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NANO LUND

AT THE FOREFRONT OF NANOSCIENCE

Quantum-dot heat engines

HEINER LINKE

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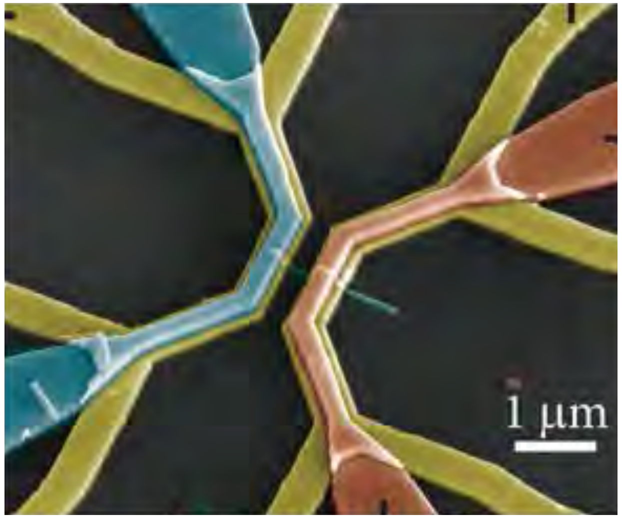
Outline

- Tutorial intro: thermoelectrics is energy filtering
- Efficiency at maximum power
- Realizing “the best thermoelectric”: quantum-dot heat engines
- Experiments: QD heat engine with > 70% of Carnot efficiency



- Application to hot-carrier solar cells

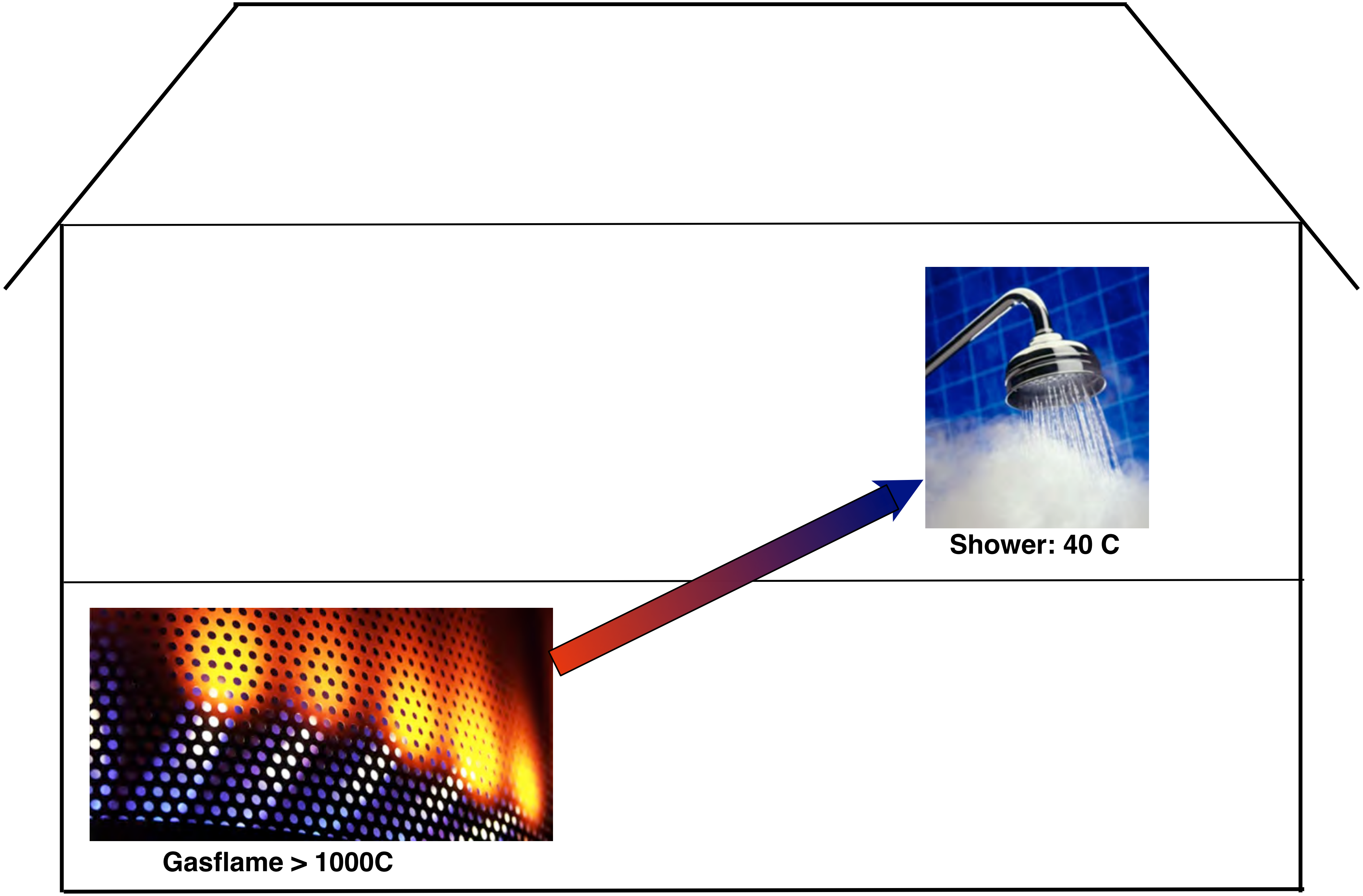
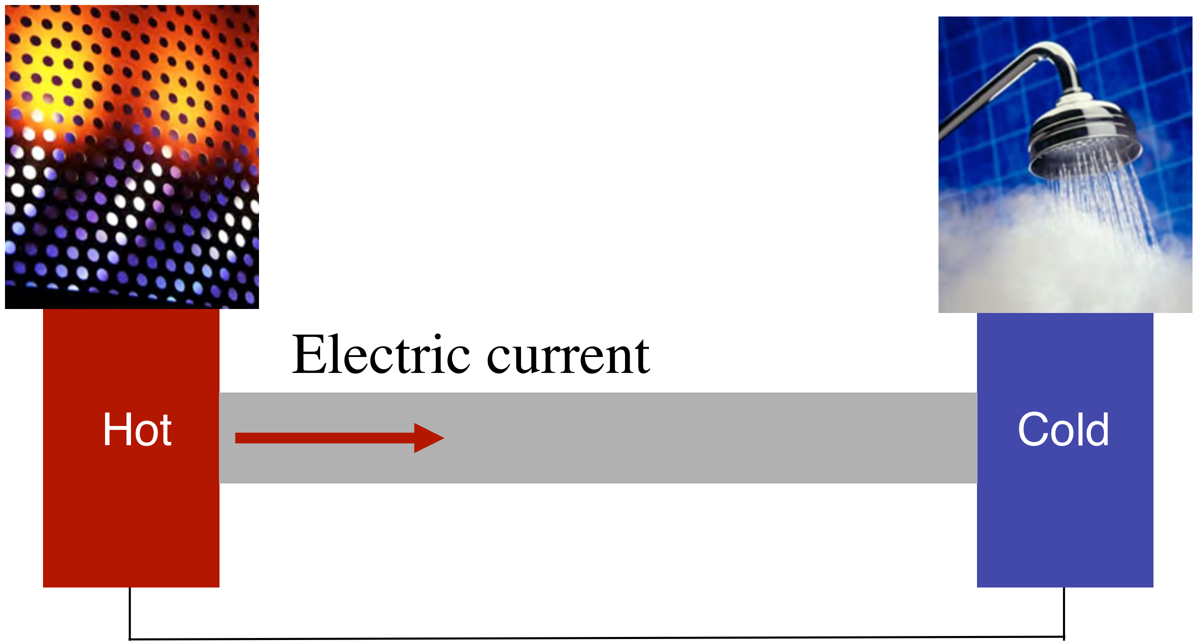
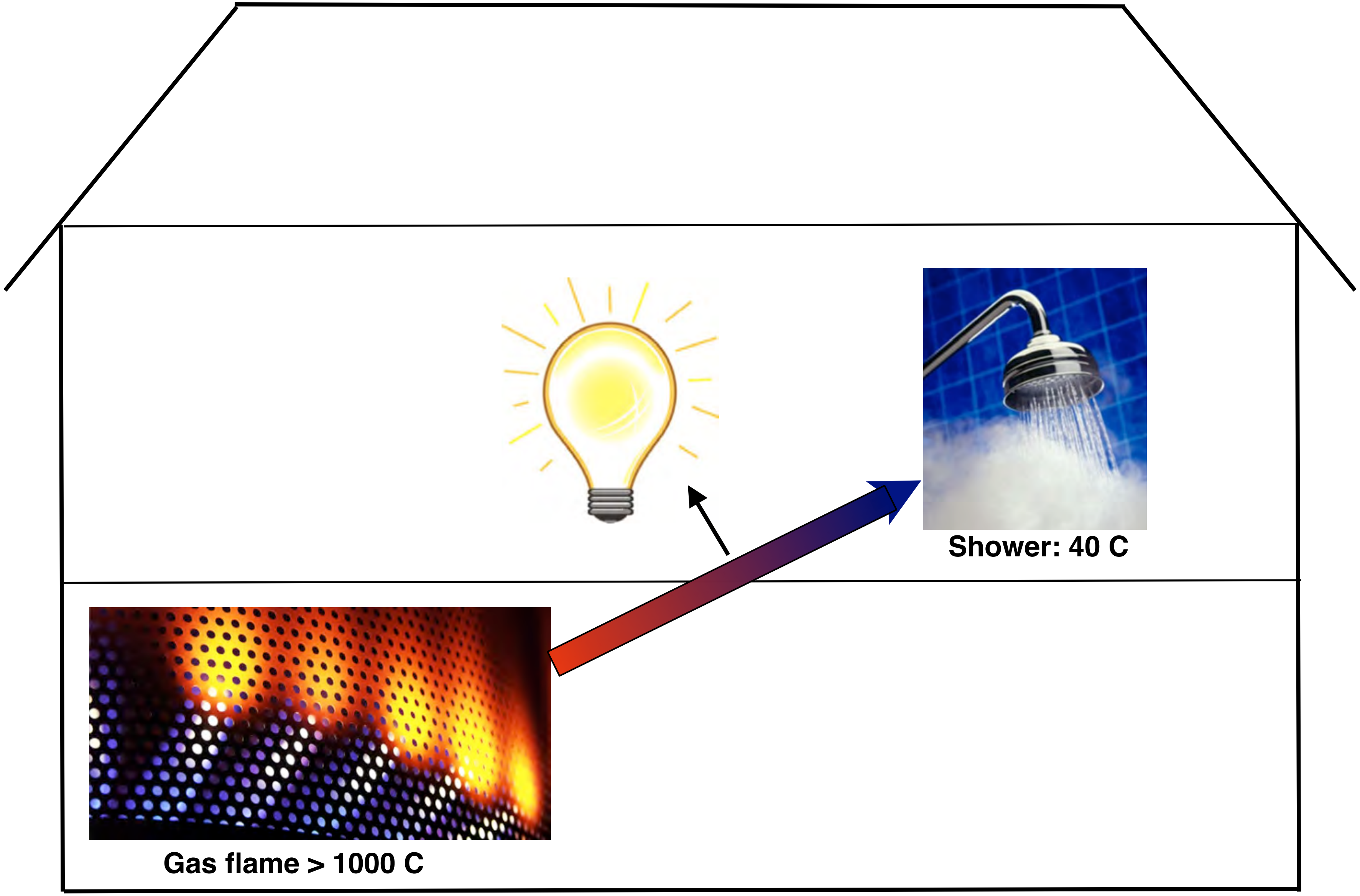


Image: homegasheaters.org

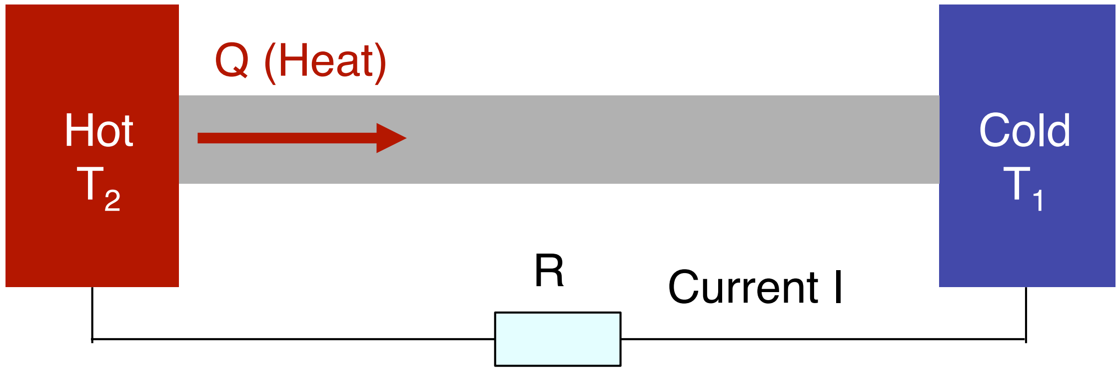
Image: naturallyhealthtips.com

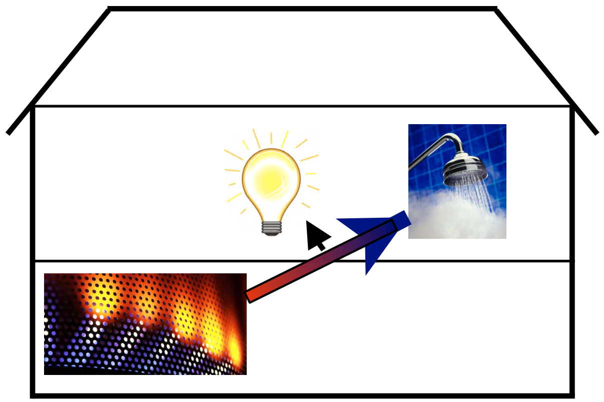
The thermoelectric effect:
Using a temperature difference to create electric current




Shower: 40 C
Gas flame > 1000 C

Thermoelectrics





- Low parasitic heat conduction by electrons (κ_{el}) and phonons (κ_{ph}).
- High Seebeck coefficient $S = \Delta V / \Delta T$
- Little Joule heating (high conductivity σ)

Figure of merit:

$$Z = \frac{S^2\sigma}{\kappa_e + \kappa_{ph}}$$

Power factor ($S^2\sigma$)

Desired is ZT > 3.
Most materials have ZT << 1. Commercial thermoelectrics have ZT ≈ 1
Record for bulk materials is ZT ≈ 2.6 (SnSe at 650 C)

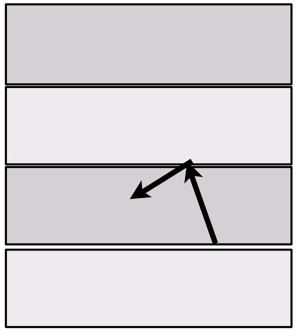
Why *nano*-thermoelectrics?

