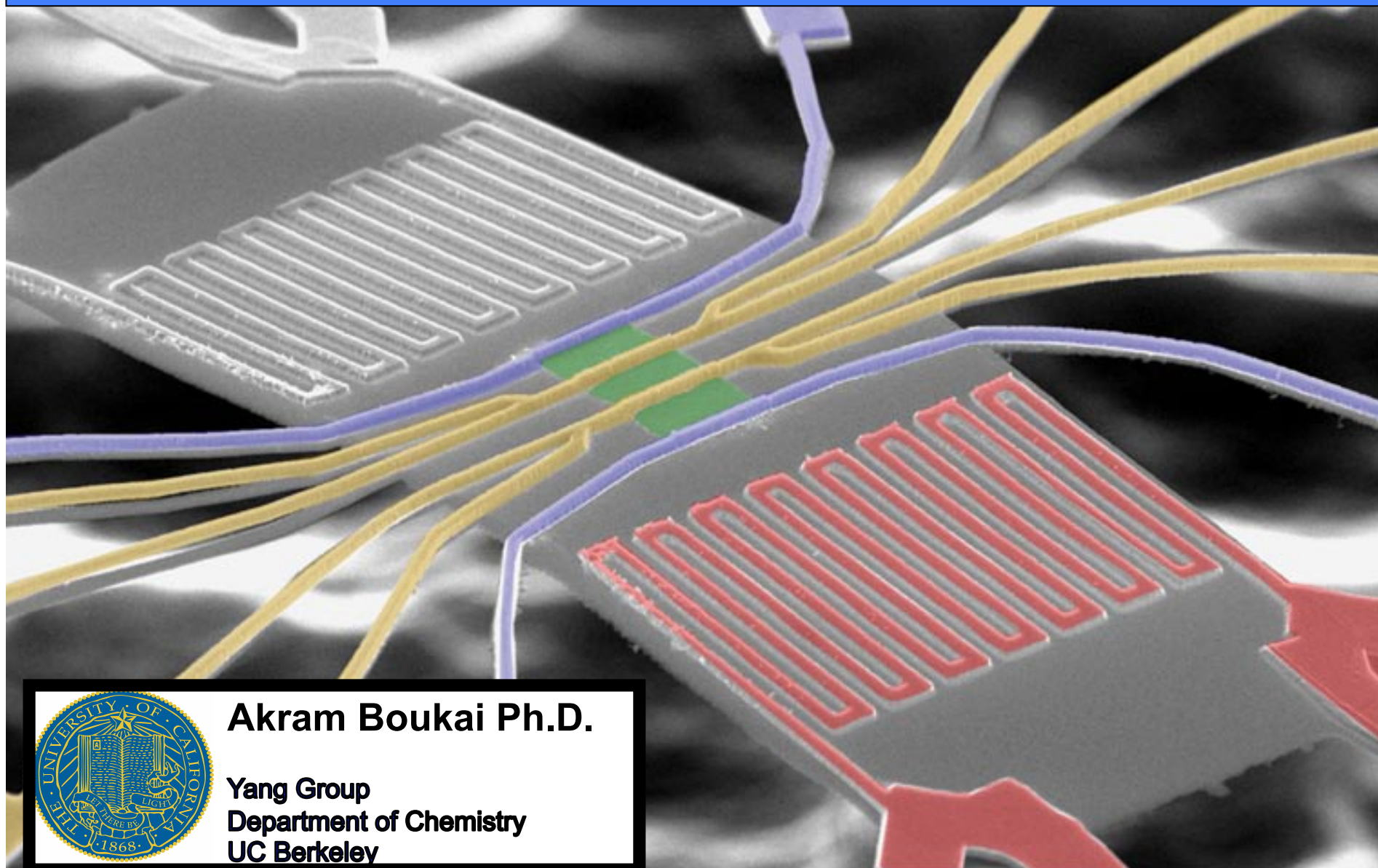


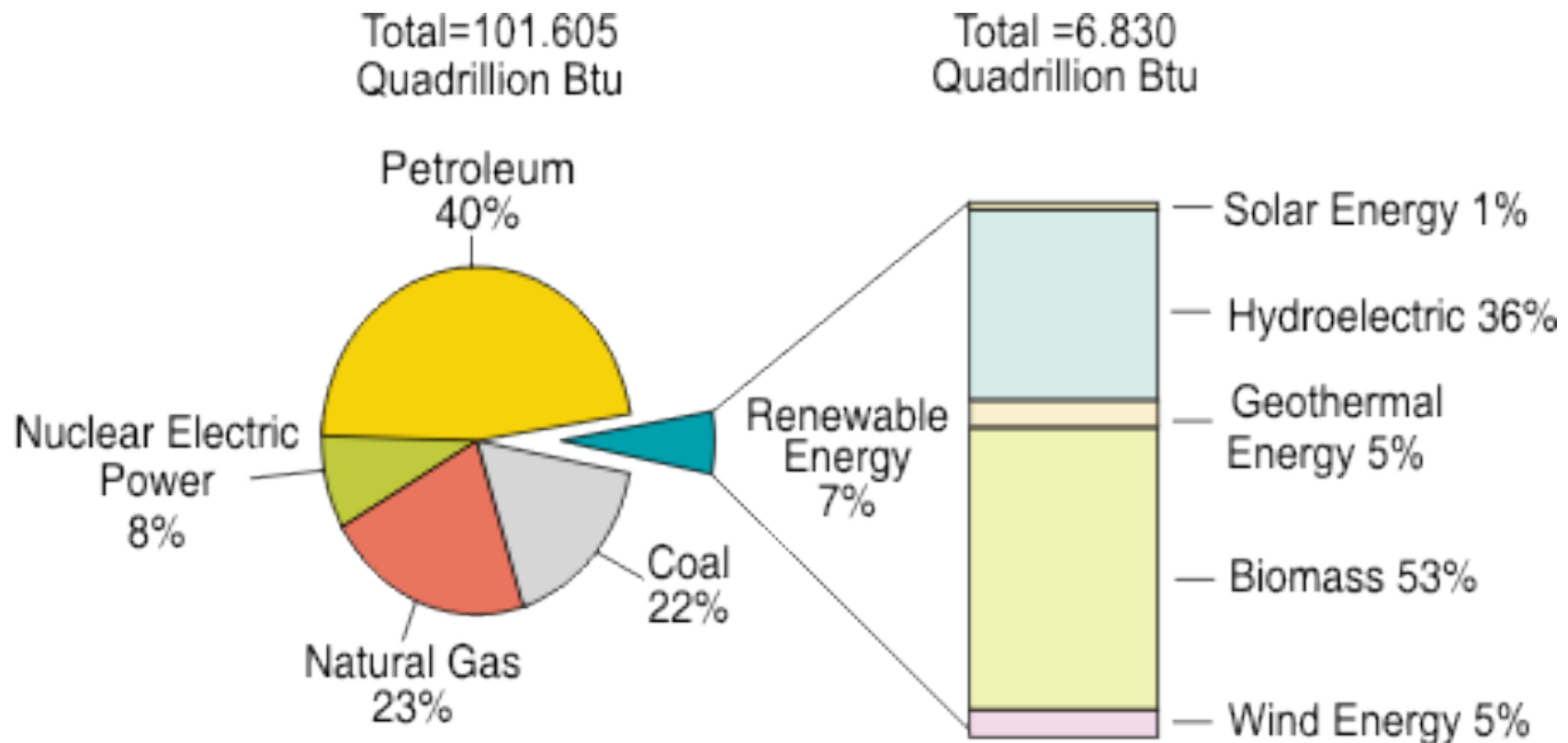
Clean Energy: Thermoelectrics and Photovoltaics



Akram Boukai Ph.D.

Yang Group
Department of Chemistry
UC Berkeley

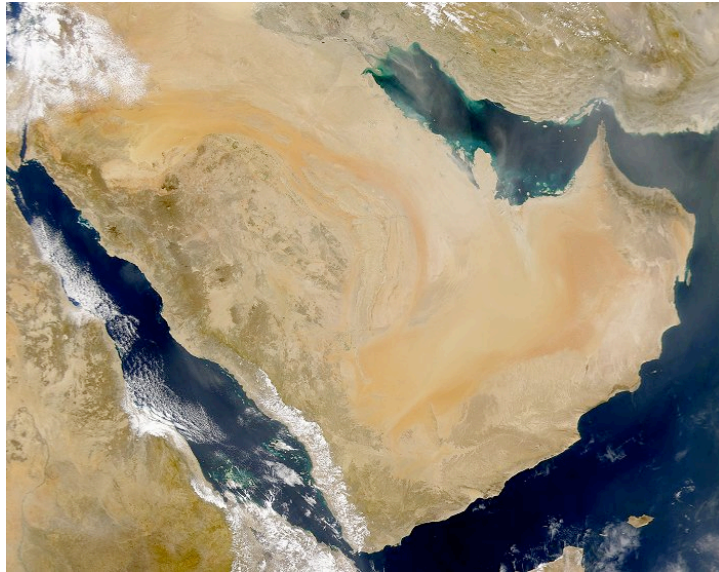
Solar Energy Use



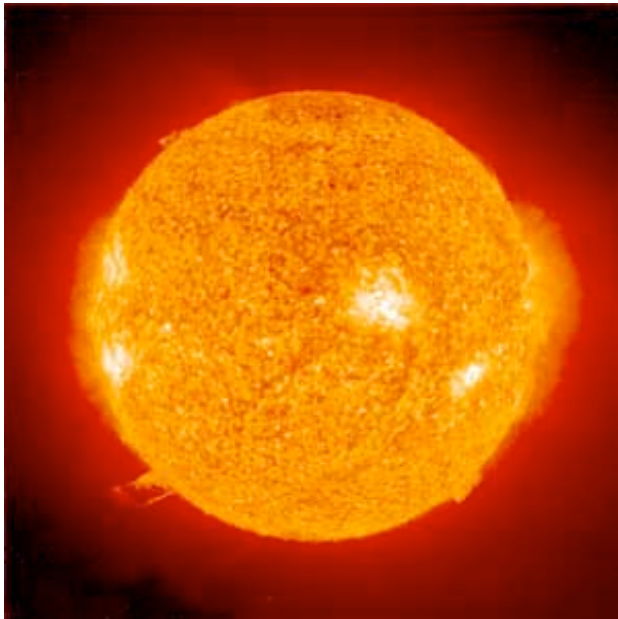
Note: Sum of components may not equal 100 percent due to independent rounding.

Source: EIA, *Renewable Energy Consumption and Electricity Preliminary 2007 Statistics*, Table 1: U.S. Energy Consumption by Energy Source, 2003-2007 (May 2008).

Hydrocarbons vs. Photons

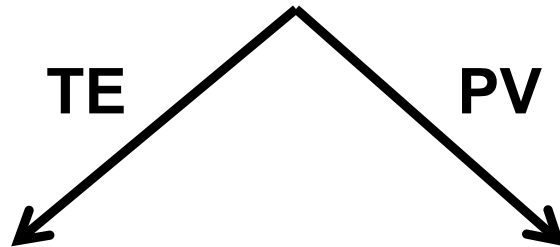
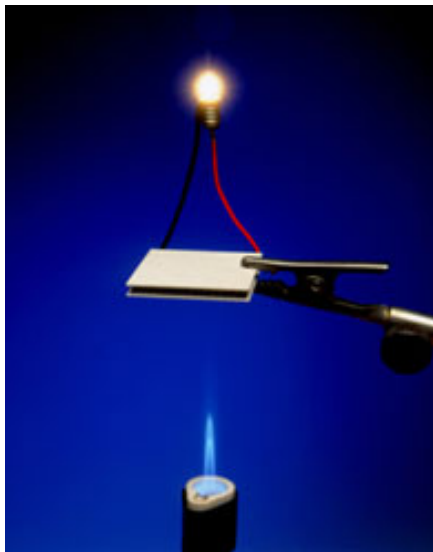
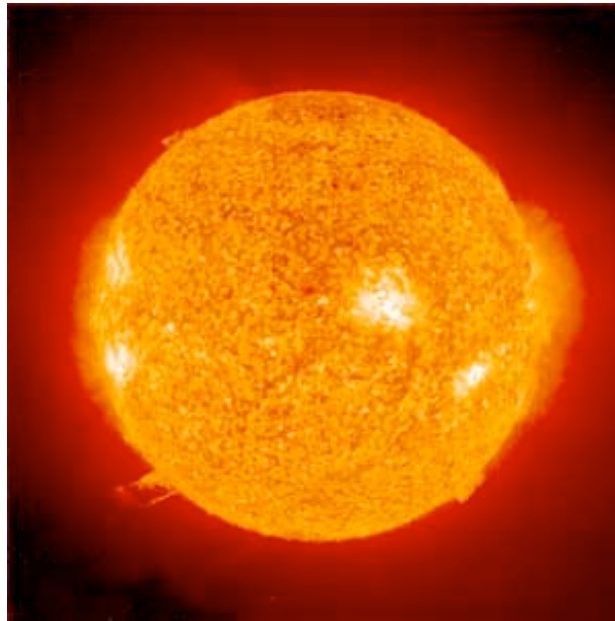


Arabian Oil: 600 years



Sun: 1.5 billion years

The Sun can Power both Solar Cells and Thermoelectrics

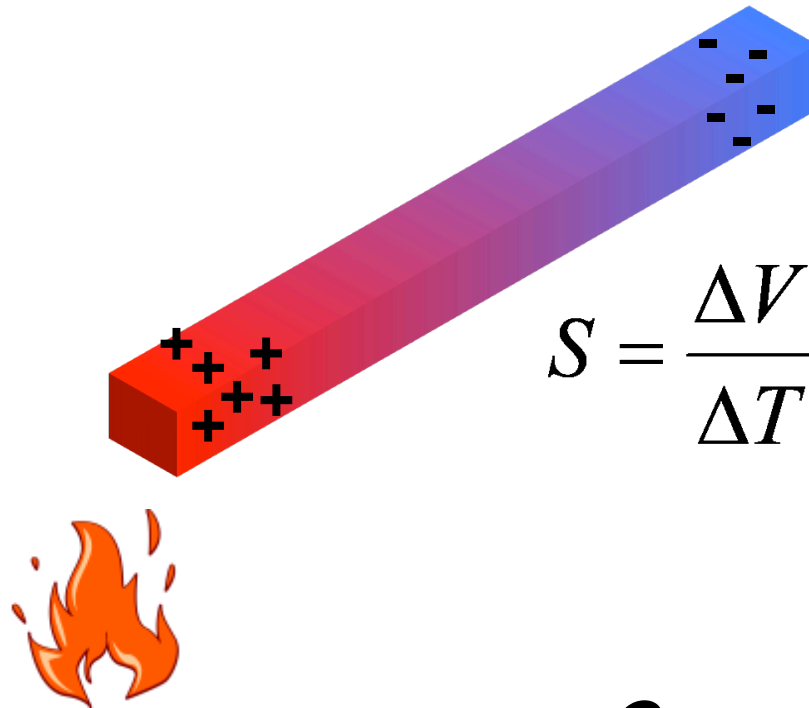


Voyager Powered by Thermoelectrics



Thermoelectrics 101

Seebeck Effect



$$S = \frac{\Delta V}{\Delta T}$$

$$\oint E \cdot dx = 0$$

L. Onsager, Physical Review 37, 405 (1931)

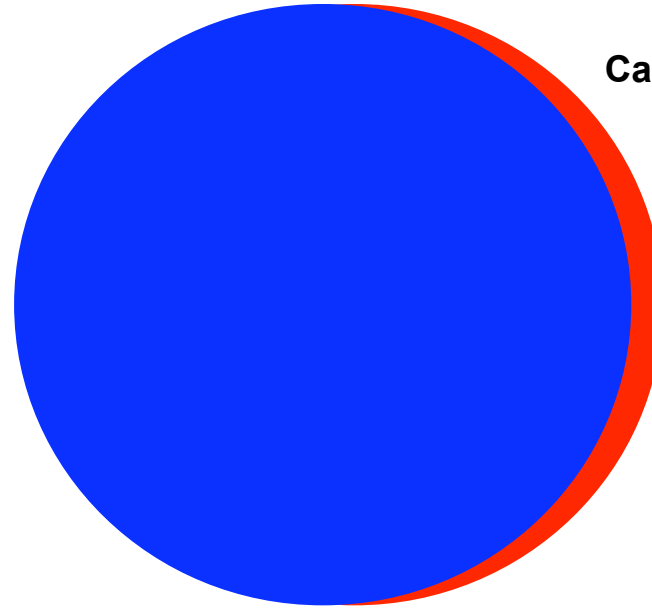
Thermoelectrics 101

FOR A METAL

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

$\sim 1 \mu\text{V/K}$

At 300K for
a typical metal



Carriers within kT are excited

FOR A SEMICONDUCTOR

$$S = \frac{Q}{eT} = \frac{k}{e}$$

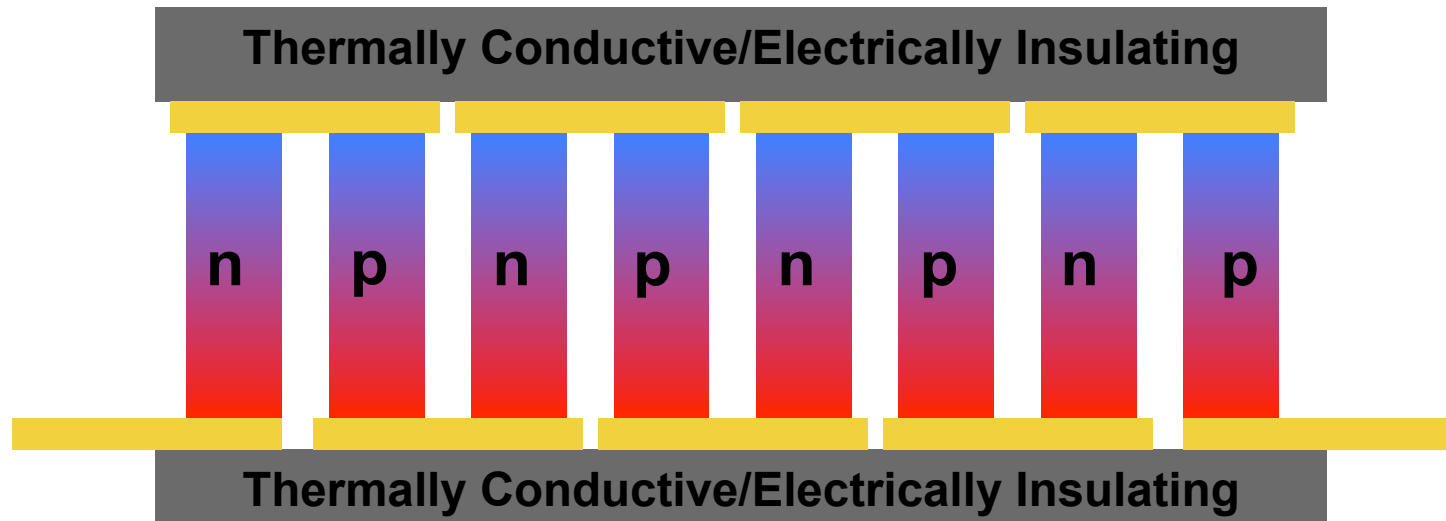


A semiconductor is like a classical gas

$\sim 100 \mu\text{V/K}$

Off the Shelf Thermoelectrics

COLD

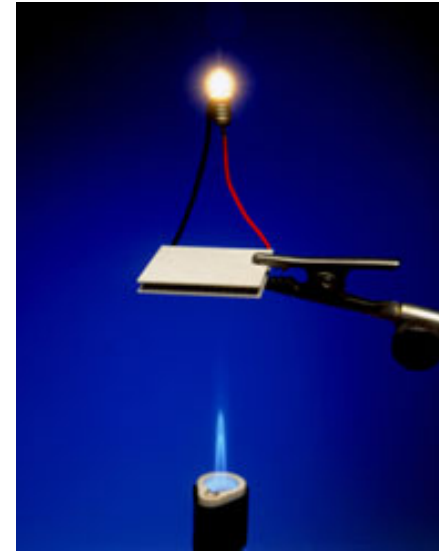
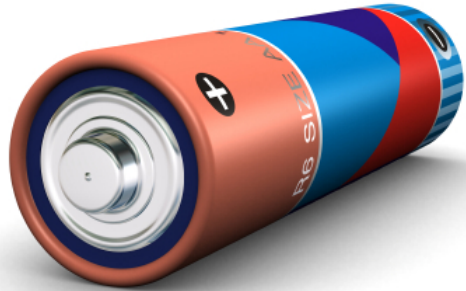


