Thermoelectric Energy Harvesting

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U.K.
The University of Glasgow

Established in 1451

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

Moved to Gilmorehill in 1870

400 years in High Street

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

- 750m² (+150 m²) cleanroom - pseudo-industrial operation
- 15 technicians + 4 PhD research technologists
- Processes include: MMICs, III-V, Si/SiGe/Ge, integrated photonics, metamaterials, MEMS (microfluidics)
- Part of EPSRC III-V National Facility & STFC Kelvin-Rutherford Facility
- Commercial access through Kelvin NanoTechnology
- http://www.jwnc.gla.ac.uk/

14 RIE / PECVD / ALD 6 Metal dep tools 4 SEMs: Hitachi S4700 Veeco: AFMs
30 years experience of e-beam lithography

Sub-5 nm single-line lithography for research

Vistec EBPG5

Measured linewidth vs dose

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

Alignment allows 1 nm gaps between different layers:

→ nanoscience: single molecule metrology
200 nm gate length
10 nm wide, 50 nm tall nanowire
10 nm Wide Si Nanowire SET

Depletion mode nanowire

Drain Current (A)

Gate Voltage (V)

1.4 K

1.9 nm

10.7 nm

10 nm
Micro and Nanotechnology from Glasgow

Nanoelectronics:
- 10 nm T-gate HEMT

Optoelectronics:
- 1.55 μm DFB laser

Hydrophobic patterns

Healthcare:
- STEM cell interrogation

Manufacture:
- AFM probes

Environment:
- Microfluidics

Sensing:
- Si nanowires
- III-V CMOS

MEMS:
- THz optics

1 nm nanogaps

Gap ~1 nm

38 nm

10 nm foot

150 nm

1 mm

1 μm

10 μm

100 μm

2 mm

10⁻⁹ 10⁻⁸ 10⁻⁷ 10⁻⁶ 10⁻⁵ 10⁻⁴ 10⁻³ 10⁻² 10⁻¹
Thermoelectrics History

- **History: Seebeck effect 1822**
  - heat → electric current

- **Peltier (1834): current → cooling**

- **Thomson effect: Thomson (Lord Kelvin) 1852**
Thermoelectric Applications

- NASA Voyager I & II
- Peltier cooler: telecoms lasers
- Cars: replace alternator
- Temperature control for CO₂ sequestration
- Buildings / industry temperature control – autonomous sensing
Energy Harvesting for Remote Sensing

Flood sensors

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

Weather monitoring

Visionary Companions: FET flagship

"Guardian Angels" aims to interlink future energy efficient technologies for a smarter life.

The project "Guardian Angels for a Smarter Life" assembles a pan-European network under the leadership of EPF Lausanne and ETH Zurich to create intelligent and autonomous systems serving society. Assisting people in all sorts of complex situations, it will meet the technological challenge of weaving together energy efficient information processing, sensing, communication and energy harvesting.

Currently, high energy consumption and the short lifespan of batteries are obstructing further progress in Information and Communication Technologies. The "Guardian Angels" (GA) are envisioned as intelligent, non-intrusive and autonomous devices featuring sensing, computation and communication. They are intended to watch out for us, providing assistance from infancy to old age. A key feature will be their zero power requirements as they will scavenge for energy, a technology that will benefit from bio-inspired concepts.

Multiple applications for smart personal companions:

Physical GA: As personal companions, these Guardian Angels will for instance be used as individual health support tools. These digital health assistants will be the key to keeping health and day care affordable and accessible to all in the ageing societies of Europe. For example, a growing number of elderly people will be able to maintain their quality of life in their familiar environment even in cases of reduced mobility or failing cognitive abilities.

Environmental GA: Furthermore, Guardian Angel devices will be able to monitor local ambient conditions for environmental danger. Communicating with each other, the devices will enlarge the personal radius of sensory perception. For example, natural disaster warnings will be issued individually and without delay. Gaining access to real time data on a grand scale will result in saving energy in heating, transportation and domestic appliances.

Emotional GA: Ultimately, the device will also perceive emotional conditions and provide helpful functions for the disabled. Thus, for example, quadriplegic patients will be empowered to interact by thought or the autistic will be enabled to read and send out emotions.

Designed in close cooperation with different social actors, interest groups and future users, paying close attention to environmentally friendly and economically feasible solutions, further beneficial applications for GA technology will be developed in the course of the project. In short, Guardian Angels devices will make our environment more interconnected and smart, more energy efficient and safe.

Guardian Angels roadmap of system complexity: main functions and supporting technologies.

Sports performance sensors

Flood sensors

Weather monitoring

Aged well being sensors

Energy harvester

Sensor

Processor

Radio

> 10 mW

> 100 µW

> 10 µW

< 100 µW/cm² !!!