$$Z = \frac{S^2\sigma}{\kappa_e + \kappa_{ph}}$$

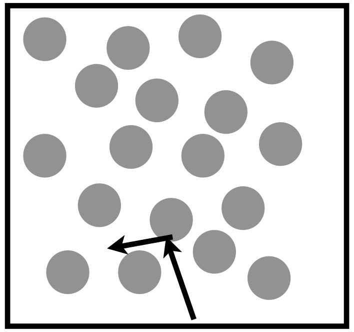
PHONONS

Phonon confinement:
Tune phonon DOS and dispersion function

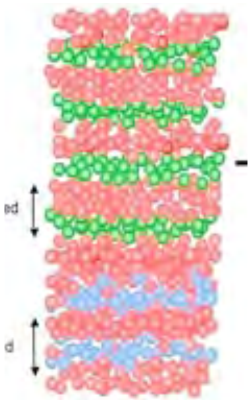
Phonons scatter off interfaces



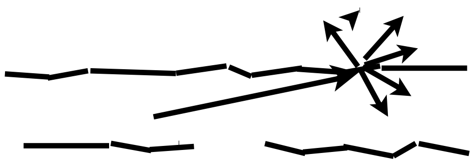
Superlattice



Nanocrystalline materials



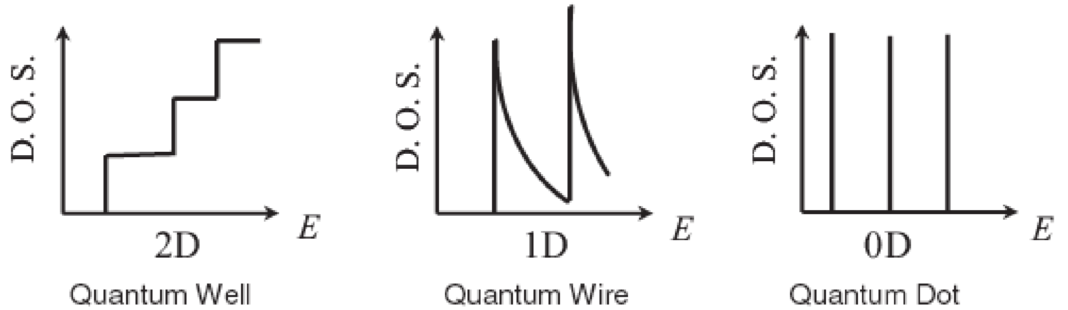
Random stacking (Johnson group)

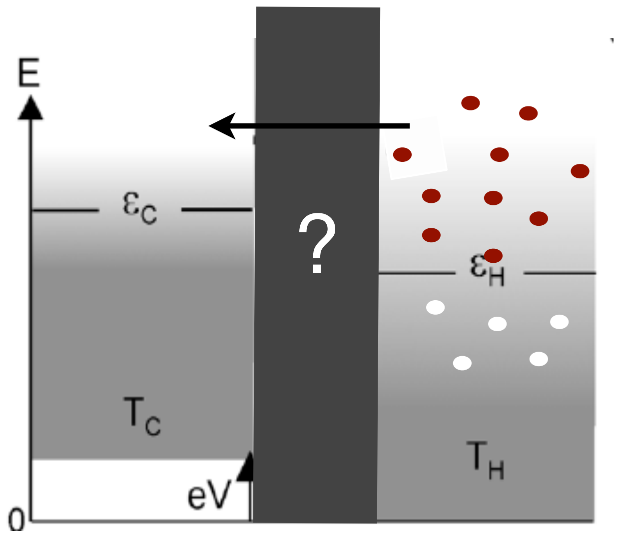


Nanowires

ELECTRONS

Electron quantum confinement:
Optimize electronic properties





Review: Dresselhaus et al, Adv. Materials **19**, 1043 (2007)

The "best thermoelectric"

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The best thermoelectric

Proc. Natl. Acad. Sci. USA
Vol. 93, pp. 7436–7439, July 1996
Applied Physical Sciences

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*Department of Physics and Astronomy, The University of Tennessee, Knoxville, TN 37996-1200; †Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6030; and ‡Instituto Balseiro, Centro Atomico Bariloche, (8400) Bariloche, Argentina

Contributed by G. D. Mahan, May 20, 1996

ABSTRACT What electronic structure provides the largest figure of merit for thermoelectric materials? To answer that question, we write the electrical conductivity, thermopower, and thermal conductivity as integrals of a single function, the transport distribution. Then we derive the mathematical function for the transport distribution, which gives the largest figure of merit. A delta-shaped transport distribution is found to maximize the thermoelectric properties. This result indicates that a narrow distribution of the energy of the electrons participating in the transport process is needed for maximum thermoelectric efficiency. Some possible realizations of this idea are discussed.

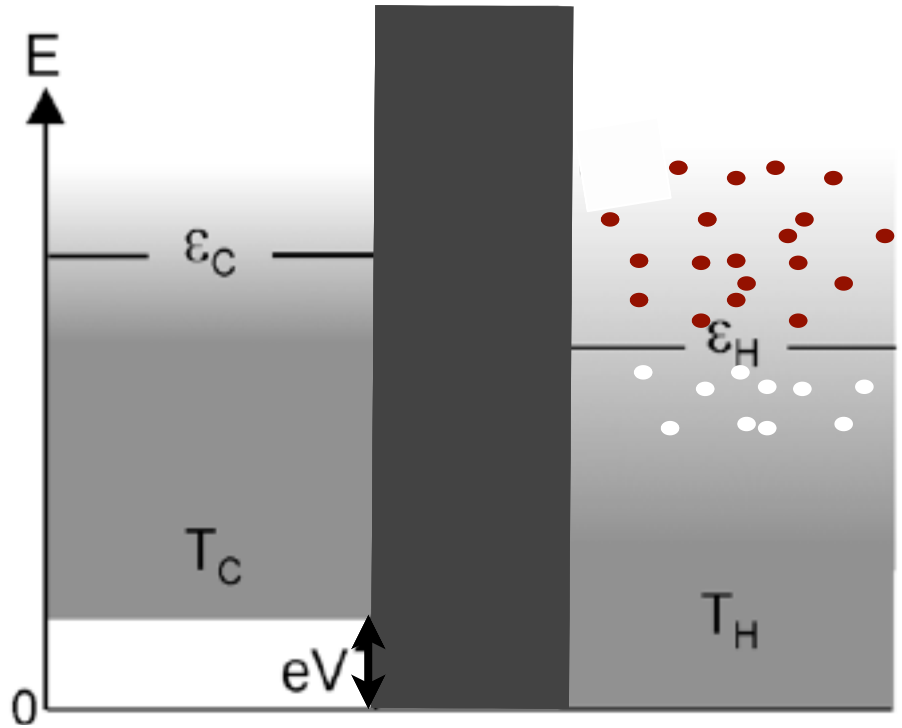
$$Z = \frac{S^2\sigma}{\kappa_e + \kappa_{ph}}$$

Figure of merit

Fundamental elements of thermoelectrics

A cold electron reservoir

A warm electron reservoir



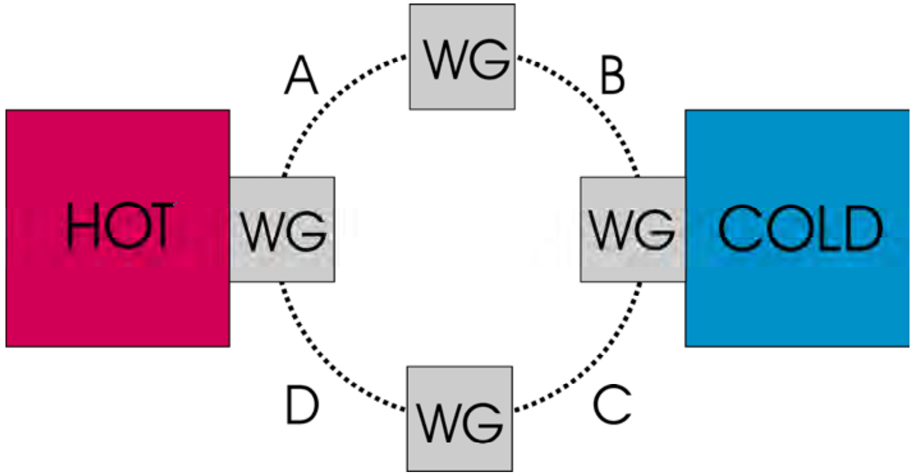
A bias voltage to do work *against.*

Energy filter

Fundamental efficiency limit of thermoelectrics?

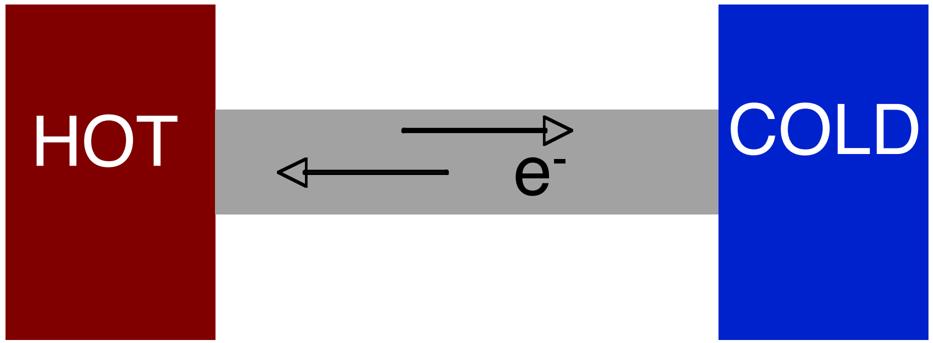
Classic, cyclic Carnot engine:
Working gas (WG) in contact with only one heat reservoir at a time.

$$\eta_C = 1 - \frac{T_C}{T_H}$$



Thermoelectric:
In contact with both reservoirs at all times.

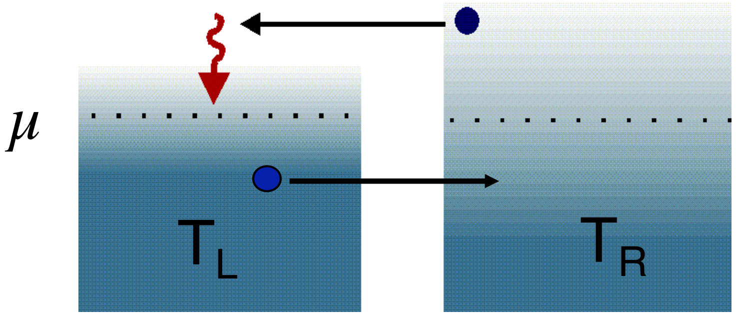
$$Z = \frac{S^2\sigma}{\kappa_e + \kappa_{ph}}$$



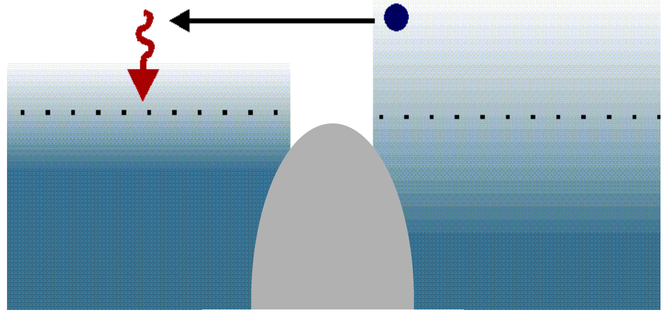
For the next few slides, S is the entropy (not Seebeck coefficient...)

$$\Delta S_L = \frac{\varepsilon - \mu}{T_L} \qquad \Delta S_R = -\frac{\varepsilon - \mu}{T_R}$$

$T_L < T_R$



$$\Delta S = \Delta S_L + \Delta S_R$$
$$= (\varepsilon - \mu)\left(\frac{1}{T_L} - \frac{1}{T_R}\right)$$

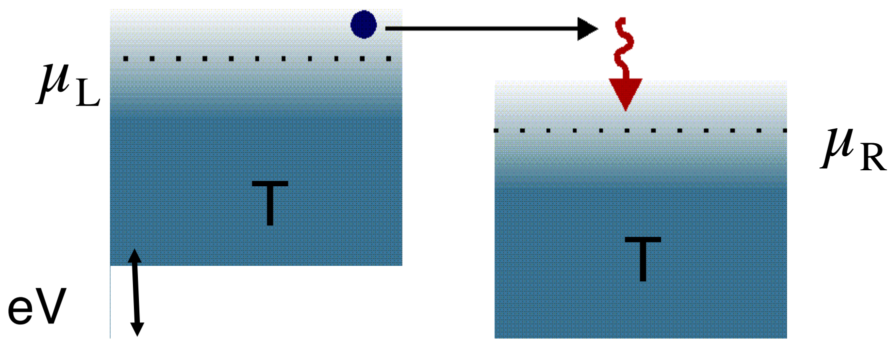


Thermovoltage!
(Seebeck effect)

Using a quantum point contact:
Molenkamp et al., PRL 65, 1052 (1990)

$$\Delta S = \frac{\Delta Q}{T} \qquad \Delta Q = \varepsilon - \mu$$

$$\Delta S_L = -\frac{\varepsilon - \mu_L}{T} \qquad \Delta S_R = \frac{+(\varepsilon - \mu_R)}{T}$$

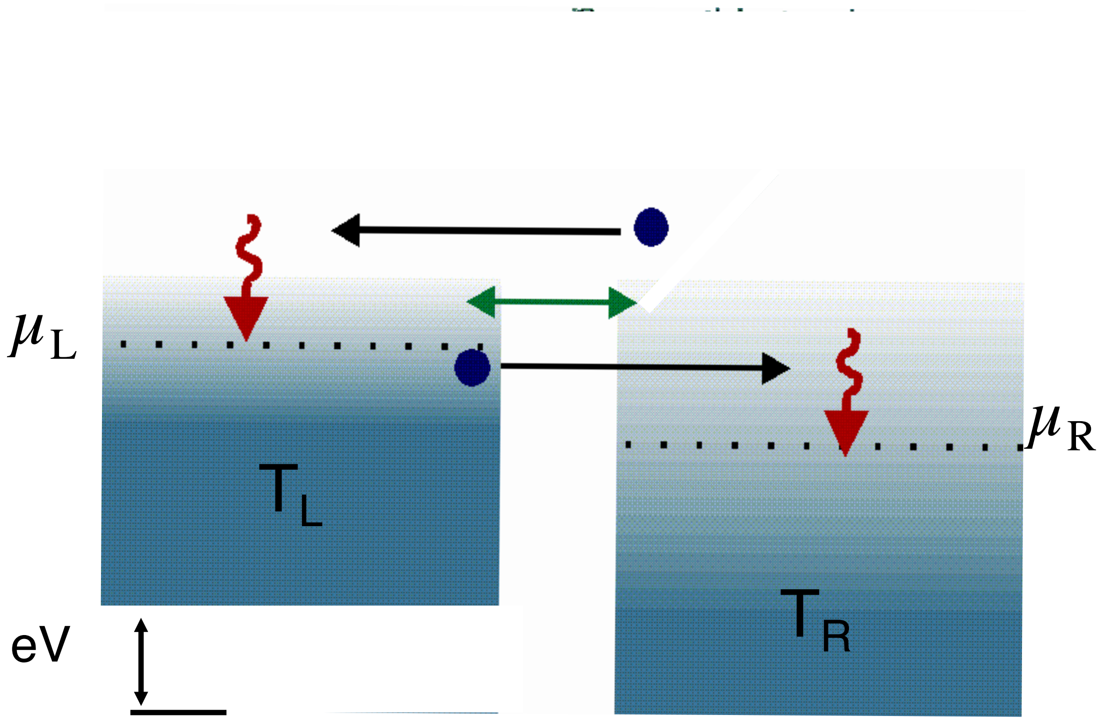


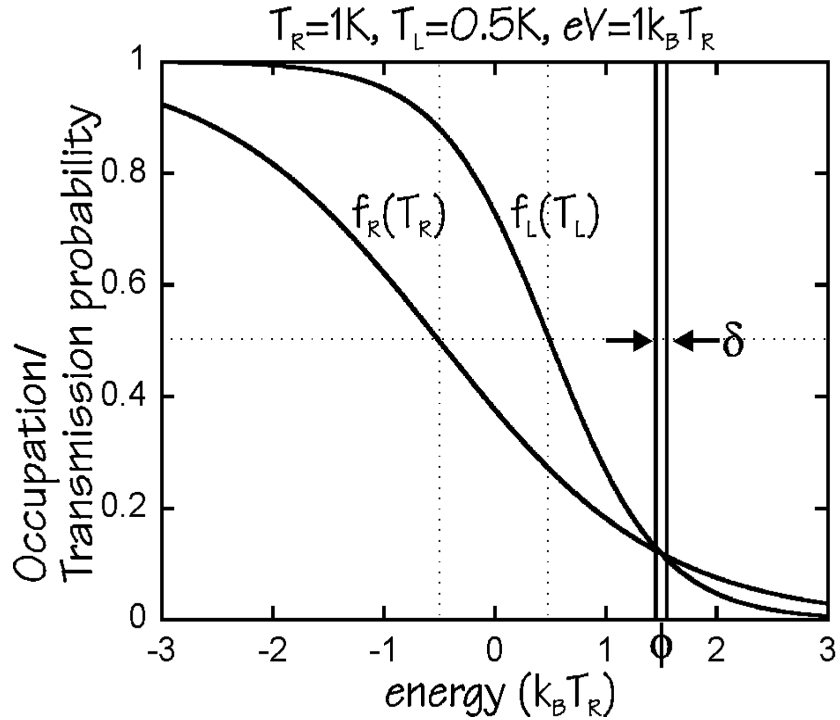
$$\Delta S = \Delta S_R + \Delta S_L = \frac{\mu_L - \mu_R}{T} = \frac{eV}{T}$$

Driven electrical current is accompanied by dissipation of kinetic energy: $\mathbf{P_{el} = I\ V}$

...accompanied by an increase of the system entropy.

