Thermoelectrics 101

Eric Pop

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http://poplab.stanford.edu

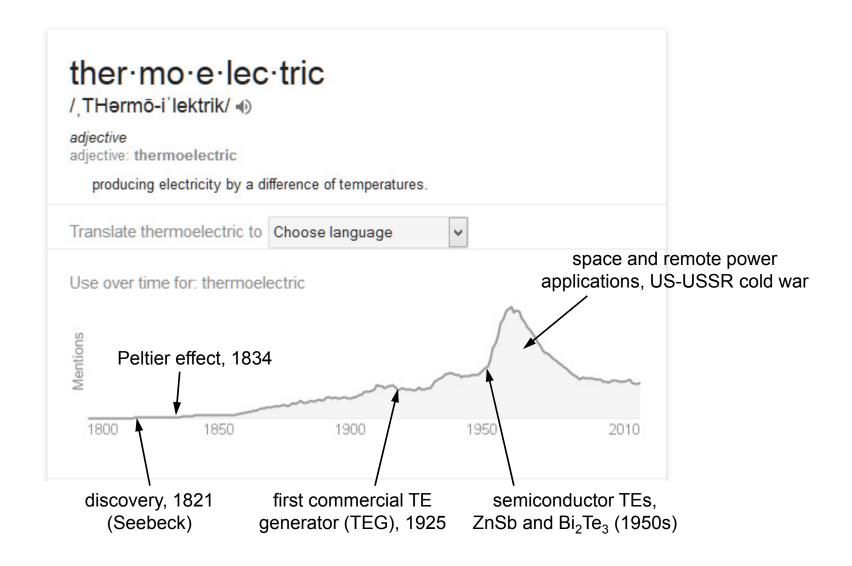
Outline

1) Fundamentals

2) Applications

3) Final Remarks

Definition and Usage

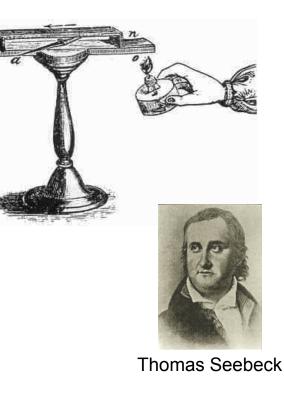


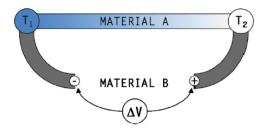
Seebeck vs. Peltier

- Seebeck effect (1821):
 - Loop of Cu and Bi wires (thermocouple)
 - Heating one end deflected magnetic needle, initial confused with thermomagnetism
 - Ørsted (1823) correctly explained that electric flow occurred due to temperature gradient

$$\Delta V \equiv (S_B - S_A) \Delta T$$

- $S_{A,B}$ = Seebeck coefficient = thermopower specific to material A or B (units of $\mu V/K$)
- Ex: $\Delta S \sim 300 \ \mu V/K$ and $\Delta T = 100 \ K$, we generate 30 mV
- Q: how do we generate 1.5 V like AA battery?

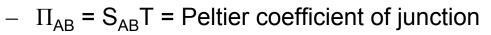




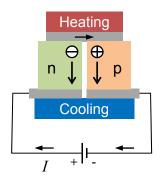
Seebeck vs. Peltier

- Peltier effect (1834):
 - Opposite of Seebeck effect
 - Electric current flow through a junction of materials A and B can be used to heat or cool

$$Q \equiv \Pi_{AB}I = (S_B - S_A)TI$$



- Heating and cooling are reversible, depending on the direction (± sign) of the current *I*
- Ex: I = 1 mA, $\Delta S \sim 300 \ \mu V/K$ and T = 300 K gives us cooling power of 90 μW
- *Q*: how do we generate greater cooling (or heating) power?

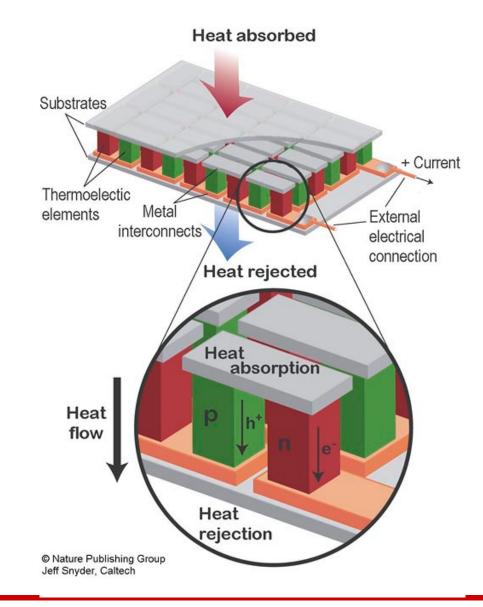




Jean Peltier

Answer (Look Ahead)

- Commercial TE modules are typically arranged in a series of alternating "n" and "p"-doped semiconductor legs
- TE legs are "electrically in series" and "thermally in parallel"



Seebeck vs. Peltier vs. Thomson Effect

- Thomson effect (1851):
 - Continuous version of Seebeck effect, no junction needed
 - Gradual change in S (∇S) due to temperature variation (∇T) inside a material creates local electric field (∇V) and local heating or cooling (Q)

$$\nabla V = T\nabla S$$



- Thomson effect directly measurable in one material
- Peltier and Seebeck more easily measurable for pairs of materials
- Seebeck, Peltier, Thomson effects are *reversible*
- Joule heating (I²R) is *not* reversible



William Thomson (Lord Kelvin)

Combining TE, Joule & Heat Flow

• Electric field:

$$\mathbf{E} = -\nabla V = \frac{\mathbf{J}}{\sigma} + S\nabla T$$

Ohm Seebeck

• Heat flux:

$$Q'' = -k\nabla T + STJ$$

• Local current density:

$$\mathbf{J} = \boldsymbol{\sigma} \left(-\nabla V - S \nabla T \right)$$

Heat diffusion equation with Seebeck effects and Joule heating

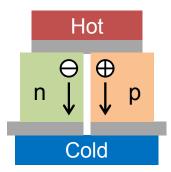
$$-Q''' = \nabla \cdot (k\nabla T) + \mathbf{J} \cdot \mathbf{E} - T\mathbf{J} \cdot \nabla S$$

Common Seebeck Coefficients

	Material	Seebeck coefficient S <i>relative to platinum</i> (µV/K)		
	Selenium	900)	acmicanductors tand to
	<u>Tellurium</u>	500		semiconductors tend to
	<u>Silicon</u>	440	7	have high $ S $, but magnitude and sign depend on doping $(S_p > 0 \text{ and } S_n < 0)$
	<u>Germanium</u>	330	J	
	<u>Antimony</u>	47		
	<u>Nichrome</u>	25	_	
Thomas Seebeck's original junction	<u>Molybdenum</u>	10	metals tend to have low S	
	Cadmium, tungsten	7.5		
	Gold, silver, copper	6.5		
	Rhodium	6.0		
	<u>Tantalum</u>	4.5		
	Lead	4.0		
	Aluminium	3.5		
	<u>Carbon</u>	3.0		
	Mercury	0.6		
	<u>Platinum</u>	0 (definition)		
	<u>Sodium</u>	-2.0		
	Potassium	-9.0		
	<u>Nickel</u>	-15		
	<u>Constantan</u>	-35		
	<u>Bismuth</u>	-72		
				source: Wikipedia

What Is the Microscopic Origin of TE?