HOT

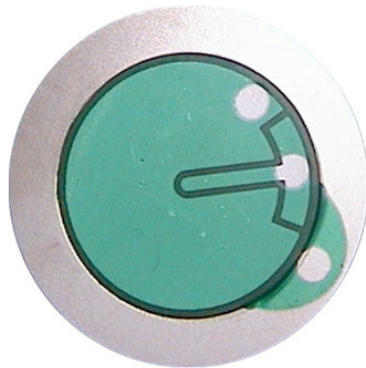
$$V_{oc} = N(S\Delta T)$$

DC and AC Power-Generating Systems

DC Power



AC Power



What Governs Particle Flow?

$$dU = TdS + pdV + \mu dN + \phi de$$

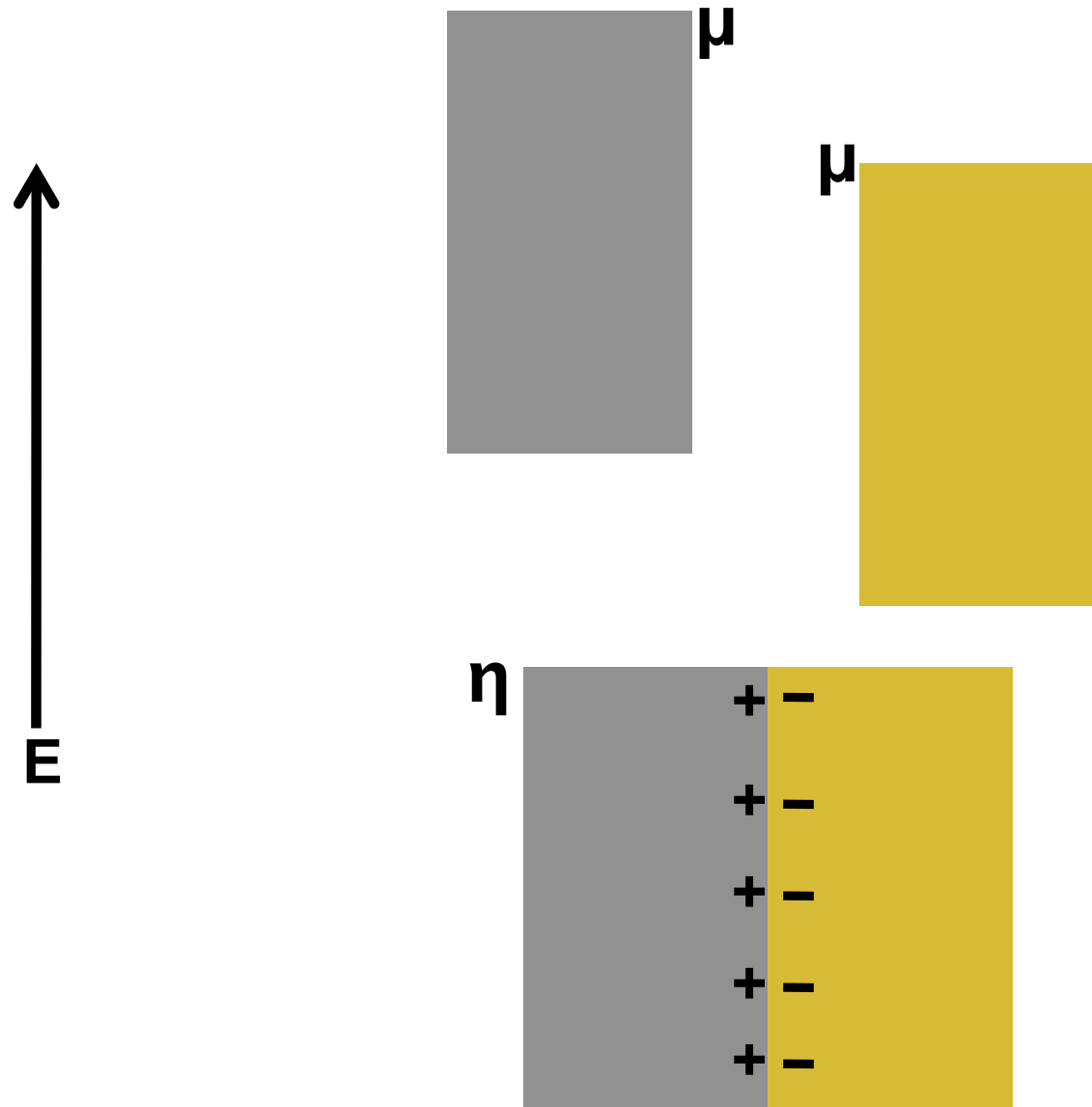
$$\eta = \mu + e\phi$$

Particles move from high electrochemical potential to low electrochemical potential

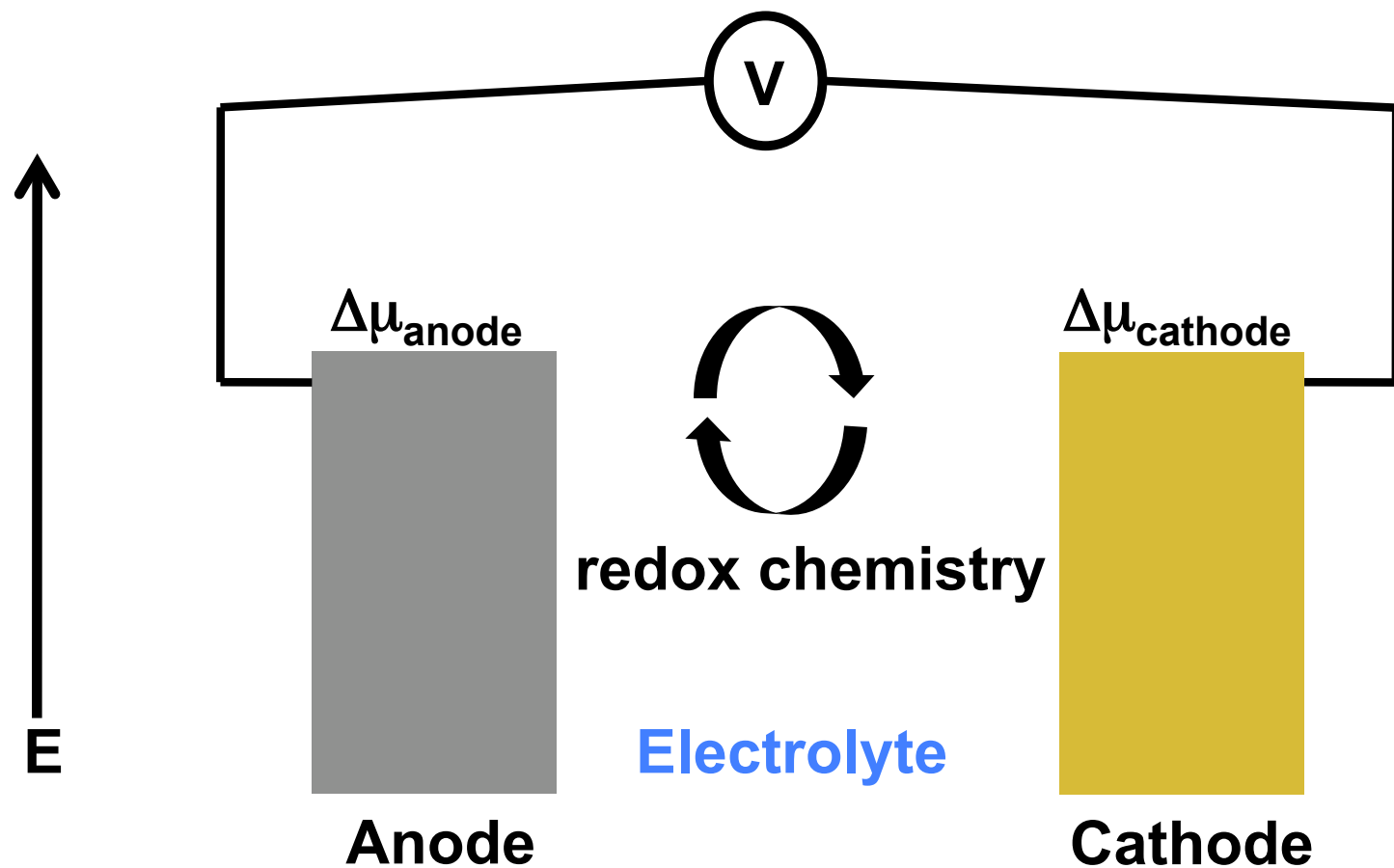
Requirements for Electric Power

- 1. An Electrochemical Potential Difference Must be Present**
- 2. A Selective Barrier Must be Present**