Reversible electron transfer





Transfer of one electron at energy ε from L to R:

$$\Delta S = \frac{-(\varepsilon - \mu_L)}{T_L} + \frac{(\varepsilon - \mu_R)}{T_R}$$

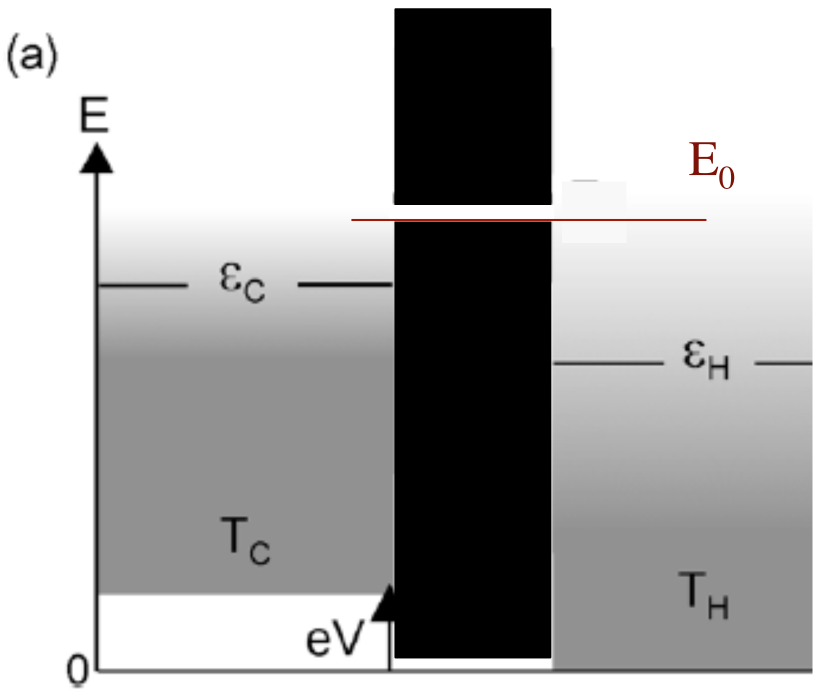
$$\Delta S = 0 \quad for \quad \varepsilon = \left(\frac{\mu_L T_R + \mu_R T_L}{T_R - T_L} \pm \right)$$

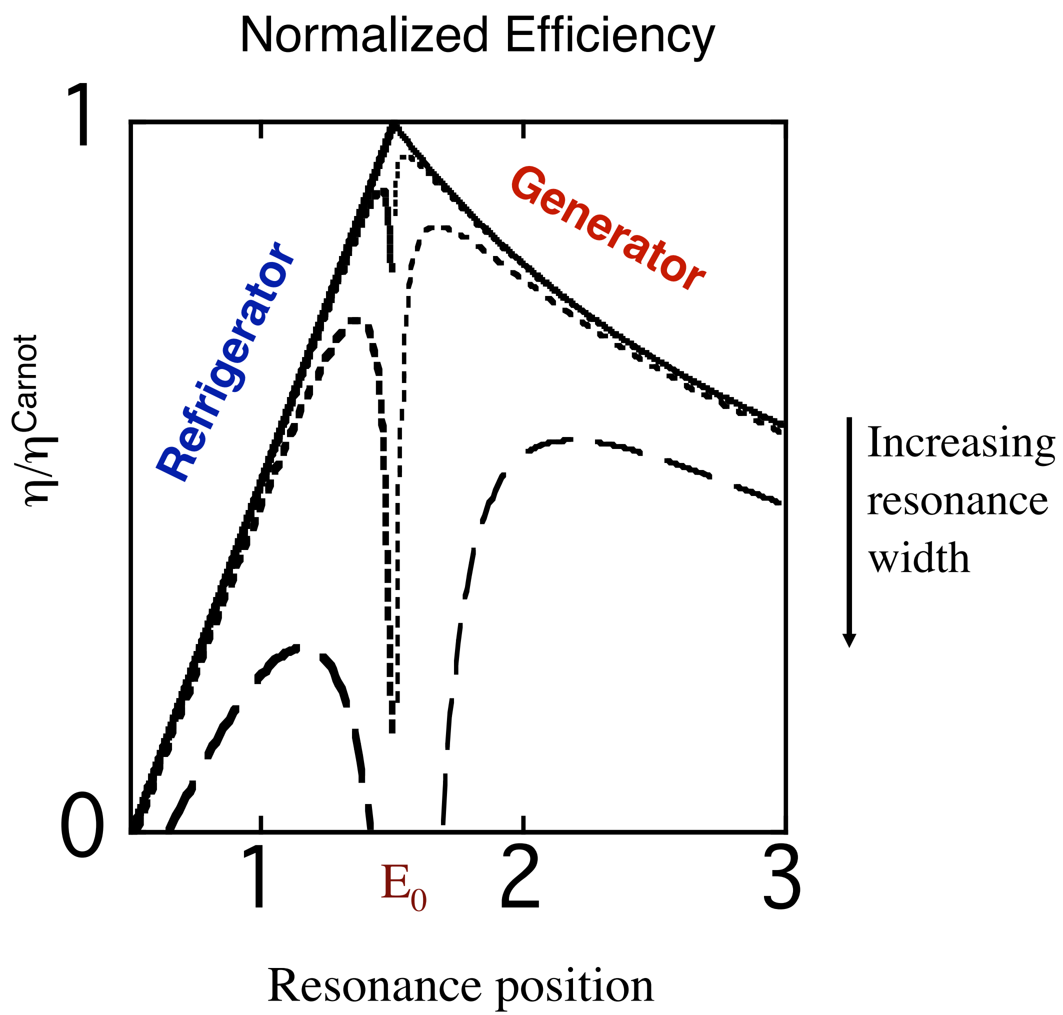
"Energy-specific equilibrium"

T. E. Humphrey and H. Linke, PRL **89,** 116801 (2002)

T. E. Humphrey, H Linke, PRL **94**, 096601 (2005)

Power generation or Refrigeration with tunable efficiency and power





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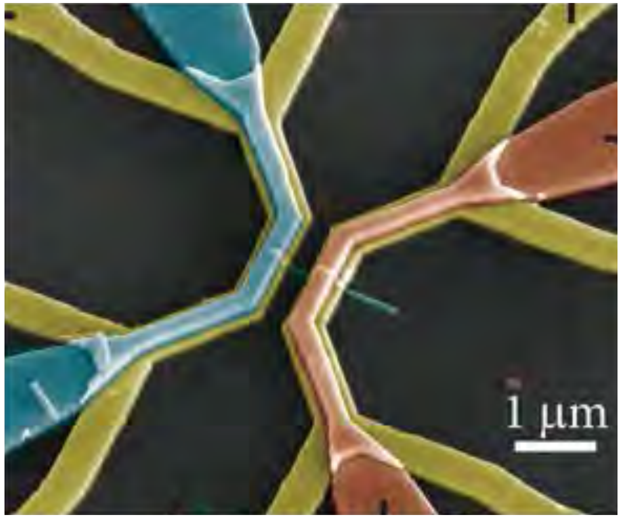


- Outlook: application to hot-carrier solar cells

Efficiency at maximum power: Curzon-Ahlborn efficiency

$$\eta_c = 1 - T_c / T_h$$

Carnot efficiency requires reversible operation, which is equivalent to zero power output.

$$\eta_{CA} = 1 - \sqrt{T_c / T_h}$$

Curzon-Ahlborn efficiency describes the efficiency of an ideal Carnot engine operated at maximum power (neglecting dissipation in reservoirs)

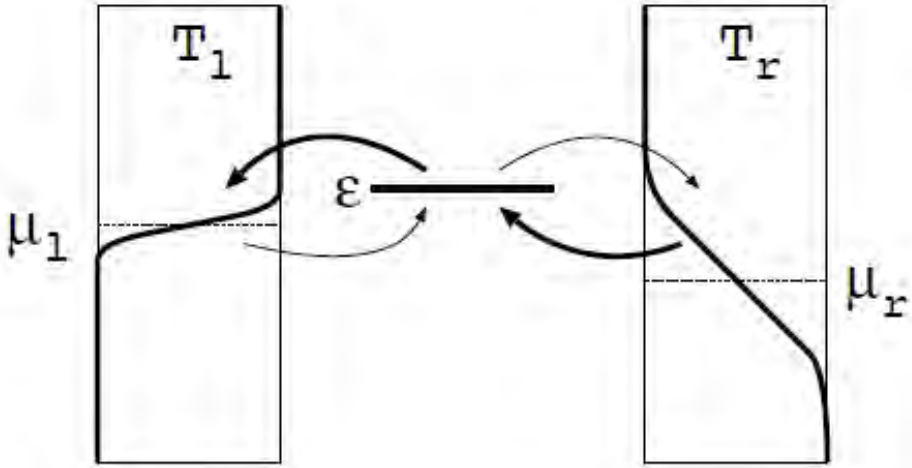
$$\eta_{CA} = 1 - \sqrt{T_c / T_h} = \eta_c / 2 + \eta_c^2 / 8 + \cdots$$

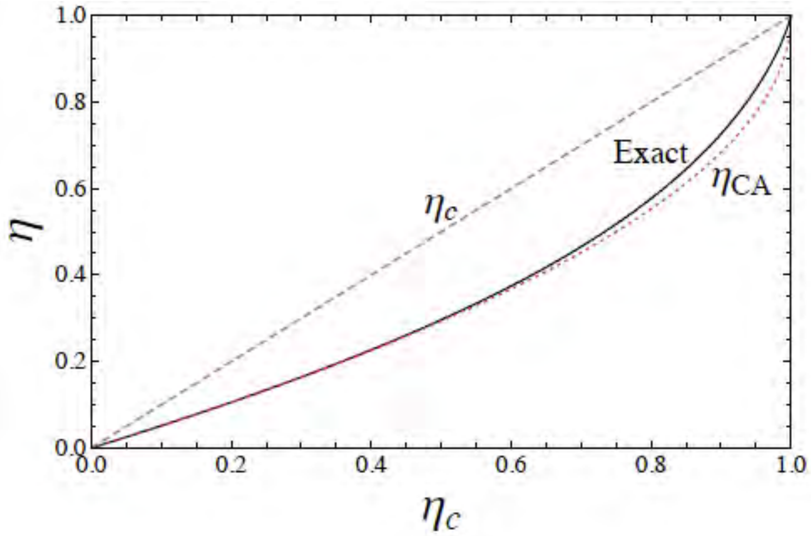
F. Curzon and B. Ahlborn, Am. J. Phys. **43**, 22 1975.

Thermoelectric efficiency at maximum power in a quantum dot

Massimiliano Esposito* and Katja Lindenberg
Department of Chemistry and Biochemistry and Institute for Nonlinear Science, University of California, San Diego, La Jolla, CA 92093-0340, USA

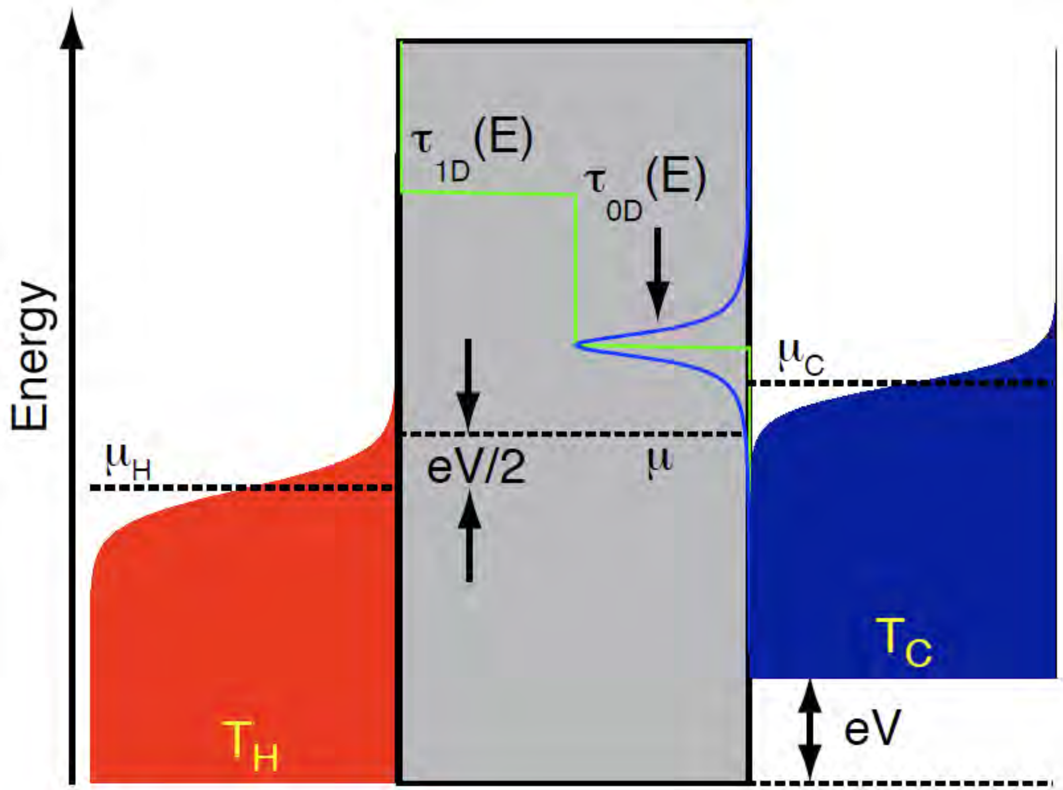
Christian Van den Broeck
Hasselt University, B-3590 Diepenbeek, Belgium





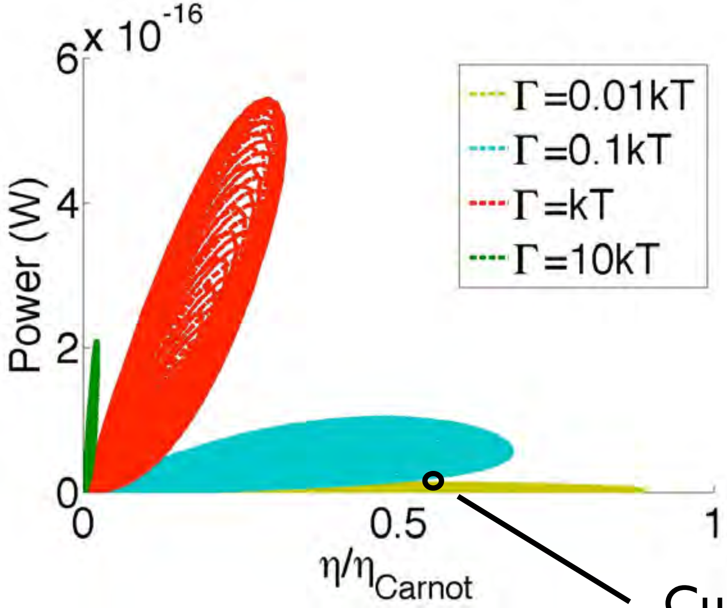
$$\eta = \frac{\eta_c}{2} + \frac{\eta_c^2}{8} + \frac{[7 + \text{csch}^2(a_0/2)]}{96}\eta_c^3 + \mathcal{O}(\eta_c^4)$$