- Seebeck = electrons (or holes*) <u>diffuse</u> in a temperature gradient, leading to ΔV
 - Diffusion from hot to cold → like hot air molecules (O₂, N₂) diffusing from space heater to farthest corners of the room
 - − Kinetic energy \rightarrow (3/2)k_BT \approx (1/2)mv² \rightarrow v = (3k_BT/m)^{1/2}
 - Hotter electrons (or holes) are faster, but they also carry charge, which sets up the voltage gradient
- Peltier = electrons (or holes*) <u>carry kinetic</u> <u>energy</u> (in addition to charge) as they move with current flow
 - Explains why we prefer materials with higher σ (electrical conductivity), i.e. metals or highly doped semiconductors



*hole = missing electron in a material = broken bond

Seebeck Coefficient (Classical & Metals)

- Seebeck coefficient can be thought of as the heat per carrier per degree K (specific heat per carrier), S ≈ C/q
- In <u>classical electron gas</u> (recall $k_B/q = 86 \mu V/K$):

$$S_{classic} \approx \frac{3}{2} \frac{k_B}{q} \approx 130 \,\mu\text{V/K}$$

 In <u>normal metals</u> only small fraction around E_F contribute, so the thermopower is very small:

$$S_{metal} \approx \left(\frac{k_B T}{E_F}\right) \frac{k_B}{q} \approx 1 \,\mu \text{V/K}$$

 In <u>semiconductors</u>, energy carriers can be "far" from E_F, so the thermopower can be large:

$$S_{semi} \approx \left| \frac{E - E_F}{qT} \right| \approx 1 \text{ mV/K}$$

Seebeck Coefficient (In General)

• Keeping track of particle motion (Boltzmann transport equation)

$$\mathbf{v} \cdot \nabla_{\mathbf{r}} f + \frac{q\mathbf{F}}{\hbar} \cdot \nabla_{\mathbf{k}} f = -\frac{f(\mathbf{r}, \mathbf{k}) - f_{eq}(\mathbf{r}, \mathbf{k})}{\tau(\mathbf{k})}$$

• Where

$$f_{\rm eq} = \frac{1}{1 + \exp{\frac{E - E_F}{k_B T}}}$$

• The electrical conductivity and Seebeck coefficient are:

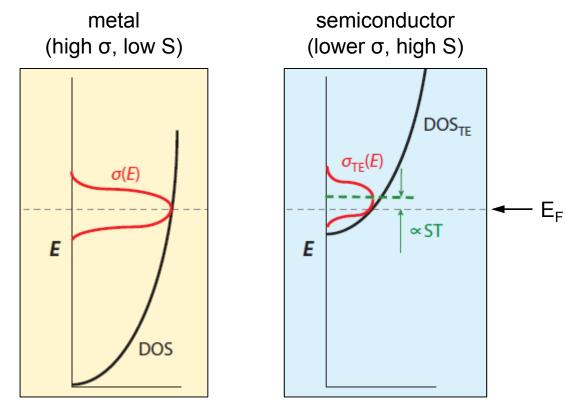
$$\sigma = \int \sigma(E) dE$$
$$S = \frac{1}{qT} \frac{\int (E - E_F) \sigma(E) dE}{\int \sigma(E) dE}$$

• Where the *differential* conductivity

$$\sigma(E) = q^{2}\tau(E)v^{2}(E)D(E)\left(-\frac{\partial f_{eq}}{\partial E}\right) \qquad \text{de} \text{states}$$

density of f states (DOS)

Picturing the Transport "Window"

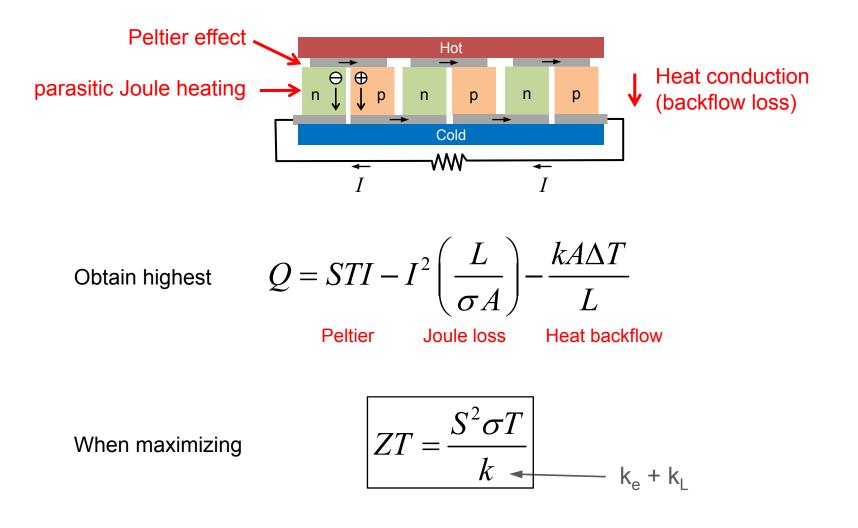


- In metals, density of states (DOS) does not vary sharply around E_F
- In doped semiconductors, E_F is at band edge where DOS varies sharply (ex: in *n*-type semiconductor, more states available for transport above than below E_F) → for high S, need asymmetric DOS near E_F

Shakouri, Annu. Rev. Mater. Res. (2011)

Thermoelectric Figure of Merit (ZT)

• How efficient are TEs?



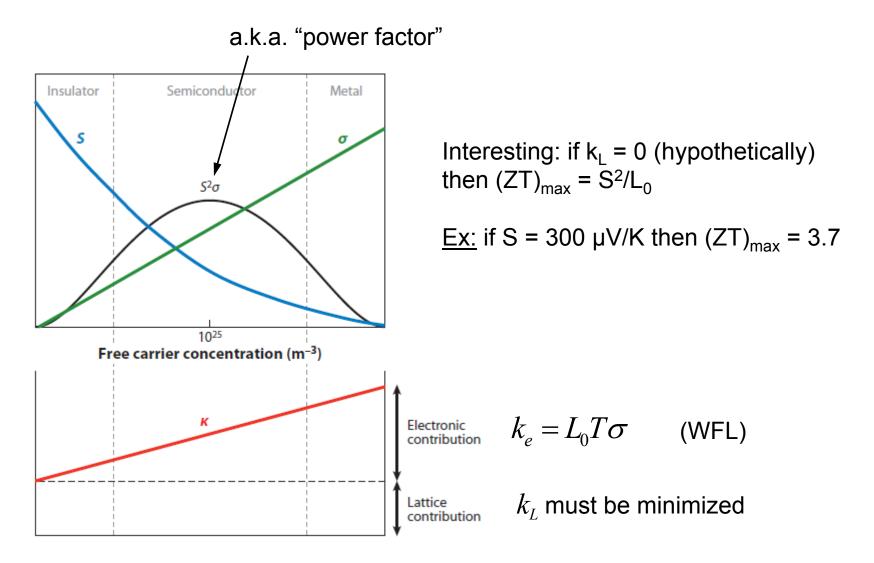
Thermoelectric Figure of Merit (ZT)

- How efficient are TEs?
- Figure of merit:

$$ZT = \frac{S^2 \sigma T}{k} - k_e + k_L$$

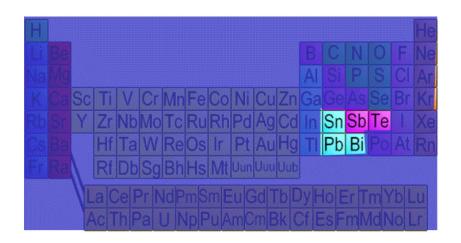
- Thus, one must simultaneously maximize S and σ (electrical conductivity) while minimizing k (thermal conductivity)
- These quantities are inter-related, such that increasing S typically leads to decreasing σ
- Also, k = k_e + k_L, thermal conductivity is sum of electron and lattice (phonon) contributions, so increasing σ leads to increasing k_e ↔ Wiedemann-Franz-Lorenz (WFL) law