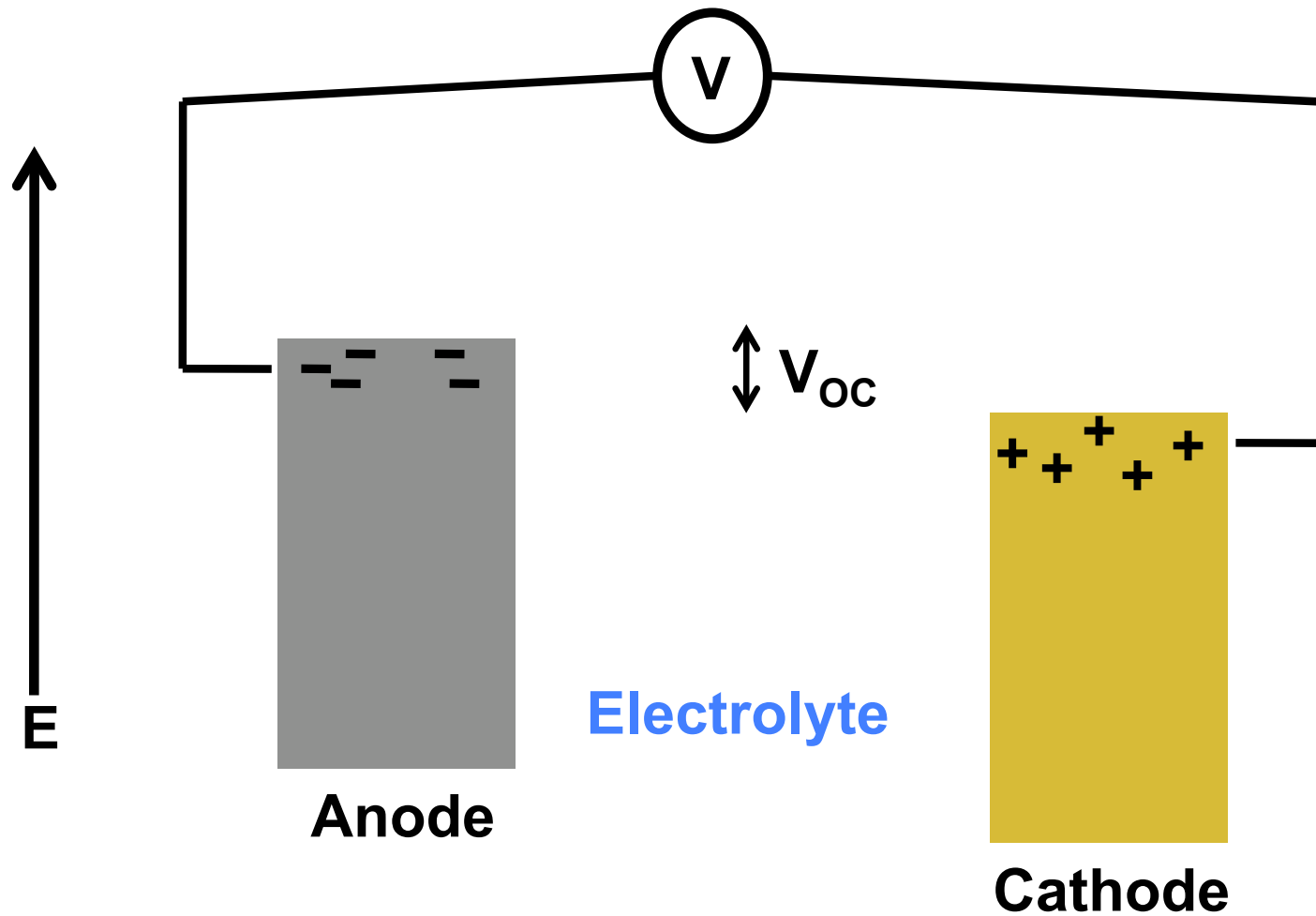
The Contact Potential



Batteries



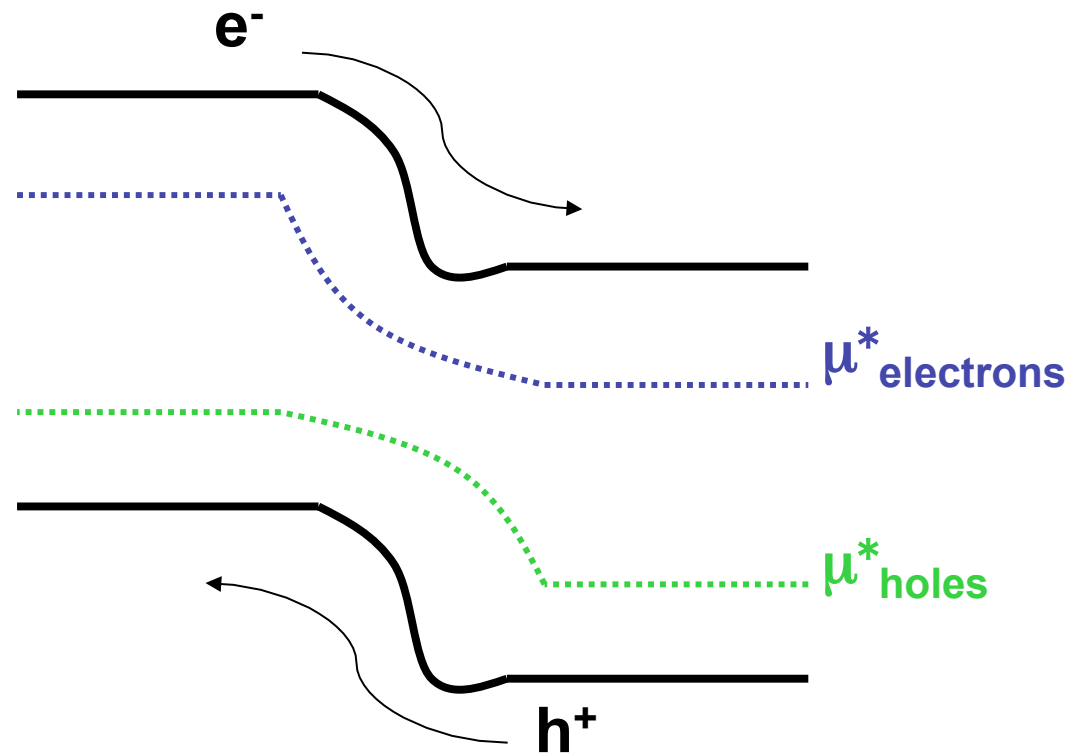
Batteries Continued



$$V_{OC} = \Delta\mu_{\text{anode}} + \Delta\mu_{\text{cathode}}$$

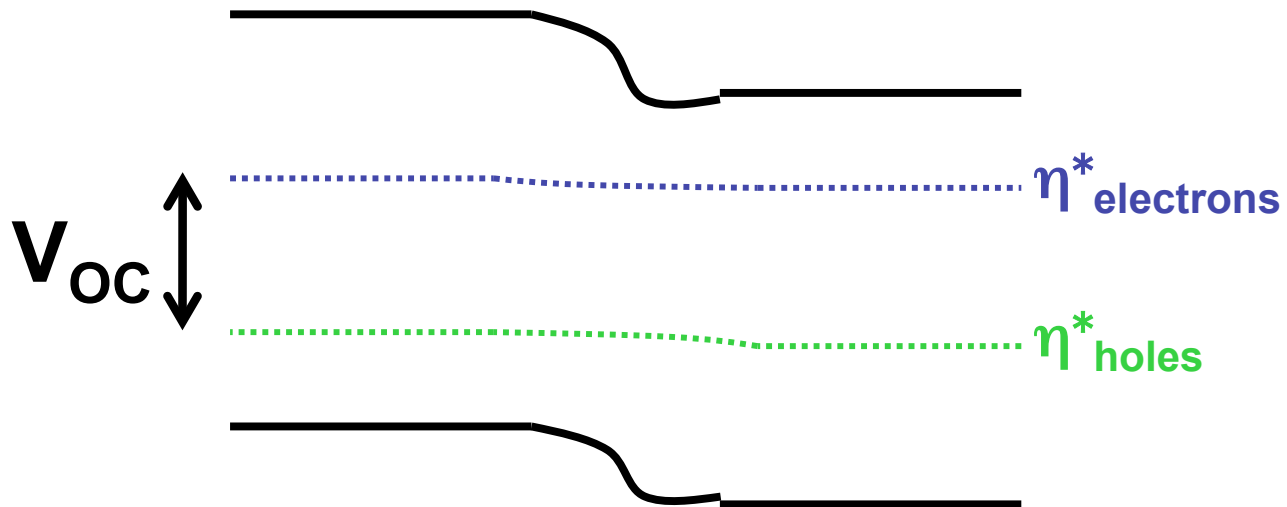
Solar Cells

Light 



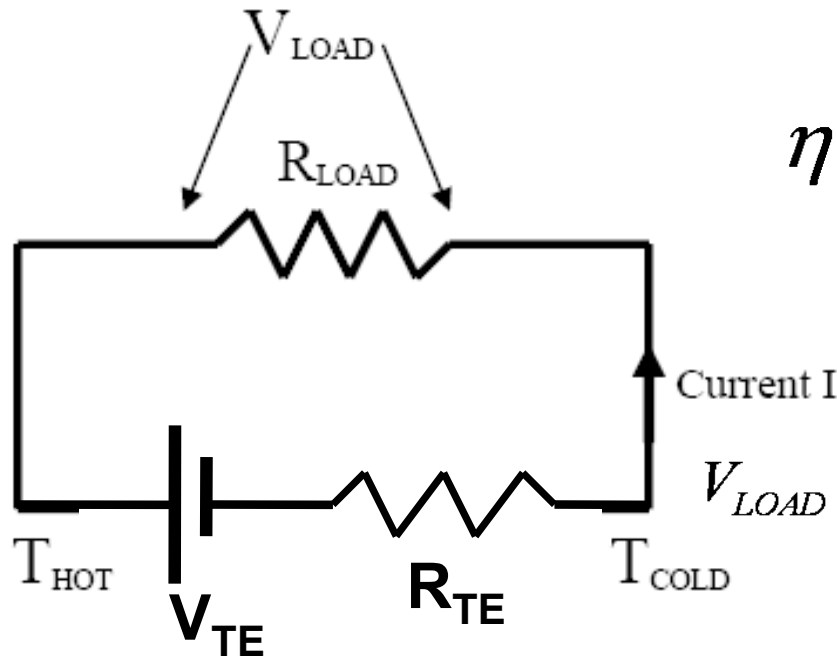
Solar Cells

Light 



$$V_{\text{oc}} = \Delta\mu_{\text{electrons}} + \Delta\mu_{\text{holes}}$$

Thermoelectrics as Heat Engines



$$\eta = \frac{W}{Q}$$

W is the work output
Q is the heat input

Work extracted is: $W = IV_{LOAD}$

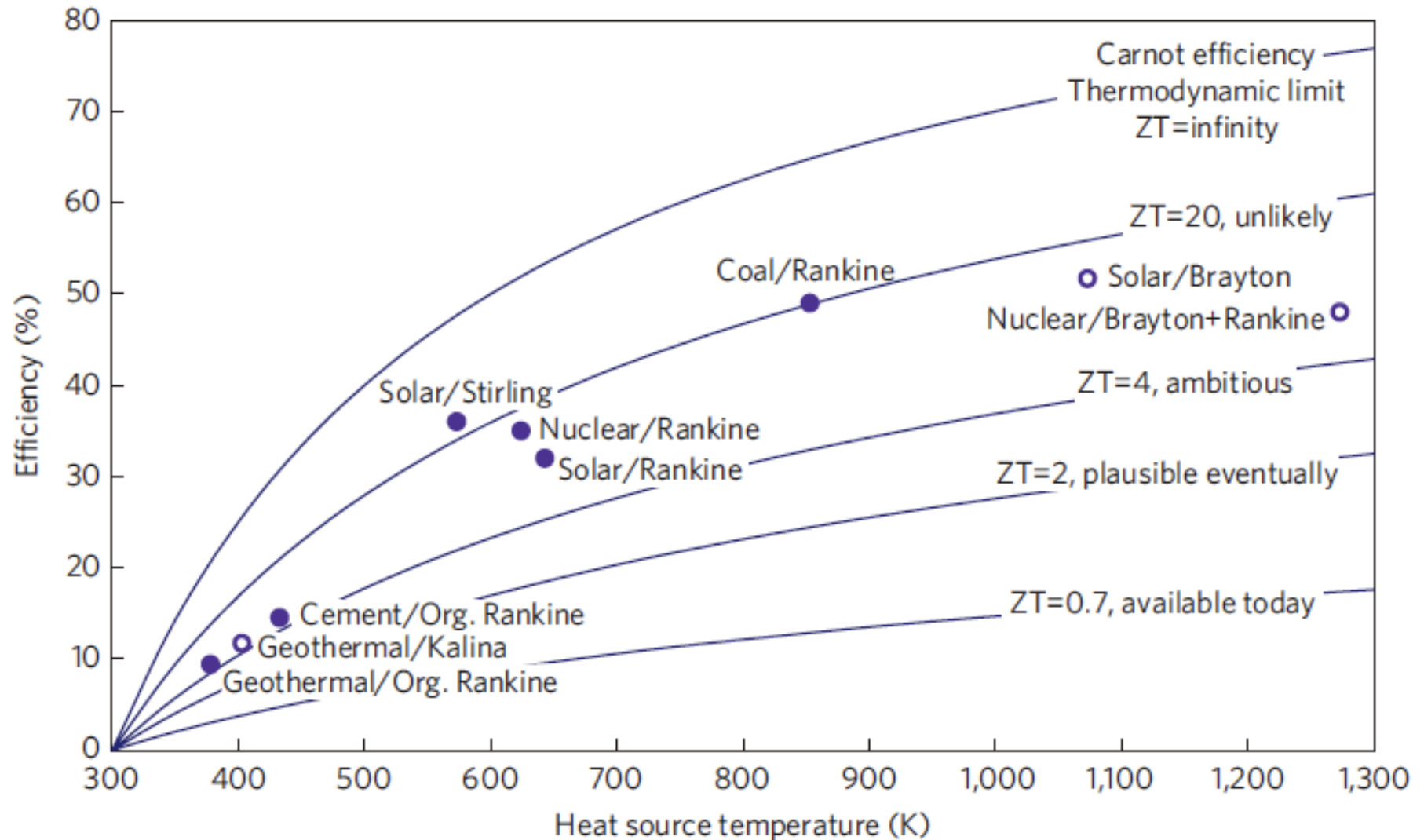
$$V_{LOAD} = V_{TE} \left(\frac{R_{LOAD}}{R_{TE} + R_{LOAD}} \right) = S\Delta T \left(\frac{R_{LOAD}}{R_{TE} + R_{LOAD}} \right)$$

$$W = S^2 \Delta T^2 \left[\frac{R_{LOAD}}{(R_{TE} + R_{LOAD})} \right]$$

Heat input consists of 3 terms: $Q_1 = \kappa \Delta T$ $Q_2 = IST_{HOT}$ $Q_3 = -\frac{1}{2} I^2 R_{TE}$

Plugging into η and maximizing: $\eta = \frac{\Delta T}{T_{HOT}} \frac{\sqrt{1 + Z\bar{T}} - 1}{\sqrt{1 + Z\bar{T}} + \frac{T_{COLD}}{T_{HOT}}}$

Heat Engines and Efficiency



Vining, C. *Nature Materials* 8, 83 (2009)

Figure of Merit for Thermoelectrics is ZT

Dimensionless number. Larger the better

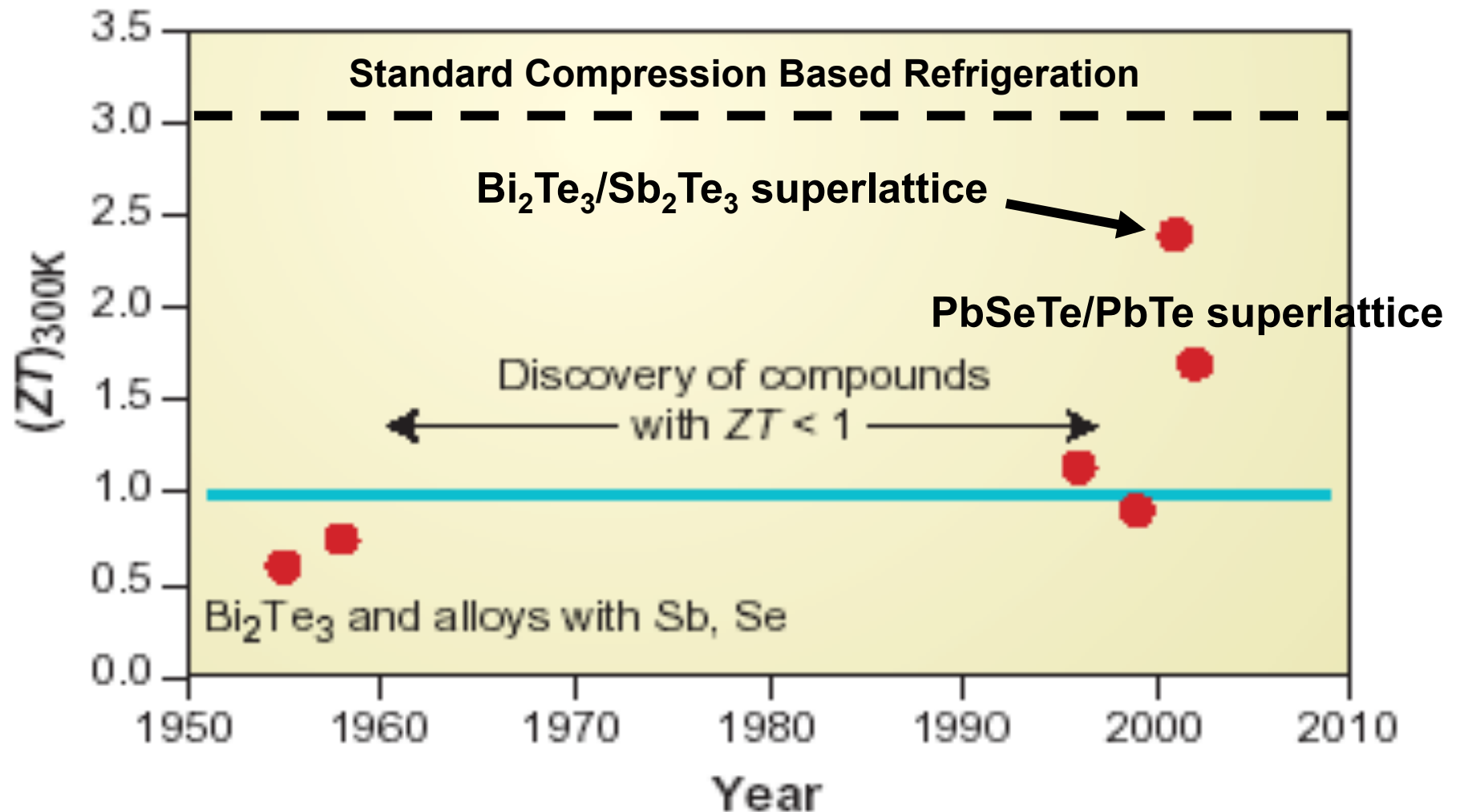
$$ZT = \frac{S^2 \sigma}{K} T$$

S Thermopower

σ Electrical conductivity

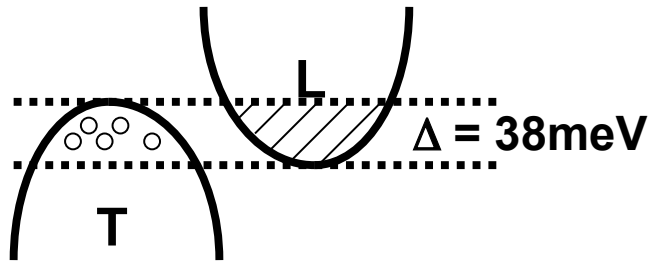
K Thermal conductivity

Is There a Ceiling to ZT?

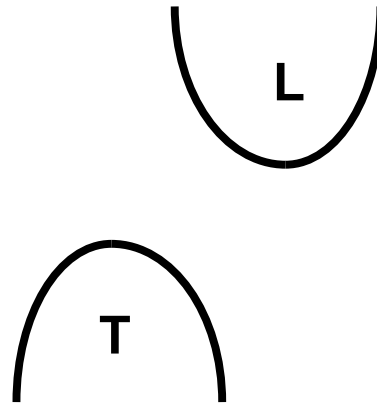


A. Majumdar, *Science* 303, 777 2004

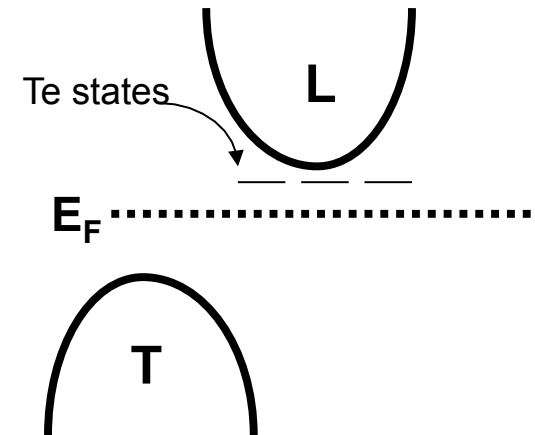
Is Bismuth a Good Thermoelectric?



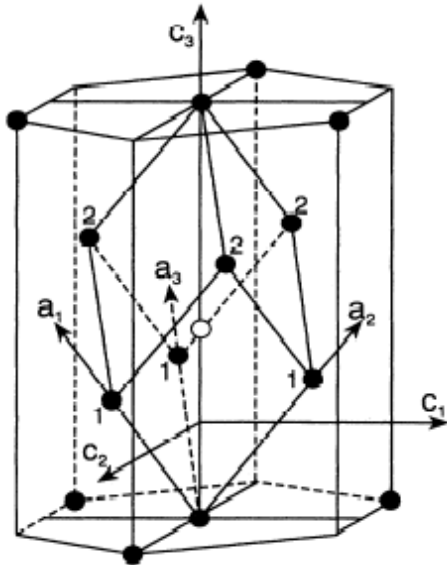
Bulk Bismuth



**Bismuth wire with
diameter $< 50 \text{ nm}$**



**Tellurium doped
Bismuth nanowires**



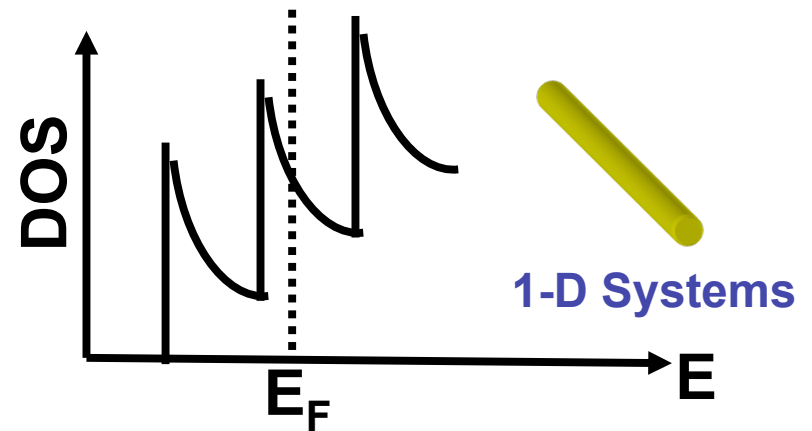
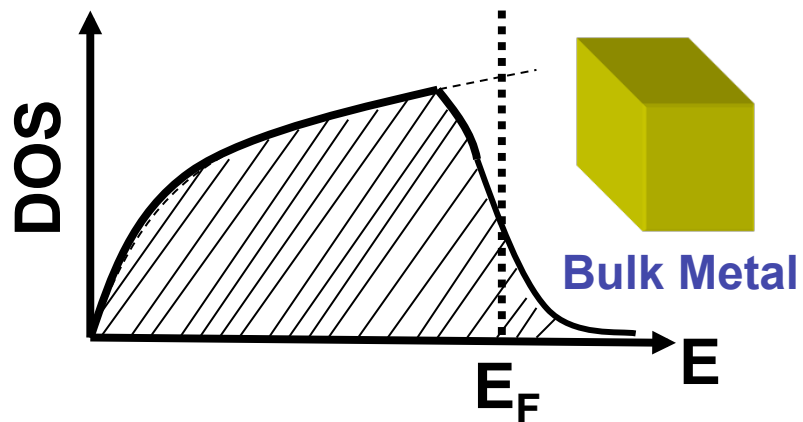
$$m^* = .001 m_e \quad \mu = 2.59 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$$

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

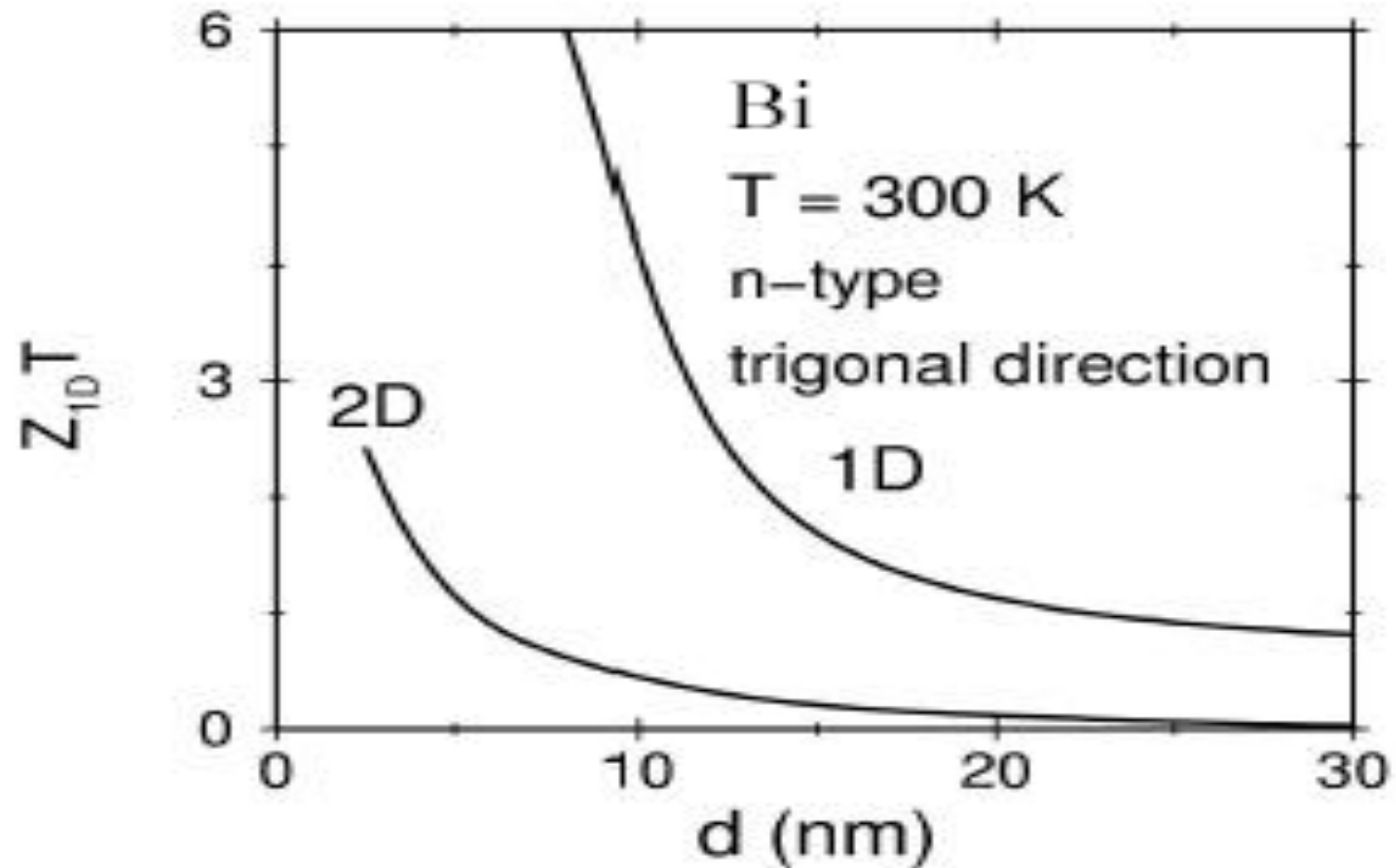
**Electron mean free path is
~30 to 50 nm at
room temperature**

Density of States

$$S \propto T \left. \frac{\partial N(E)}{\partial E} \right|_{E_F}$$

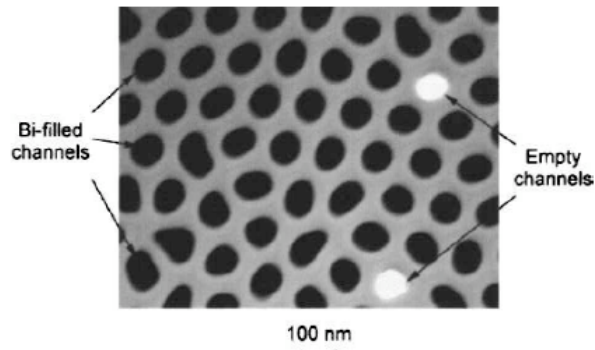


ZT for Bismuth Nanowires



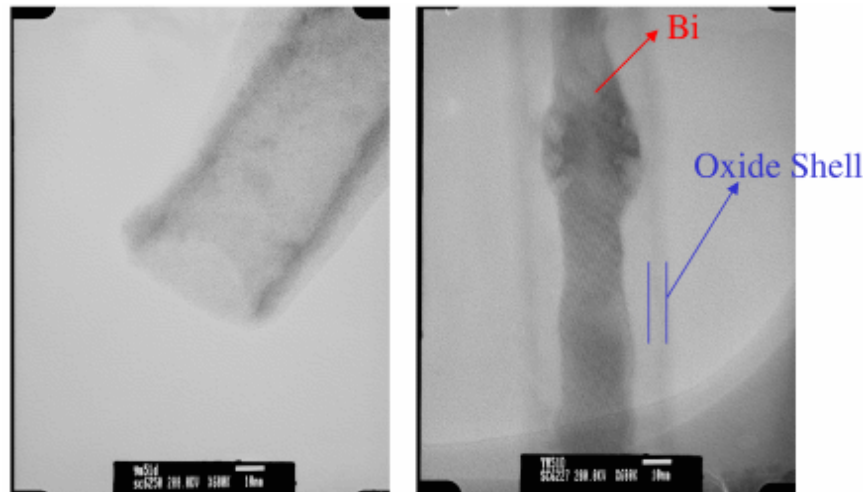
M.S. Dresselhaus, *Phys. Rev. B* 62, 4610 2000

