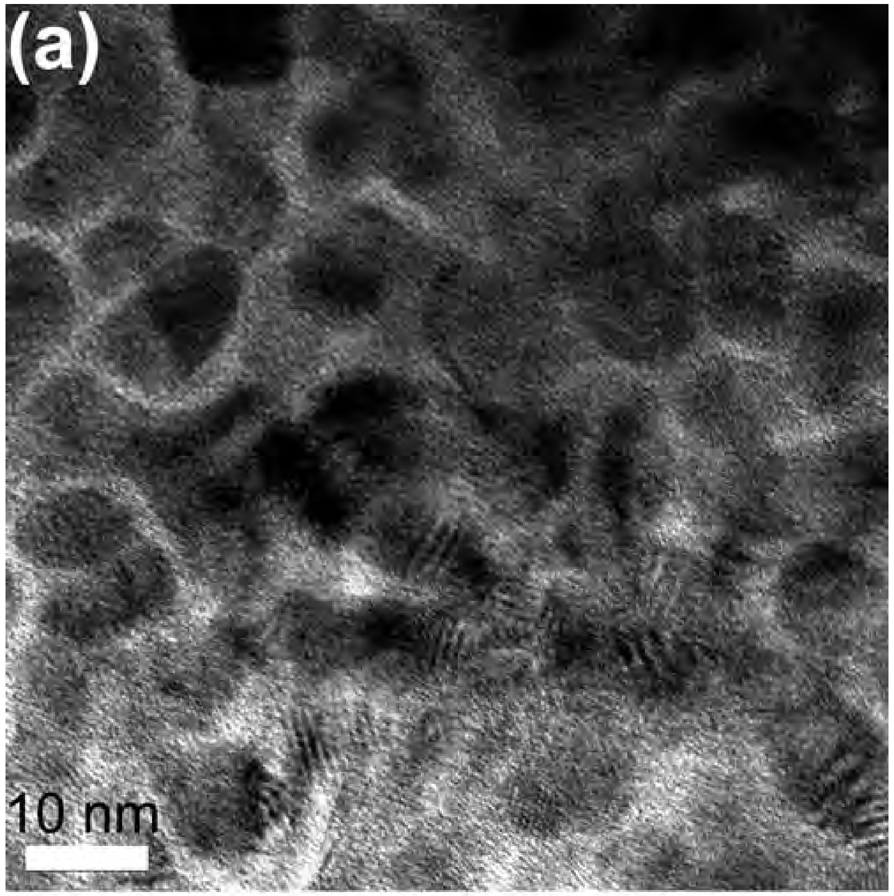
- **Many orders of magnitude change in ZT for small change in density (few %)**
- **Technology immature and process dependent**