Trade-Offs in Maximizing ZT

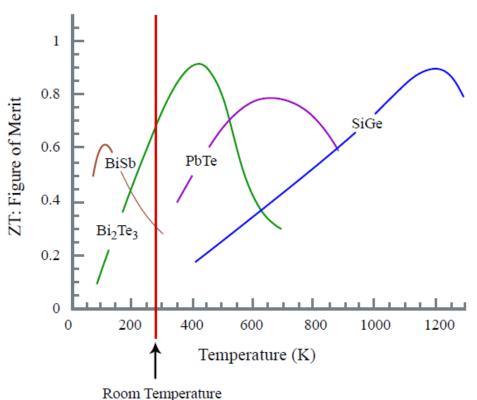


Lorenz constant $L_0 = 2.45 \times 10^{-8} W\Omega/K^2$

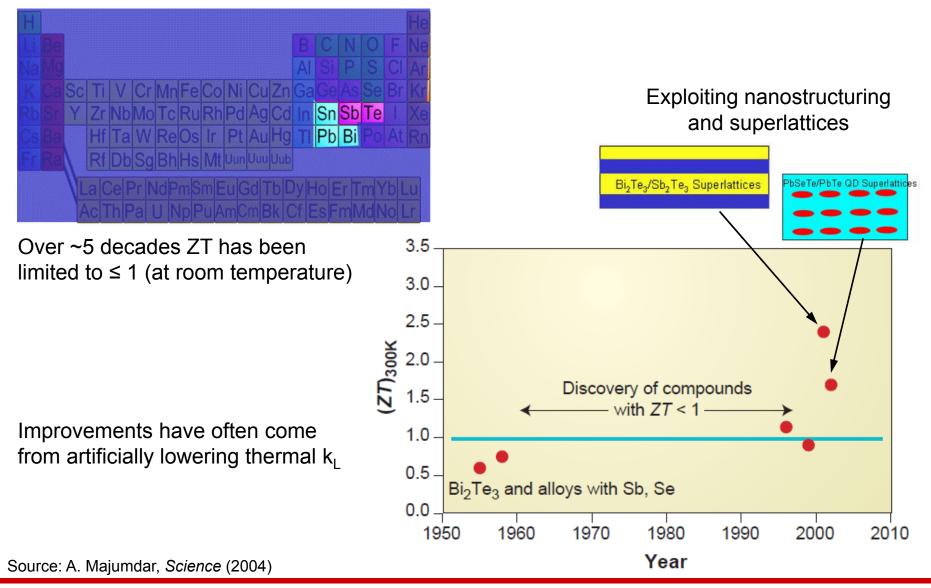
ZT for Commercial Materials



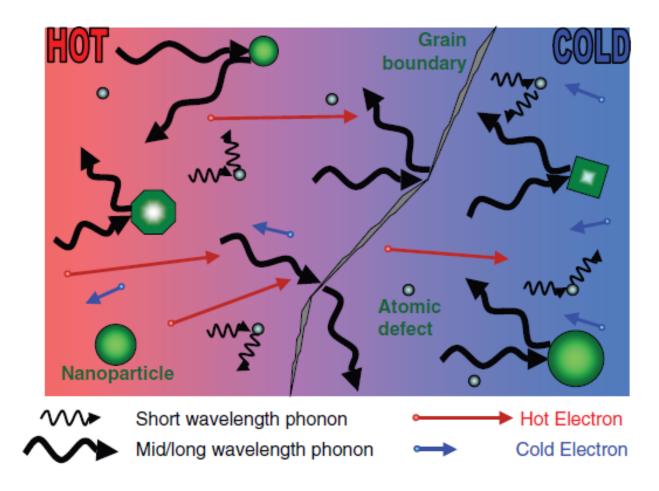
- 0.6 < ZT < 1 for commercially available materials over 300-1200 K temperature range
- Note different materials are best at different temperatures



Evolution of ZT over Time



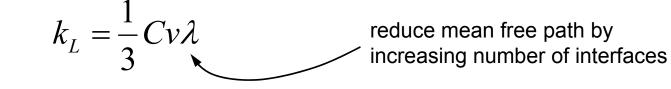
How Can We Lower Thermal K?

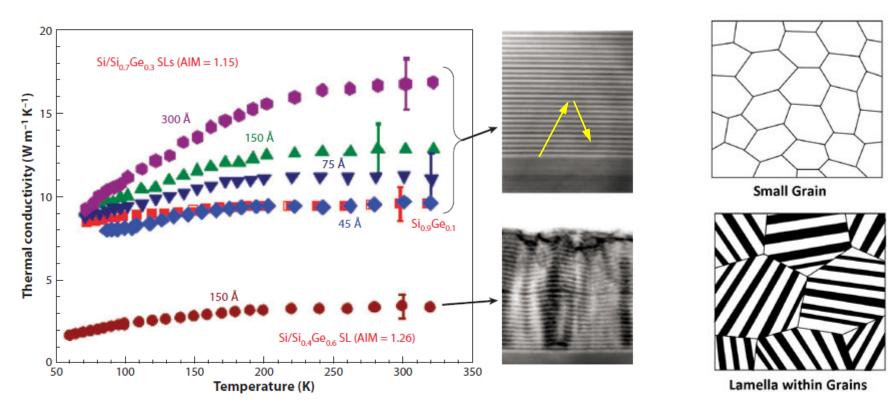


- Introduce features that scatter phonons, not electrons
- "Phonon glass, electron crystal" (G. Slack, 1960s)

Reducing Thermal Conductivity

Reduce thermal k_L using nanoscale scattering features





Reducing Thermal Conductivity

• Using edge roughness of Si nanowires

Vol 451 10 January 2008 doi:10.1038/nature06381

Enhanced thermoelectric performance of rough silicon nanowires

Allon I. Hochbaum¹*, Renkun Chen²*, Raul Diaz Delgado¹, Wenjie Liang¹, Erik C. Garnett¹, Mark Najarian³, Arun Majumdar^{2,3,4} & Peidong Yang^{1,3,4}

PRL 102, 125503 (2009) PHYSICAL REVIEW LETTERS

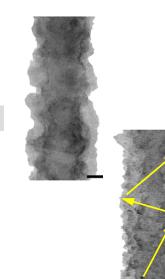
Impact of Phonon-Surface Roughness Scattering on Thermal Conductivity of Thin Si Nanowires

Pierre Martin,^{1,*} Zlatan Aksamija,¹ Eric Pop,^{1,2,†} and Umberto Ravaioli¹

¹Beckman Institute and Department of Electrical and Computer Engineering, University of Illinois, Urbana-Champaign, Urbana, Illinois 61801, USA

²Micro- and Nano-Technology Laboratory, University of Illinois, Urbana-Champaign, Urbana, Illinois 61801, USA (Received 24 November 2008; published 27 March 2009)

We present a novel approach for computing the surface roughness-limited thermal conductivity of silicon nanowires with diameter D < 100 nm. A frequency-dependent phonon scattering rate is computed from perturbation theory and related to a description of the surface through the root-mean-square roughness height Δ and autocovariance length L. Using a full phonon dispersion relation, we find a quadratic dependence of thermal conductivity on diameter and roughness as $(D/\Delta)^2$. Computed results show excellent agreement with experimental data for a wide diameter and temperature range (25–350 K),