Bismuth is Not an Easy Material to Work With



State of the art: Alumina assisted electrodeposition

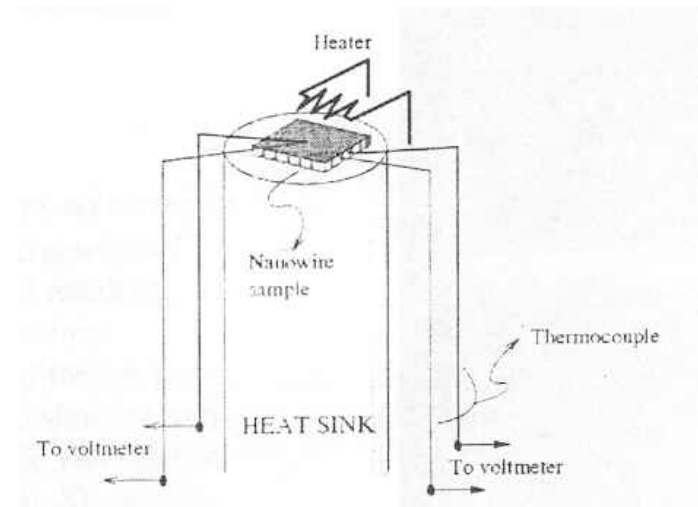
M.S. Dresselhaus *et. al.*, *Int. Mater. Rev.* 48, 45-66 2003



Bismuth is sensitive to acids and bases and oxidizes readily

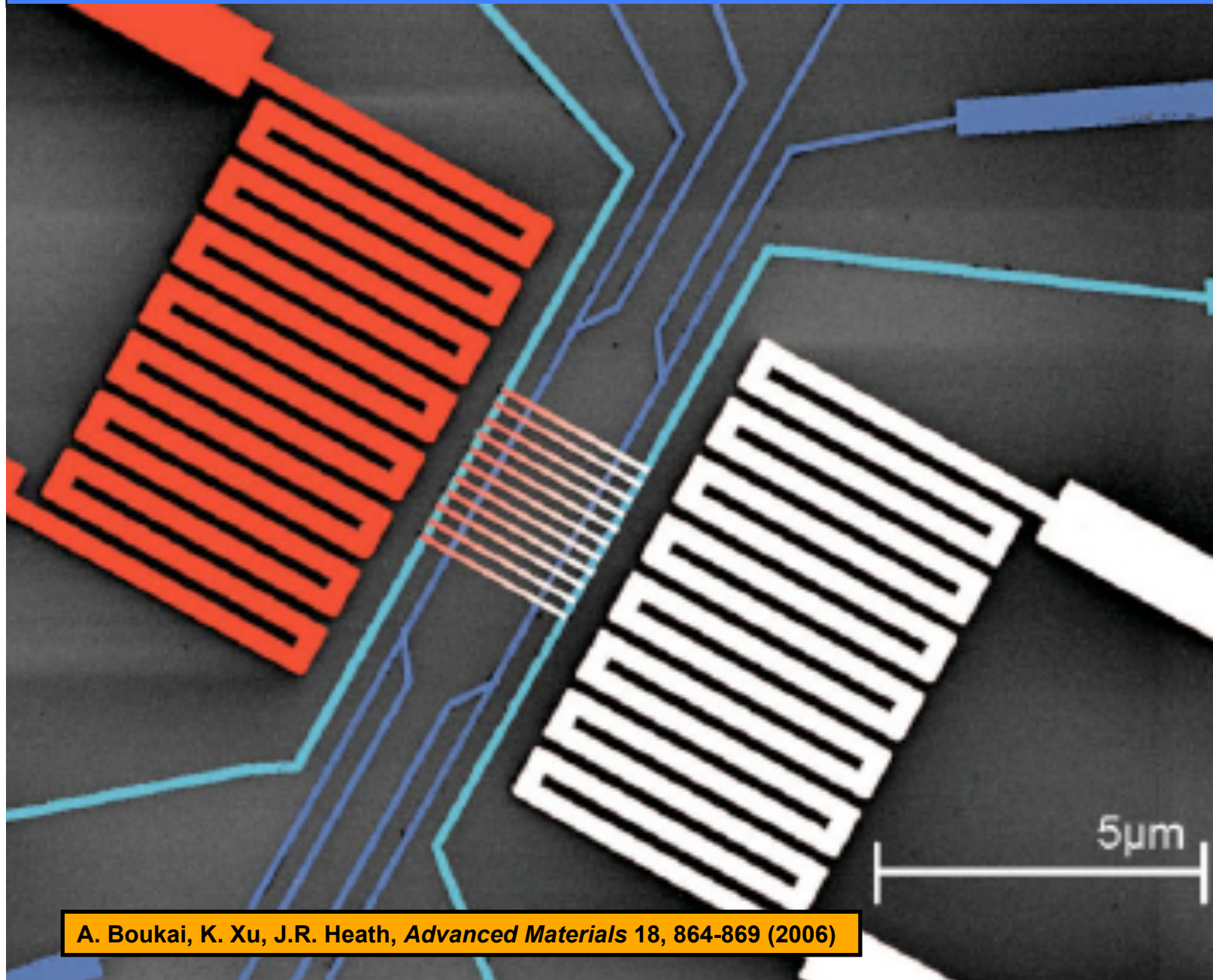
S.B. Cronin *et. al.*, *Nanotechnology* 13, 653-658 2002

Measurement limited to 2-point and large thermocouples



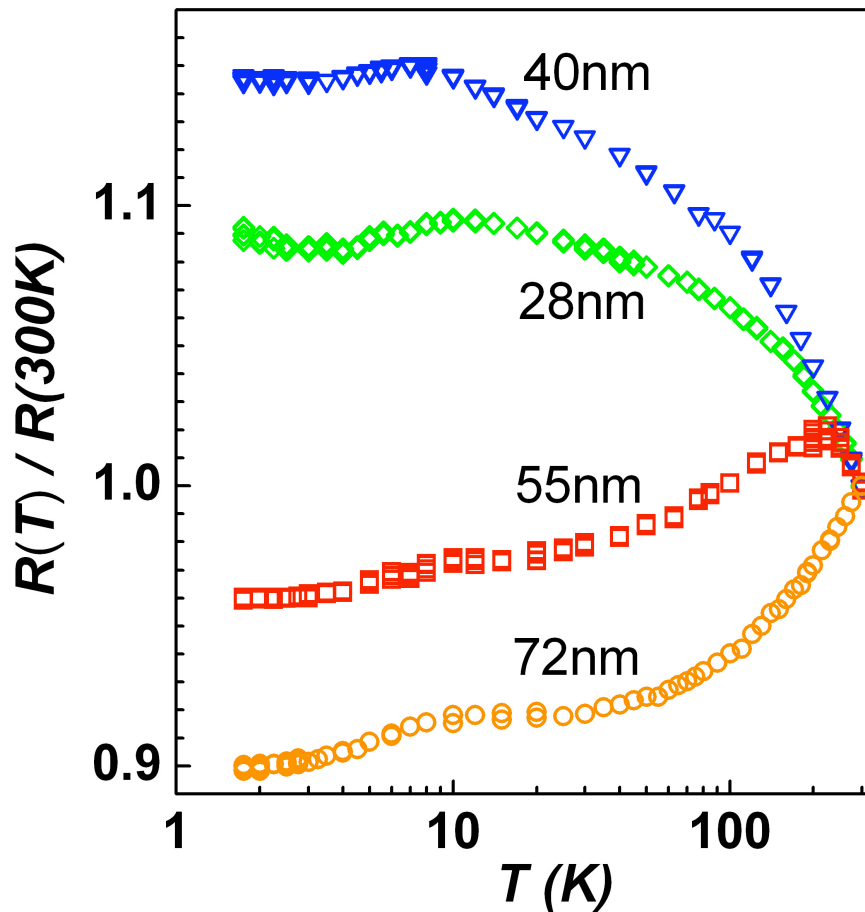
Y.M. Lin *et. al.*, *Mat. Res. Soc. Symp. Proc.* 691, 377-382 2002

Bismuth Nanowire Thermoelectric Devices

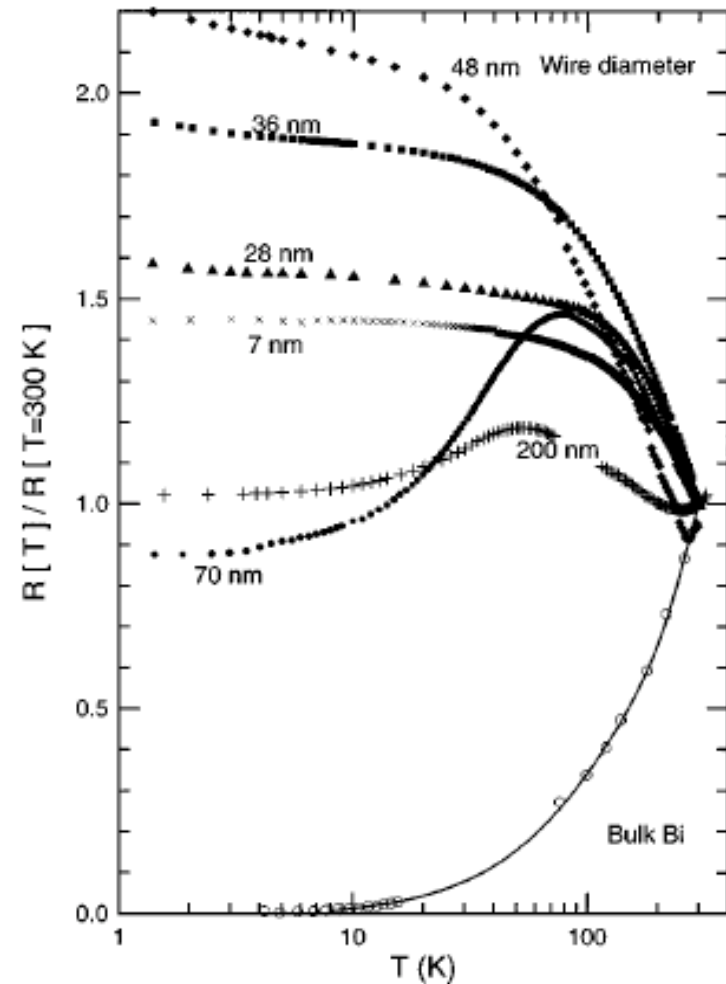


A. Boukai, K. Xu, J.R. Heath, *Advanced Materials* 18, 864-869 (2006)

Bi Nanowire Electrical Conductivity Results



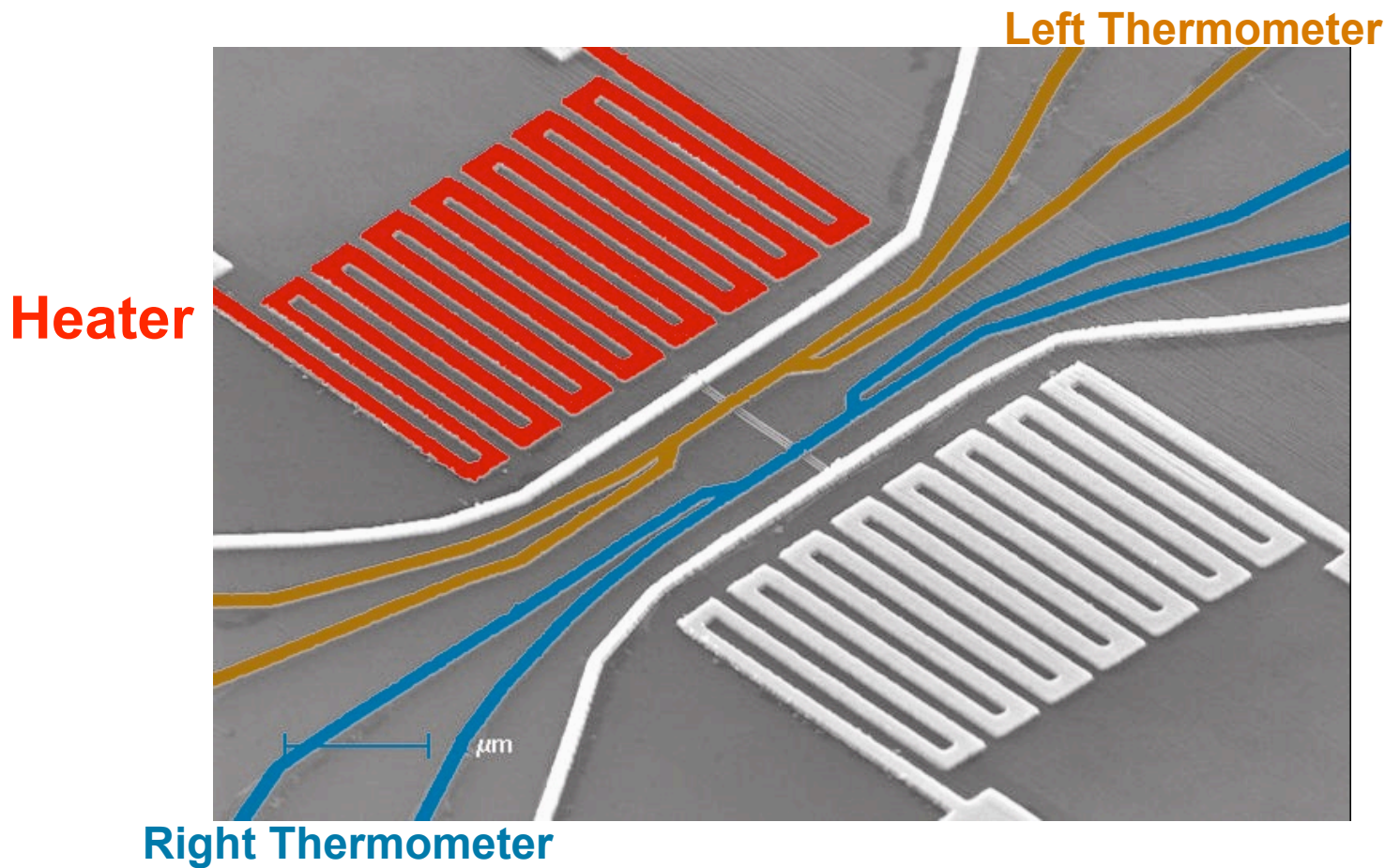
A. Boukai, K. Xu, J.R. Heath, *Advanced Materials* 18, 864-869 2006



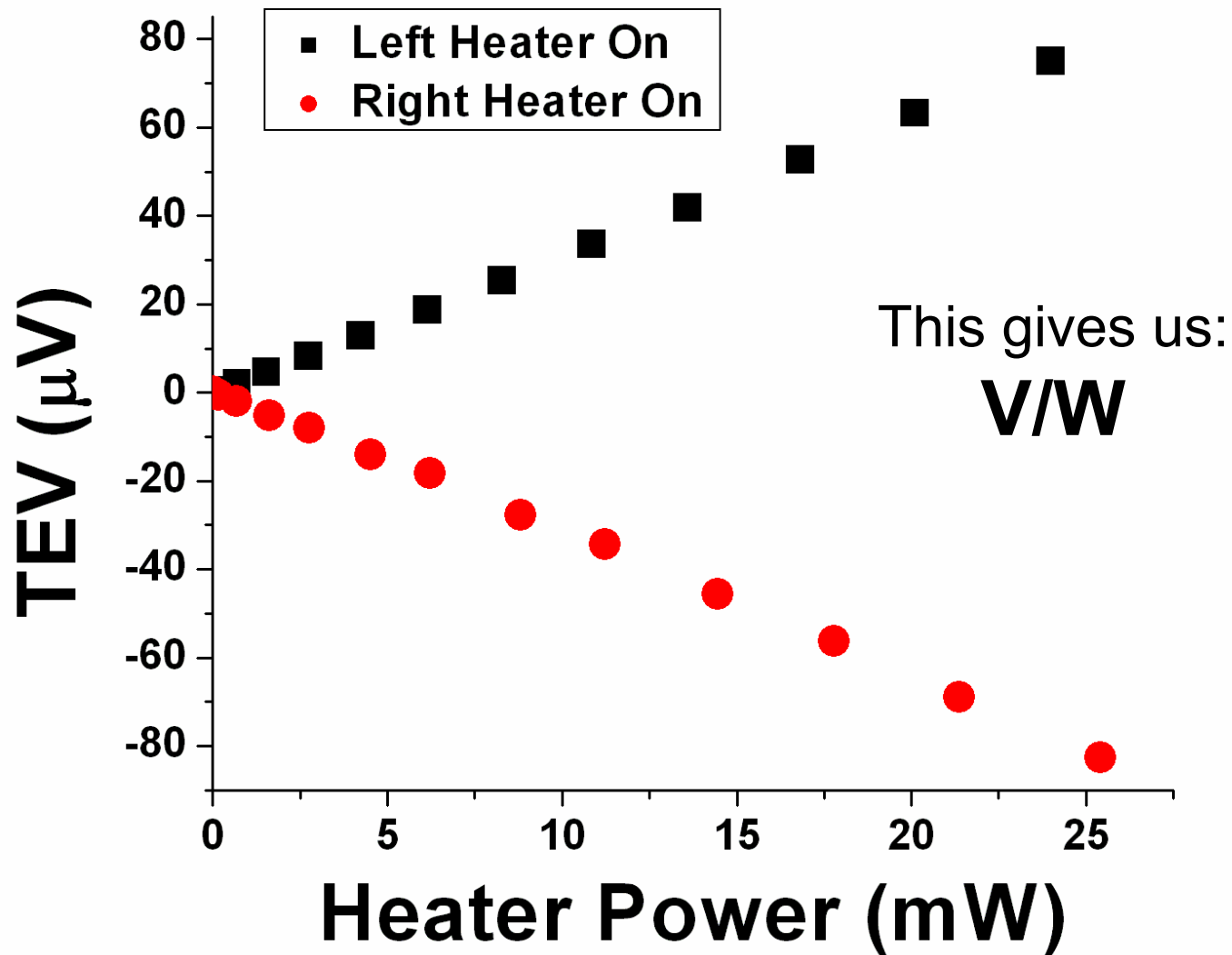
Heremans et. al., *Phys. Rev. B* 61, 2921-2930 2000

