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

- E-beam lithography
- Vistec VB6

- 900 m² cleanroom - pseudo-industrial operation
- 14 technicians + 4 PhD research technologists
- Processes include: MMICs, III-V, Si/SiGe/Ge, integrated photonics, metamaterials, MEMS (microfluidics)

- Süss MA6 optical lith
- Süss MA6 optical lithography

- Part of EPSRC III-V National Facility & STFC Kelvin-Rutherford Facility

- Commercial access through Kelvin NanoTechnology

- 14 RIE / PECVD / ALD
- 6 Metal dep tools
- 4 SEMs: Hitachi S4700
- Veeco: AFMs

- http://www.jwnc.gla.ac.uk/
Electron Beam Lithography Capability

30 years experience of e-beam lithography

Sub-5 nm single-line lithography for research

Vistec EBPG5

Vistec VB6

Measured linewidth vs dose

<table>
<thead>
<tr>
<th>Width (nm)</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dose (µC cm⁻²)</td>
<td>16000</td>
<td>20000</td>
<td>24000</td>
<td>28000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

HSQ

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

Alignment allows 1 nm gaps between different layers:

→ nanoscience: single molecule metrology
10 nm Width Si Nanowire FET

200 nm gate length
10 nm wide,
50 nm tall nanowire

$I_{on} = 2.4 \text{ mA/\mu m} @ 1.2 \text{ V}$

$66 \text{ mV/dec}$
Depletion mode nanowire

10 nm Wide Si Nanowire SET
Micro and Nanotechnology from Glasgow

Nanoelectronics: 10 nm T-gate HEMT

Optoelectronics: 1.55µm DFB laser

Hydrophobic patterns

Healthcare: STEM cell interrogation

Manufacture: AFM probes

Environment: Microfluidics

Sensing: Si nanowires

III-V CMOS

MEMS: THz optics
Thermoelectric 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

Micropelt

Temperature control for CO₂ sequestration

Buildings / industry temperature control – autonomous sensing
Energy Harvesting for Remote Sensing

Sports performance sensors

Flood sensors

Weather monitoring

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.

The Physical Guardian Angels will record vital body functions with quasi-invisible zero-power technology.

Guardian Angels for a Smarter Life

+++ Collaboration of more than two dozen universities, research institutions and industrial R&D labs in 13 countries +++ Project will use scavenger powered sensors to provide intelligent personal health and safety measures, environmental monitoring and support for disabilities +++ One year research pilot will bid for EU's 10 year, 1 billion EUR flagship project.
Fourier thermal transport

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

Area, \( A \)

Heat (energy/t) = \( Q \)

hot side, \( T_h \)

cold side, \( T_c \)

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

Joule heating

\[ Q = I^2 R \]

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

resistance, \( R \)
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

\( \kappa \) = thermal conductivity

\( \sigma \) = electrical conductivity

\( \alpha \) = Seebeck coefficient

\( \mu(E) \) = 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

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

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

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 electron
The Seebeck Coefficient

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

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

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

For electrons in the conduction band, \( E_c \) of a semiconductor

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

see Mott and Jones (1974) and H. Fritzscbe, 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 \( E = E_F \)

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

(Mott’s formula for metals)


i.e. Seebeck coefficient depends on the asymmetry of the current contributions above and below \( E_F \)
3D Electronic and Thermal Transport

3D electronic transport

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

3D thermal transport

\[ f(E) \]
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
Semiconductor Example: SiGe Alloys

Seebeck coefficient, $\alpha$ (µV K$^{-1}$) decreases for higher $n$

For SiGe, $\alpha$ increases with $T$

Degenerately doped p-Si$_{0.7}$Ge$_{0.3}$

Mott criteria $\sim 2 \times 10^{18}$ cm$^{-3}$

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

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

\[ \frac{dQ}{dx} = \beta I \frac{dT}{dx} \]

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 \( \beta \)
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
Energy Conversion: Electricity

The Rankine Cycle

William John Macquorn Rankine

Energy stored in fuel → heat → kinetic energy → electric energy
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 \( J = \frac{1}{A} \)

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

Seebeck effect: electricity generation

[Diagram showing a device with a heat source \( T_h \) and a heat sink \( T_c \), with an n-p junction and a load.]