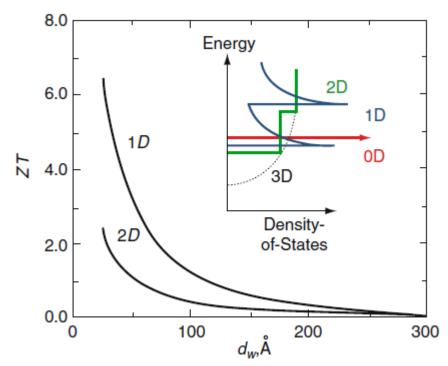
week ending

27 MARCH 2009

nature

Effects of Nanostructuring on TEs

- Hicks and Dresselhaus (1993)* pioneered concept of quantum confinement effects for TEs
- Sharp features in the 1D and 2D density of states (DOS) lead to asymmetric $\sigma(E)$ and should increase S
- Challenge: sharp DOS features become "blurred" if there is size non-uniformity in the system
- Most recent breakthroughs benefitted from reduction in k_L



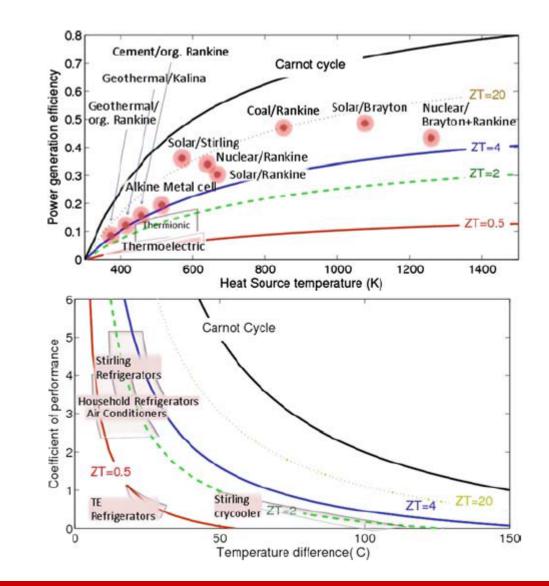
*http://dx.doi.org/10.1103/PhysRevB.47.12727

How High ZT?

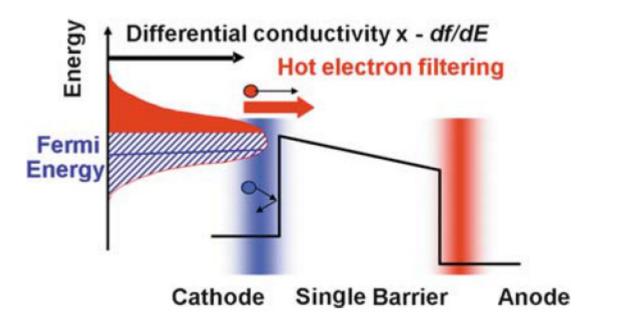
• TE efficiency

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

- Cooling comparison: modern (mechanical) refrigerator efficiency equivalent to ZT ~ 3
- Power generation comparison: steam power plants are ~40% efficient



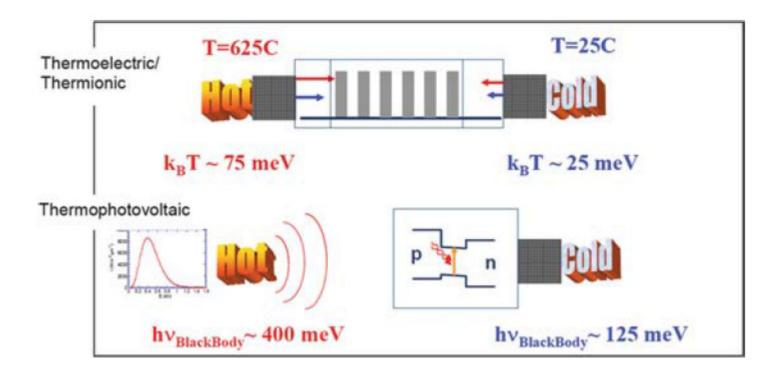
<u>Alternative:</u> Thermionic (TI) Energy Conversion



- Design tunnel barrier that blocks (filters out) the cold electron distribution, to obtain maximum energy transmission
- Nanoscale vacuum gap is best electron (tunneling) conductor and worst thermal (phonon) conductor
- Challenges in controlling uniform tunnel gaps and efficiency only at higher temperatures

source: Shakouri (2010)

Alternative: Thermophotovoltaics (TPV)



- Filter peak emission of thermal radiation from hot source
- Transmitted photons converted to electron-hole pairs in pn junction
 - TPV avoids some losses of conventional PV and heat backflow problem of TE
 - However, must avoid non-radiative recombination in pn junction

Questions?

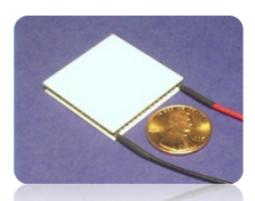


1) Fundamentals

2) Applications

3) Final Remarks

Thermoelectric Applications





Electric Cooling



Power Generation

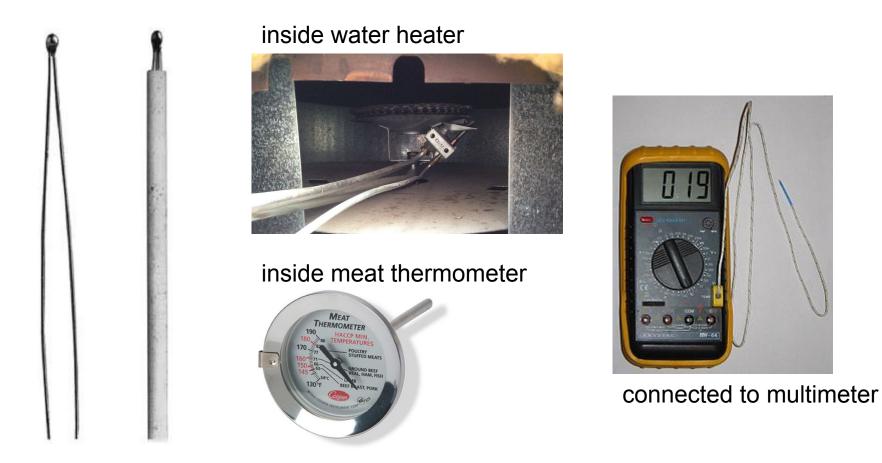








Thermocouples



 Junction of two dissimilar materials, used to measure temperature (based on Seebeck's original experiment)

Recap: Thermoelectric Modules

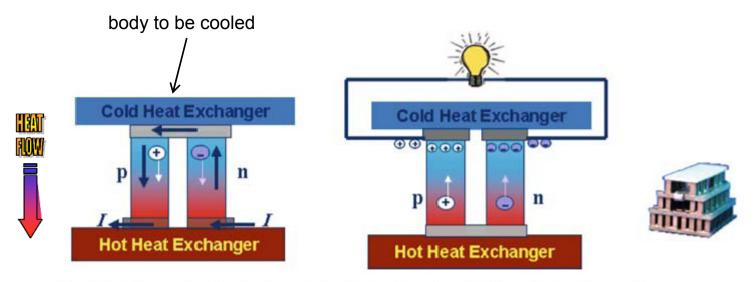


Fig. 9.1 Thermoelectric devices. *Left*: Cooler based on Peltier effect. *Center*: Power generator based on Seebeck effect. *Right*: An actual module

- Use electrons and holes to carry heat and cool a body (e.g. cup holder)
 - Must have good electron and hole conductivity (high σ , S)
 - Must block heat "backflow" through (low k)
- Use temperature gradient (e.g. hot engine to ambient) to generate power
- No moving parts (=quiet and reliable), no freon (=clean)

More Historical Perspective

- During and after world wars TE research grew, for both cooling and power generation for military and civilian uses
- Some advances could not be shared or were slow (US vs. USSR)
- 1950s: cooling from ambient to 0 °C demonstrated (with Bi₂Te₃)
- Energy harvesting from oil lamp or camp fire to power radios



Kerosene Radio Made in Moscow for use in rural areas, this all-wave radio is reportedly powered by the kerosene lamp hanging above it. A group of thermocouples is heated internally to 570 degrees by the flame. Fins cool the outside to about 90 degrees. The temperature differential generates enough current to operate the low-drain receiver. Regular listeners may want fur-lined union suits, though: It works best in a room with open windows.

