Thermoelectric Energy Harvesting

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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
James Watt Nanofabrication Centre @Glasgow

- 750m² 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

Vistec VB6 & EBPG5

Süss MA6 optical & nanoimprint lithography

8 RIE / PECVD  3 Metal dep tools  4 SEMs: Hitachi S4700  Veeco: AFMs

http://www.jwnc.gla.ac.uk
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)
Penrose tile: 0.46 nm rms alignment

Sub-5nm e-beam lithography

Measured linewidth vs dose

Probing molecules

Gap ~1nm

Ni

Pt

Photonic bandgaps

Si nanowire cavity

Q = 177,000

22 nm T-gate HEMTs

HSQ

Dose (µC cm⁻²)

Width (nm)

16000

20000

24000

28000

38nm

200 nm

5.00µm

11.9mm x 9.00k SE(U)

Tapered outside Cavity, Nₜₒ

Tapered within Cavity, Nₜᵢ

Cavity length, c

SiO₂

S470 100µm 10.0 µm × 15.0 µm SE(U) 139097
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
Why Use Thermoelectrics?

- No moving parts → no maintenance
- Peltier Coolers: fast feedback control mechanisms → $\Delta T < 0.1 \, ^\circ C$
- 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
The Peltier Effect

- Hot reservoir $T_h$
- Cold reservoir $T_c$
- Heat transfer, $Q$
- 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)
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 = \( \frac{1}{q} \times \text{entropy} \left( \frac{Q}{T} \right) \) transported with charge carrier
Measuring Seebeck Coefficient

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

$V_\sigma$, $I_\sigma$, $I_{heater}$, $T_h$, $T_c$, $\Delta T$
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)
The Seebeck Coefficient for Metals

\[ f(1 - f) = -k_B T \frac{df}{dE} \]

Expand \( g(E) \mu(E) \) in Taylor’s series at \( E = E_F \)

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

(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:

\[ \alpha = -\frac{8\pi^2 k_B^2}{3e^2 h^2} m^* T \left( \frac{\pi}{3n} \right)^{\frac{2}{3}} \]

\( n = \text{carrier density} \)

M. Cutler et al., Phys. Rev. 133, A1143 (1964)
Seebeck coefficient, $\alpha (\mu V K^{-1})$

- For SiGe, $\alpha$ increases with $T$
- $\alpha$ decreases for higher $n$
- Mott criteria $\sim 2 \times 10^{18} \text{ cm}^{-3}$
- Degenerately doped p-Si$_{0.7}$Ge$_{0.3}$

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

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

Hot reservoir $T_h$

Cold reservoir $T_c$

$\beta$ is temperature dependent

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

Thomson coefficient, $\beta$

$$ dQ = \beta I dT $$

units: V/K
The Kelvin Relationships

Derived using irreversible thermodynamics

\[ \Pi = \alpha T \]

\[ \beta = T \frac{d\alpha}{dT} \]

These relationships hold for all materials

Seebeck, \( \alpha \) is easy to measure experimentally

Therefore measure \( \alpha \) to obtain \( \Pi \) and \( \beta \)
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 =

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

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

\[
Q = \alpha IT - \kappa A \nabla T
\]
Semiconductors and Thermoelectrics

Seebeck effect:
- electricity generation

Peltier effect:
- electrical cooling

Heat source $T_h$
- heat source $T_h$

Metal
- metal

n p
- n p

Heat sink $T_c$
- heat sink $T_c$

Load
- Load

Battery
- Battery

Heat transfer $Q$
- Heat transfer $Q$
Conversion Efficiency

\[ \eta = \frac{\text{power supplied to load}}{\text{heat absorbed at hot junction}} \]

Power to load (Joule heating) = \( I^2 R_L \)

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

\[ = \kappa A (T_h - T_c) - \frac{1}{2} I^2 R \]

NB half Joule heat returned to hot junction
Conversion Efficiency

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

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

For maximum value

\[ \frac{d\eta}{d(\frac{R_L}{R})} = 0 \]

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

\[ \eta_{\text{max}} = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + Z T} - 1}{\sqrt{1 + Z T} + \frac{T_c}{T_h}} \]

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

\[ \eta_{\text{max}} = \text{Carnot} \times \text{Joule losses and irreversible processes} \]
Thermoelectric Power Generating Efficiency

\[ \eta = \frac{\Delta T}{T_h} \cdot \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + \frac{T_c}{T_h}} \]