*D.J. Paul*
*School of Engineering*

# Nanoparticle / Quantum Dot Materials

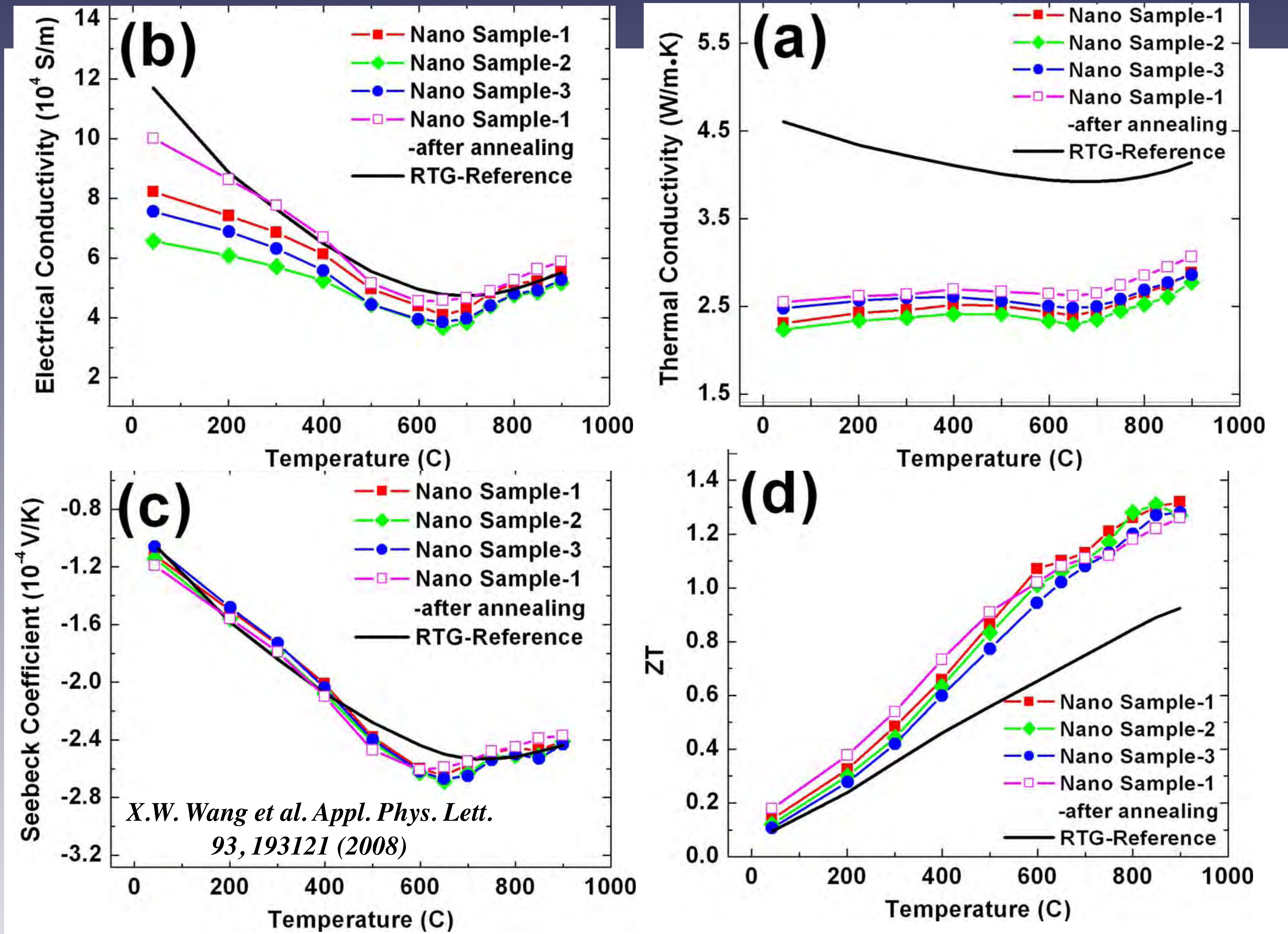



**Ball milled bulk alloy**

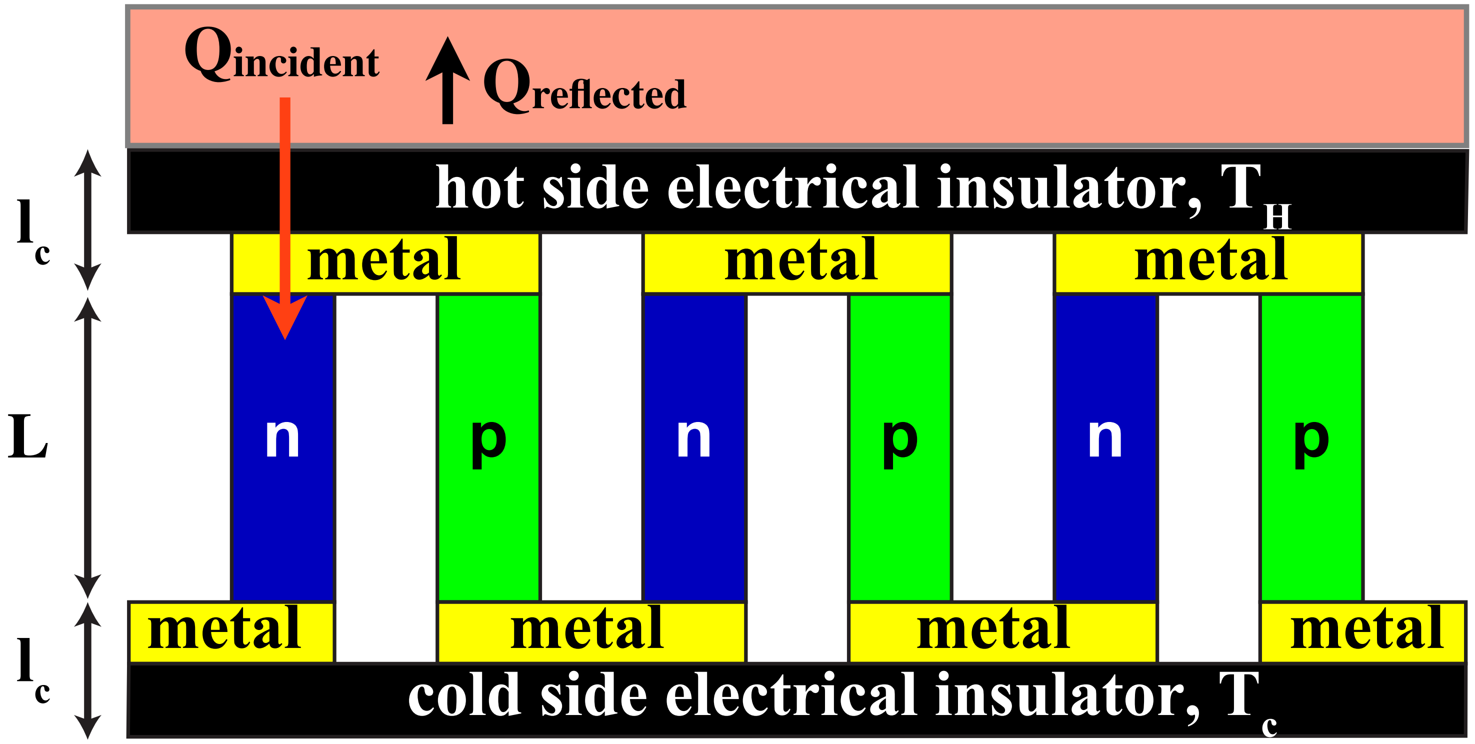



**Hot pressed material with ~ 10 nm nanoparticles**

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