More Historical Perspective

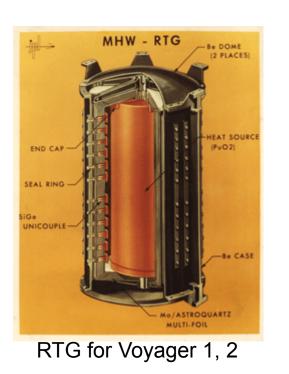
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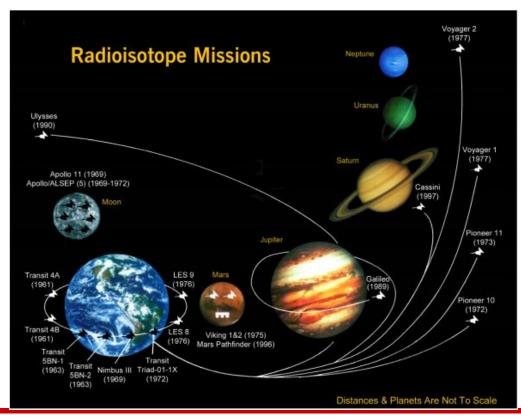


today: the BioLite camp stove phone charger (\$130 at REI.com)

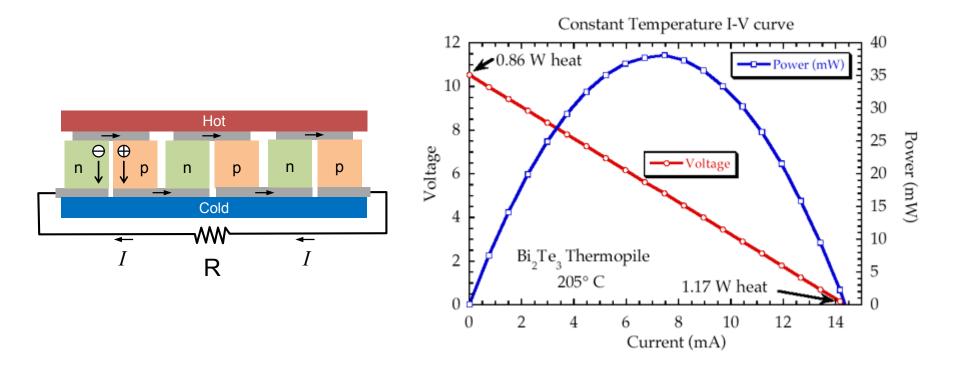
Radioisotope Thermoelectric Generators (RTGs)

- For remote applications (e.g. lighthouses) and space exploration, electrical power provided by RTG
- RTG converts heat from decaying Pu-238 into electricity
 - Half-life of 90 years and 1 g sufficient for ~0.5 W power
- NASA used RTGs to power Apollo, Voyager, Viking, Curiosity...



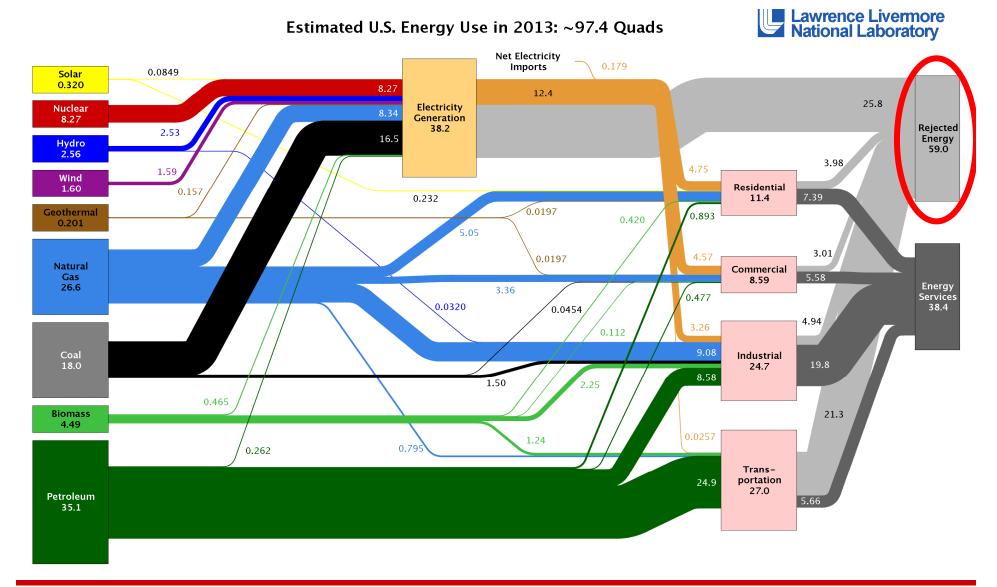


Current-Voltage-Power Curve of a TEG



- In practice, the internal resistance of TEG and the external load resistance both matter
- Open circuit \rightarrow max voltage, but no power produced
- High current \rightarrow voltage is lost on the internal TEG resistance

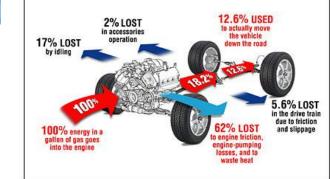
National Energy Perspective



Energy Harvesting from Waste Heat

- Almost everything we do wastes heat
 - Power generation
 - Transportation (engine + friction)
 - Computing
- 15 TW (60%) wasted as heat in the world*
- Most is "low-grade" *T* ≤ 200 °C
- Recovering even a few percent would be HUGE, equivalent of several power plants (GW)





thermoelectrics could be a solution

*Dept. of Energy (2012). By comparison, ALL data center power consumption world-wide is ~30 GW!

Recap: TEs for Refrigeration

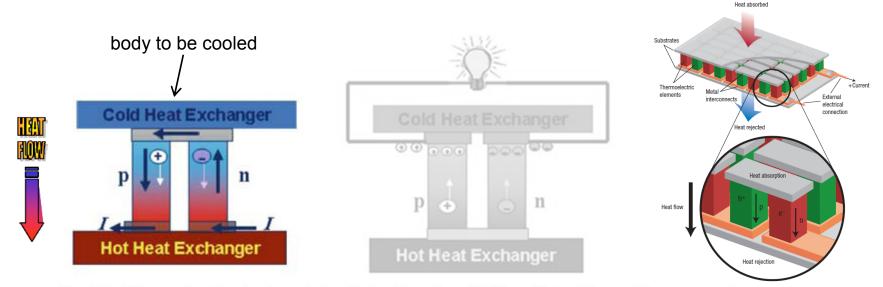


Fig. 9.1 Thermoelectric devices. *Left*: Cooler based on Peltier effect. *Center*: Power generator based on Seebeck effect. *Right*: An actual module (sources: A. Shakouri, G. Snyder)

• Use junction (ΔS) and current to electrically heat or cool

- Peltier effect:
$$Q_{heat,cool} = \pm I \Delta ST$$

- Used in small refrigerators, cooled car seats, cup holders
- No moving parts (=quiet and reliable), no freon (=clean)