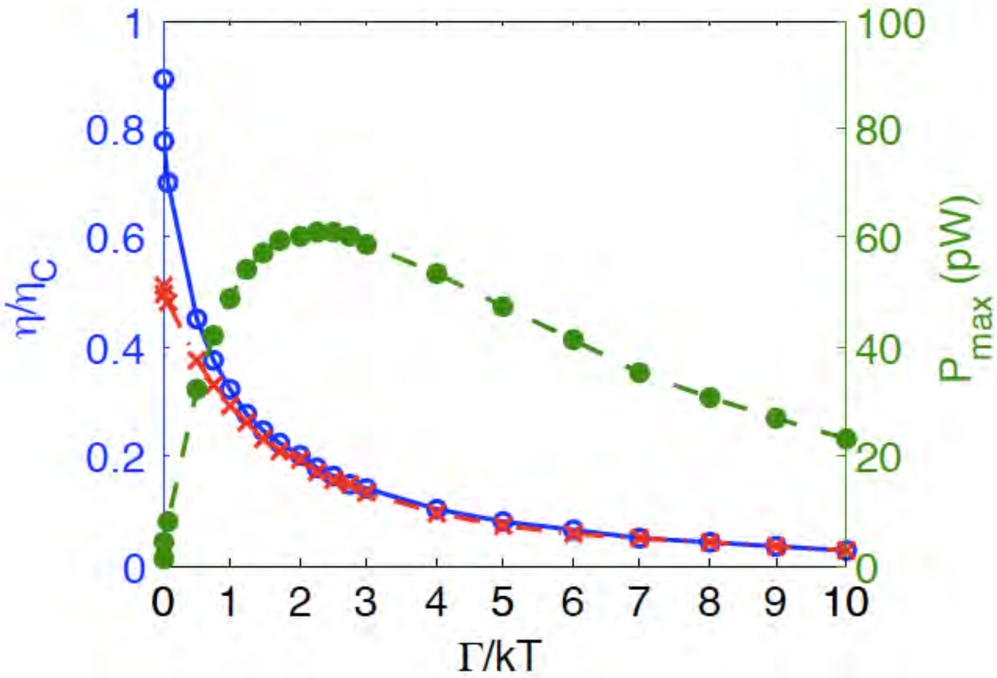
Esposito, Lindenberg, van den Broeck, PRL **102**, 130602 (2009)



Energy
$\tau_{1D}(E)$
$\tau_{0D}(E)$
μ_H
eV/2
μ
μ_C
T_C
T_H
eV

Quantum dots





Curzon-Ahlborn value: 51.1%

- Carnot efficiency obtained when transmission resonance becomes delta-function like.
- In this limit, efficiency at "maximum" power is $\eta_C/2 + \eta_C^2/8$ = 51. 1%
- Increasing transmission width increases power at reduced efficiency.

N. Nakpathomkun, H. Xu, H. Linke
Phys. Rev. B **82**, 235428 (2010)

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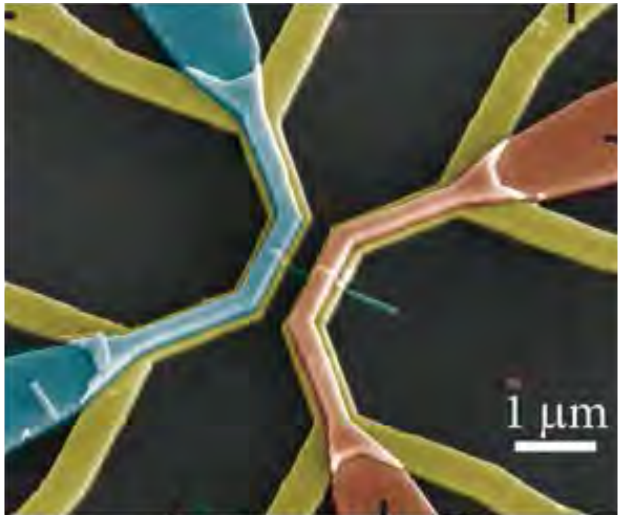
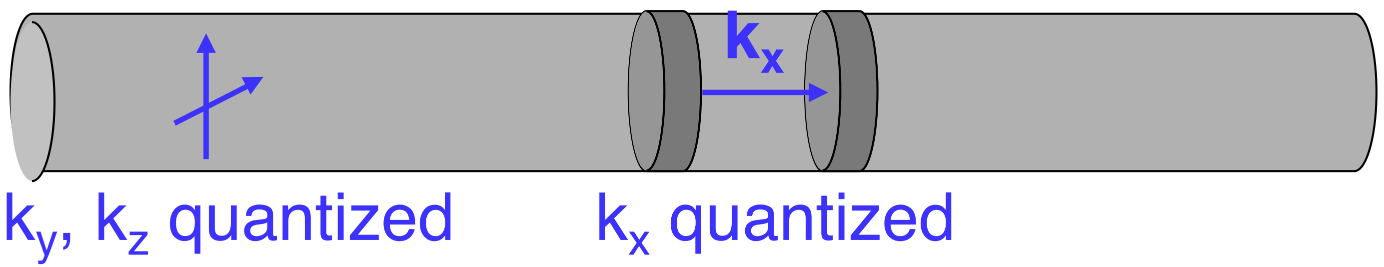
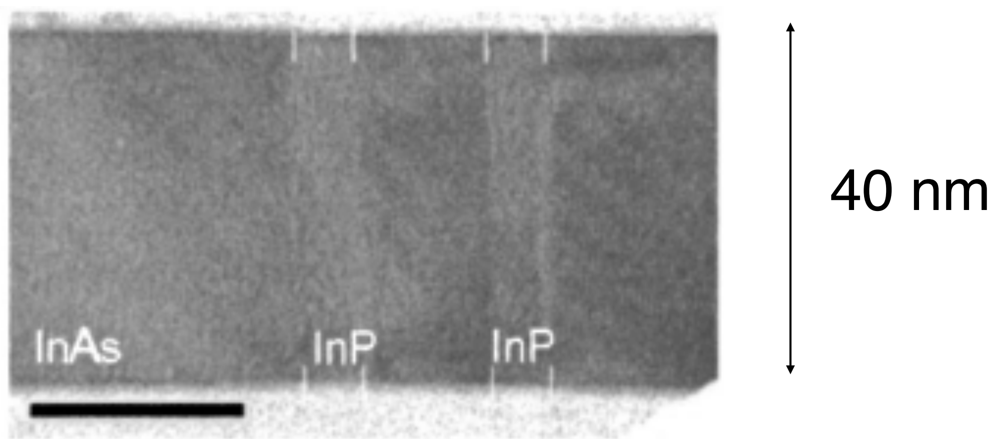


- Application to hot-carrier solar cells

Energy-filtering using nanowires

1D - 0D -1D resonant tunneling in a heterostructure nanowire.

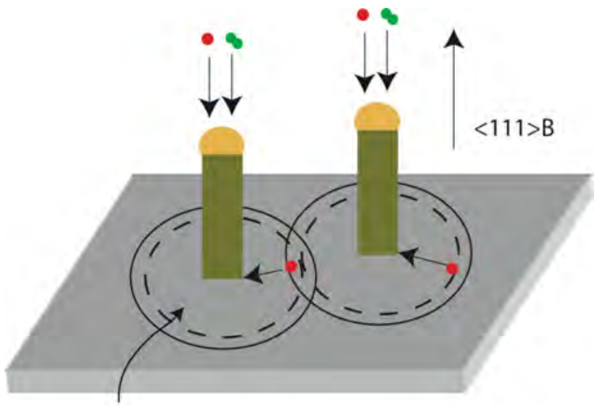




Björk *et al.*

Appl. Phys. Lett., Vol. 81, No. 23, 2 December 2002

Epitaxially grown nanowires, e.g. InAs/InP

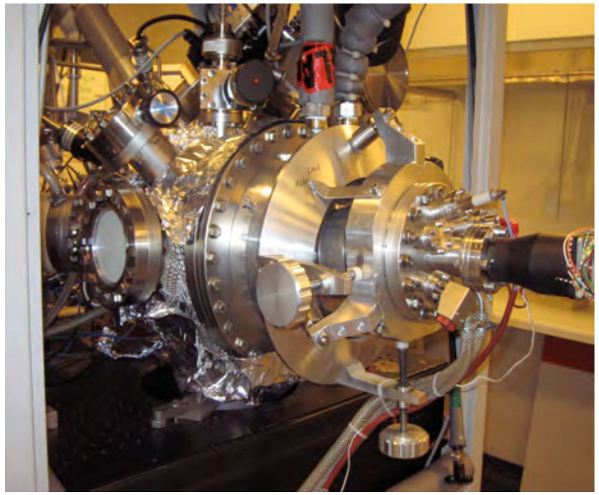


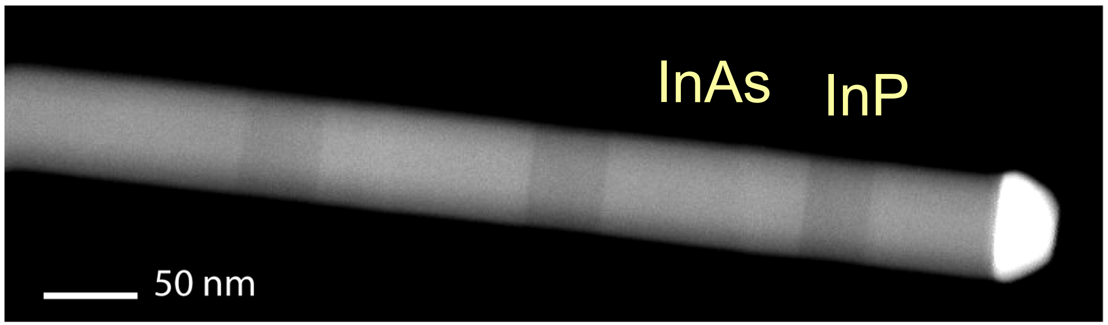
TBAs (group-V)

TMIn (group-III)