Battery free autonomous sensors: ECG, blood pressure, etc.
Fourier thermal transport

\[ Q = -\kappa A \nabla T \]

**Heat (energy/t)**

- **Area,** \( A \)
- **Hot side,** \( T_h \)
- **Cold side,** \( T_c \)
- **Heat (energy/t) =** \( Q \)

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

Joule heating

\[ Q = I^2 R \]

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

Peltier coefficient, \( \Pi = \frac{Q}{I} \)

units: \( W/A = V \)

Peltier coefficient is the heat energy carried by each electron per unit charge & time.
The Seebeck Effect

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

Seebeck coefficient, \( \alpha = \frac{dV}{dT} \) units: V/K

Seebeck coefficient = \( \frac{1}{q} \) x entropy \( \left( \frac{Q}{T} \right) \) transported with electron
If we ignore energy dependent scattering (i.e. $\tau = \tau(E)$) then from J.M. Ziman

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

Thermoelectric power requires asymmetry in red area under curve

$$\alpha = \frac{q^2}{3T\sigma} \int \tau(E) \nu^2(E) \left[ -g(E) \frac{df}{dE} \right] (E - E_F) dE$$
Seebeck coefficient, $\alpha$ (µV K$^{-1}$)

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

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

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

The Thomson Effect is a property of certain materials that allows for the generation of electric current due to a temperature gradient. In the context of this diagram, we have a Hot reservoir at temperature $T_h$ and a Cold reservoir at temperature $T_c$. The temperature gradient $dT$ is present, and the current $I$ flows from the Hot reservoir to the Cold reservoir.

Mathematically, the change in heat $dQ$ with respect to distance $dx$ can be expressed as:

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

where $\beta$ is the Thomson coefficient, a measure of the efficiency of the Thomson effect. The units of $\beta$ are $V/K$.

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 \( \beta \)
Carnot Efficiency for Thermal Engines

Efficiency \( \eta = \frac{\text{net work output}}{\text{heat input}} \) = \( \frac{W_t - W_{\text{com}}}{Q_1} \)

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

\( \eta = \frac{Q_1 - Q_2}{Q_1} \)

\( \eta = 1 - \frac{Q_2}{Q_1} \)
Carnot Efficiency

Efficiency =

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

\[ \eta = 1 - \frac{Q_2}{Q_1} \]

Carnot: maximum \( \eta \) only depends on \( T_c \) and \( T_h \)

\[ \eta_c = 1 - \frac{T_c}{T_h} \]

Higher temperatures give higher efficiencies

\( T_c = 293 \text{ K} = 20 \text{ °C} \)
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 $J = \frac{1}{A}$

\[ Q = \alpha IT - \kappa A \nabla T \]
Seebeck effect: electricity generation

Peltier effect: electrical cooling i.e. heat pump

Heat transfer $Q$

Load

Battery
Conversion Efficiency

η = \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 = \alpha IT_h

I = \frac{\alpha (T_h - T_c)}{R + R_L} \quad \text{(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
Thermoelectric Conversion Efficiency

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

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

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

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

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

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

\[ = \text{Carnot} \times \text{Joule losses and irreversible processes} \]
Thermodynamic Efficiency

Figure of merit

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

\[ \eta = \frac{\Delta T}{T_H} \left( \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + \frac{T_c}{T_H}} \right) \]

\[ \Delta T \ (°C) \]

Efficiency, \( \eta \) (%)

Temperature (K)

Carnot

ZT = 20

ZT = 10

ZT = 5

ZT = 2

Today ZT = 0.7

Solar–Stirling

Nuclear–Rankine

Carbon–capture

Coal–Rankine
At large scale, thermodynamic engines more efficient than TE

ZT average for both n and p over all temperature range

Diagram assumes high $\Delta T$

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)
NASA with finite Pu fuel for RTG requires high efficiency

Automotive requires high power (heat is abundant)

Industrial sensing requires high power (heat is abundant)

Autonomous sensing requires high power (heat is abundant)

As heat is abundant the issue is how to maximise power output NOT efficiency for most applications

\[ \text{Power } \propto \alpha^2 \sigma \]
As the system has thermal conductivity $\kappa$, a maximum $\Delta T$ can be sustained across a module limited by 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.
Thermoelectric vs Doping of Semiconductors

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

- **n-Type $zT$**

  - $zT$ vs Temperature for different materials:
    - $\text{Bi}_2\text{Te}_3$
    - $\text{PbTe}$
    - $\text{CoSb}_3$
    - $\text{SiGe}$

- **p-Type $zT$**

  - $zT$ vs Temperature for different materials:
    - $\text{Sb}_2\text{Te}_3$
    - $\text{TAGS}$
    - $\text{CeFe}_4\text{Sb}_{12}$
    - $\text{Yb}_{14}\text{MnSb}_{11}$
    - $\text{SiGe}$

*Nature Materials 7, 105 (2008)*

- **Bulk $\text{n-Bi}_2\text{Te}_3$ and $\text{p-Sb}_2\text{Te}_3$ used in most commercial thermoelectrics & Peltier coolers**