Recap: TEs for Power Generation

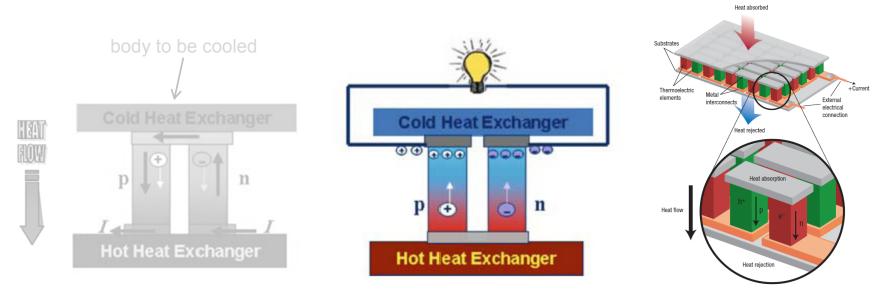


Fig. 9.1 Thermoelectric devices. *Left*: Cooler based on Peltier effect. *Center*: Power generator based on Seebeck effect. *Right*: An actual module (sources: A. Shakouri, G. Snyder)

- Use temperature gradient (ΔT) to generate power
 - Seebeck effect: $\Delta V \equiv S \Delta T$
- Used in car engines & exhaust, Mars rover (~100 W)
- No moving parts (=quiet and reliable), no freon (=clean)

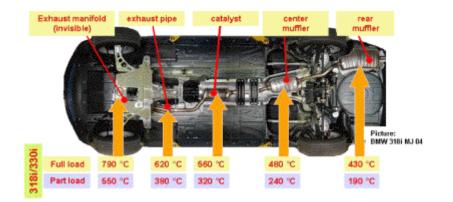




Ex: Automobile Waste Heat Recovery

- About 75% of energy from combustion lost as heat in exhaust or coolant
- Catalytic converters reach 300-500 C and TEGs can be used to harvest 100s of W
- Small fraction power recovery (consider 1 HP ≈ 750 W) but sufficient to power radio or AC and lessen alternator load





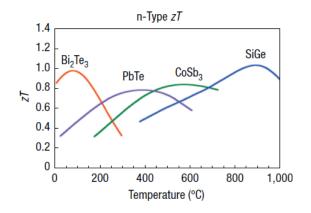
An Important Perspective

- "Thermoelectric energy conversion will never be as efficient as steam engines. That means thermoelectrics will remain limited to applications served poorly or not at all by existing technology" (Vining, 2009*)
- However:
 - TEs could play a big role in waste heat recovery
 - Cooling in small size applications (e.g. lasers, seats, cup holders)
 - What matters is not just efficiency (ZT), but cost per Watt
 - Many groups are looking at polymer TEs even though efficiency is lower than traditional semiconductors, paralleling work in solar cell community
 - Power generation in communities without power plants and electric grid
 - *TE modules in cooking stoves and solar thermal systems*

*Vining, "An Inconvenient Truth About TEs" (2009)

New Materials for Thermal Energy Harvesting

• Traditional thermoelectrics: Bi, Te, Pb \rightarrow rare, <u>expensive</u>, toxic, brittle

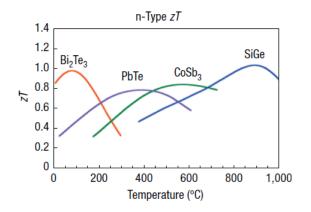


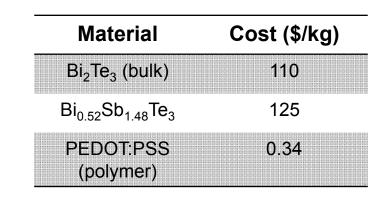
Material	Cost (\$/kg)
Bi ₂ Te ₃ (bulk)	110
$\mathrm{Bi}_{0.52}\mathrm{Sb}_{1.48}\mathrm{Te}_3$	125
PEDOT:PSS (polymer)	0.34

G. Snyder, Nature Mat. (2008); S. Yee et al. (2013)

New Materials for Thermal Energy Harvesting

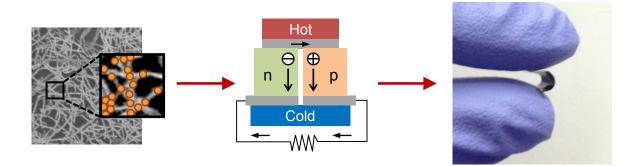
• Traditional thermoelectrics: Bi, Te, Pb \rightarrow rare, <u>expensive</u>, toxic, brittle







- Start with **low-cost polymers*** that already have low k, high σ
- Use nanostructuring (nanotubes, nanowires) to increase S

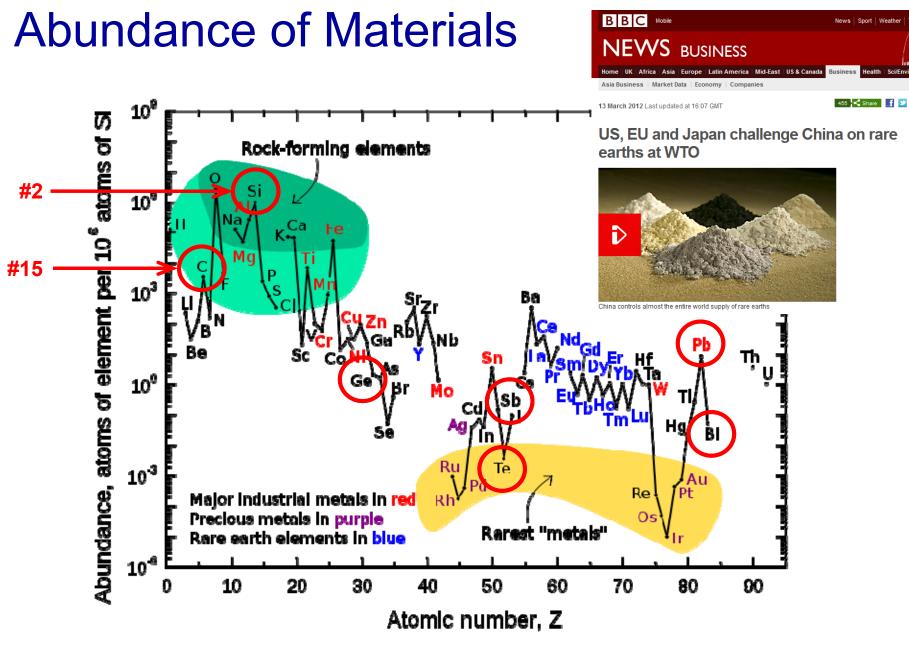


Bonus:

- mechanically flexible
- solution processable

G. Snyder, Nature Mat. (2008); S. Yee et al. (2013)

*Berkeley and LBNL (J. Urban and R. Segalman)