Measuring the Thermopower

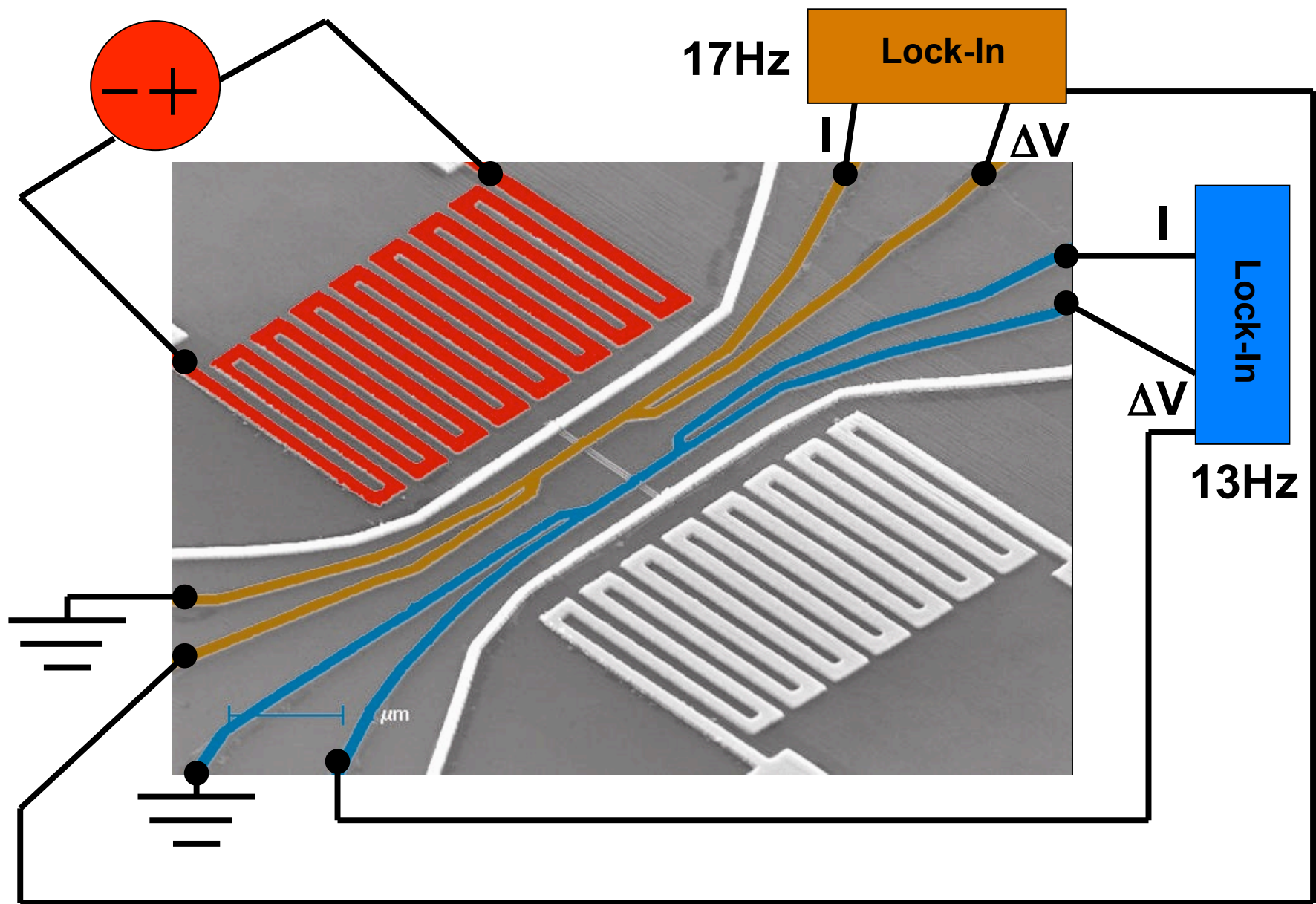
$$S = \frac{\Delta V}{\Delta T}$$



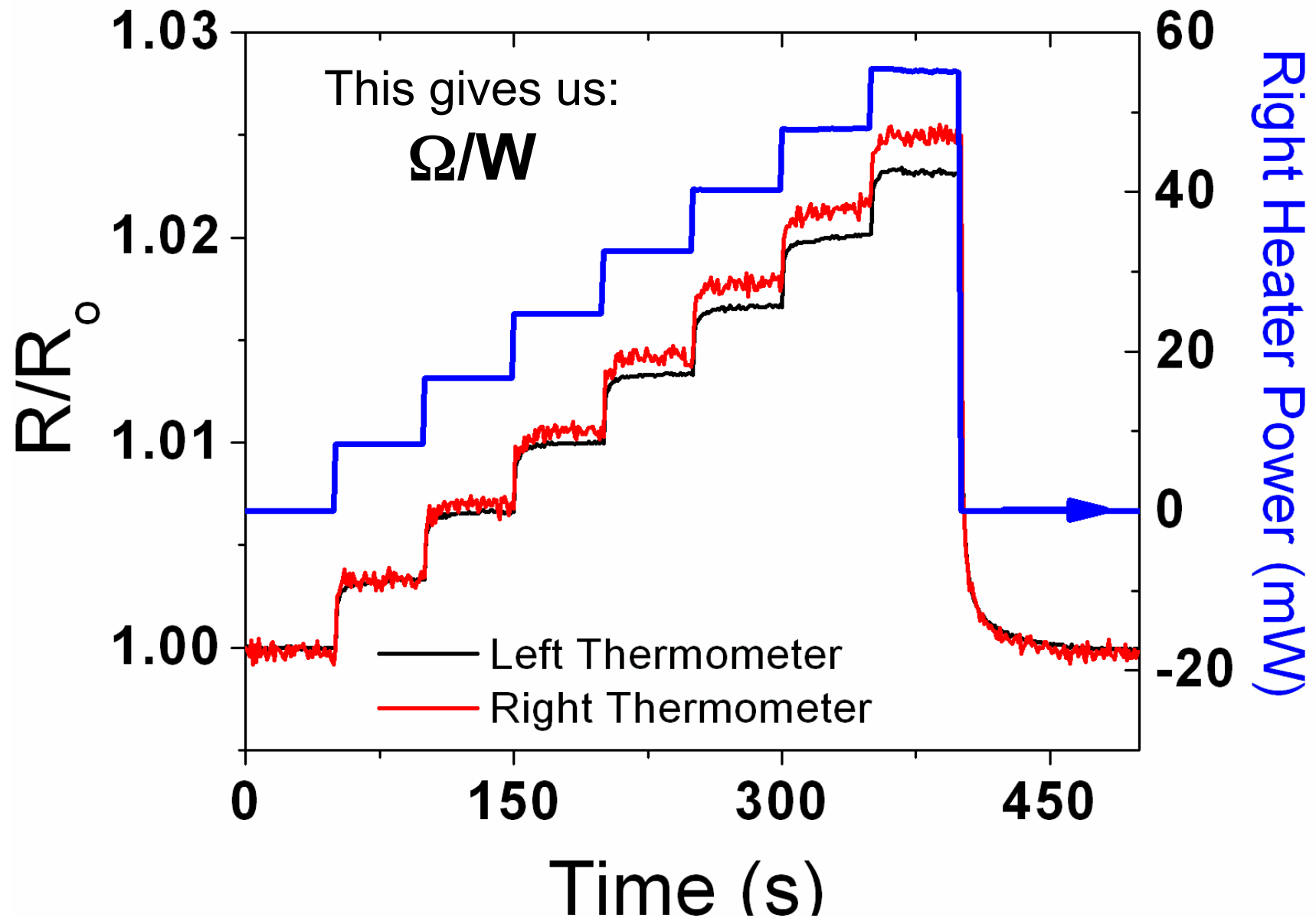
Measuring the Thermoelectric Voltage (TEV)