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

# Maximum Output Power




A = module leg area

L = module leg length

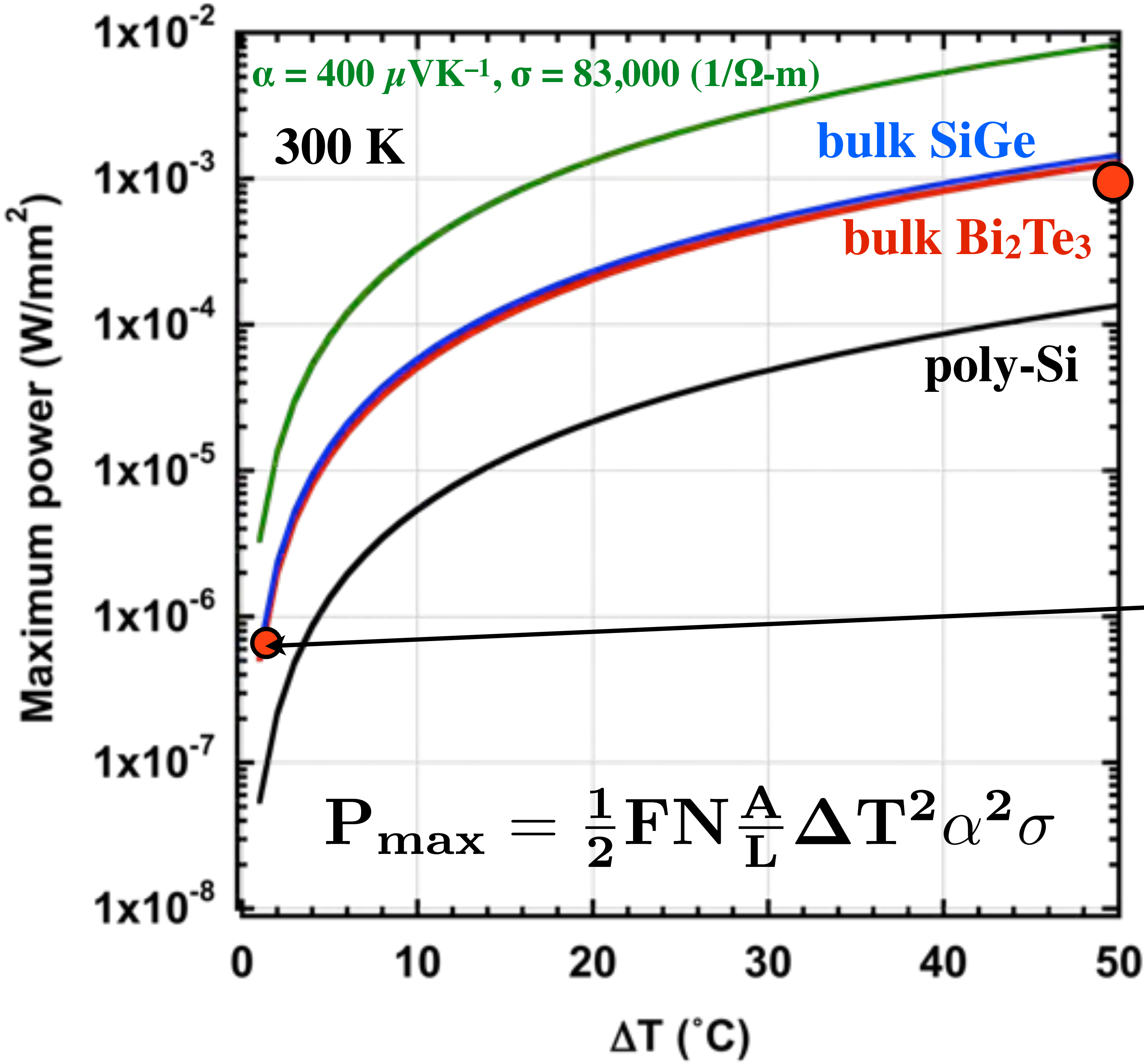
N = number of modules

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

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

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