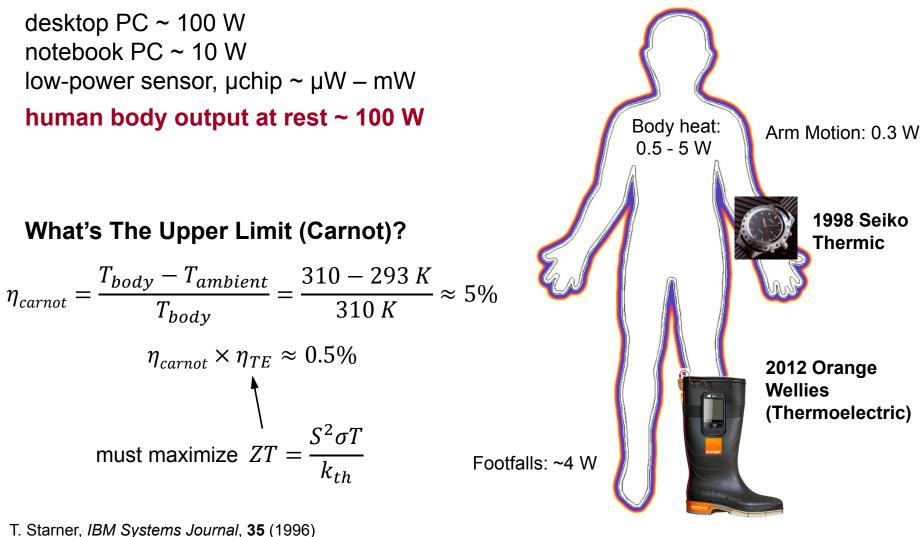


source: http://pubs.usgs.gov/fs/2002/fs087-02

Energy Harvesting From the Human Body

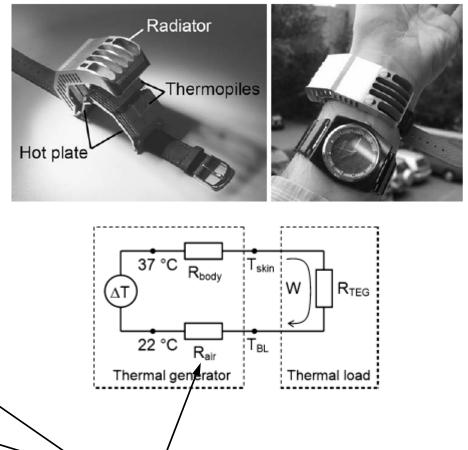
Usable Power From The Body:

Power Consumption



Optimizing Human Energy Harvesting

- Body heat powered watches, boots already demonstrated
- Maximum power harvested is ~180 µW/cm² between skin (34 °C) and air (22 °C)
- However, full ∆T = 12 °C is not dropped across TEG
- Key is maximizing internal TEG thermal resistance (R_{TEG}) and minimizing TEG-air thermal resistance (R_{air})



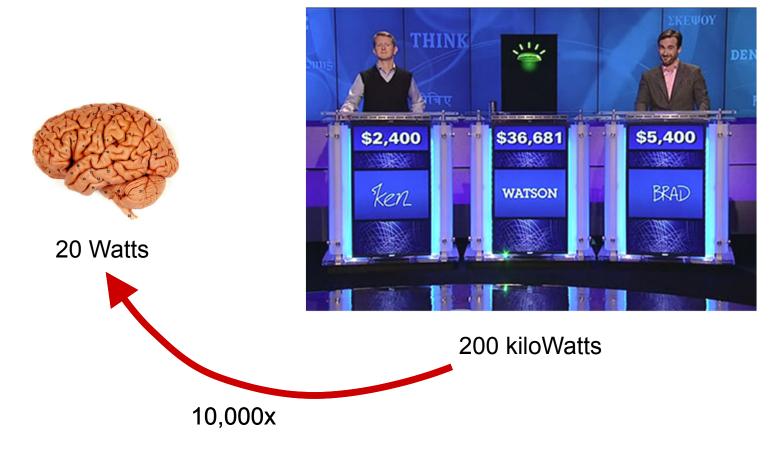
parasitics!

source: V. Leonov (2009)

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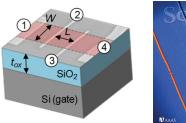
What Motivates Our Research Group



(IBM Watson, *Jeopardy!* champion)

(conventional Moore's Law size scaling can get us ~10x)

Our Work: Two Sides of the Same Coin

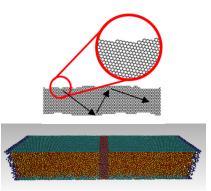




Lower power at its source

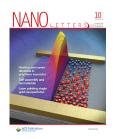
(devices, sensors, circuits)

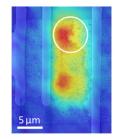




Harvest and manage heat

(energy, thermoelectrics)



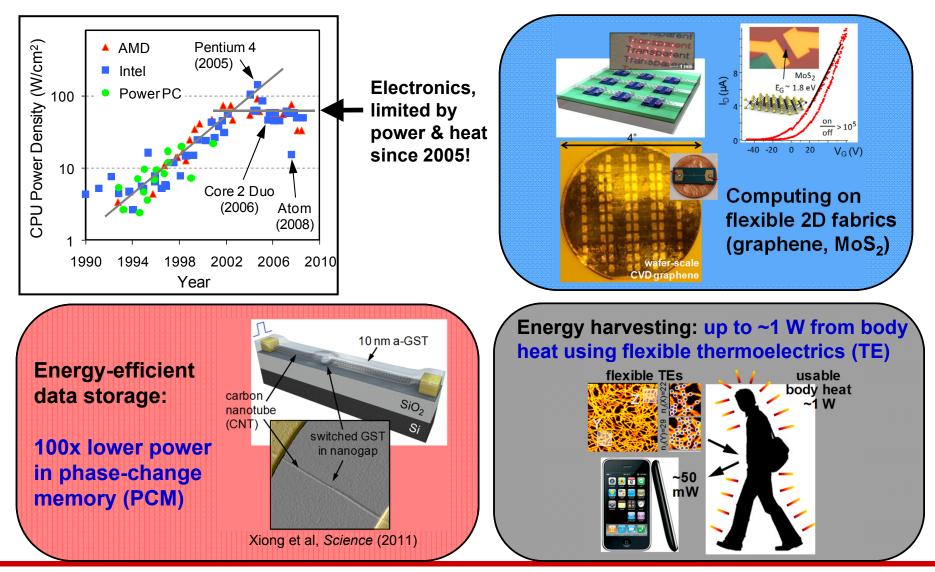


fundamental understanding practical applications

Pop Lab: Energy and Electronics

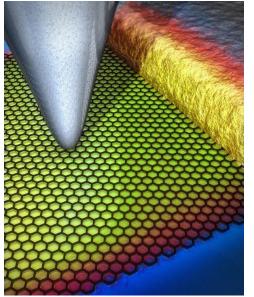
http://poplab.stanford.edu

review: E. Pop, *Nano Research* 3, 147 (2010) new course: EE 323 "Energy in Electronics" in Autumn 2014

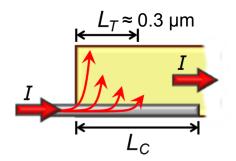


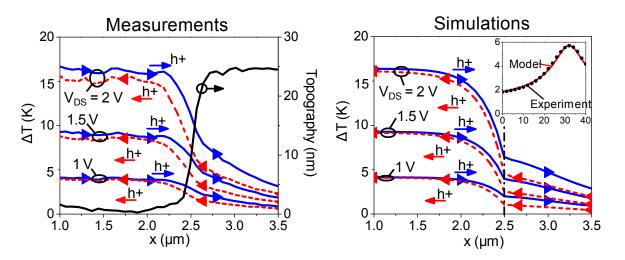
Thermoelectric Effects at Nanoscale Contacts

K. Grosse, M.-H. Bae, F. Lian, E. Pop, W. King, Nature Nano 6, 287 (2011)



scanning Joule expansion microscopy (SJEM)



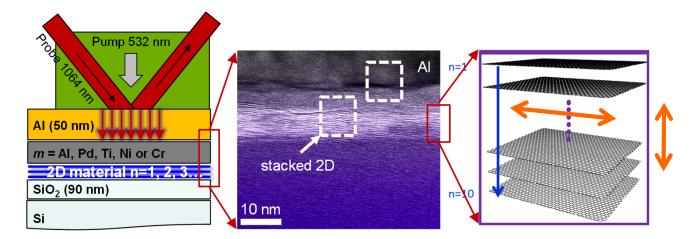


- AFM-based thermometry (SJEM)
- Contact temperature due to:
 - Current crowding (CC)
 - Thermoelectric effect (TE) $\}$ 1/3
- Some 2D materials have large thermopower S
 - Engineer cooling at device contacts?
 - Design built-in TE coolers?

