Clean Energy: Thermoelectrics and Photovoltaics

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Solar Energy Use

Total = 101.605 Quadrillion Btu

- Petroleum 40%
- Nuclear Electric Power 8%
- Natural Gas 23%
- Coal 22%
- Renewable Energy 7%

Total = 6.830 Quadrillion Btu

- Solar Energy 1%
- Hydroelectric 36%
- Geothermal Energy 5%
- Biomass 53%
- Wind Energy 5%

Note: Sum of components may not equal 100 percent due to independent rounding.
Hydrocarbons vs. Photons

Arabian Oil: 600 years

Sun: 1.5 billion years
The Sun can Power both Solar Cells and Thermoelectrics
Voyager Powered by Thermoelectrics
Seebeck Effect

\[ S = \frac{\Delta V}{\Delta T} \]

\[ \oint E \cdot dx = 0 \]

L. Onsager, Physical Review 37, 405 (1931)
Carriers within $kT$ are excited.

**FOR A METAL**

\[ S = \frac{Q}{eT} = \frac{k}{e} \frac{kT}{E_F} \]

\[ \sim 1 \, \mu V/K \]

At 300K for a typical metal

**FOR A SEMICONDUCTOR**

\[ S = \frac{Q}{eT} = \frac{k}{e} \]

A semiconductor is like a classical gas

\[ \sim 100 \, \mu V/K \]
Off the Shelf Thermoelectrics

\[ V_{OC} = N(S\Delta T) \]
DC and AC Power-Generating Systems

**DC Power**

- Battery
- Solar panel
- Light bulb

**AC Power**

- Turbine
- Transformer
What Governs Particle Flow?

\[ dU = TdS + pdV + \mu dN + \phi de \]

\[ \eta = \mu + e\phi \]

Particles move from high electrochemical potential to low electrochemical potential.
Requirements for Electric Power

1. An Electrochemical Potential Difference Must be Present
   2. A Selective Barrier Must be Present
The Contact Potential
Batteries

Anode

\[ \Delta \mu_{\text{anode}} \]

Electrolyte

redox chemistry

Cathode

\[ \Delta \mu_{\text{cathode}} \]
Batteries Continued

\[ V_{OC} = \Delta \mu_{\text{anode}} + \Delta \mu_{\text{cathode}} \]
Solar Cells

Light

\[ V_{OC} = \Delta \mu_{\text{electrons}} + \Delta \mu_{\text{holes}} \]
Thermoelectrics as Heat Engines

Heat input consists of 3 terms:

\[ Q_1 = \kappa \Delta T \quad Q_2 = I S T_{HOT} \quad Q_3 = -\frac{1}{2} I^2 R_{TE} \]

Plugging into \( \eta \) and maximizing:

\[ \eta = \frac{\Delta T}{T_{HOT}} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_{COLD}}{T_{HOT}}} \]

\[ \eta = \frac{W}{Q} \quad \text{W is the work output} \]
\[ \text{Q is the heat input} \]

Work extracted is:

\[ W = I V_{LOAD} \]

\[ V_{LOAD} = V_{TE} \left( \frac{R_{LOAD}}{R_{TE} + R_{LOAD}} \right) = S \Delta T \left( \frac{R_{LOAD}}{R_{TE} + R_{LOAD}} \right) \]

\[ W = S^2 \Delta T^2 \left[ \frac{R_{LOAD}}{R_{TE} + R_{LOAD}} \right] \]
Heat Engines and Efficiency

Figure of Merit for Thermoelectrics is $ZT$

Dimensionless number. Larger the better

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

$S$  Thermopower

$\sigma$  Electrical conductivity

$\kappa$  Thermal conductivity
Is There a Ceiling to ZT?

A. Majumdar, Science 303, 777 2004
Is Bismuth a Good Thermoelectric?

Bulk Bismuth

\[ \Delta = 38 \text{meV} \]

Bismuth wire with diameter < 50nm

Tellurium doped Bismuth nanowires

\[ m^* = 0.001 m_e \quad \mu = 2.59 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \]

\[ S = 100 \mu \text{V/K} \quad \kappa = 8 \text{ W m}^{-1} \text{ K}^{-1} \]

Electron mean free path is ~30 to 50nm at room temperature
Density of States

\[ S \propto T \frac{\partial N(E)}{\partial E} \bigg|_{E_F} \]
ZT for Bismuth Nanowires