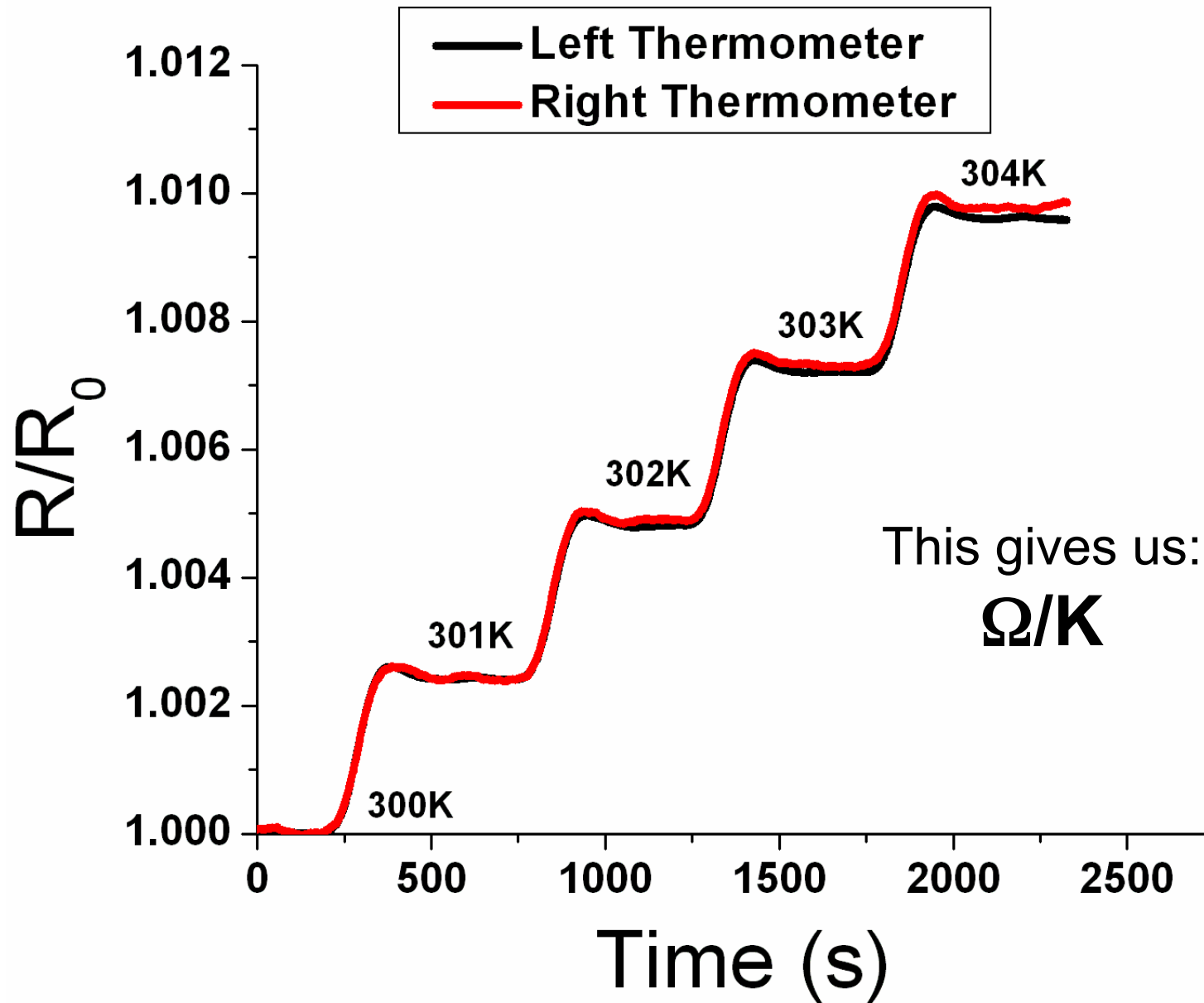
Measuring ΔT



Measuring ΔT

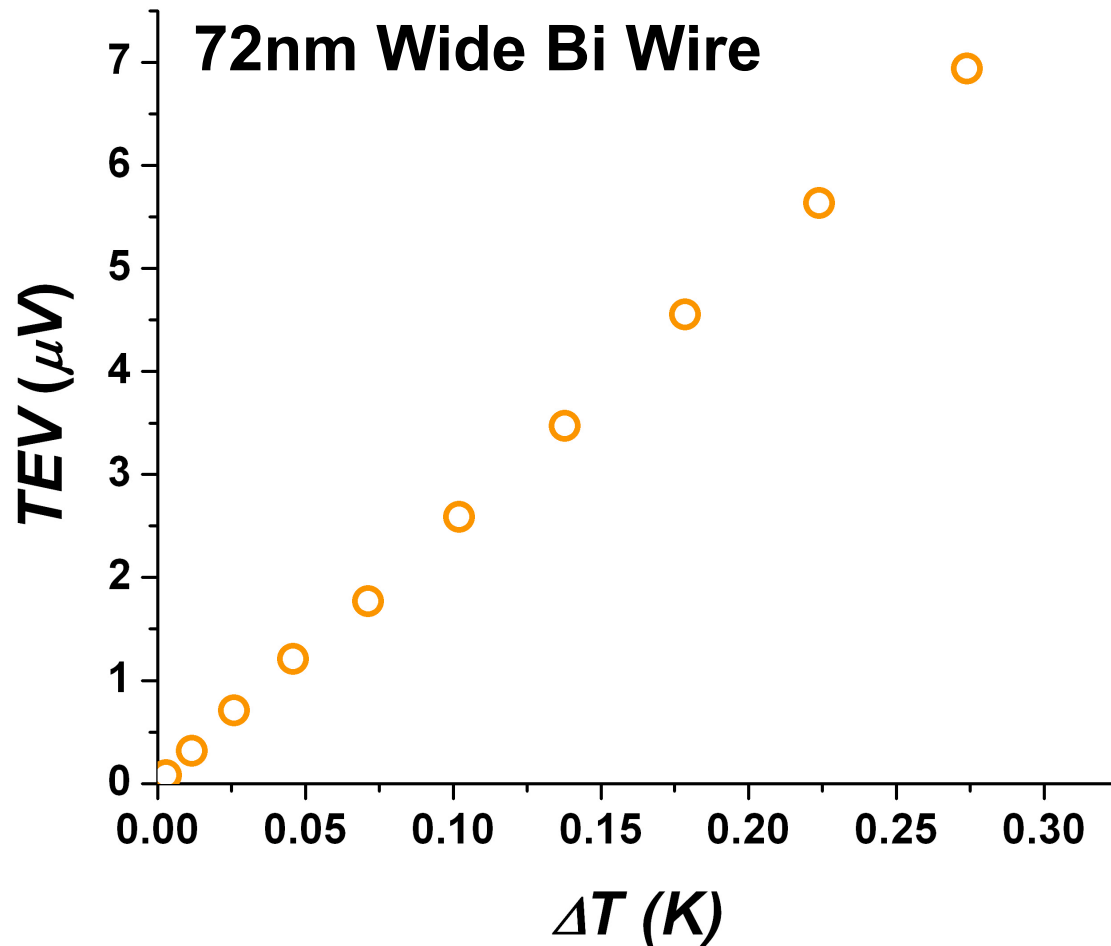


Measuring ΔT

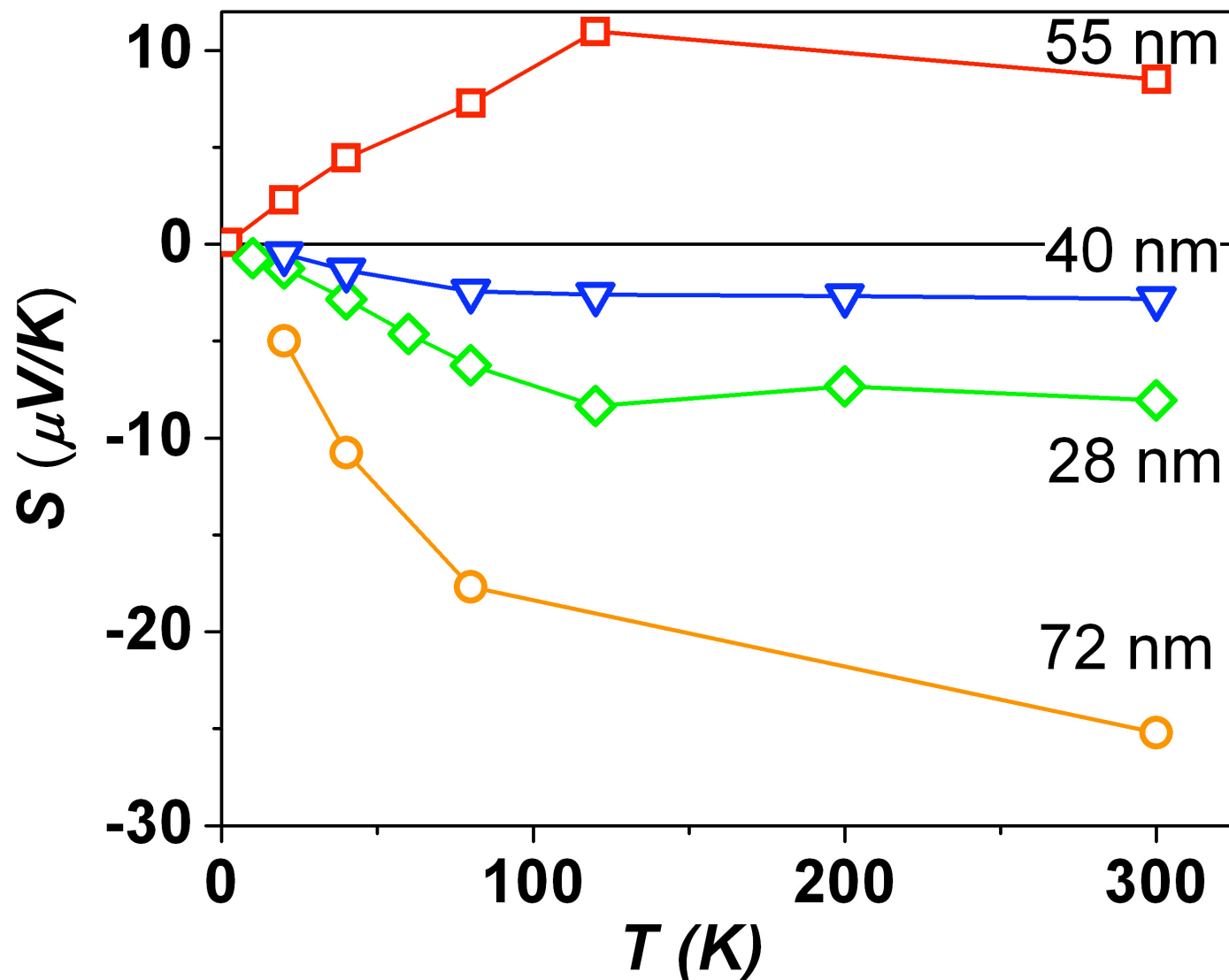


Measuring ΔT

Multiply: $\frac{V}{W} \times \frac{W}{\Omega} \times \frac{\Omega}{K}$

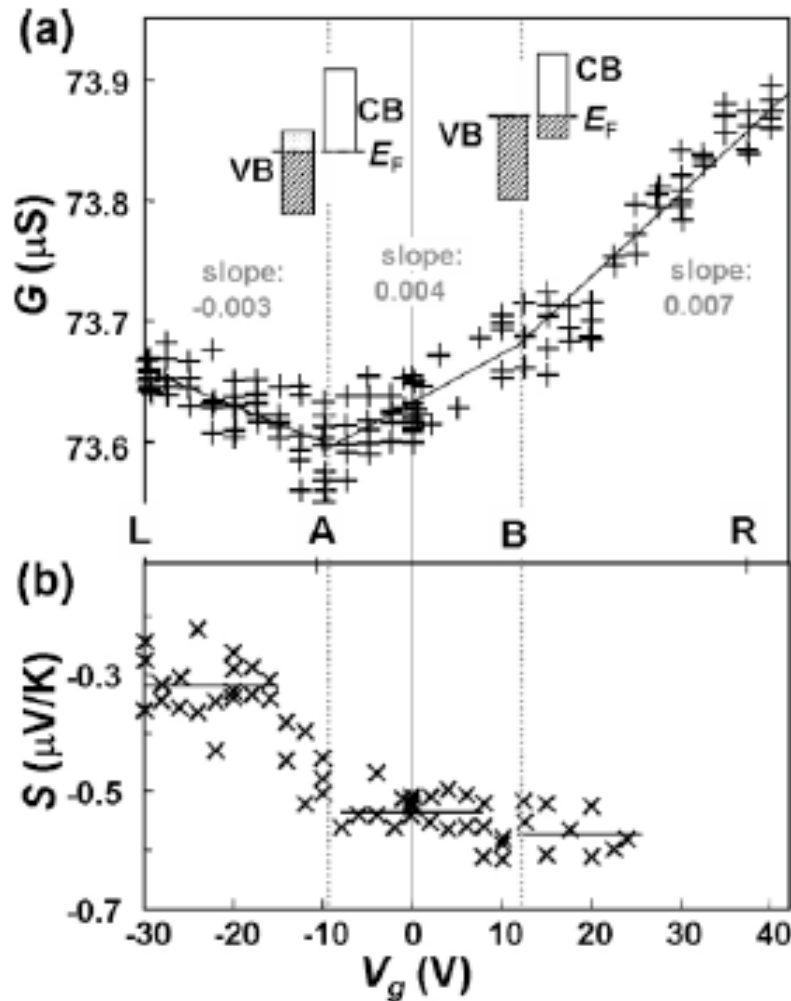


Bi Nanowire Thermopower Results



Surface States Dominate Carrier Transport

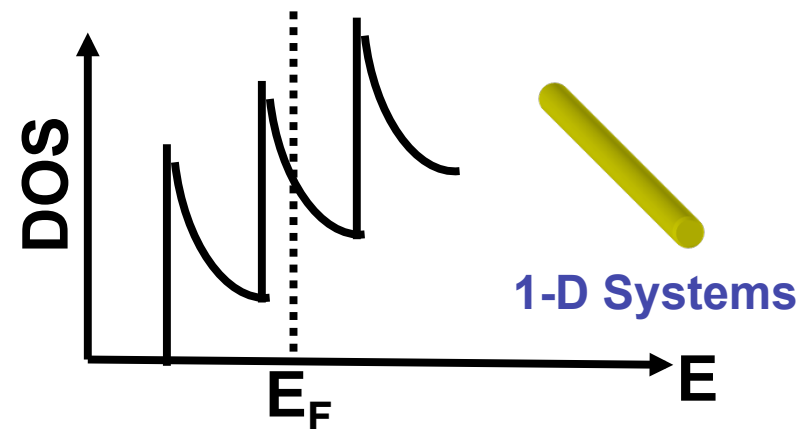
40nm wide Bi wire at 20K Results



Our results indicate that surface states dominate the carrier transport

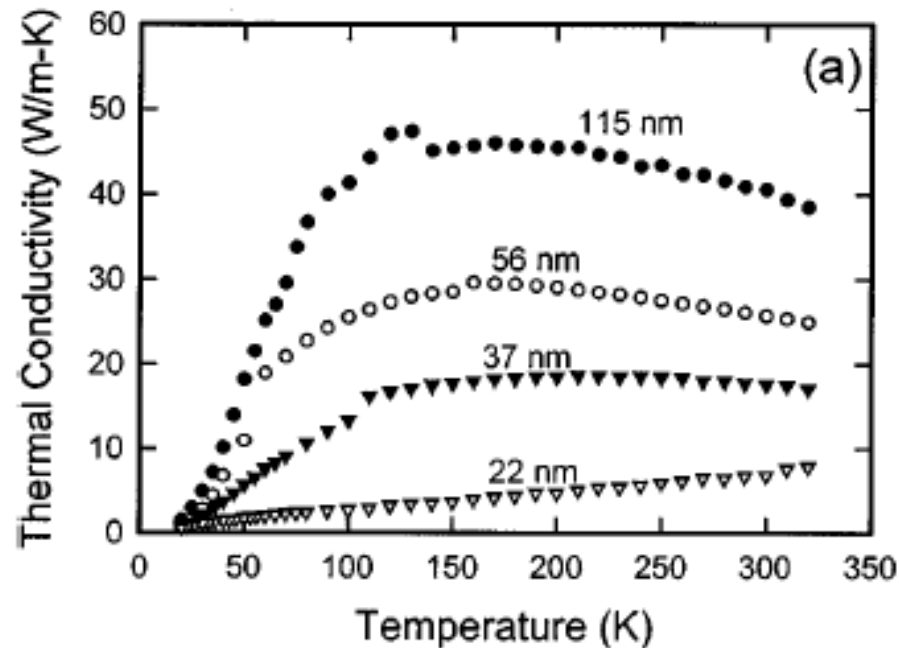
Thermopower is well correlated to Mott diffusion formula

$$S \propto \left. \frac{dN}{dE} \right|_{E_F}$$



And God Said, “Let there be Silicon and it was good.”

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

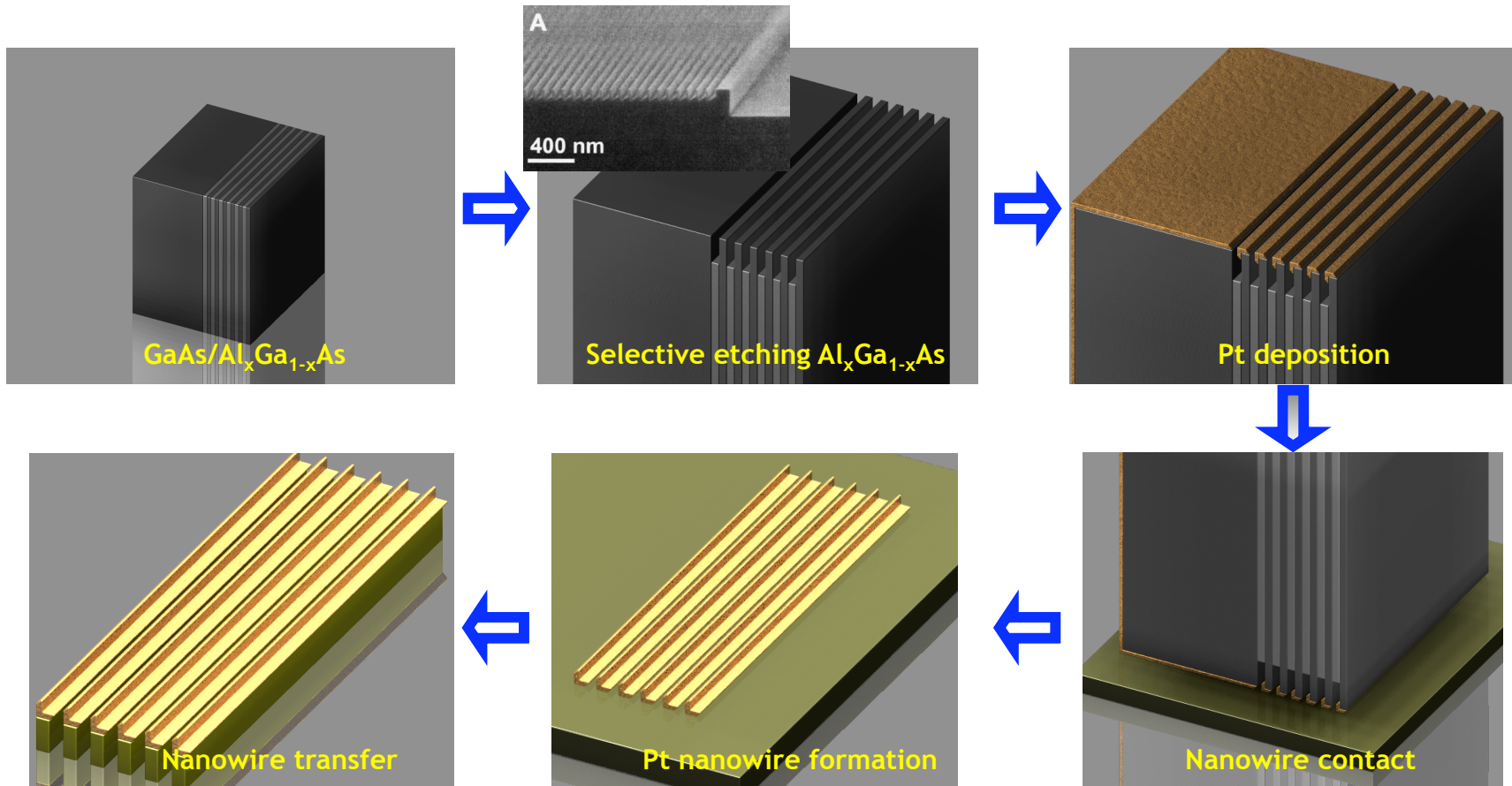


D. Li, et al. *APL* 83, 2935 2003

κ for bulk Si is ~ 150 W/(m-K) @300K

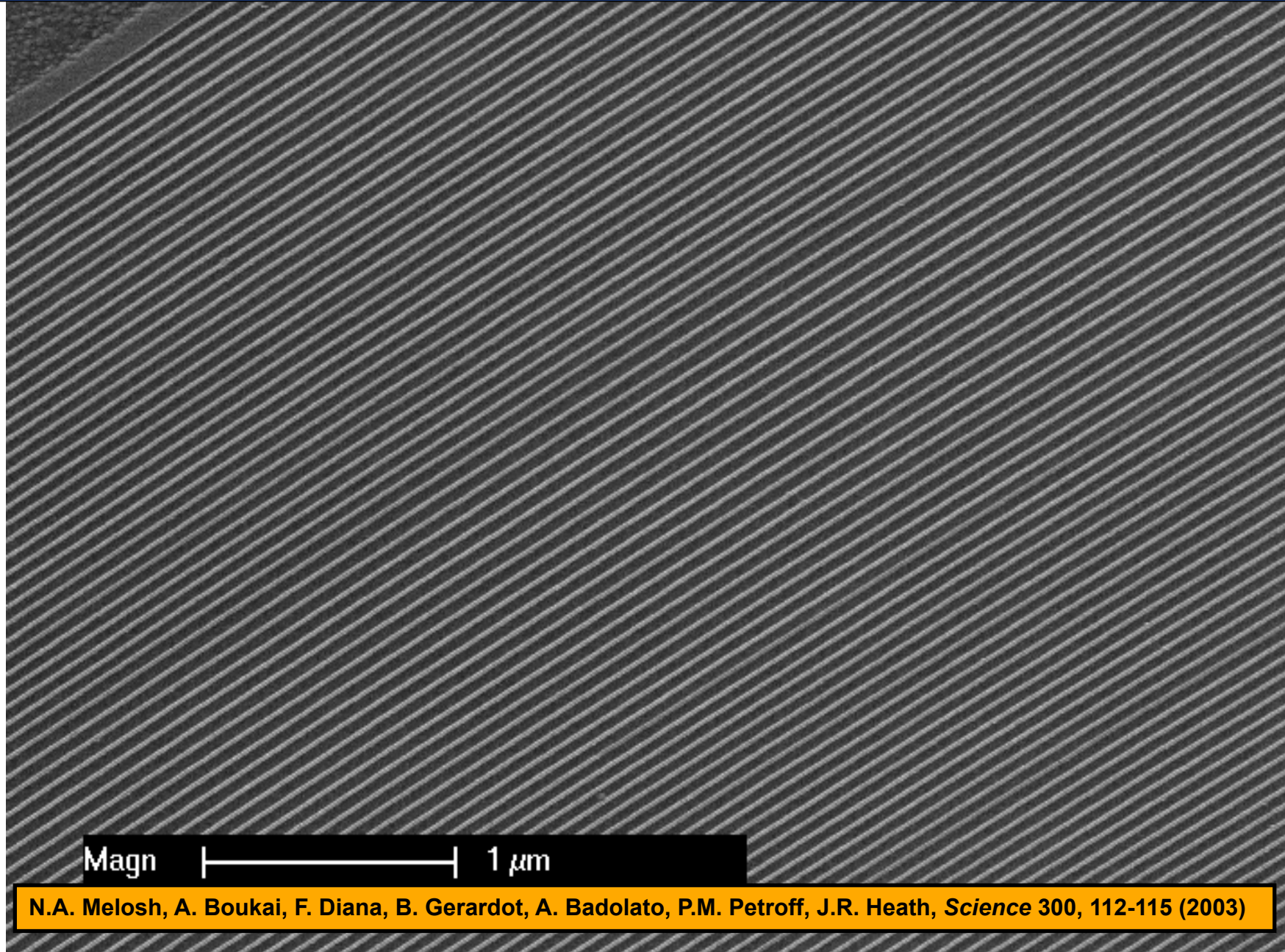
With SNAP, we have control over wire width, doping, crystal orientation, etc.

Superlattice Nanowire Pattern Transfer (SNAP)



N.A. Melosh, A. Boukai, F. Diana, B. Gerardot, A. Badolato, P.M. Petroff, J.R. Heath, *Science* 300, 112-115 (2003)

Array of Si Nanowires Made With SNAP



SNAP's Versatility

↓
20nm
↑

7.5nm

200 nm
Gen VI Drive-In Doped 400 Si Wires

Acc.V	Spot	Magn	Det	WD	Exp		200 nm
30.0 kV	1.0	150000x	SE	11.1	1	032906-Sample12-Si NWs-15 nm pitch	