2/3

Looking Ahead: Unusual 2D Materials

- Large in-plane thermal conductivity of graphene (>1000 W/m/K)
- Ultra-low cross-plane thermal conductivity of layered WSe₂ (<0.1 W/m/K)
 - Lower than plastics and comparable to air*
- Huge thermal anisotropy in all layered 2D materials (>10-100x)**



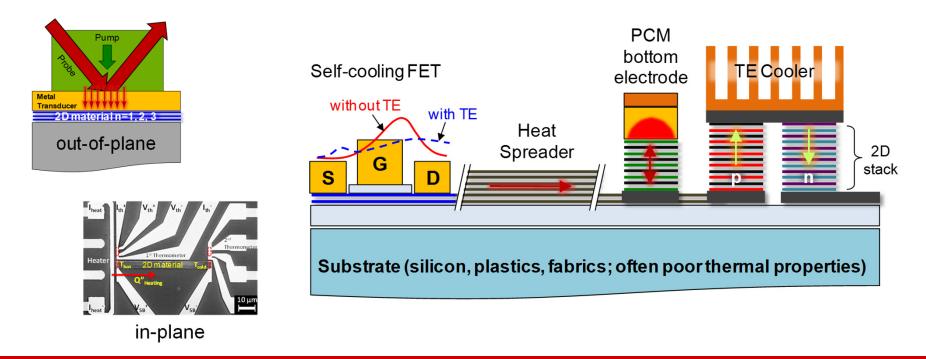
- Large thermopower in some 2D materials (~0.5 mV/K)
- Favorable properties for thermoelectrics

*C. Chiritescu et al., *Science* (2007) **E. Pop, V. Varshney, A. Roy, *MRS Bulletin* (2012) **D. Estrada, Z. Li, F. Lian, [...], F. Pop. *in preparation* (2014)

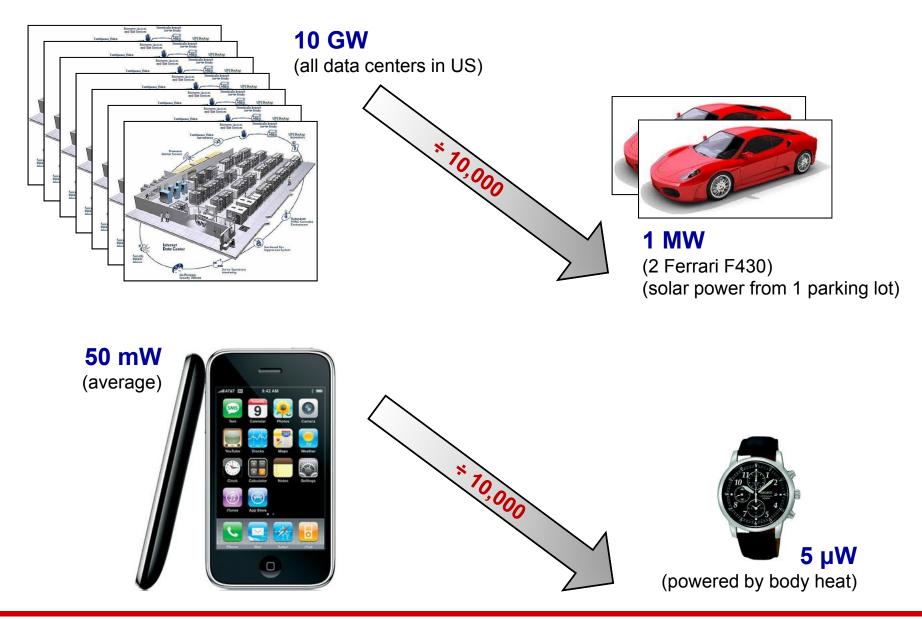
Looking Ahead: Future Opportunities

Could we:

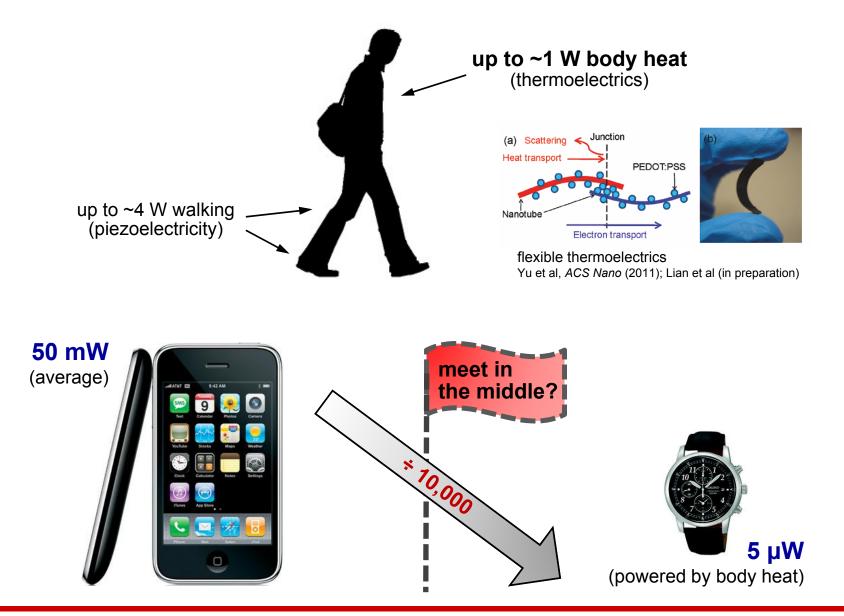
- Exploit **anisotropy** for low-power electronics? (e.g. phase-change memory)
- Separate thermal and electrical flow? (thermal transistor)
- Design electronics with built-in thermoelectric cooling?
- Achieve transparent heat spreaders and flexible thermoelectrics?



What Is 10,000x Electrical Power Reduction?



Low Power Devices + Energy Harvesting



Summary

lower power

energy harvesting

- Moore's Law ~10x → slowing down
- Energy scaling & harvesting $\sim 10^4 x$ \rightarrow exciting
- Opportunity for convergence of:
 - Low power electronics
 - Energy harvesting
 - Novel nanomaterials
 - Towards fundamental limits of energy use (up to 10,000x improvements may be possible)

MUCH room for optimization of energy dissipation, use, and harvesting from the "atomic" level

Key References

- <u>http://www.thermoelectrics.caltech.edu</u> (web tutorial)
- <u>http://core.kmi.open.ac.uk/download/pdf/11784960.pdf</u> (historical)
- <u>http://www.crcnetbase.com/isbn/978-0-8493-0146-9</u> (CRC Handbook of TEs)
- <u>http://dx.doi.org/10.1002/adma.201000839</u> (nanostructured TEs)
- <u>http://dx.doi.org/10.1146/annurev-matsci-062910-100445</u> (recent developments)
- <u>http://dx.doi.org/10.1038/nmat2361</u> (inconvenient truth)
- <u>http://dx.doi.org/10.1039/C3EE41504J</u> (\$/W metrics)
- <u>http://dx.doi.org/10.1016/j.rser.2013.12.030</u> (material and manufacturing costs)
- <u>http://dx.doi.org/10.1063/1.4803172</u> (nanoscale Peltier in data storage)
- <u>http://dx.doi.org/10.1007/s11664-008-0638-6</u> (wearable TEGs)