Substrate surface
InAs (111)B

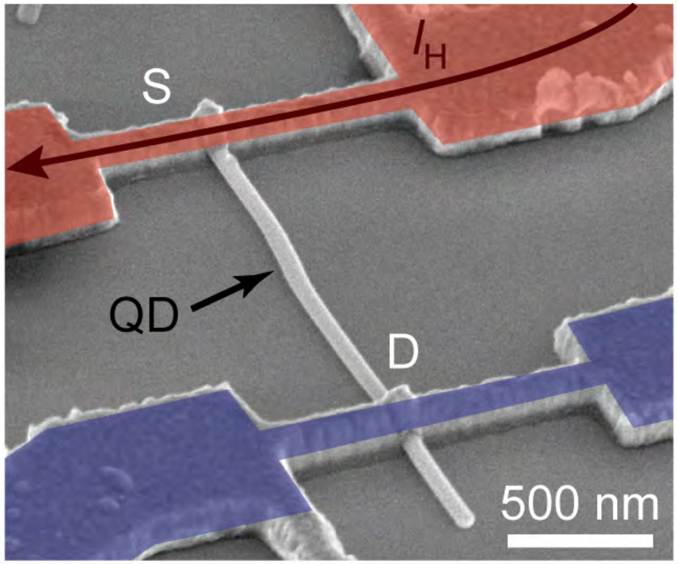
CBE

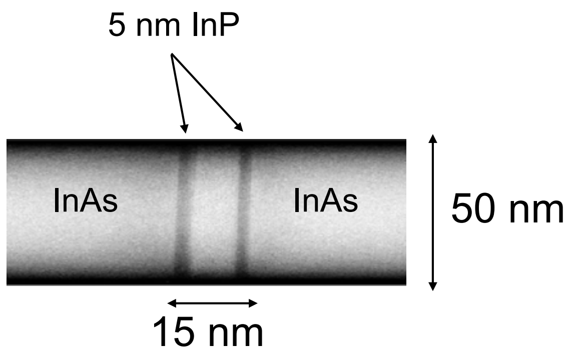




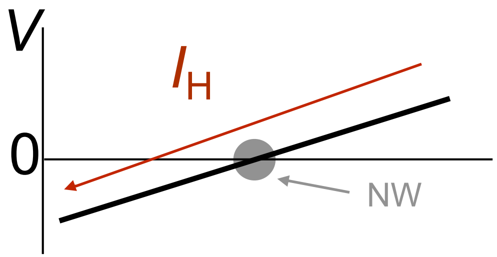
Ann Persson, Linus Fröberg

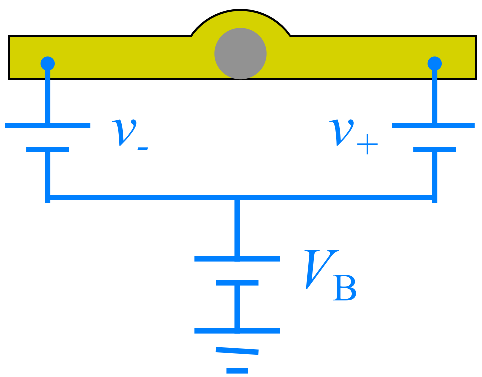
Device

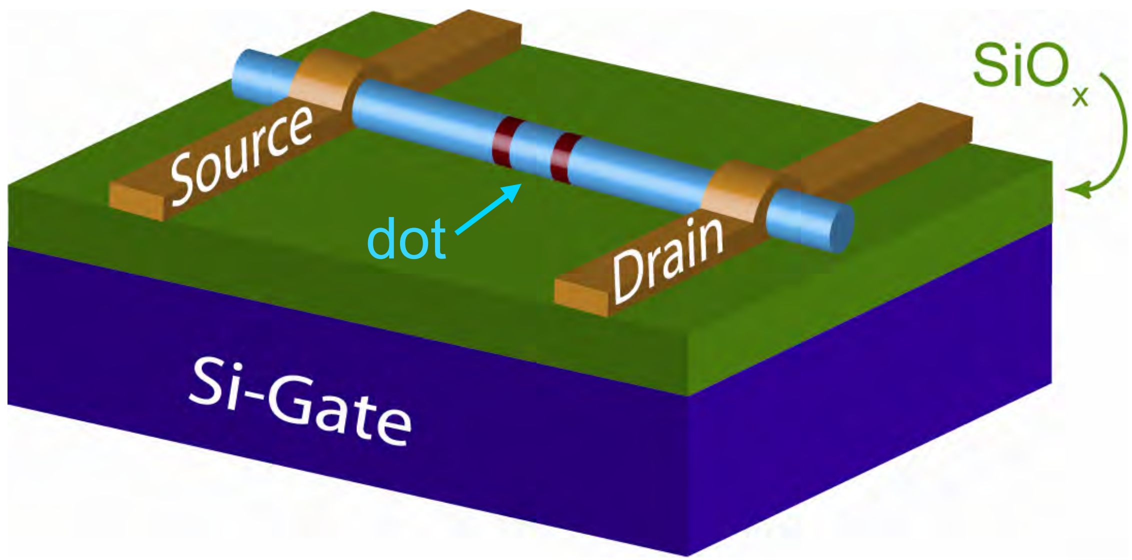




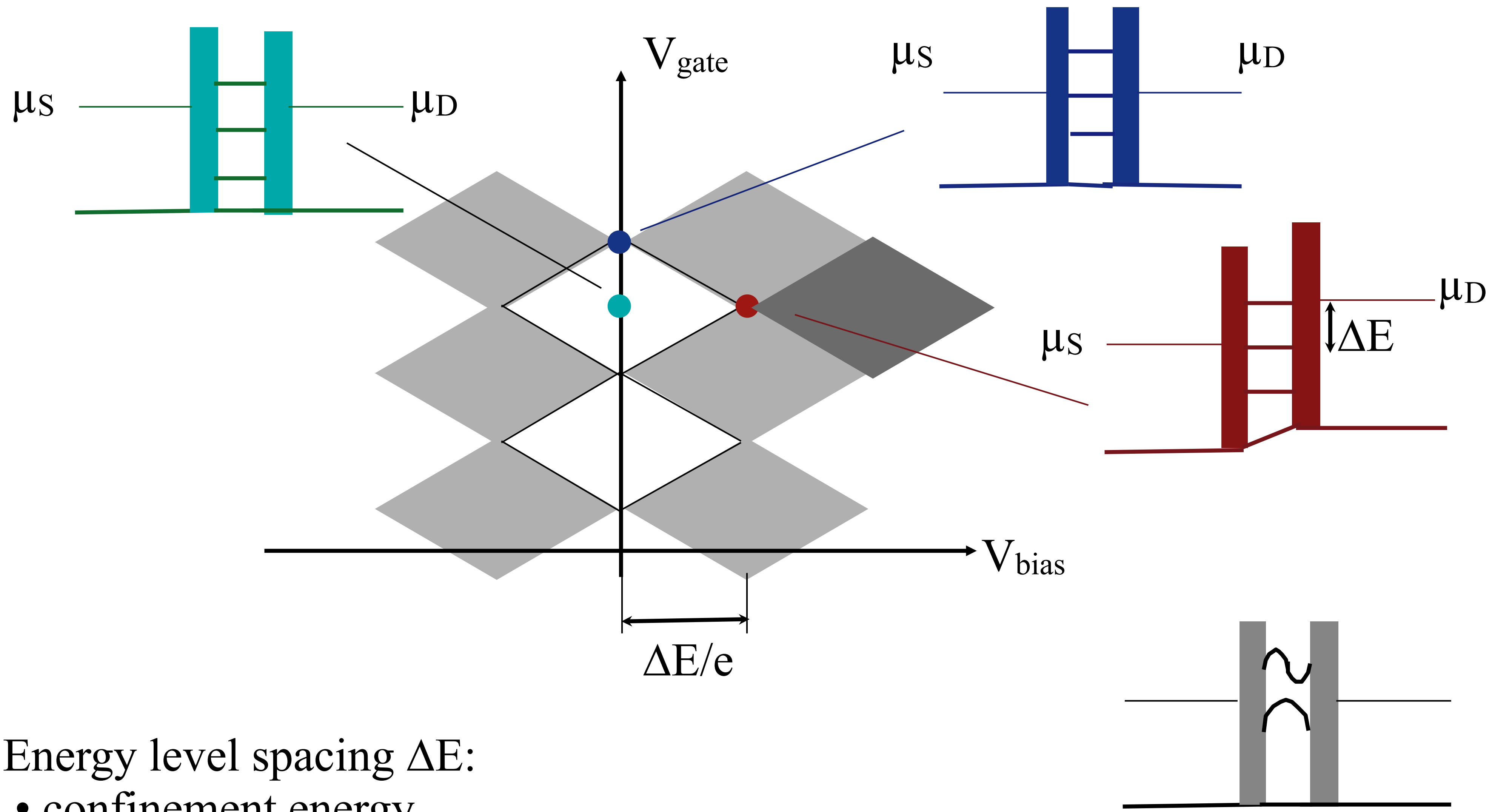
T = 250 mK to 10 K





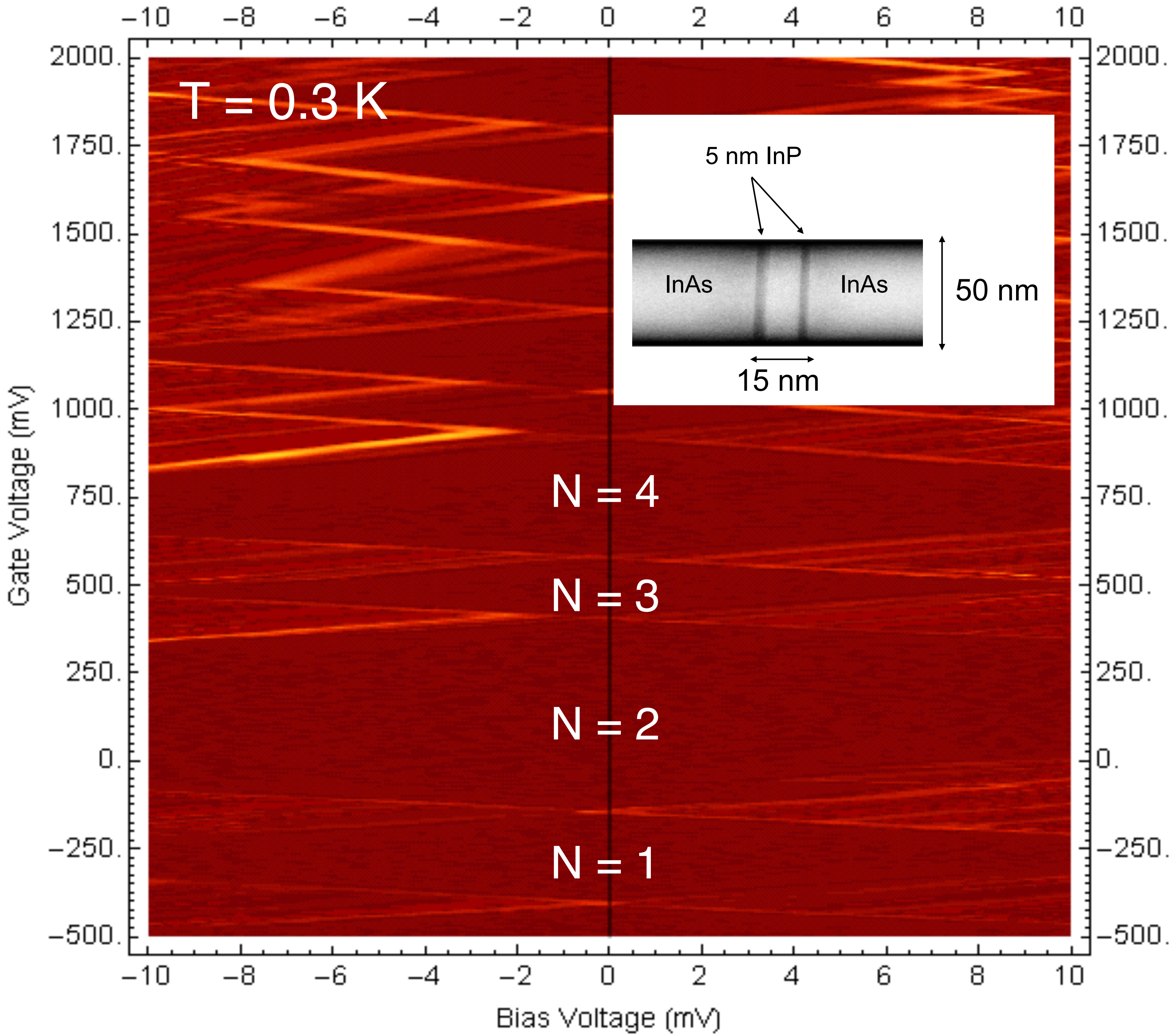


Quantum dot energy level spectroscopy



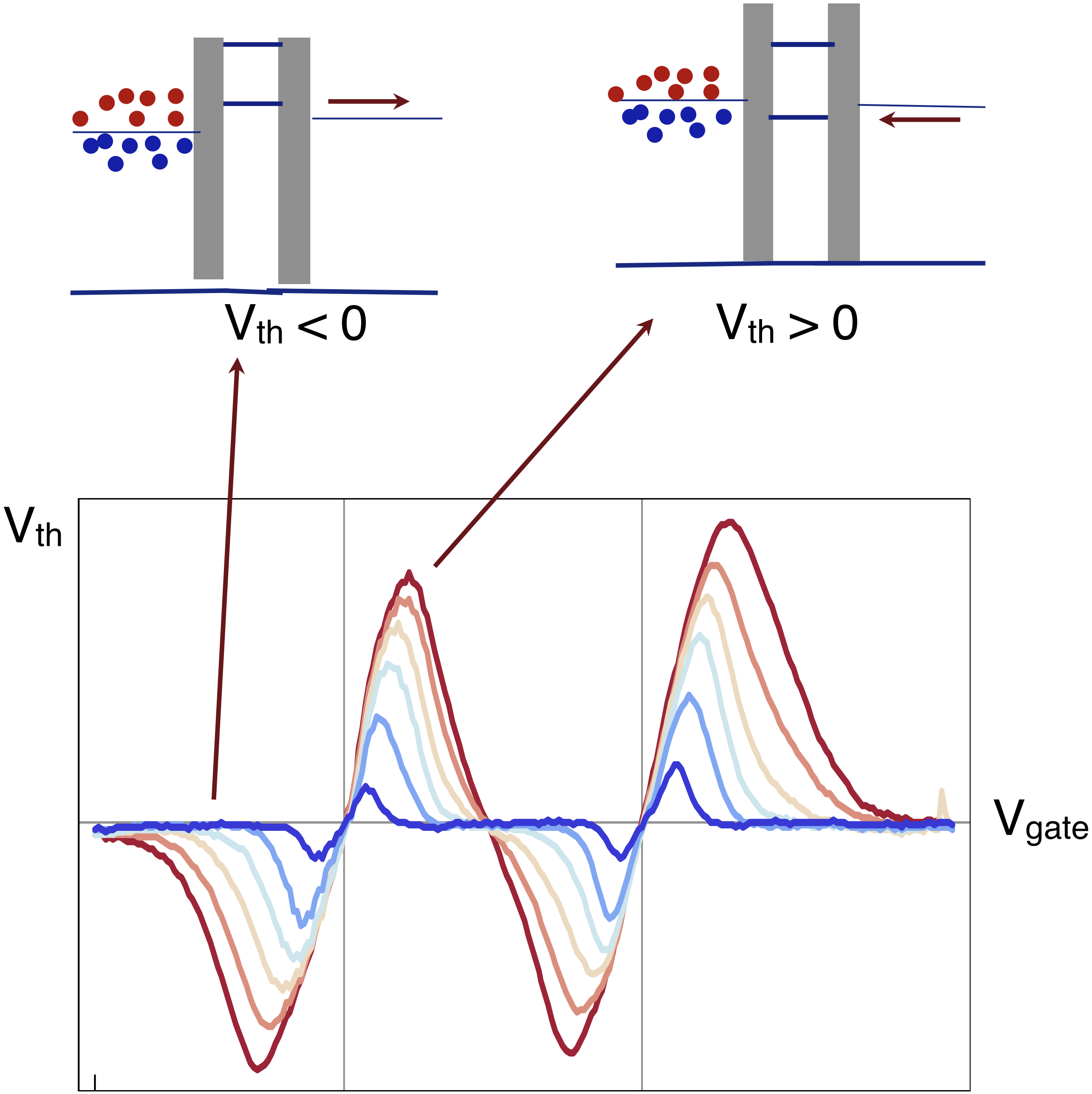
Energy level spacing ΔE:

- confinement energy
- single electron charging energy $e^2/2C$

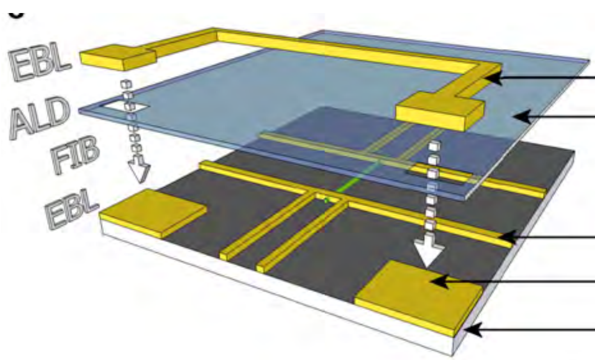


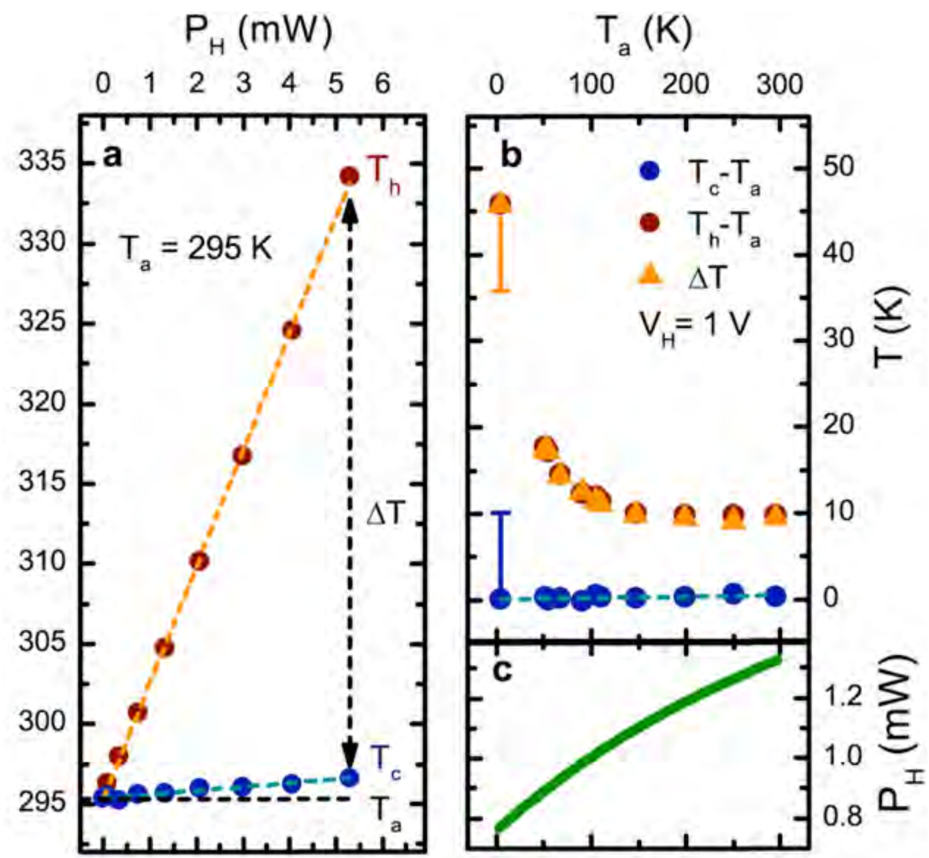
Eric Hoffmann

Thermovoltage data



Top-heaters to enable high ΔT with minimal heating

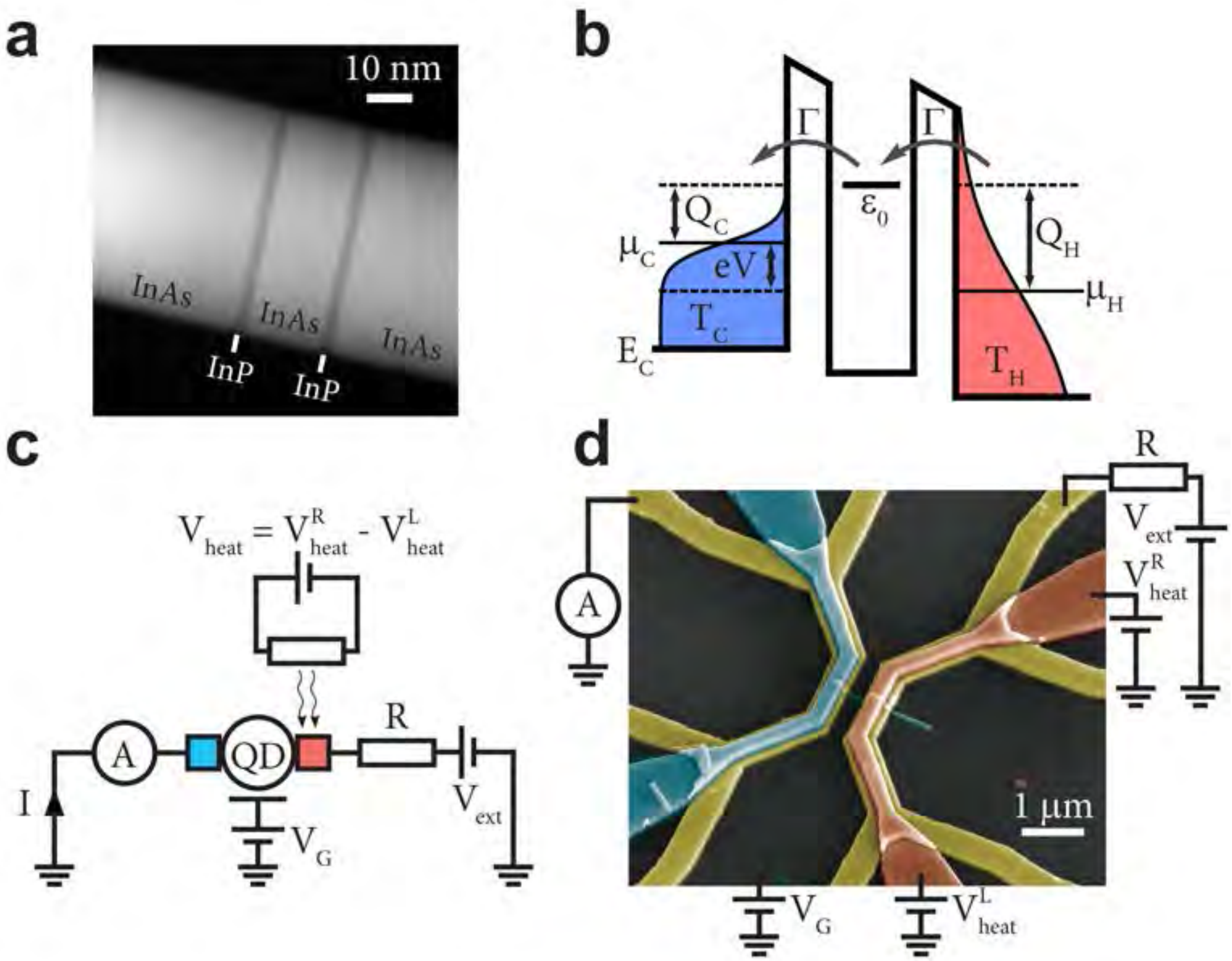




J. Gluschke et al

Nanotechnology **25**, 385704 (2014)