# Maximum Power Examples




Dense microfabricated module

N = 2500

L = 10 $\mu$m

$l_c$ = 1 $\mu$m

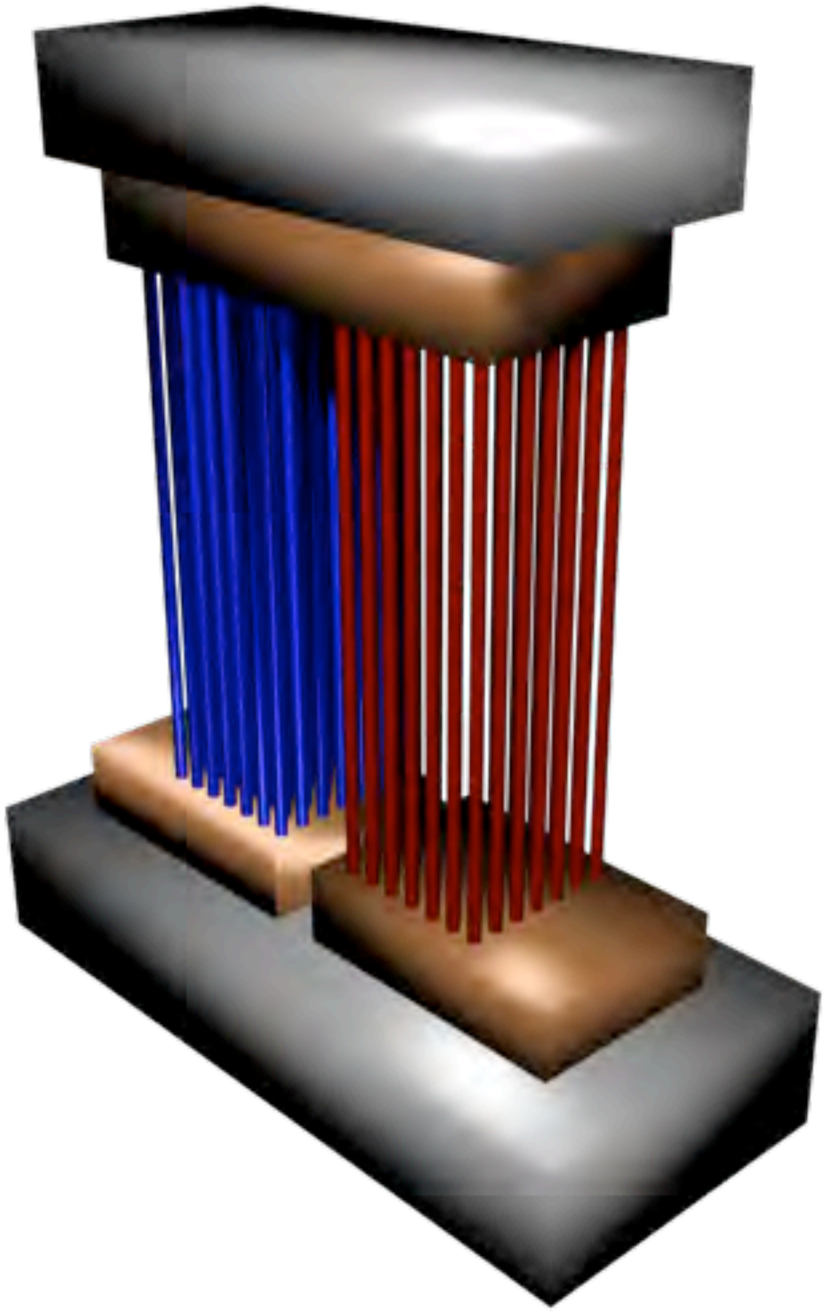
A = 10 x 10 $\mu m^2$

F = 0.2

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

N.B. The thermal conductivity must also be considered for $\Delta T_{max}$!