Peltier effect: electrical cooling i.e. heat pump

[Diagram showing a device with a heat source \( T_h \), metal layers, and a battery.]

Heat transfer \( Q \)

Load

Battery

[Diagram indicating the direction of heat transfer and the current flow.]
Conversion Efficiency

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

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

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

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

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

Figure of merit

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

Power factor = \( \alpha^2 \sigma \)

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

Impedance matching and maximum power point tracking are key for thermoelectrics.
### Energy Quality

<table>
<thead>
<tr>
<th>Highest Quality</th>
<th>Lowest Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electromagnetic</td>
<td></td>
</tr>
<tr>
<td>Mechanical (kinetic)</td>
<td></td>
</tr>
<tr>
<td>Photon (light)</td>
<td></td>
</tr>
<tr>
<td>Chemical</td>
<td></td>
</tr>
<tr>
<td>Heat (thermal)</td>
<td></td>
</tr>
</tbody>
</table>

First proposed as **availability** by Kelvin in 1851 refined by Ohta

Energy quality describes the ease (i.e. $\eta$) with which energy can be transformed

A transition down the table will be more efficient than moving up the table

Therefore solar heating is more efficient than photovoltaic electrical generation

Expanded version from chemistry developed by Odum
Solar Thermal Water Heating System

Thermosiphon – natural convection & no pump

46% to 74% $\eta$ for solar energy $\rightarrow$ heat conversion are typical
Carnot Limit for Radiative Absorption

Thermal limit i.e. heating for the sun as a 6000 K black body emitter with a 300 K solar cell black body absorber

Sun: 6000 K

Maximum Carnot efficiency is 85% for absorber at 2470 K: all photons absorbed, maximum heat from every photon, zero thermal dissipation from absorber

Actual efficiencies for a room temperature absorber are < 85%
How Much Continuous Solar Energy?

Due to clouds, day/night & seasons, average energy << peak energy

Available energy needs to be averaged over 365 days and 24 hours

![Bar chart showing average solar irradiance (W/m²) for various cities: Glasgow, London, Paris, New York, Rome, Madrid, Athens, San Francisco, Cairo, Honolulu, Nouakchott.](chart.png)

Average solar irradiance (W/m²)
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..)

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.
Solar Thermal Water Heating

Efficiency can be high as $\eta$ is dominated by absorption of photons

Optimisation is all about maximum photon absorption and minimum heat loss

46% to 74% $\eta$ for solar energy $\rightarrow$ heat conversion are typical

$\eta$ heavily dependent on amount of solar energy available and required hot water temperature
Application Reality Check

- NASA with finite Pu fuel for RTG requires high efficiency
- Automotive requires high power (heat is abundant)
- Industrial sensing requires high power (heat is abundant)
- Autonomous sensing requires high power (heat is abundant)
- As heat is abundant the issue is how to maximise power output NOT efficiency for most applications

\[ \text{Power} \propto \alpha^2 \sigma \]
The majority of heat in solids is transported by acoustic phonons.
Thermal Conductivity

Lattice contribution:

\[ \kappa_{\text{ph}} = \frac{k_B}{2\pi^2} \left( \frac{k_B}{\hbar} \right)^3 T^3 \int_0^{\theta_D} \frac{\tau_c(x)x^4e^x}{\nu(x)(e^x-1)^2} \, dx \]

\[ \theta_D = \text{Debye temperature (640 K for Si)} \]

\[ x = \frac{\hbar\omega}{k_B T} \]

\[ \tau_c = \text{combined phonon scattering time} \]

\[ \nu(x) = \text{velocity} \]

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

Electron (hole) contribution:

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

\[ \tau(E) = \text{total electron momentum relaxation time} \]

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

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

- **But tellurium is 9$^{th}$ rarest element on earth !!!**

- **Bulk Si$_{1-x}$Ge$_x$ (x~0.2 to 0.3) used for high temperature satellite applications**

*Nature Materials 7, 105 (2008)*
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:

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

Seebeck Enhancement at Low Dimensions

Increase $\alpha$ through enhanced DOS:

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

3D bulk

2D quantum well

1D quantum wire

0D quantum dot

$g(E)$

$E_F$ $E$

$E_F$ $E$

$E_F$ $E$

$E_F$ $E$

$\alpha$ increasing

Length Scales: Mean Free Paths

3D electron mean free path

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

3D phonon mean free path

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

- \( C_v = \text{specific heat capacity} \)
- \( \langle v_t \rangle = \text{average phonon velocity} \)
- \( \rho = \text{density of phonons} \)

A structure may be 2D or 3D for electrons but 1 D for phonons (or vice versa!)
## Phonon Mean Free Paths

<table>
<thead>
<tr>
<th>Material</th>
<th>Model</th>
<th>Specific Heat (x10^6 Jm^-3K^-1)</th>
<th>Group velocity (ms^-1)</th>
<th>Phonon mean free path, Λ_{ph} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Debye</td>
<td>1.66</td>
<td>6400</td>
<td>40.9</td>
</tr>
<tr>
<td>Si</td>
<td>Dispersion</td>
<td>0.93</td>
<td>1804</td>
<td>260.4</td>
</tr>
<tr>
<td>Ge</td>
<td>Debye</td>
<td>1.67</td>
<td>3900</td>
<td>27.5</td>
</tr>
<tr>
<td>Ge</td>
<td>Dispersion</td>
<td>0.87</td>
<td>1042</td>
<td>198.6</td>
</tr>
</tbody>
</table>

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 \( \propto \frac{dE}{dk_q} \)
isolated Sb anions. The Zintl formalism describes these units as covalently bound with electrons donated from the ionic Yb\textsuperscript{2+} sublattice (yellow).

The alloying used in the state-of-the-art materials. For example, rare-

most state-of-the-art thermoelectric alloys (Bi\textsubscript{2}Te\textsubscript{3}, Caltech unpublished data; such as CoSb\textsubscript{3}, contain corner-sharing CoSb\textsubscript{6} octahedra, which can

due to the large number of random vacancies (PbTe and GeTe) continues to be an active area of research\textsuperscript{29–32}. Many

thermal conductivity\textsuperscript{28}. Alloying the binary tellurides (Bi\textsubscript{2}Te\textsubscript{3}, Sb\textsubscript{2}Te\textsubscript{3},

Wright discusses how alloying Bi\textsubscript{2}Te\textsubscript{3} with other isoelectronic cations

systems (such as Yb\textsubscript{14}MnSb\textsubscript{11}, ref. 45; CeFe\textsubscript{3}CoSb\textsubscript{12}, ref. 34; Ba\textsubscript{8}Ga\textsubscript{16}Ge\textsubscript{30}, ref. 79; and Zn\textsubscript{4}Sb\textsubscript{3}, ref. 80; Ag\textsubscript{9}TlTe\textsubscript{5}, ref. 40; and La\textsubscript{3–}Th

Figure 2

Skutterudite structure: filling voids with heavy atoms

\textit{p-Yb\textsubscript{14}MnSb\textsubscript{11} – ZT \sim 1 @ 900 °C}

\textit{G.J. Snyder et al., Nat. Mat. 7, 105 (2008)}
Principle: trying to copy “High Tc” superconductor structures

Heavy ion / atom layers for phonon scattering

High mobility electron layers for high electrical conductivity

Only small improvements to ZT observed

$\text{Na}_x\text{CoO}_2$  $\text{Ca}_x\text{Yb}_{1-x}\text{Zn}_2\text{Sb}_2$
AgPb$_{18}$SbTe$_{20}$ – Nanoparticle Scattering?

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

at 700 K

Nanostructures can improve Seebeck coefficient and/or decrease thermal conductivity
GREEN Silicon Approach

Low dimension technology

- superlattices
- quantum dots
- nanowires

Si/SiGe technology → cheap and back end of line compatible
Thermoelectric Low Dimensional Structures

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

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

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

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

378 QWs

10 nm

100 nm

Energy (meV)

-0.5 -0.4 -0.3 -0.2 -0.1 0.0 0.1 0.2 0.4 0.6 0.8 1

Distance (nm)

0 0.5 1 1.5 2 2.5 3 3.5 4

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

Theory for sample

Width of 3.43 nm and barriers 1.17 nm.