- **But tellurium is 9th rarest element on earth !!!**

- **Bulk $\text{Si}_{1-x}\text{Ge}_x$ ($x \sim 0.2$ to 0.3) used for high temperature satellite applications**
Main Strategies for Optimising ZT

Reducing thermal conductivity faster than electrical conductivity:

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

Low-dimensional structures:

- Increase $\alpha$ 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 $\kappa$ and $\sigma$ almost independent
- Reduce $\kappa$ through phonon scattering on heterointerfaces

Energy filtering:

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

Increase $\alpha$ through enhanced DOS:

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

3D bulk

2D quantum well

1D quantum wire

0D quantum dot

$g(E)$ vs $E$

$\alpha$ increasing

The majority of heat in solids is transported by acoustic phonons.
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 $\rightarrow$ stationary phonons or bandgaps

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

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

![Graph showing phonon dispersion](image)
Nanostructures can improve Seebeck coefficient and/or decrease thermal conductivity.
Thermoelectric Low Dimensional Structures

Lateral superlattice
- Heat source $T_h$
- Metal
- Heat sink $T_c$
- n p

Vertical superlattice
- Heat source $T_h$
- Metal
- Heat sink $T_c$
- n p

Quantum Dots
- Heat source $T_h$
- Metal
- Heat sink $T_c$
- n p

Nanowires
- Heat source $T_h$
- Metal
- Heat sink $T_c$
- n p

378 QWs

10 nm

100 nm

2 nm
Vertical (Cross-plane) Superlattice TEs

- Use of transport perpendicular to superlattice quantum wells
- Higher $\alpha$ from the higher density of states
- Lower electron conductivity from tunnelling
- Lower $\kappa_{ph}$ from phonon scattering at heterointerfaces
- Able to engineer lower $\kappa_{ph}$ with phononic bandgaps

Overall $Z$ and $ZT$ should increase

Figure of merit

$$ZT = \frac{\alpha^2 \sigma}{\kappa} T$$
p-type Wafer Designs

SL1 to SL4: 922 x

- 2.85 ± 1.5 nm p-Ge QW
- 1.1 ± 0.6 nm p-Si$_{0.5}$Ge$_{0.5}$

SL5: 2338 x

- Si$_{0.175}$Ge$_{0.825}$
- 1.1 ± 0.2 nm p-Ge QW
- 0.5 ± 0.1 nm p-Si$_{0.5}$Ge$_{0.5}$

- Si$_{0.175}$Ge$_{0.825}$
Holes (Electronic Dispersion)

Distance (nm)

Energy (eV)

Energy (meV)

SL2

SL5

HH1 dispersion
HH2 dispersion
LH1 dispersion
HH dispersion
LH dispersion
SO dispersion

Rytov model

Half structure allows parasitics to be measured and removed for more accurate heat flux determination.
Thermal Measurements

Measured 41% of heat in vertical transport
Bulk SiGe ZT Comparisons

MIT, Nano Lett. 8, 4670 (2008)

J.P. Dismukes et al., J. Appl. Phys. 35, 2899 (1964)
Nanowire Fabrication on Suspended Hall Bar

100 x 45 nm wide Si nanowires with integrated heaters, thermometers and electrical probes
Si Nanowires: How many atoms wide?

Pt coat for TEM

Si

1.9 nm

10.7 nm

SiO$_2$

10 nm

17.8 nm

silicon

27.8 nm

SiO$_2$
45 nm Wide n-Silicon Nanowires

@ 300 K:
- $\sigma = 20,300$ S/m
- 4 terminal
- $\kappa = 7.78$ W/mK
- $\alpha = -271$ $\mu$V/K
- $ZT = 0.057$

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

n-Bi$_2$Te$_3$

p-Sb$_2$Te$_3$

20 µm Bi$_2$Te$_3$

http://www.micropelt.com/
System Design: Power Output

\[ P = \frac{\alpha^2 \sigma A N \Delta T^2}{2(\rho_c \sigma + L)(1 + 2 \frac{\kappa_c l}{\kappa_c L})^2} \]

A = module leg area  
L = module leg length  
N = number of modules  
\( \kappa_c \) = thermal contact conductivity  
\( \rho_c \) = electrical contact resistivity


System: power in BiTe alloys limited by Ohmic contacts

\( \rho_c \) (Bi\(_2\)Te\(_3\)) \( \equiv \) 1 x 10\(^{-7}\) \(\Omega\)-cm\(^2\)

\( \rho_c \) (Si\(_{1-x}\)Ge\(_x\)) = 1.2 x 10\(^{-8}\) \(\Omega\)-cm\(^2\)

300 K data

Power density (mW/cm\(^2\))

Delta temperature (K or °C)
122 Leg Modules

- n-type
- p-type

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


Further Information

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http://userweb.eng.gla.ac.uk/douglas.paul/index.html

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