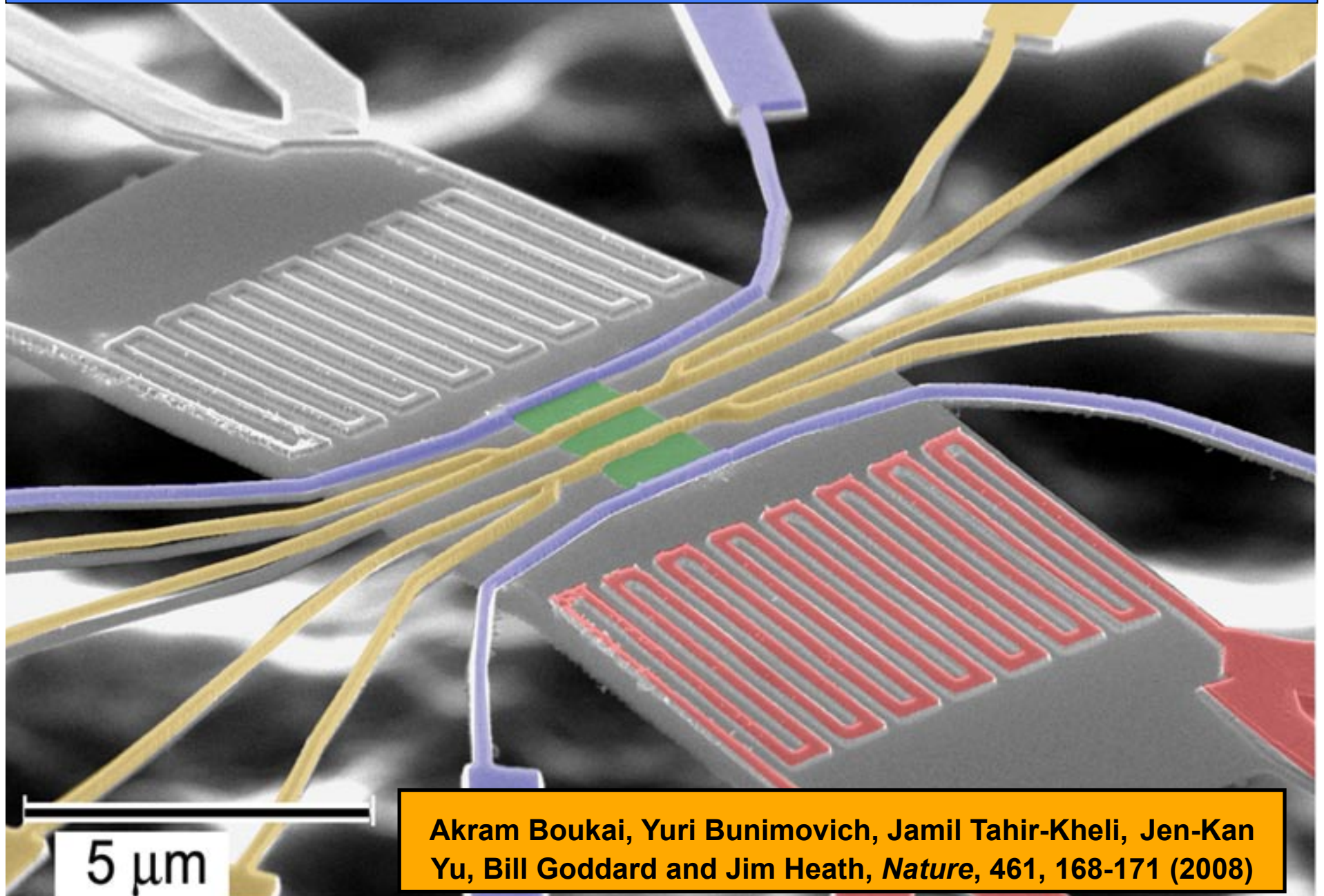
400 NWs

5 μ m
Gen VI Drive-In Doped 400 Si Wires

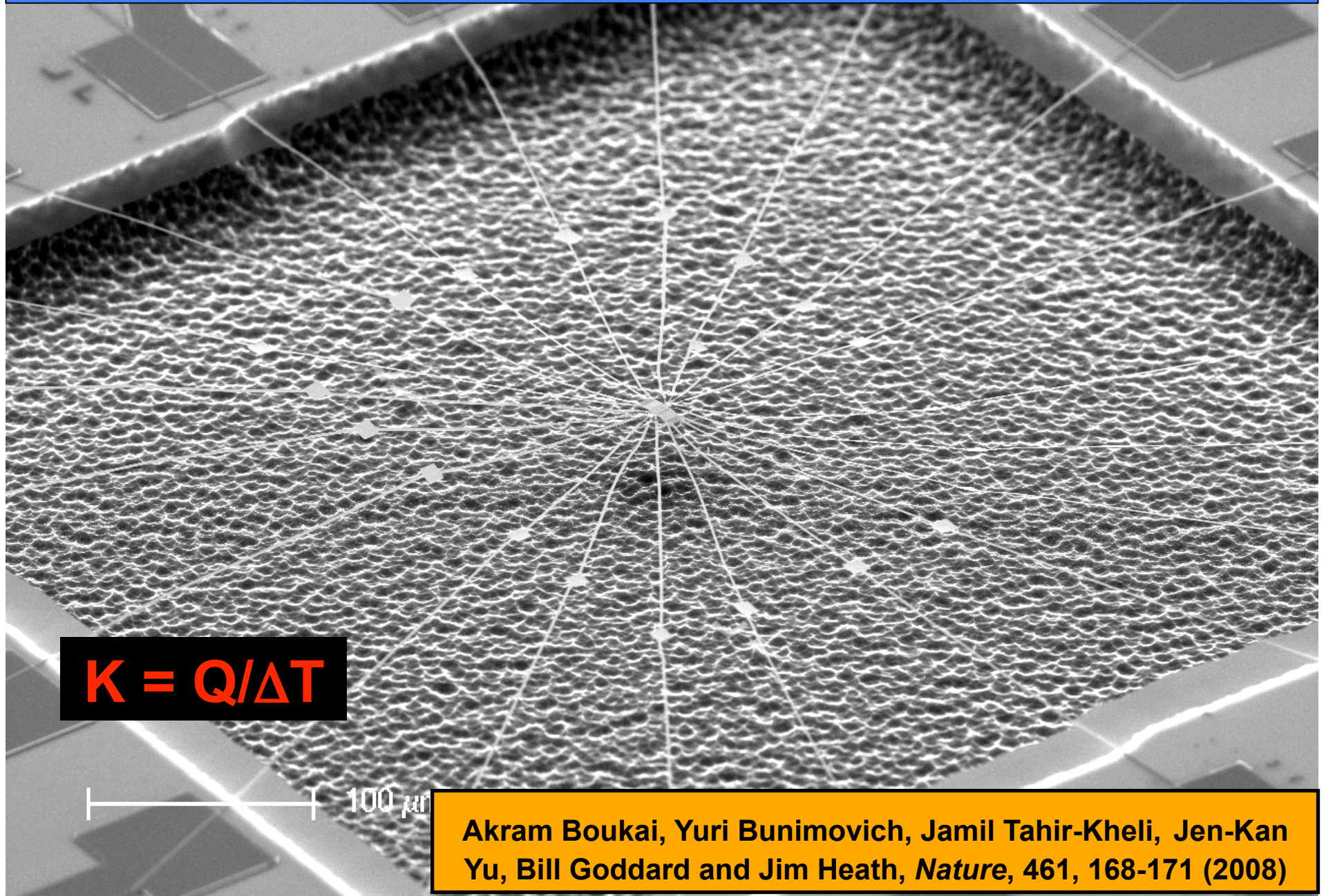
1400 NWs

20 μ m
061205 1400 Si Wires

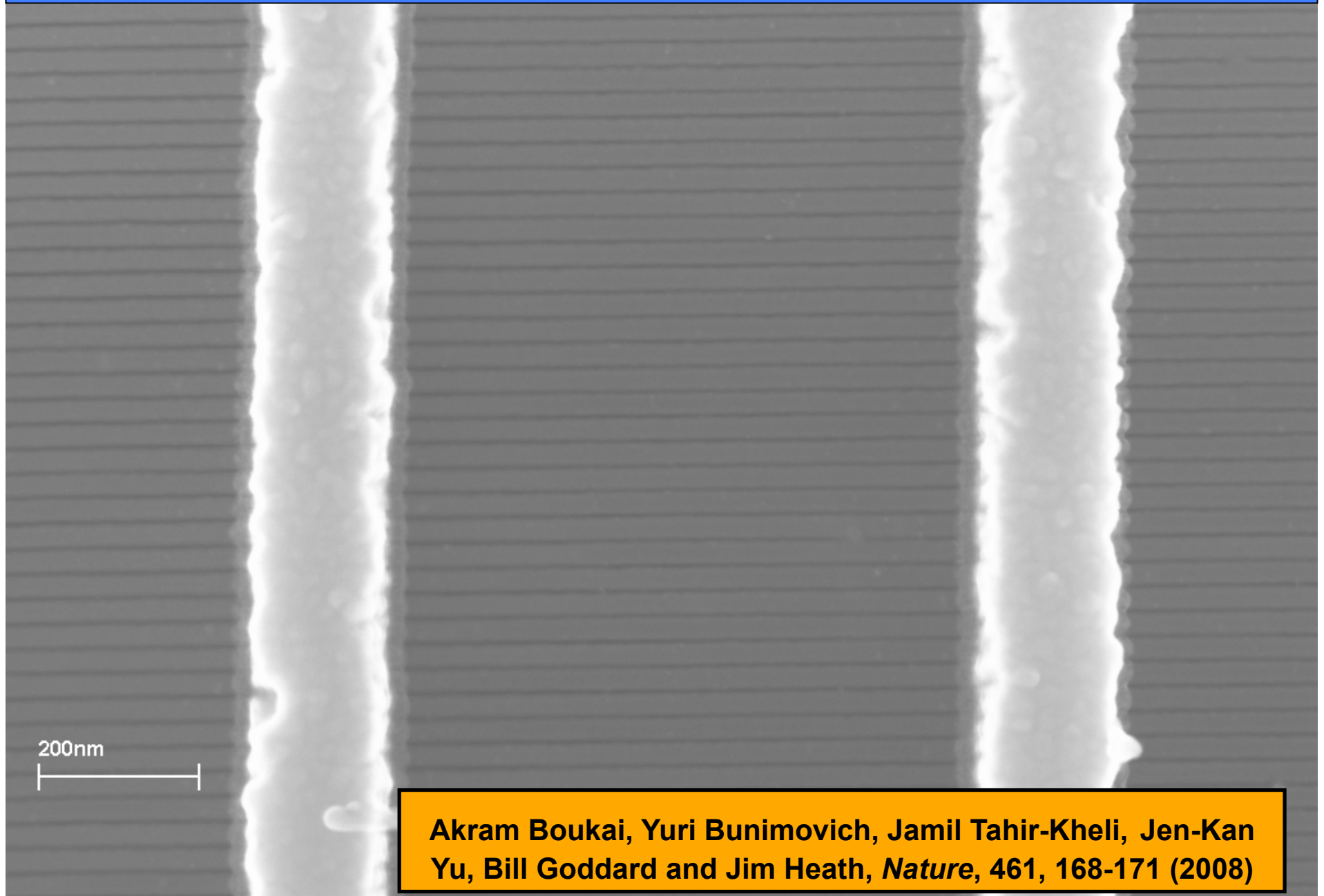
Si Nanowire Thermoelectrics



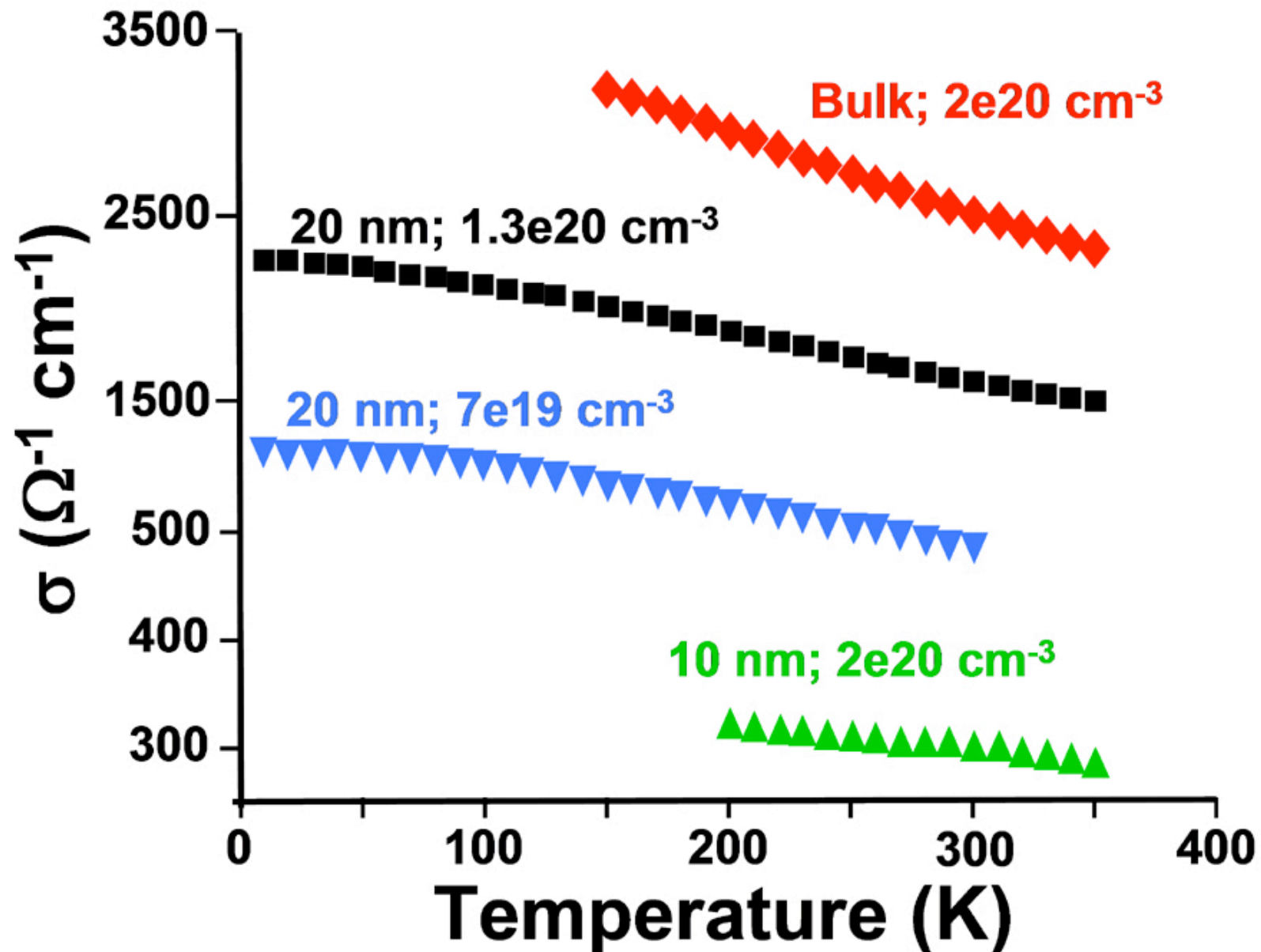
Suspended Platform Allows Measurement of ZT



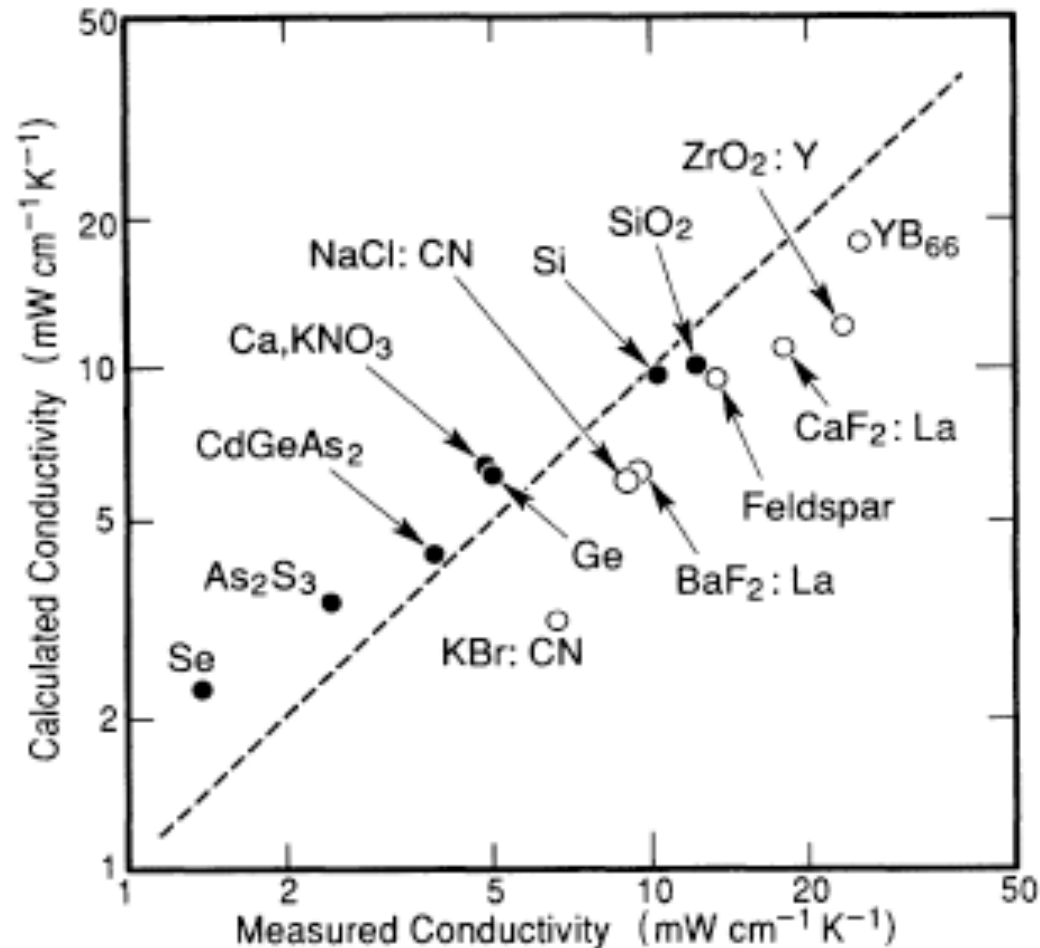
Measurements are Taken on an Array of Si NWs



Si Nanowire Electrical Conductivity



Minimum Thermal Conductivity

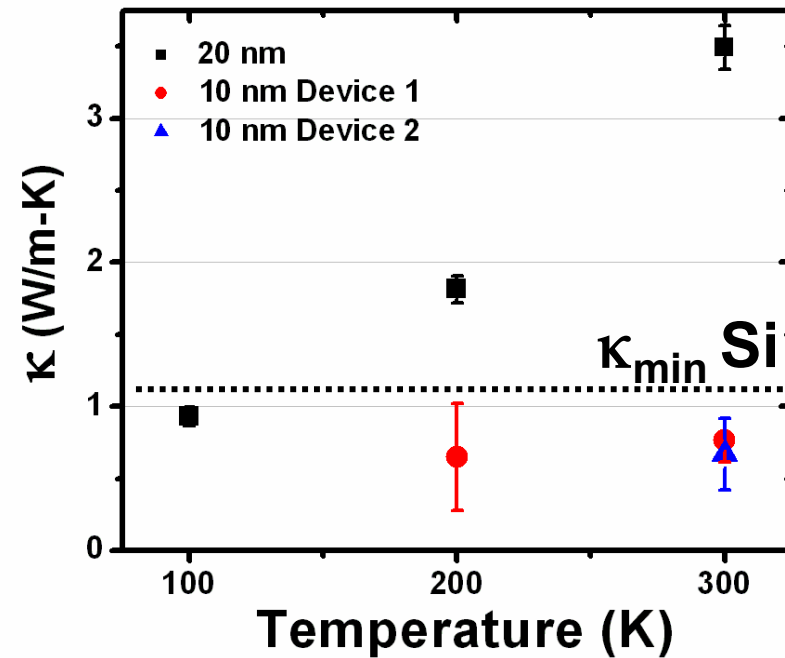
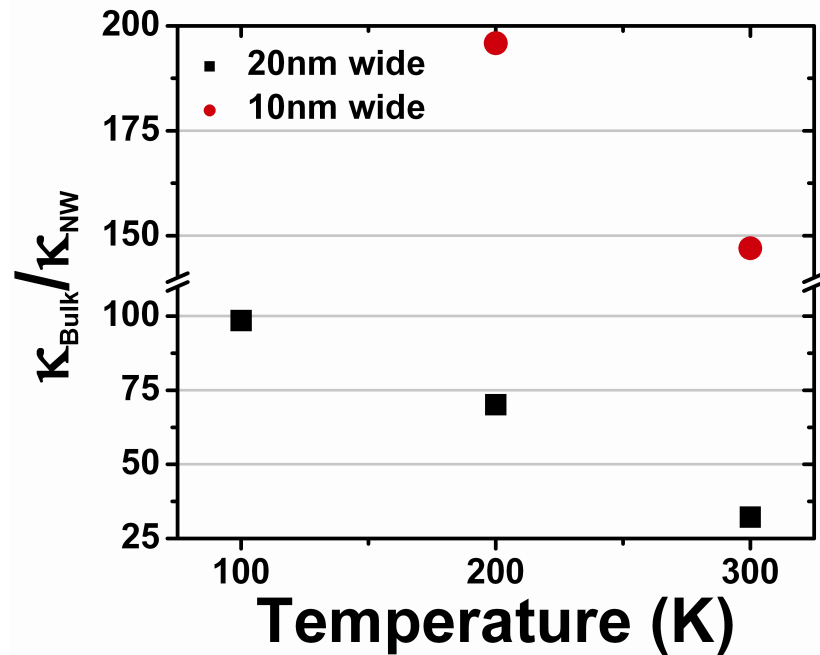


D.G. Cahill, et al. Phys. Rev. B 46, 6131 (1992)