Temperature difference, \( \Delta T \) (°C)

- \( ZT=0.5 \)
- \( ZT=1 \)
- \( ZT=2 \)
- \( ZT=3 \)
- \( ZT=4 \)
- \( ZT=5 \)

Efficiency (%)

Temperature (K)

- Carnot

Figure of merit

\[ ZT = \frac{\alpha^2 \sigma}{\kappa} T \]
Heat Transfer in Thermoelectric Element

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

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

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

area, \( A_n \)

heat source \( T_h \)

area, \( A_p \)

heat sink \( T_c \)

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

\[ Z \text{ for a couple depends on relative dimensions} \]

\[ Z \text{ is maximum for } \frac{L_n A_p}{L_p A_m} = \sqrt{\frac{\sigma_n \kappa_n}{\sigma_p \kappa_p}} \]
Maximising ZT for an Unbalanced Couple

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

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

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

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

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

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Thermodynamic Efficiency: The Competition

Carnot efficiency
Thermodynamic limit
ZT=∞
ZT=20, unlikely
ZT=4, ambitious
ZT=2, plausible eventually
ZT=0.7, available today

Heat source temperature (K)

Efficiency (%)

ZT of 4 start to become seriously competitive

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

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At large scale, thermodynamic engines more efficient than TE

ZT average for both n and p over all temperature range

Diagram assumes high T

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

C.B. Vining, Nature Mat. 8, 83 (2009)
Thermal Conductivity of Bulk Materials

Both the lattice and electron current can contribute to heat transfer

\[
\kappa = \kappa_{el} + \kappa_{ph}
\]

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

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

Good thermoelectric materials should ideally have \( \kappa_{el} \ll \kappa_{ph} \)

i.e. electrical and thermal conductivities are largely decoupled
Phonons: Lattice Vibration Heat Transfer

- **Frequency (THz)**
  - LO
  - TO
  - LA

- **Energy (meV)**
  - 0
  - 10
  - 20
  - 30
  - 40
  - 50
  - 60

- **Wavenumber**
  - \(\Gamma\)
  - \(\Delta\)
  - \(X\)

- **Optic modes** - neighbours in **antiphase**
  - \(\delta+\) and \(\delta-\)

- **Acoustic modes** - neighbours in **phase**
  - \(\Delta\) and \(\Xi\)

Materials:
- SiGe

Diagram showing phonon modes and their frequencies and energies in a lattice structure.
Wiedemann-Franz Law

Empirical law from experimental observation that \( \frac{\kappa}{\sigma T} = \text{constant for metals} \)

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 $\kappa_{el}$

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

$L = \text{Lorentz number}$

$$= 2.45 \times 10^{-8} \text{ W}\cdot\Omega\cdot\text{K}^{-2}$$

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

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

Exceptions:
- most exceptions systems with $\kappa_{el} \ll \kappa_{ph}$
- some pure metals at low temperatures
- certain alloys where small $\kappa_{el}$ results in significant $\kappa_{ph}$ contribution
- certain low dimensional structures where $\kappa_{ph}$ can dominate
Renewed interest in thermoelectrics is motivated by the realization that complexity at multiple length scales can lead to new avenues for energy conversion. An optimized ZT (reduced), leading to both a decrease in thermal conductivity as possible. Traditional thermoelectric materials may decouple the Seebeck coefficient and electrical conductivity (efficiency). An optimized ZT requires compromises with α, σ & κ.

Limited by the Wiedemann-Franz law, the standard computation of electrical resistivity, which are likewise due to bipolar effects.

Maximum ZT requires 1 + l = 0.8

Maximum ZT ~ 1 at ~100 °C

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

- Example for Bi$_2$Te$_3$ where $\kappa_{\text{ph}}$ is theoretically reduced by x 4
- Polycrystalline or defects can be used to reduce $\kappa_{\text{ph}}$ faster than $\sigma$

$$ZT = \frac{\alpha^2}{L(1 + \frac{\kappa_{\text{ph}}}{\kappa_{\text{el}}})}$$

“Phonon glasses” search to improve ZT

Bulk Thermoelectric Materials Performance

![Graph showing n-Type and p-Type zT values for various materials](image)

- **Bulk n-Bi<sub>2</sub>Te<sub>3</sub> and p-Sb<sub>2</sub>Te<sub>3** used in most commercial Peltier coolers

- **Bulk Si<sub>1-x</sub>Ge<sub>x** (x~0.2 to 0.3) used for high temperature satellite applications