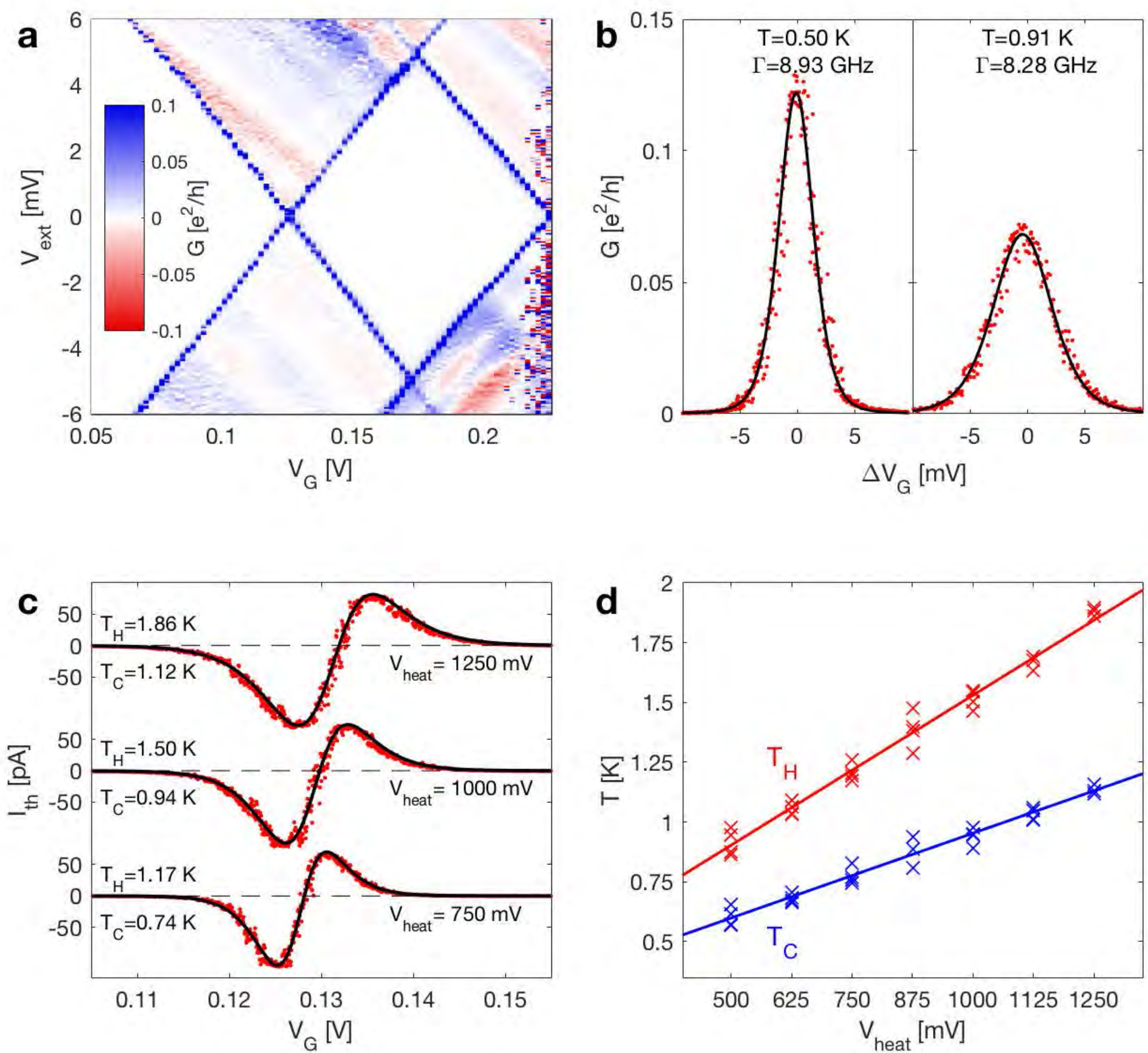
Quantum-dot heat engine: device



Artis Svilans

A. Svilans,
M. Josefsson,
M. Leijnse, et al.
arXiv:1710.00742

Quantum-dot heat engine: characterisation



Artis Svilans

Martin Josefsson

A. Svilans,
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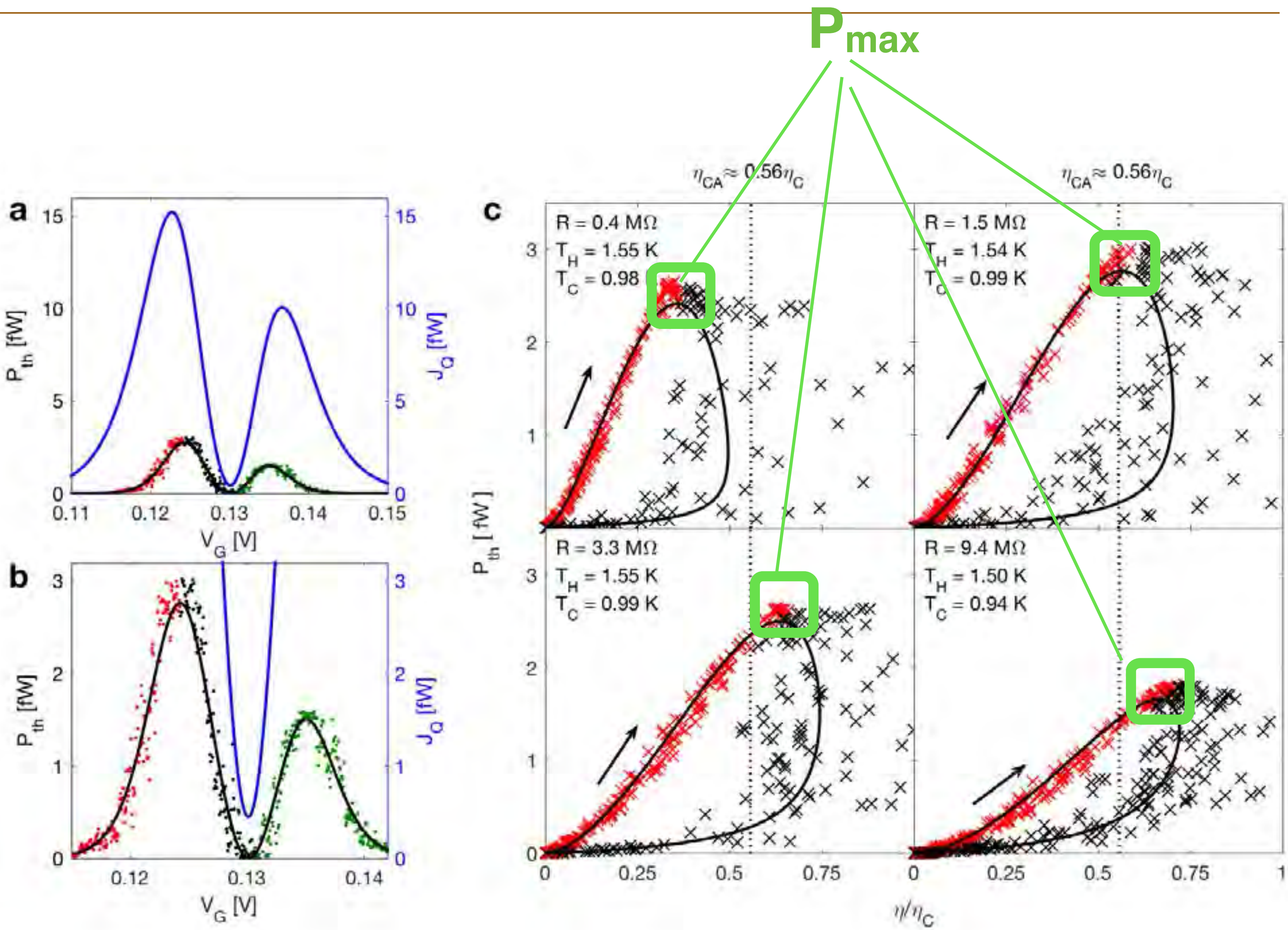
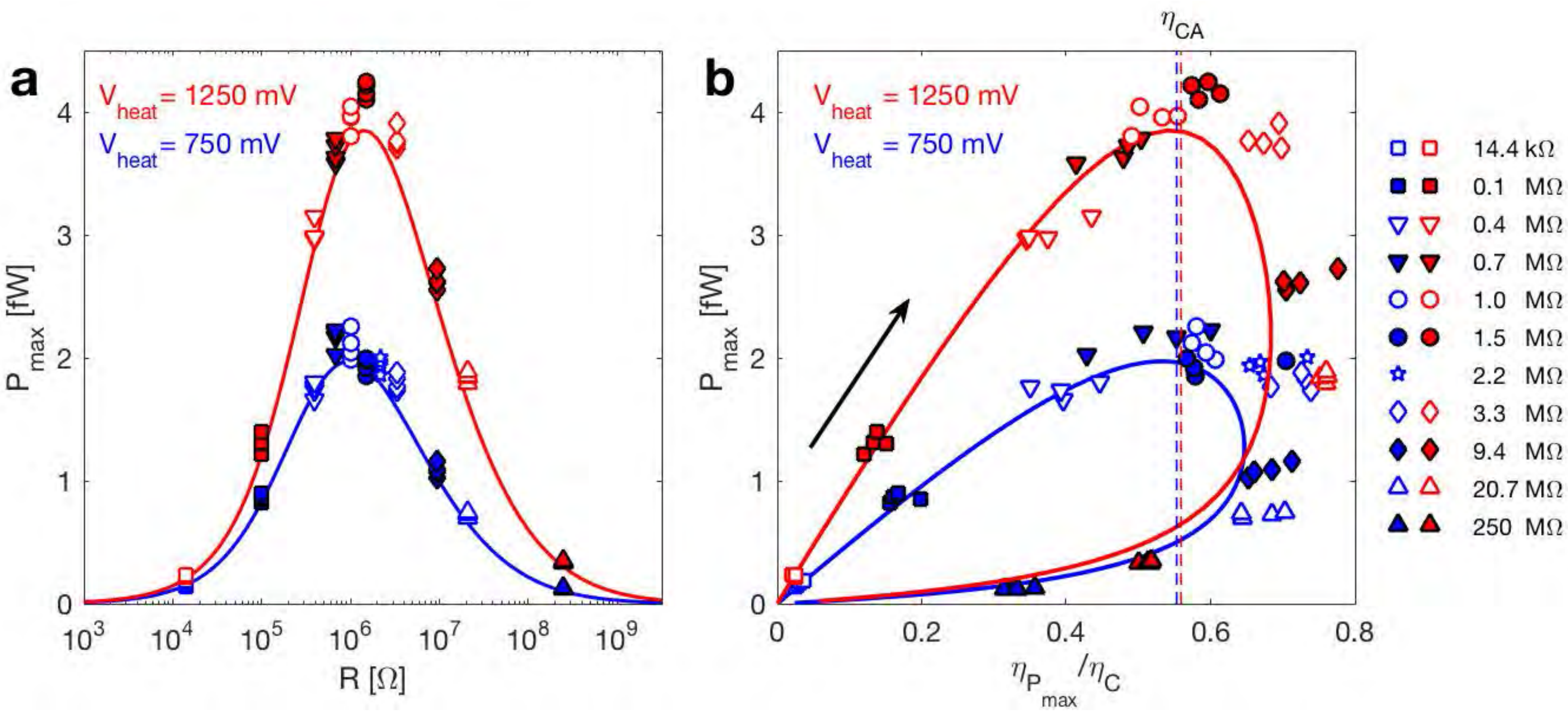
arXiv:1710.00742

Quantum-dot heat engine: performance



Quantum-dot heat engine: performance



Quantum-dot heat engine achieves Curzon-Ahlborn efficiency at maximum power and about 70 % of Carnot efficiency with finite power output

A. Svilans, M. Josefsson, M. Leijnse, et al. arXiv:1710.00742

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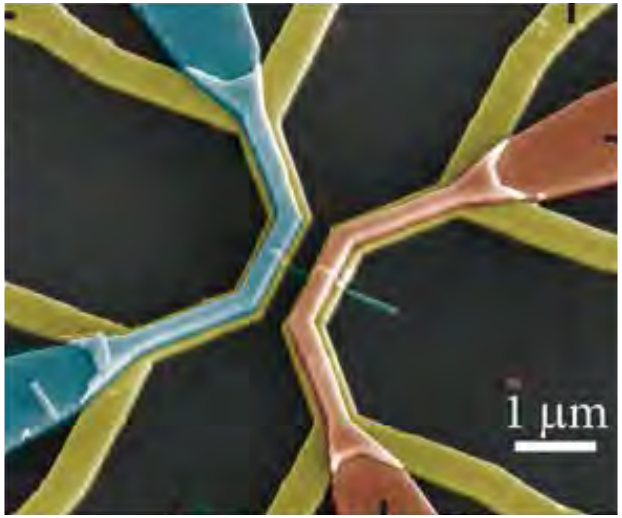