Width of 2.48 nm and barriers 1.12 nm.
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
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$_{0.5}$

Si$_{0.175}$Ge$_{0.825}$

SL5: 2338 x
1.1 ± 0.2 nm p-Ge QW
0.5 ± 0.1 nm p-Si$_{0.5}$Ge$_{0.5}$

Si$_{0.175}$Ge$_{0.825}$
Rytov 1D Continuum Model for Layered Materials

Superlattice N → ∞

QW: mass density ρ_a, phase velocity v_a

Barrier, ρ_b, v_b

Acoustic mismatch: \[ \eta = \frac{\rho_b v_b}{\rho_a v_a} \]

Superlattice zone boundaries:

\[ q_z = \frac{n\pi}{a + b} \]

\[ \cos q_z (a + b) = \cos q_a a \cos q_b b - \left[ \frac{1 + \eta^2}{2\eta} \right] \sin q_a a \sin q_b b \]

Acoustic mismatch:

Electron and Phonon Dispersion

Holes (Electronic Dispersion)

Distance (nm)

Distance (nm)

Energy (eV)

Measuring Seebeck Coefficient

- Physically heat one side of sample
- Cold sink on other side of sample
- Thermocouples top and bottom to measure $\Delta T$
- 4 terminal electrical measurements
- $\alpha$ and $\sigma$ easy to measure
- Thermal conductivity, $\kappa$ very difficult to measure
Vertical structure characterisation device

1. Mesa structure
2. Top Ohmic contact
3. Bottom Ohmic contact
4. Top Heater

30 nm Si₃N₄
50 nm Si₃N₄
Thermal Parasitic Removal

Isotropic structure

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

Measured 41% of heat in vertical transport
Transfer Line Measurements (TLMs)

Any misalignment or gaps results in errors → circular TLMs

Contact spacing, $d$

Resistance, $R$

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

$\rho_c = L_T^2 R_{sh}$
Vertical Electrical Conductivity I

Circular Transfer Line Method

Higher accuracy than TLM but correction factor required
Vertical Electrical Conductivity II

- 20 µm
- 30 µm
- 50 µm

- $R_{\text{contact}}$ $R_{\text{contact}}$
- $R_{\text{SL}}$ $R_{\text{SL}}$
- $R_{\text{lateral}}$

$\sigma = 2,215.7 \pm 61.7$ S/m

Corrected Resistance (Ohm)

Total resistance (Ω)

Spacing (µm)

Etch depth (µm)
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

\[ \frac{\Delta(ZT)}{ZT} = 2 \frac{\Delta\alpha}{\alpha} + \frac{\Delta\sigma}{\sigma} + \frac{\Delta\kappa}{\kappa} + \frac{\Delta T}{T} \]

\( \Delta x = \text{uncertainty in } x = \text{standard deviation in } x \)

- Measurements are conceptually simple but results vary considerably due to thermal gradients in the measurements \( \rightarrow \) systematic inaccuracies

- Total ZT uncertainty can be between 25% to 50%
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

SiO₂

Si

1.9 nm

10.7 nm

10 nm

17.8 nm

27.8 nm

silicon
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?
10 nm wide
500 nm tall
Si nanowire

Si etch

High density nanowires
50 nm Ge/SiGe nanowires
4 µm deep etched
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

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

- 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**

- \( \rho_c (\text{Bi}_2\text{Te}_3) \approx 1 \times 10^{-7} \ \Omega\text{-cm}^2 \)
- \( \rho_c (\text{Si}_{1-x}\text{Ge}_x) = 1.2 \times 10^{-8} \ \Omega\text{-cm}^2 \)


**Graph:**
- Power density (mW/cm²) vs. \( \Delta \) temperature (K or °C)
- Data for BiTe Micropelt ZT = 0.6, SiGe Dismukes ZT = 0.11, Nano SiGe ZT = 0.26, Nano BiTe ZT = 0.9
D.M. Rowe (Ed.), “Thermoelectrics Handbook: Macro to Nano”


Further Information

Contact: Prof Douglas Paul
Douglas.Paul@glasgow.ac.uk
Tel:- +44 141 330 5219

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

Address: School of Engineering,
University of Glasgow,
Rankine Building,
Oakfield Avenue,
Glasgow,
G12 8LT,
U.K.

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