_D.J. Paul_
_School of Engineering_
Thermoelectric Generators / Peltier Coolers

Bulk $n$-Bi$_2$Te$_3$ and $p$-Sb$_2$Te$_3$ devices
Small Scale Microfabricated Energy Harvesting

ΔT = 5 K → 5 V and 1 µW

Si process: poly-Si

α_{n+p} = 160 µV/K

κ = 31.4 Wm⁻¹K⁻¹

ρ = 1.5 mΩ-cm

Micropelt: Microfabricated Bi$_2$Te$_3$ Technology

http://www.micropelt.com/

20 µm Bi$_2$Te$_3$
D.J. Paul  
School of Engineering

Micropelt Peltier Coolers for Lasers

Microfabricated Bi$_2$Te$_3$ thermoelectric devices

http://www.micropelt.com/
Micropelt Bi$_2$Te$_3$ Thermoelectric Energy Harvester

3.4 mm x 3.4 mm thermoelectric chip

ZT $\sim$ 1

http://www.micropelt.com/
VW and BMW announced TE on exhaust in 2008: 24 Bi$_2$Te$_3$ modules

600 W under motorway driving $\rightarrow$ 30% of car’s electrical requirement

5% reduction in fuel consumption through removing alternator
NASA Radioisotope Thermoelectric Generator

Radioisotope heater → thermoelectric generator → electricity

Voyager – Pu$^{238}$

Pu$^{238}$ fuel pellet

Half-life = 87 years

470 W @ 30 V on launch, after 33 years power = $470 \times 2^{-\frac{33}{87}} = 361$ W
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
U.K. Electricity Generation 2007

- Nuclear
- Other
- Coal
- Renewables
- Gas
- Oil

80% generate CO₂

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

Energy filtering:

\[
\alpha = -\frac{k_B}{q} \left[ \frac{E_c - E_F}{k_B T} + \int_{0}^{\infty} \frac{(E-E_c)}{k_B T} \frac{\sigma(E) dE}{\int_{0}^{\infty} \sigma(E) dE} \right]
\]


Carrier Pocket Engineering – strain & band structure engineering
Length Scales: Mean Free Paths

3D electron mean free path

\[ \ell = v_F \tau_m = \frac{\hbar}{m^*} \left( 3\pi^2 n \right)^{\frac{1}{3}} \frac{\mu m^*}{q} \]

3D phonon mean free path

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

- \( C_v = \) specific heat capacity
- \( \langle v_t \rangle = \) average phonon velocity
- \( q = \) density of phonons

A structure may be 2D or 3D for electrons but 1 D for phonons (or vice versa!)
The high thermal conductivity of CoSb3 is lowered when the electrical conductivity is optimized by doping (doped CoSb3). The thermal conductivity is further reduced by the presence of large void spaces shown in blue.

For example, rare-occupancies, or rattling atoms in addition to the disorder inherent in the alloying used in the state-of-the-art materials. For example, rare-earth elements such as CoSb3 and IrSb3, there is a high degree of covalent bonding between the elements.

In contrast, the clathrates, which contain large, complex unit cells, may be tuned by moving the composition slightly off equilibrium. The room-temperature structure of Zn4Sb3 has a crystalline Sb sublattice (blue) and a highly disordered Zn sublattice containing a variety of interstitial sites (in polyhedra) along with the primary sites (purple).

As disorder is achieved through interstitial sites, partial filling establishes a random alloy mixture of elements. For skutterudites containing elements with low electronegativity such as Bi2Te3 and anions does not reduce the electrical conductivity but lowers the potential to reduce thermal conductivity through disorder.

The half-Heusler alloys have a relatively low lattice thermal conductivity (Fig. 2a) presumably because of the mass ratio of the alloy constituents. It can be expected that random vacancies are ideal scattering sites.

A clear correlation has been found with the size and vibrational motion of the constituent atoms and the thermal conductivity leading to high lattice thermal conductivities. For example, in the clathrates such as CeFe3CoSb12, La3–xTe4, TAGS, SiGe, and the half-Heusler alloy Hf0.75Zr0.25NiSn.

Filling these voids with ions adds additional electrons that may be tuned by moving the composition slightly off equilibrium. One class of such materials are clathrates, which contain large, complex unit cells. Complex crystal structures that yield low lattice thermal conductivity.