Bismuth is Not an Easy Material to Work With

State of the art: Alumina assisted electrodeposition

M.S. Dresselhaus et. al., Int. Mater. Rev. 48, 45-66 2003

Bismuth is sensitive to acids and bases and oxidizes readily

S.B. Cronin et. al., Nanotechnology 13, 653-658 2002

Measurement limited to 2-point and large thermocouples

Bismuth Nanowire Thermoelectric Devices

Bi Nanowire Electrical Conductivity Results

A. Boukai, K. Xu, J.R. Heath, Advanced Materials 18, 864-869 2006

Measuring the Thermopower

\[ S = \frac{\Delta V}{\Delta T} \]
Measuring the Thermoelectric Voltage (TEV)

This gives us:

\[
V/W
\]
Measuring $\Delta T$
Measuring $\Delta T$

This gives us:

$$\frac{\Omega}{W}$$

![Graph showing the relationship between R/R₀ and time with different power levels for left and right thermometers.](image)
Measuring $\Delta T$

This gives us: $\Omega/K$
Measuring $\Delta T$

Multiply: \[
\frac{V}{W} \times \frac{W}{\Omega} \times \frac{\Omega}{K}
\]

72nm Wide Bi Wire

Graph showing $TEV (\mu V)$ vs $\Delta T (K)$
Bi Nanowire Thermopower Results

A. Boukai, K. Xu, J.R. Heath, *Advanced Materials* 18, 864-869 2006
40nm wide Bi wire at 20K Results

Our results indicate that surface states dominate the carrier transport.

Thermopower is well correlated to Mott diffusion formula:

\[ S \propto \left| \frac{dN}{dE} \right|_{E_F} \]

1-D Systems

DOS

1-D Systems
And God Said, “Let there be Silicon and it was good.”

Chemistry of Si is well understood
+50 years of Silicon R&D

κ for bulk Si is ~150 W/(m-K) @300K

With SNAP, we have control over wire width, doping, crystal orientation, etc.
Superlattice Nanowire Pattern Transfer (SNAP)

GaAs/Al₆Ga₁₋ₓAs

Selective etching AlₓGa₁₋ₓAs

Pt deposition

Nanowire transfer

Pt nanowire formation

Nanowire contact

Array of Si Nanowires Made With SNAP

SNAP’s Versatility

20nm

400 NWs

1400 NWs

7.5nm

Gen VI Drive-In Doped 400 Si Wires

Acc.V Spot Magn Det WD Exp
30.0 kV 1.0 15000x SE 11.1 1 032906 · Sample 12 · Si NWs · 15 nm pitch
Si Nanowire Thermoelectrics

Suspended Platform Allows Measurement of ZT

\[ K = \frac{Q}{\Delta T} \]

Measurements are Taken on an Array of Si NWs

Si Nanowire Electrical Conductivity

![Graph showing electrical conductivity of Si nanowires versus temperature. The graph includes lines for bulk, 20 nm, and 10 nm nanowires with different carrier densities.](image-url)
Minimum Thermal Conductivity

$\kappa_{\text{min}}$ for Si $\sim 1 \text{ W/(m-K)}$ @300K

This occurs when Si is amorphous
\( \kappa \) for bulk Si is \( \sim150 \text{ W/(m-K)} \) @300K
Diffuse vs Specular Scattering
Our error in the temperature measurement is ~ .01%!!!
Si Nanowire Thermopower

\[ S^2 / K^2 \times 10^{-7} \]

\[ \propto \frac{1}{T} \]

- 20 nm wide; 7e19 cm\(^{-3}\)
- 20 nm wide; 3e19 cm\(^{-3}\)
- Bulk; 5e19 cm\(^{-3}\)
- 20 nm wide; 2e20 cm\(^{-3}\)

Temperature (K)
Phonon Drag

Bulk Silicon

Phonons are not in equilibrium. Longitudinal modes push the electrons down the temperature gradient.

Phonon Drag in Our Si NWs

Thermopower $S$ ($\mu$V·K$^{-1}$)

Temperature (K)

- $1 \times 10^{17}$ (estimated)
- $3 \times 10^{19}$
- $1.3 \times 10^{20}$
Phonon Drag is Supposed to Disappear at the Nanoscale


Thank you Jamil and Bill!
Phonon Drag in a 1-D System

\[ S = S_{\text{diffusion}} + S_{\text{phonon drag}} \]
Efficient Si Nanowires

20nm wide; 7e19 cm⁻³

10nm wide; 2e20 cm⁻³

Temperature (K)