- Application to hot-carrier solar cells

Conventional, single-junction silicon solar cell at short circuit

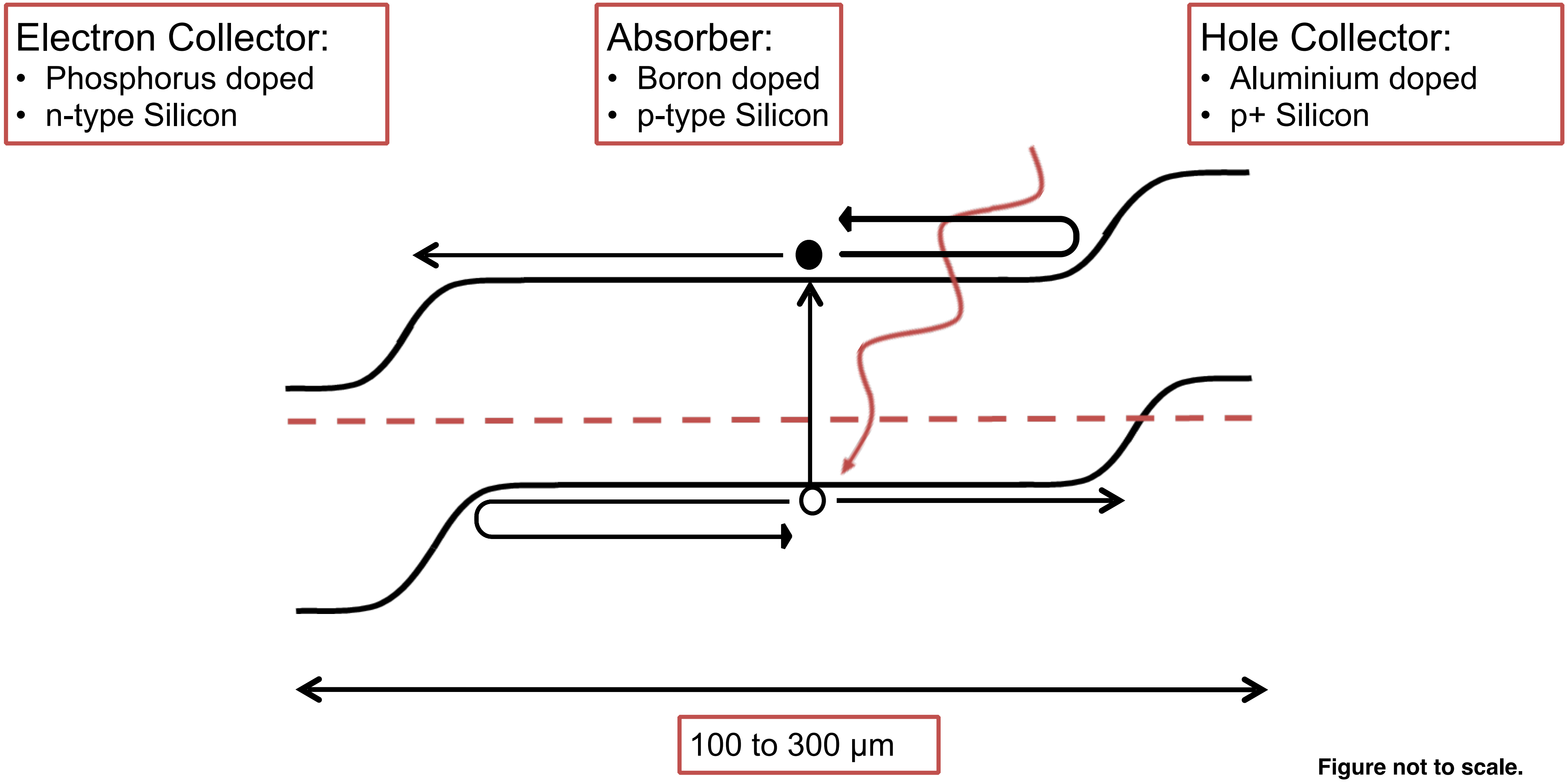


Figure not to scale.

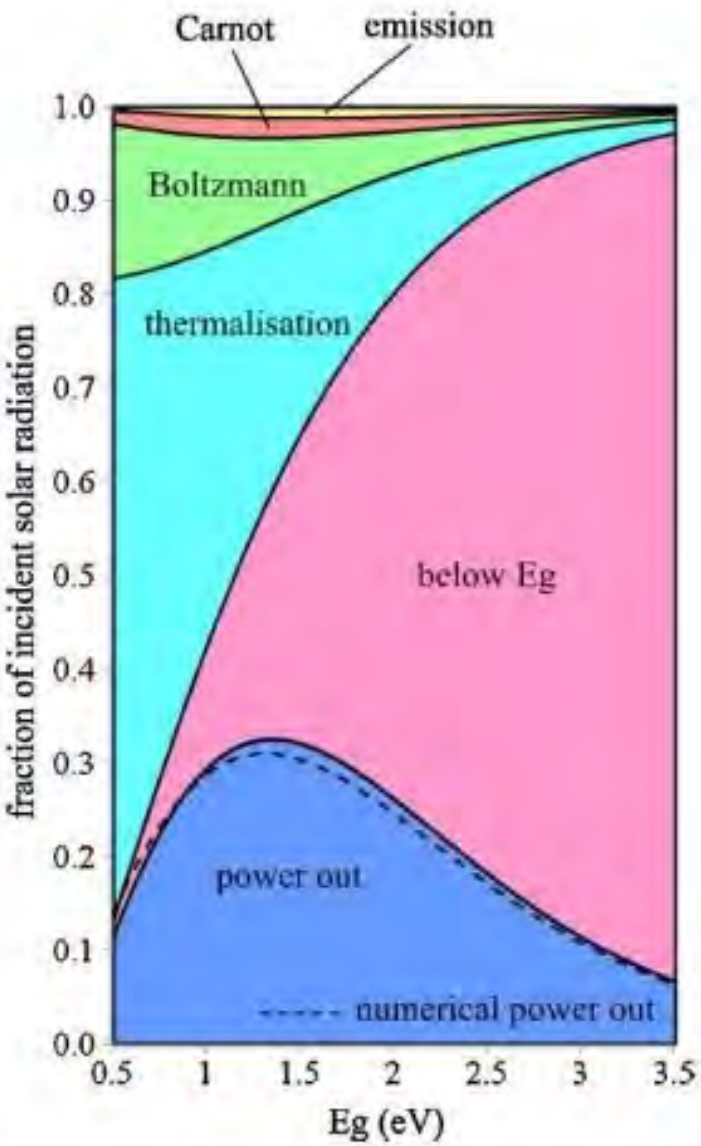
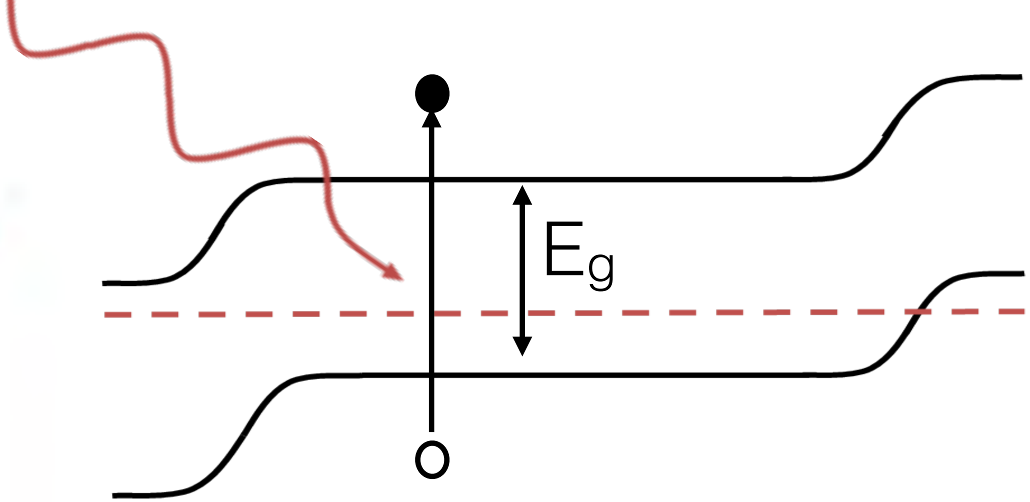


Figure 6. Intrinsic loss processes and hence, power out are shown to be dependent on E_g. All incident radiation is accounted for, illustrating why intrinsic loss mechanisms lead to fundamental limiting efficiency.



- Carrier cooling decreases the energy each carrier can provide to an external circuit.
- pn-junction solar cells of small bandgap materials are rarely made due to the magnitude of thermalisation losses.

L. C. Hirst and N. J. Ekins-Daukes, "Fundamental losses in solar cells," *Progr. in Photovolt.: Res. Appl.*, **19** 286–293 (2011)

Targeted time scale for carrier collection in this work

Time scale of pn-junction solar cell carrier collection.

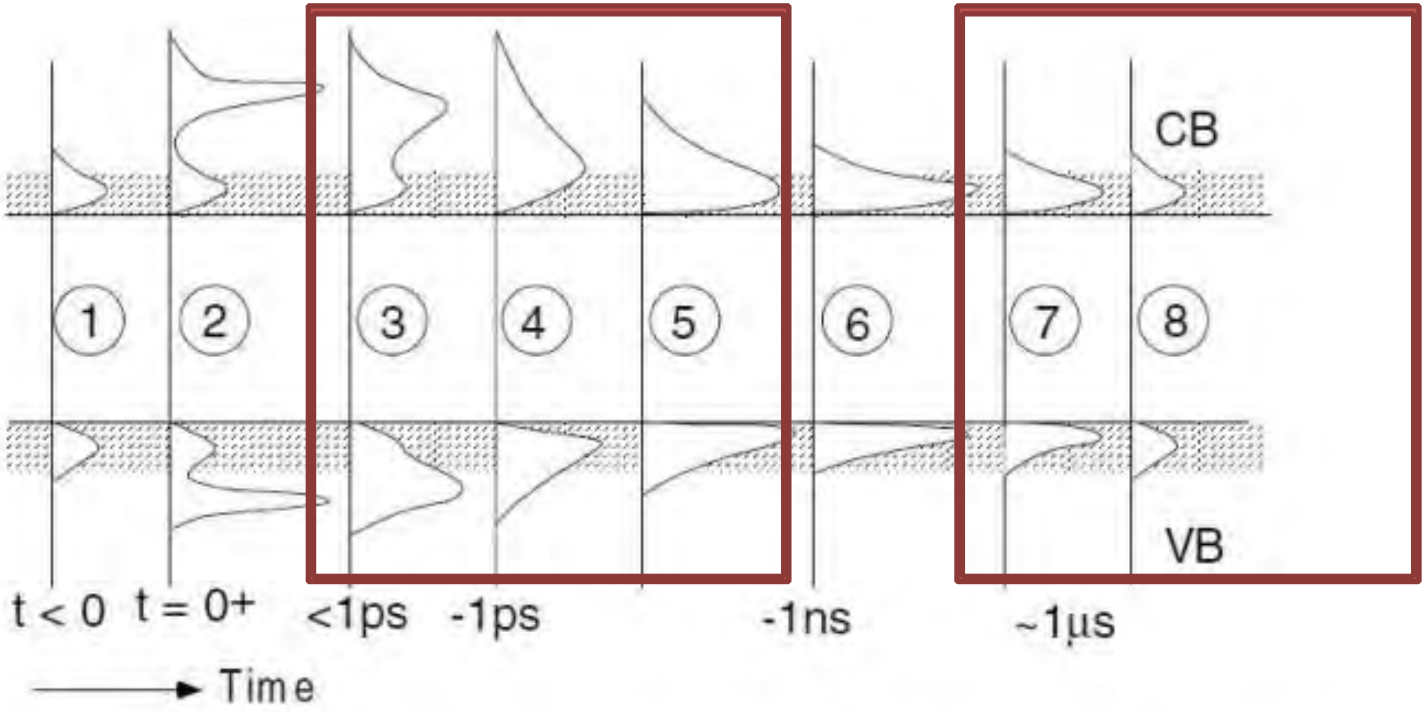
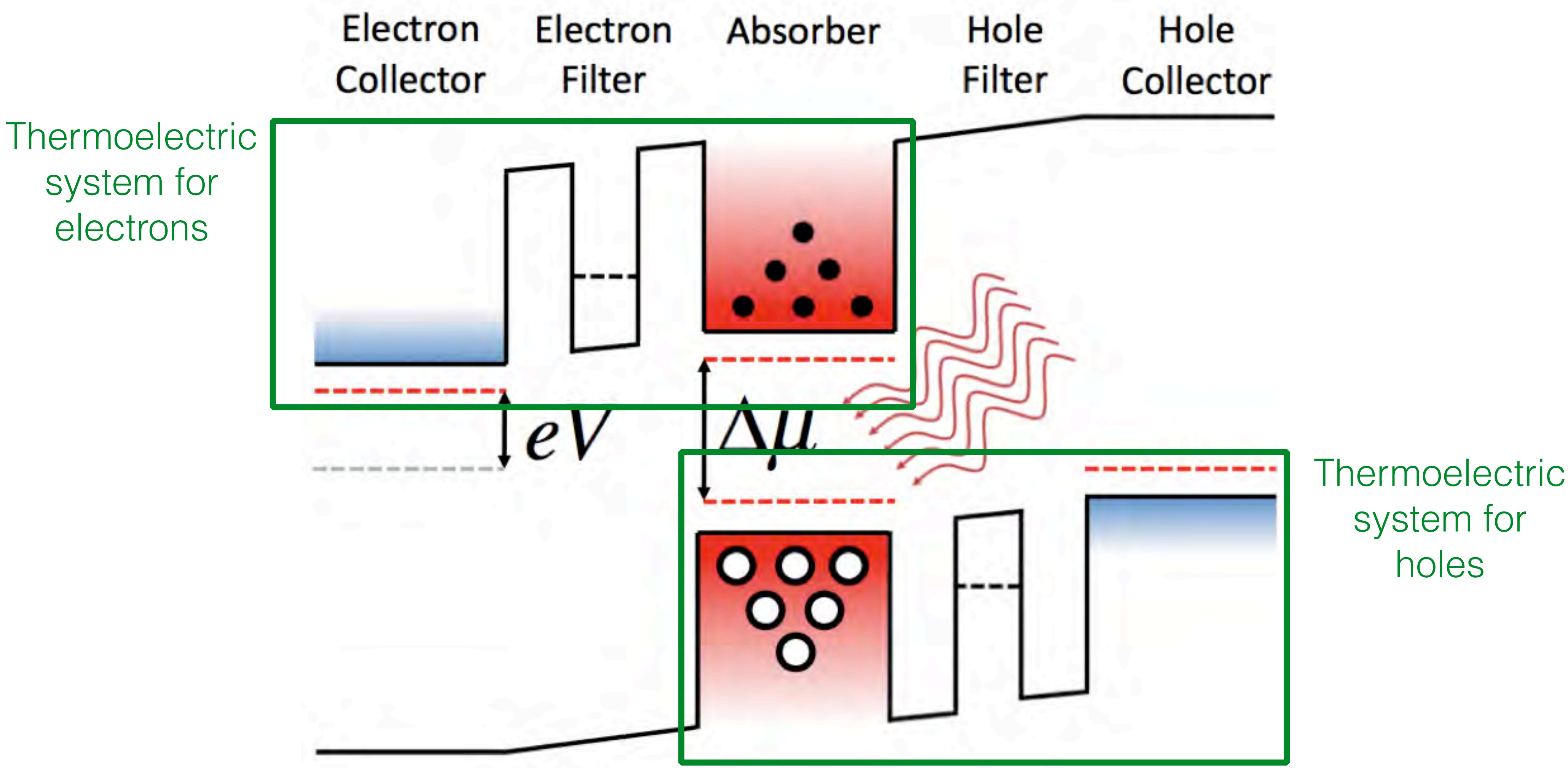