Figure 2

Skutterudite structure: filling voids with heavy atoms

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

Temperature °C

<table>
<thead>
<tr>
<th>Material</th>
<th>$\kappa_0$ (W m$^{-1}$ K$^{-1}$)</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Te$_3$</td>
<td>0.05</td>
<td>300</td>
</tr>
<tr>
<td>PbTe</td>
<td>0.00</td>
<td>300</td>
</tr>
<tr>
<td>CeFe$<em>3$CoSb$</em>{12}$</td>
<td>0.01</td>
<td>300</td>
</tr>
<tr>
<td>Hf$<em>{0.75}$Zr$</em>{0.25}$NiSn</td>
<td>0.02</td>
<td>300</td>
</tr>
<tr>
<td>SiGe</td>
<td>0.03</td>
<td>300</td>
</tr>
<tr>
<td>TAGS</td>
<td>0.04</td>
<td>300</td>
</tr>
<tr>
<td>Ag$_8$TiTe$_5$</td>
<td>0.05</td>
<td>300</td>
</tr>
<tr>
<td>La$_{3-x}$Te$_4$</td>
<td>0.06</td>
<td>300</td>
</tr>
<tr>
<td>Yb$<em>{14}$MnSb$</em>{11}$</td>
<td>0.07</td>
<td>300</td>
</tr>
<tr>
<td>Zn$_4$Sb$_3$</td>
<td>0.08</td>
<td>300</td>
</tr>
<tr>
<td>Ba$<em>{8}$Ga$</em>{16}$Ge$_{30}$</td>
<td>0.09</td>
<td>300</td>
</tr>
</tbody>
</table>

The graph shows the variation of thermal conductivity with temperature for different materials. The $p$-type Yb$_{14}$MnSb$_{11}$ has a $zT$ of 1 at 900 °C.

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?

\[ \alpha = -335 \, \mu \text{V K}^{-1} \]
\[ \sigma = 30,000 \, \text{S/m} \]
\[ \kappa = 1.1 \, \text{W m}^{-1}\text{K}^{-1} \]
at 700 K


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Low Dimensional Structures: 2D Superlattices

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

$L.D.\ Hicks\ and\ M.S.\ Dresselhaus,\ Phys.\ Rev.\ B\ 47,\ 12737\ (1993)$
2D Bi$_2$Te$_3$ Superlattices

$$E_{F2D} = E_{F3D} - \frac{\hbar^2 \pi^2}{2m^*_z a^2}$$

Both doping and quantum well width, $a$, can now be used to engineer ZT

$$Z2D T = \text{(1)} \quad \text{ZT for 3D Bi}_2\text{Te}_3$$

$$Z2D T = \text{(2)}$$

m$_x$ = 0.021 m$_0$

m$_y$ = 0.081 m$_0$

m$_z$ = 0.32 m$_0$

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

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

**p-Bi$_2$Te$_3$ / Sb$_2$Te$_3$ Superlattices**

Bi$_2$Te$_3$  \( \kappa_{ph} = 1.05 \text{ Wm}^{-1}\text{K}^{-1} \)

3/3 nm, 1/5 nm, 2/4 nm Bi$_2$Te$_3$ / Sb$_2$Te$_3$ periods almost identical \( \kappa_{ph} \)

**p-Bi$_2$Te$_3$ / Sb$_2$Te$_3$ Superlattices**

Bulk Bi$_2$Te$_3$ ZT $\sim$ 1.0
Superlattice ZT = 2.6

<table>
<thead>
<tr>
<th>Electrons</th>
<th>Phonons</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$ = 383 cm$^2$V$^{-1}$s$^{-1}$</td>
<td>$\Lambda_{ph}$ = 3 nm</td>
</tr>
<tr>
<td>$\ell$ = 11.4 nm</td>
<td>$k_{el}\ell$ $\sim$ 7.6</td>
</tr>
<tr>
<td>$k_{ph}\Lambda$ $\sim$ 0.5</td>
<td></td>
</tr>
</tbody>
</table>

$=>$ Phonon blocking

1 nm: 5 nm p-Bi$_2$Te$_3$ QW / Sb$_2$Te$_3$ barrier superlattices

Thermal conductivity reduced more than electrical conductivity

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

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The more heterointerfaces, the lower the thermal conductivity.