# 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

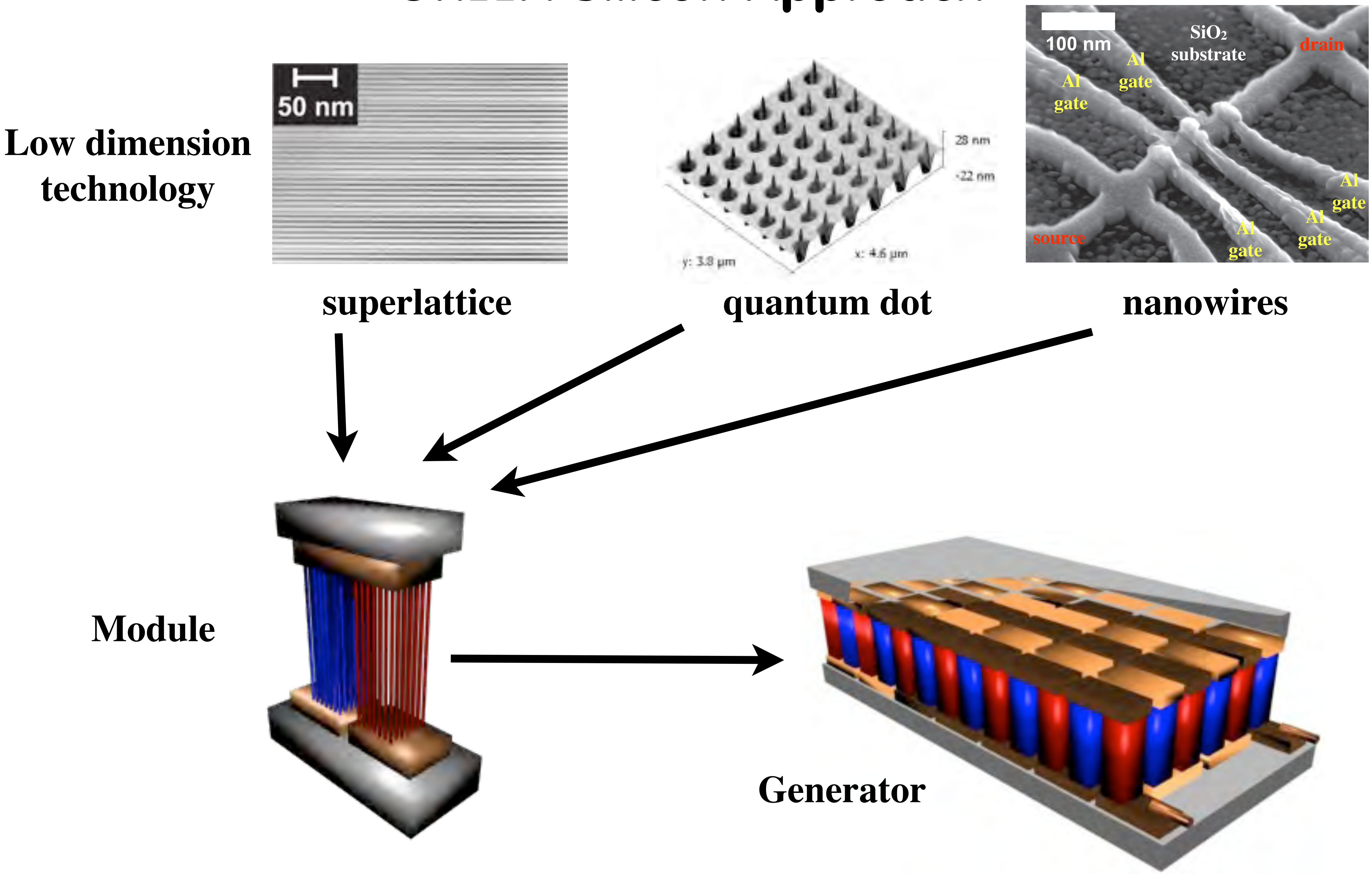
**E. Müller**

ETH Zürich, Switzerland



*D.J. Paul – Co-ordinator GREEN Si*
*EC FP7 ICT FET*
*"2ZeroPowerICT" No.: 257750*

# GREEN Silicon Approach




*D.J. Paul – Co-ordinator GREEN Si*
*EC FP7 ICT FET*
*"2ZeroPowerICT" No.: 257750*

# Summary

- Waste heat is everywhere –> enormous number of applications
- Low dimensional structures are yet to demonstrate the predicted increases in $\alpha$ due to DOS
- Reducing $\kappa_{\mathrm{ph}}$ faster than $\sigma$ has been the most successful approach to improving ZT to date
- Heterointerface scattering of phonons has been successful in reducing $\kappa$
- 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)