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

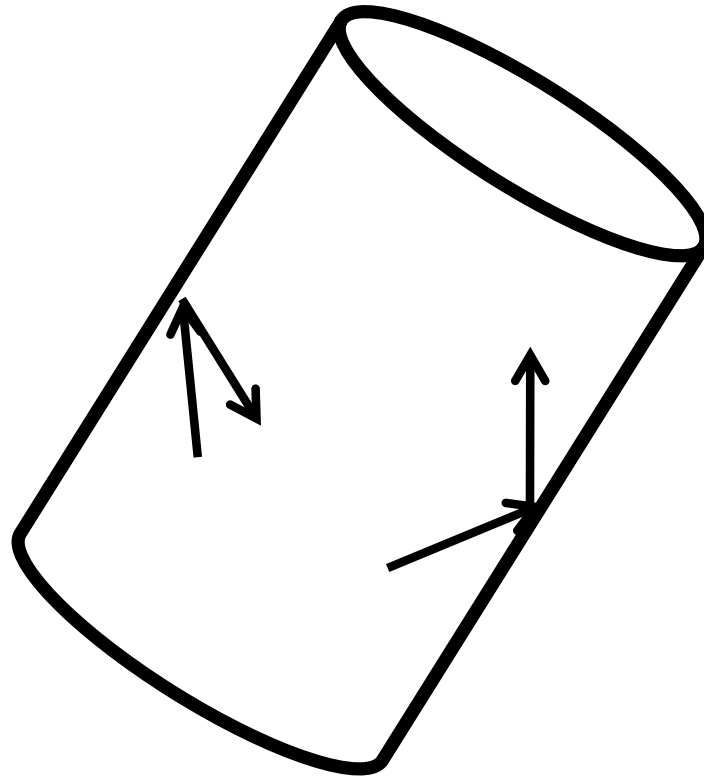
This occurs when Si is amorphous

Si Nanowire Thermal Conductivity

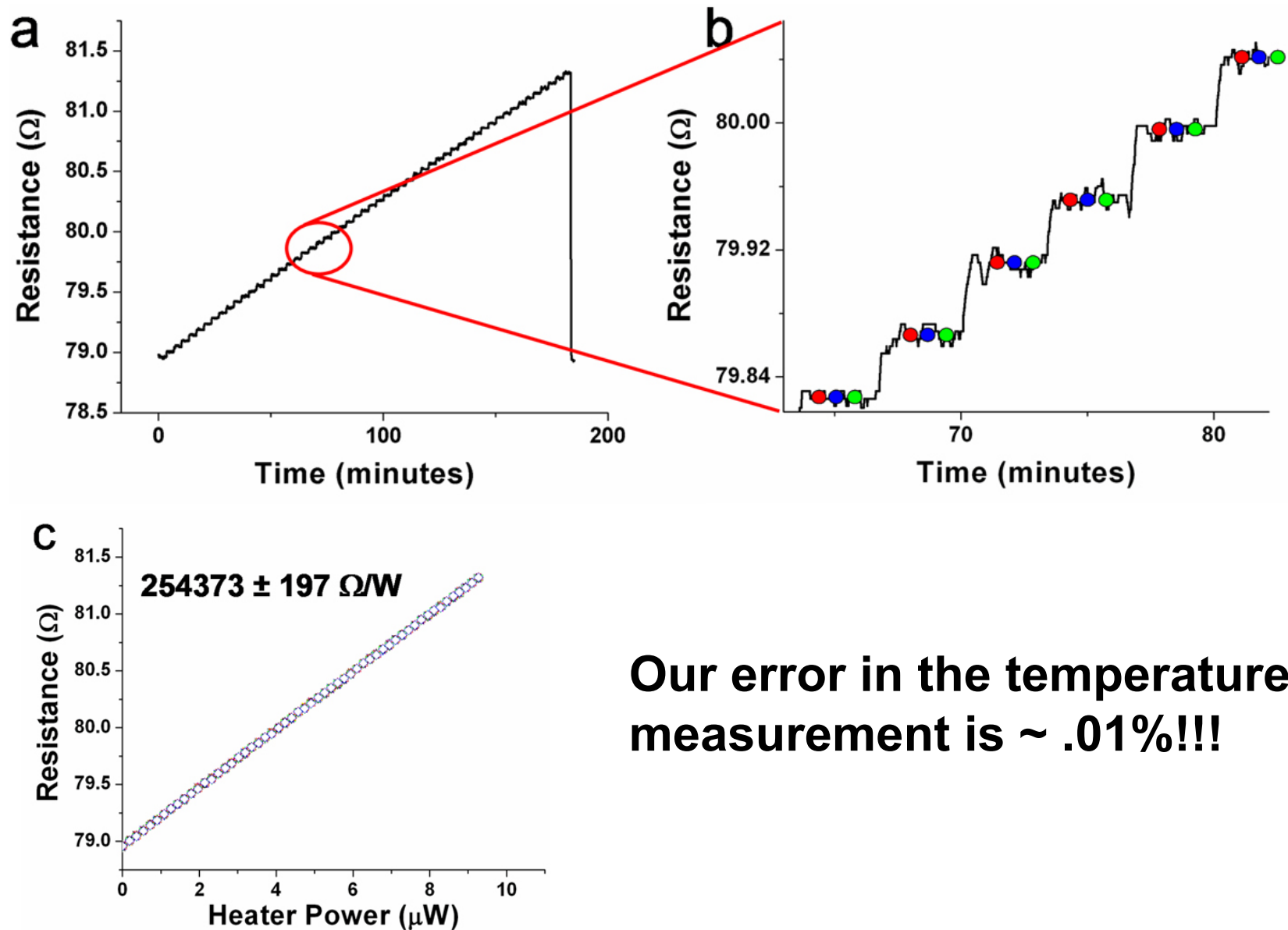


κ for bulk Si is ~ 150 W/(m-K) @300K

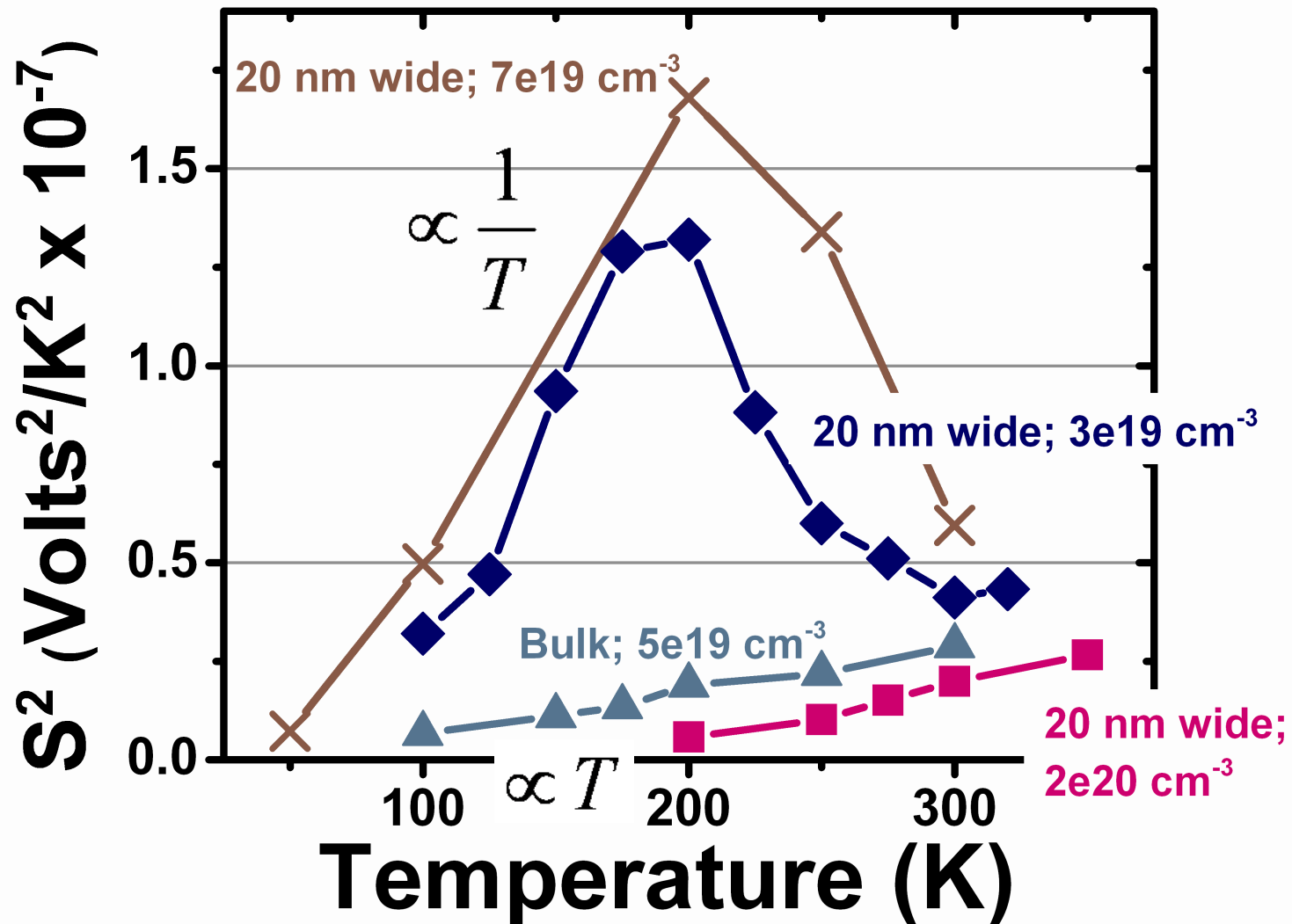
Diffuse vs Specular Scattering



Lots of Data to Minimize Error Bars

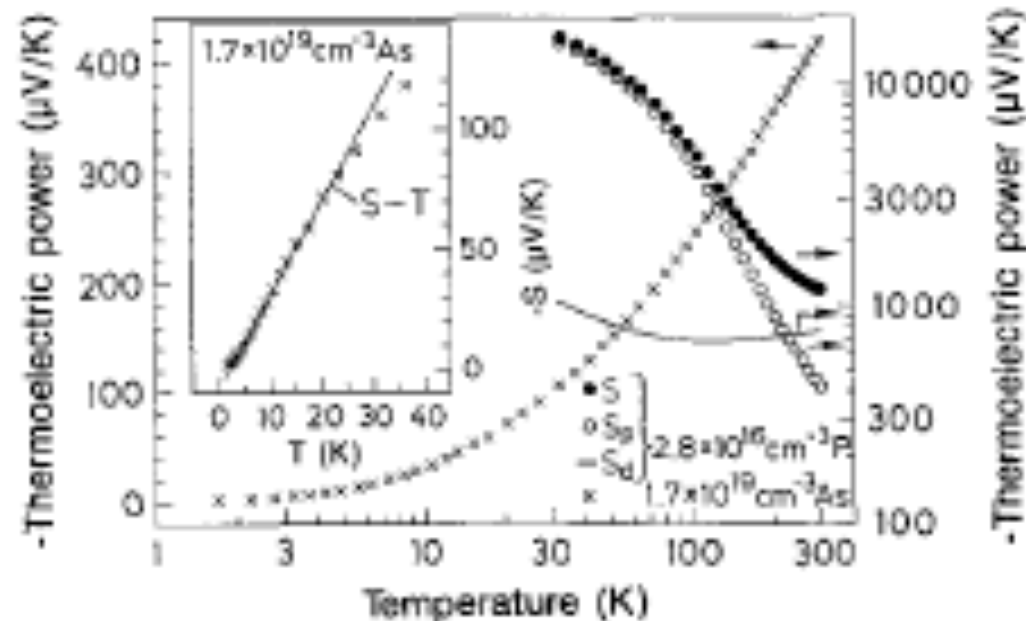


Si Nanowire Thermopower

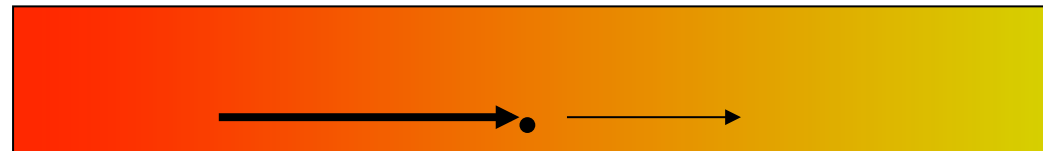


Phonon Drag

Bulk Silicon

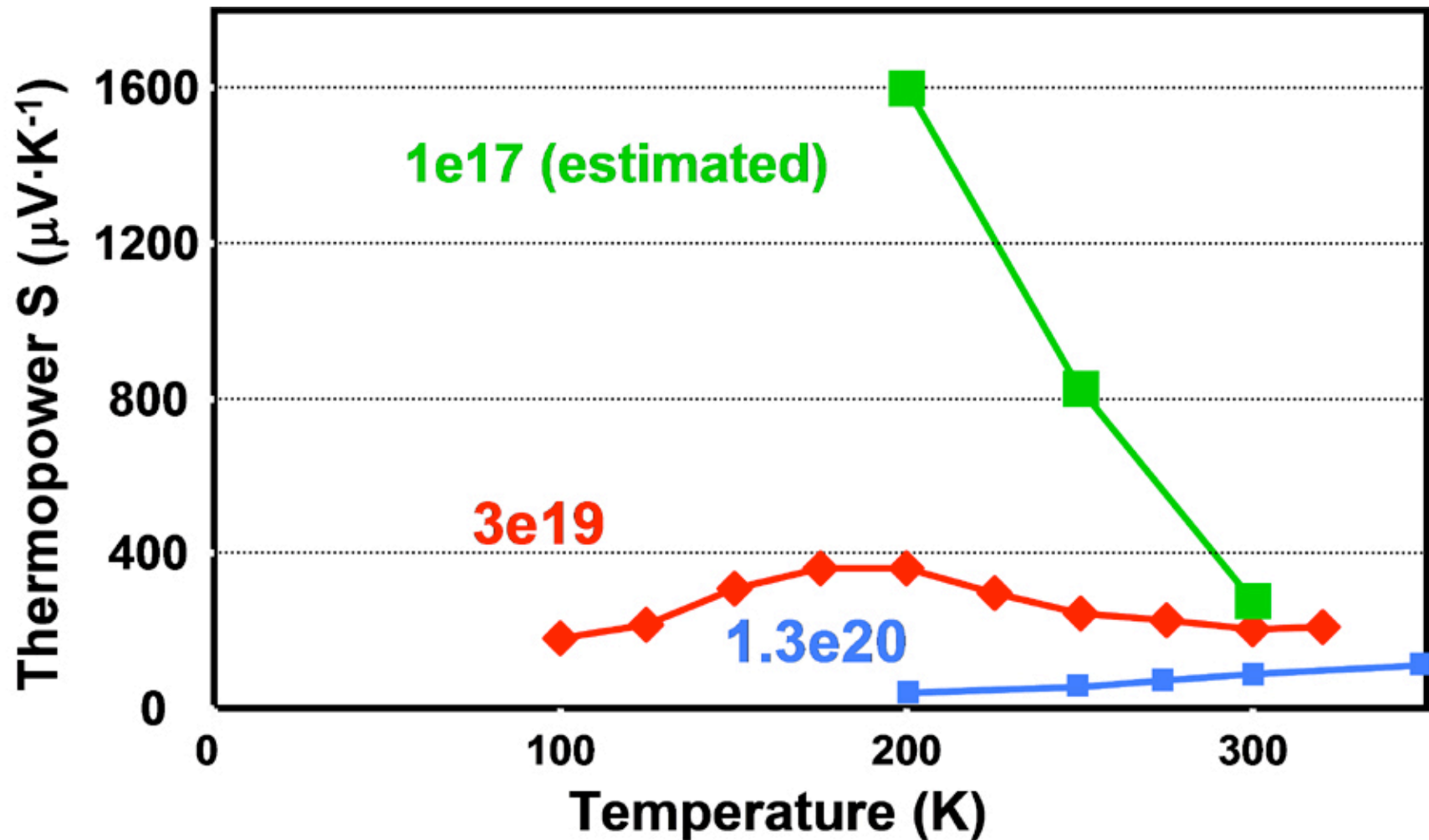


L. Weber, E. Gmelin, *Applied Physics A* 53, 136-140 (1991)

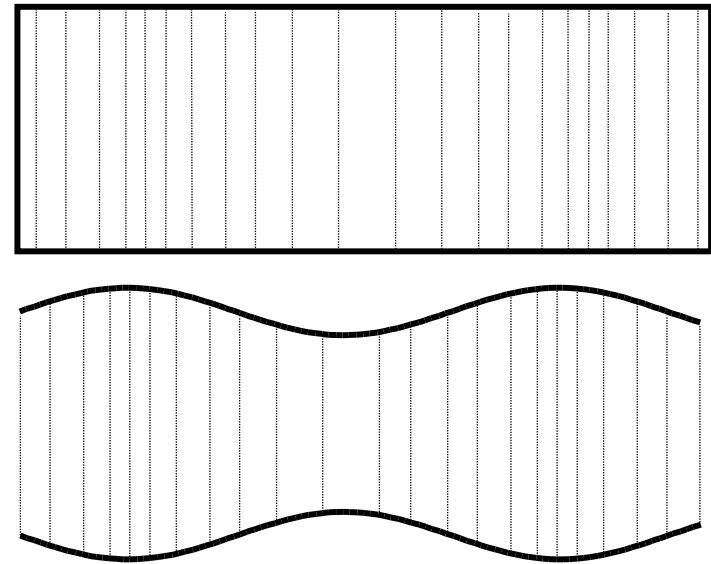
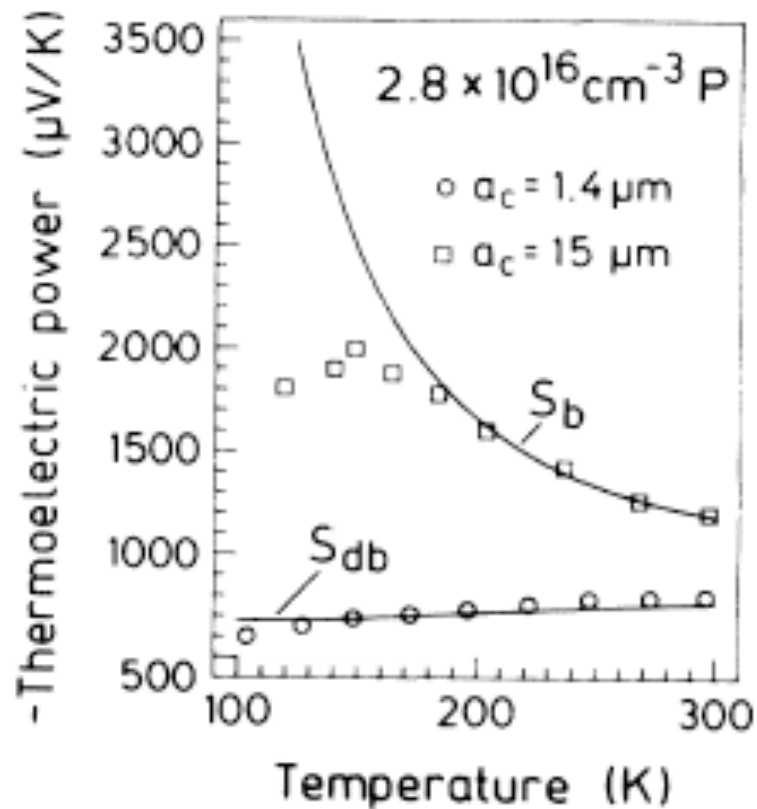


Phonons are not in equilibrium
Longitudinal modes push the electrons
down the temperature gradient

Phonon Drag in Our Si NWs



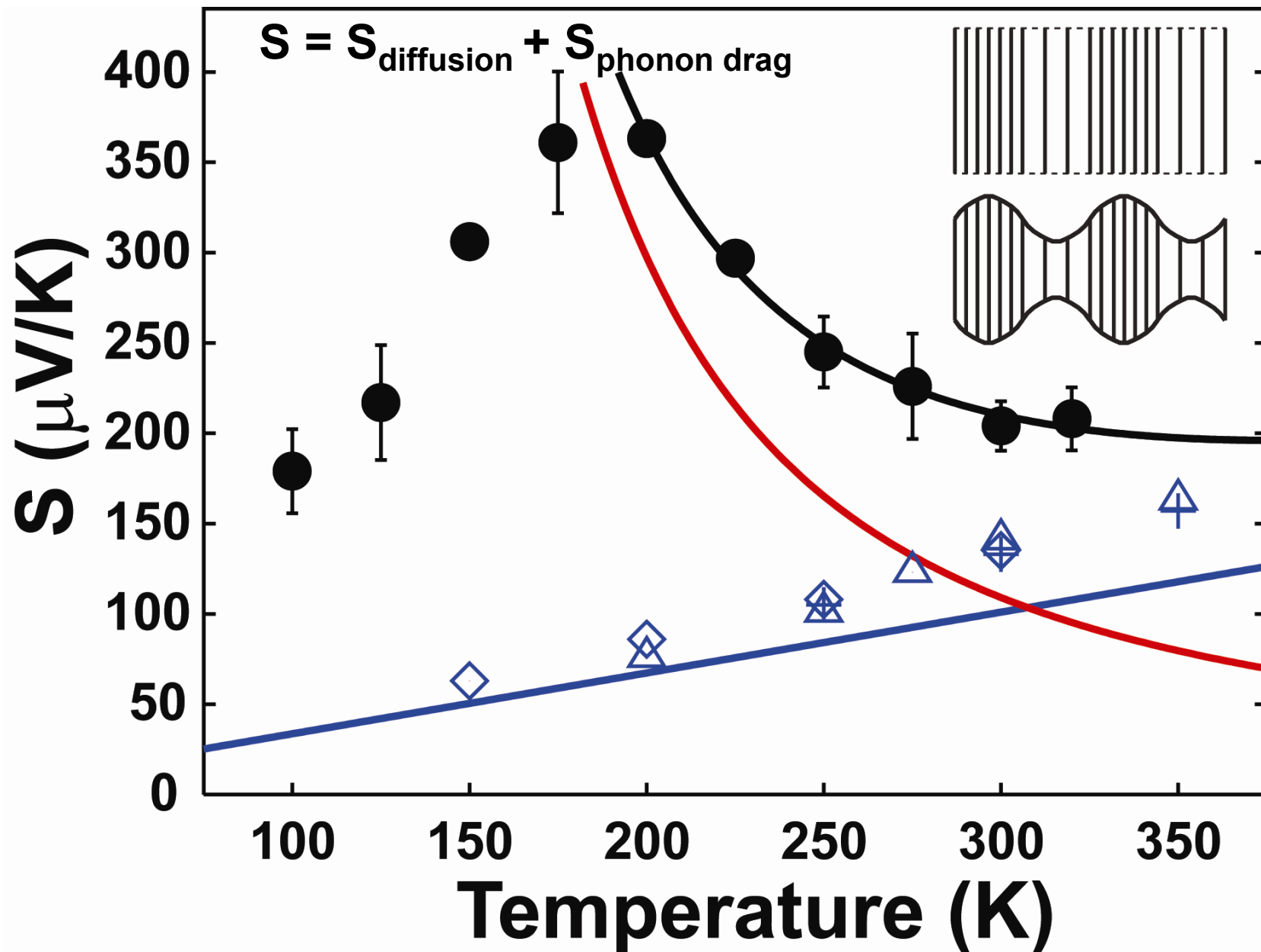
Phonon Drag is Supposed to Disappear at the Nanoscale



Thank you Jamil and Bill!

L. Weber, et al. Phys. Rev. B 46, 9511 (1992)

Phonon Drag in a 1-D System



Efficient Si Nanowires