Physically: more heterointerfaces $\rightarrow$ 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

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

10 µm n-Si / Si_{0.8}Ge_{0.2} superlattice

- $\alpha = -1260 \, \mu V K^{-1}$
- $\sigma = 95,200 \, 1/(\Omega-m)$
- $\kappa = 14.6 \, W m^{-1}K^{-1}$
- $ZT = 3.1$ 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 $\Delta T = 200 \, ^\circ C \Rightarrow ZT_{module} \sim 3$

Thermal Conductivity of Silicon Nanowires

For bulk Si
\[ \kappa \sim 149 \text{ Wm}^{-1}\text{K}^{-1} \]
at 300 K

For bulk Si
\[ \Lambda_{ph} = \frac{3 \kappa_{ph}}{C_v \langle v_t \rangle \rho} \]
\[ \sim 300 \text{ nm} \]

Phonon scattering at boundaries increases for smaller dia. wires

**Thermal Conductivity of 1D Silicon Nanowires**

\[
\Lambda_{ph} = \frac{3\kappa_{ph}}{C_{v} \langle v_t \rangle \rho}
\]

\(\sim 300 \text{ nm}\)

\(\ell = 110 \text{ nm}\)

Phonon scattering >> electron scattering

Red data from nanowires with rough boundaries

1D Nanowires

4 terminal Si nanowires

Substrate removed by etching

Heaters


D.J. Paul
School of Engineering
1D Silicon Nanowires

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

For Module Require Vertical Nanowires

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

Heat absorber
metal interconnects
Heat rejector
thermoelectric elements
nanowire elements
electrical connections
Seebeck $\alpha$: bulk < superlattice < QD

Thermal conductivity reduced more than electrical conductivity

SiGe Quantum Dots

G. Perot et al., Nat. Mat. 9, 491 (2010)
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
Nanoparticle / Quantum Dot Materials

(b) Ball milled bulk alloy

(a) Hot pressed material with ~ 10 nm nanoparticles

The significant enhancement of ZT shows the maximum of 0.93 for the sample between 400 and 700 °C.

Enhanced thermoelectric properties have been achieved in nanostructured dense bulk SiGe alloy. The thermal conductivity reduction is strongly correlated with the nanostructure features that can lead to large reduction in the thermal conductivity while maintaining the power factor.

The thermal conductivity reduction is mainly attributed to the thermal conductivity reduction, which is strongly correlated with the nanostructure features. The enhanced Seebeck coefficient shows a maximum of 1.26.

We are grateful to Dr. Jean-Pierre Fleurial and Dr. M.D., and Z.R. and G.C. for their contribution to this work.

In summary, enhanced thermoelectric properties have been achieved in nanostructured dense bulk SiGe alloy. The enhancement that is obtained is the result of a significant reduction in the thermal conductivity while maintaining the power factor.

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In summary, enhanced thermoelectric properties have been achieved in nanostructured dense bulk SiGe alloy. The enhancement that is obtained is the result of a significant reduction in the thermal conductivity while maintaining the power factor.
\[ P_{\text{max}} = \frac{1}{2} FN \frac{A}{L} \Delta T^2 \alpha^2 \sigma \]

- \( F \) = fabrication factor
- \( N \) = number of modules
- \( A \) = module leg area
- \( L \) = module leg length
- Practical systems: both electrical and thermal impedance matching is required

Maximum Power Examples

\[ P_{\text{max}} = \frac{1}{2} FN \frac{A}{L} \Delta T^2 \alpha^2 \sigma \]

\( \alpha = 400 \, \mu V K^{-1}, \sigma = 83,000 (1/\Omega \cdot m) \)

300 K

bulk SiGe

bulk Bi\(_2\)Te\(_3\)

poly-Si

Micropelt

N = 2500

L = 10 \, \mu m

l\(_c\) = 1 \, \mu m

A = 10 \times 10 \, \mu m^2

F = 0.2

Dense microfabricated module

bulk Bi\(_2\)Te\(_3\) experiment

Nat. Mat. 2, 528 (2003)

(scaled from L = 20 \rightarrow 10 \, \mu m)

N.B. The thermal conductivity must also be considered for \( \Delta T_{\text{max}} \)!
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
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J. Stangl, T. Fromherz & G. Bauer
University of Linz, Austria

E. Müller
ETH Zürich, Switzerland
GREEN Silicon Approach

Low dimension technology

superlattice

quantum dot

nanowires

Module

Generator

D.J. Paul – Co-ordinator GREEN Si EC FP7 ICT FET “22eroPowerICT” 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 $\kappa_{\text{ph}}$ 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”