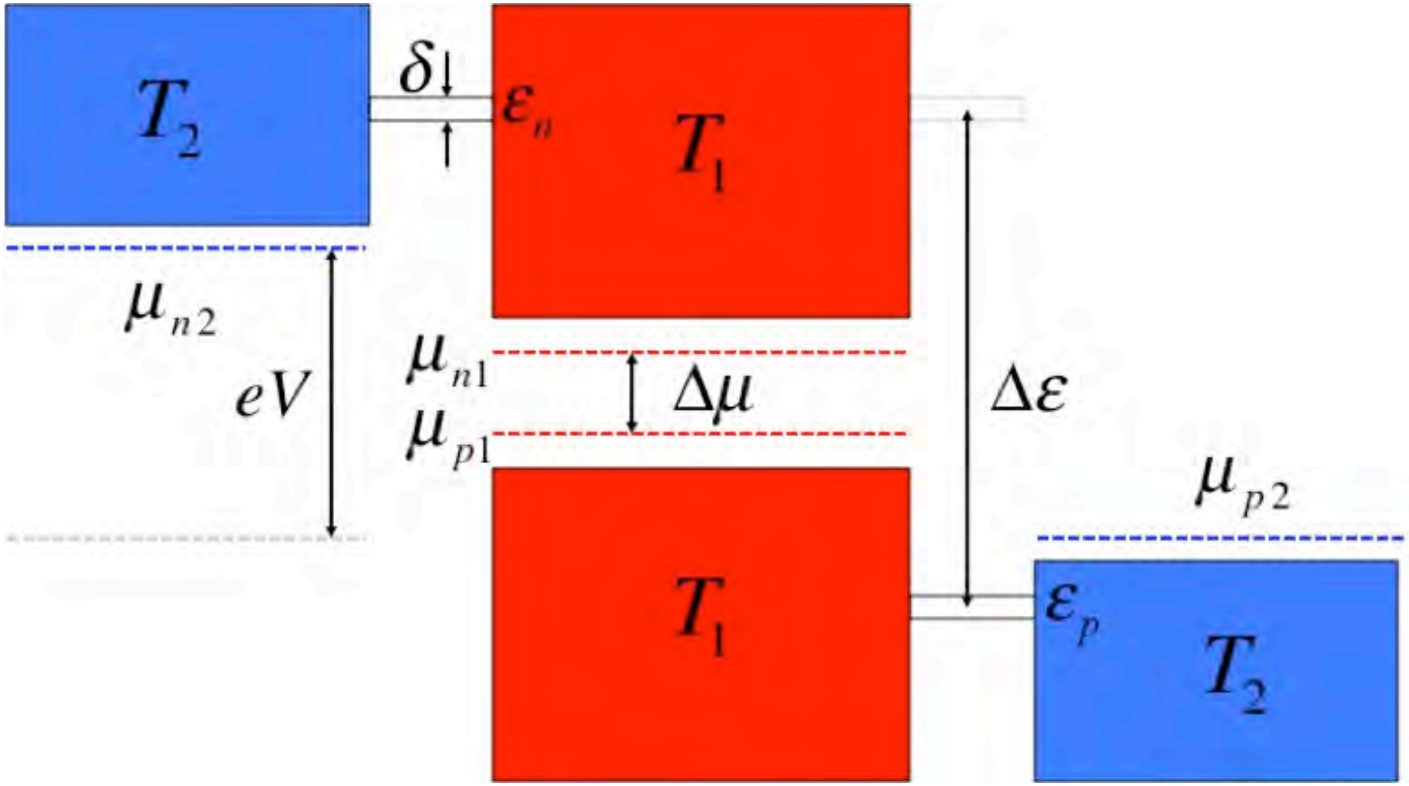
Fig. 6.2: Time evolution of electron and hole distributions in a semiconductor subject to a short, high intensity, monochromatic pulse of light from a laser: (1) Thermal equilibrium before pulse; (2) "coherent" stage straight after pulse; (3) carrier scattering; (4) thermalisation of "hot carriers"; (5) carrier cooling; (6) lattice thermalised carriers; (7) recombination of carriers; (8) return to thermal equilibrium.

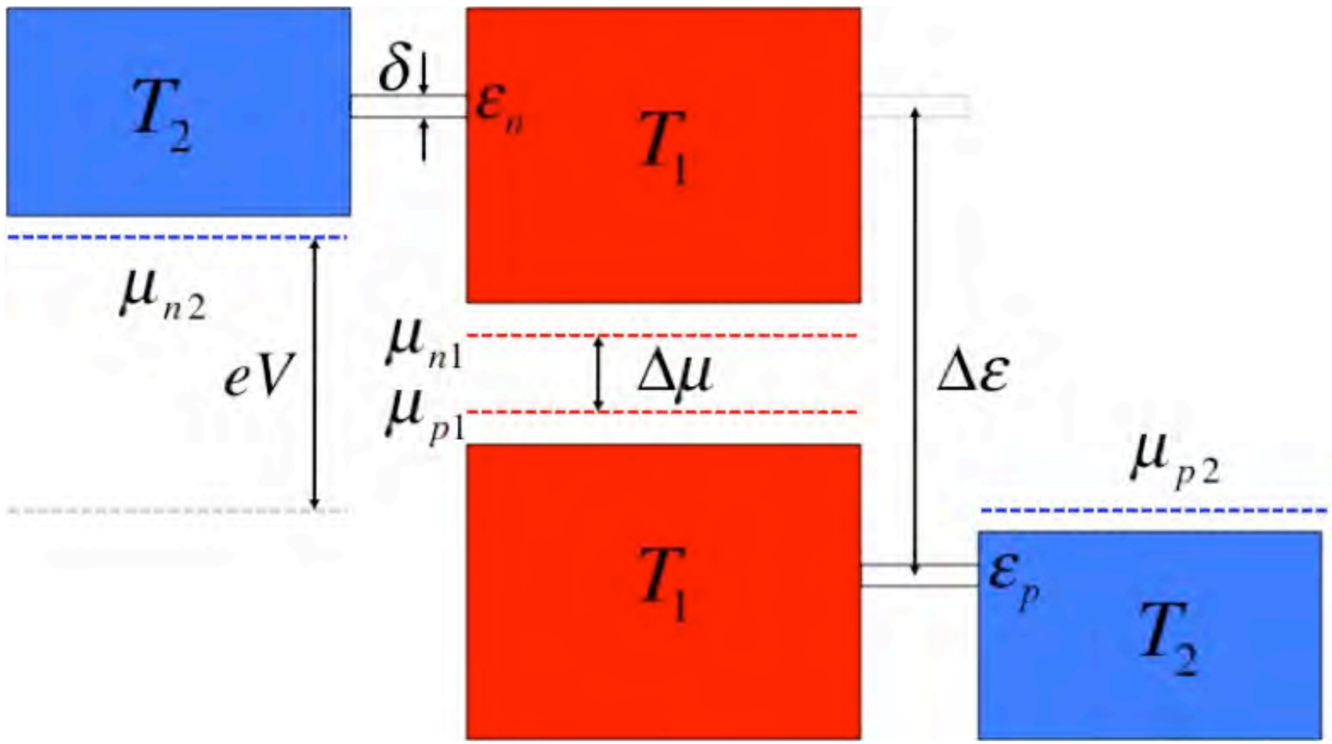
M. A. Green, Third Generation Photovoltaics. Heidelberg: Springer, 2006.

Basic idea of a hot-carrier cell: photothermoelectrics



Can a hot-carrier photovoltaic system be run reversibly?





$$\Delta S = \Delta S_{n1,ext} + \Delta S_{n2,inj} + \Delta S_{p1,ext} + \Delta S_{p2,inj}$$
$$= \frac{\Delta\varepsilon - eV}{T_2} - \frac{\Delta\varepsilon - \Delta\mu}{T_1}.$$

ΔS = 0 when $$\frac{\Delta\varepsilon - \Delta\mu}{T_1} = \frac{\Delta\varepsilon - eV}{T_2}$$

(equivalent to energy-specific equilibrium across both junctions)

S. Limpert, S. Bremner, H. Linke,
New J. Phys. (2015)

Open-circuit voltage

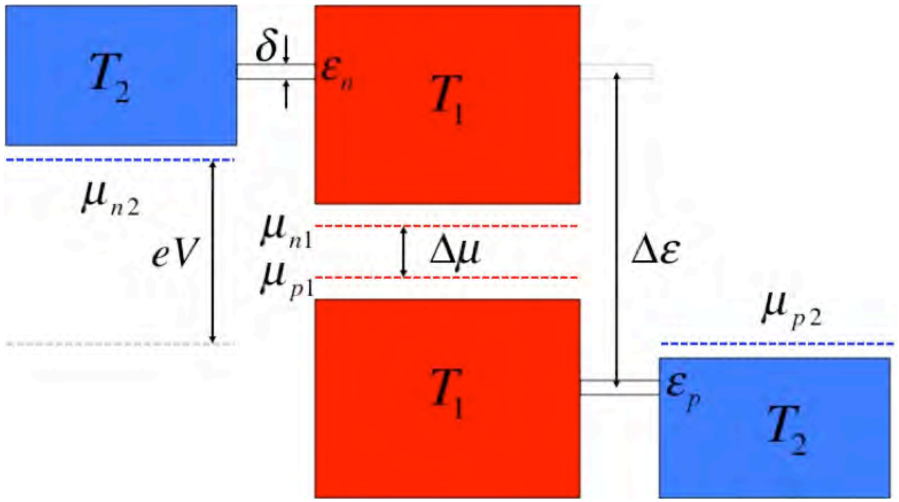
Steven Limpert

$$\Delta S = \Delta S_{n1,ext} + \Delta S_{n2,inj} + \Delta S_{p1,ext} + \Delta S_{p2,inj}$$
$$= \frac{\Delta\varepsilon - eV}{T_2} - \frac{\Delta\varepsilon - \Delta\mu}{T_1}.$$

$$eV = \Delta\varepsilon\left(1 - \frac{T_2}{T_1}\right) + \Delta\mu\frac{T_2}{T_1} - T_2\Delta S.$$

$$= Q_1\eta_{Carnot} + \Delta\mu - T_2\Delta S.$$

Heat engine | Solar cell



Explicit term describing the reduction of voltage due to irreversibility

$$Q_1 = Q_{n1} + Q_{p1} = \left(\varepsilon_n - \mu_{n1}\right) + \left(\mu_{p1} - \varepsilon_p\right) = \Delta\varepsilon - \Delta\mu$$

Key results from theory

- In principle, there is one operation point (V, T_1, T_2) where a hot-carrier solar cell (solar cell plus two energy filters) can be operated reversibly.

- The achievable open-circuit voltage is higher than that of a single pn-junction.

Basic idea for hot-carrier experiments

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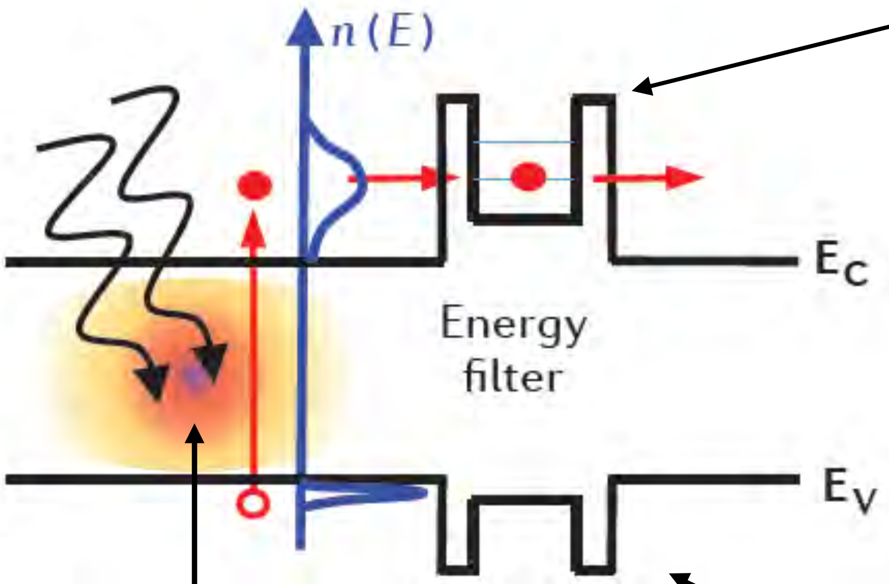
Heterostructure nanowire with small band gap and high electron-hole mass asymmetry (e.g. InAs/InP)

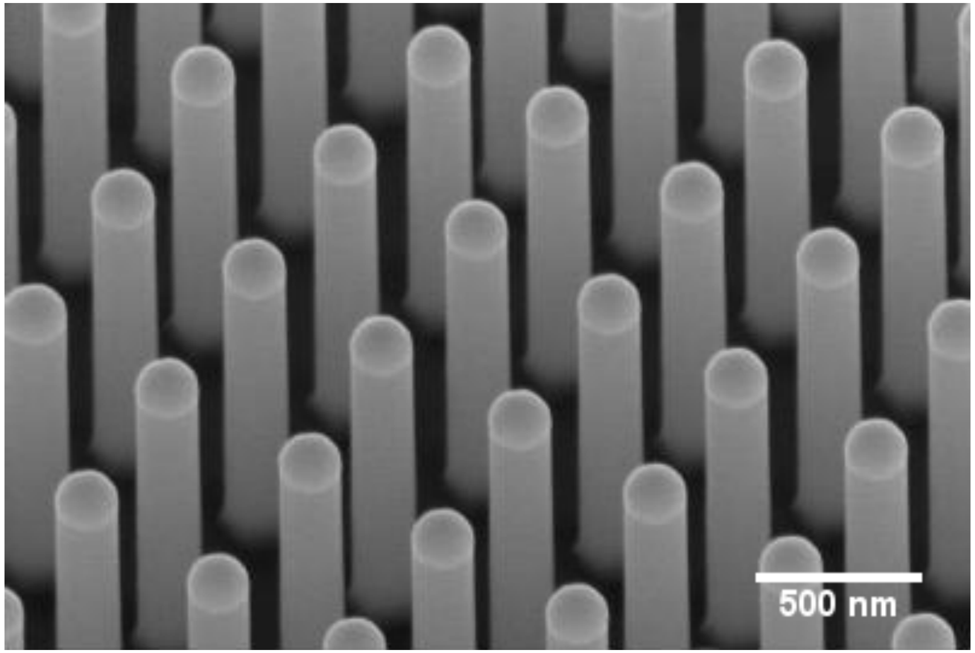
Energy filter (or thermionic barrier) for hot electrons



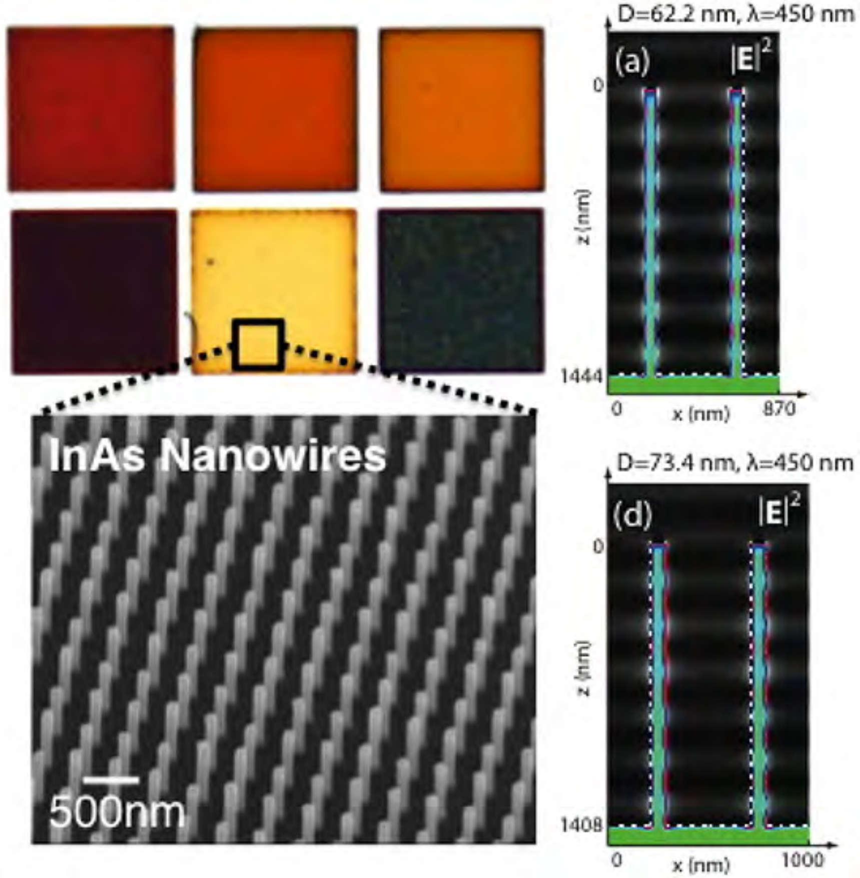
Local light absorption (photonic hot spot)

Block for holes (high mass -> small kinetic energy)

III-V nanowires and photonic behaviour



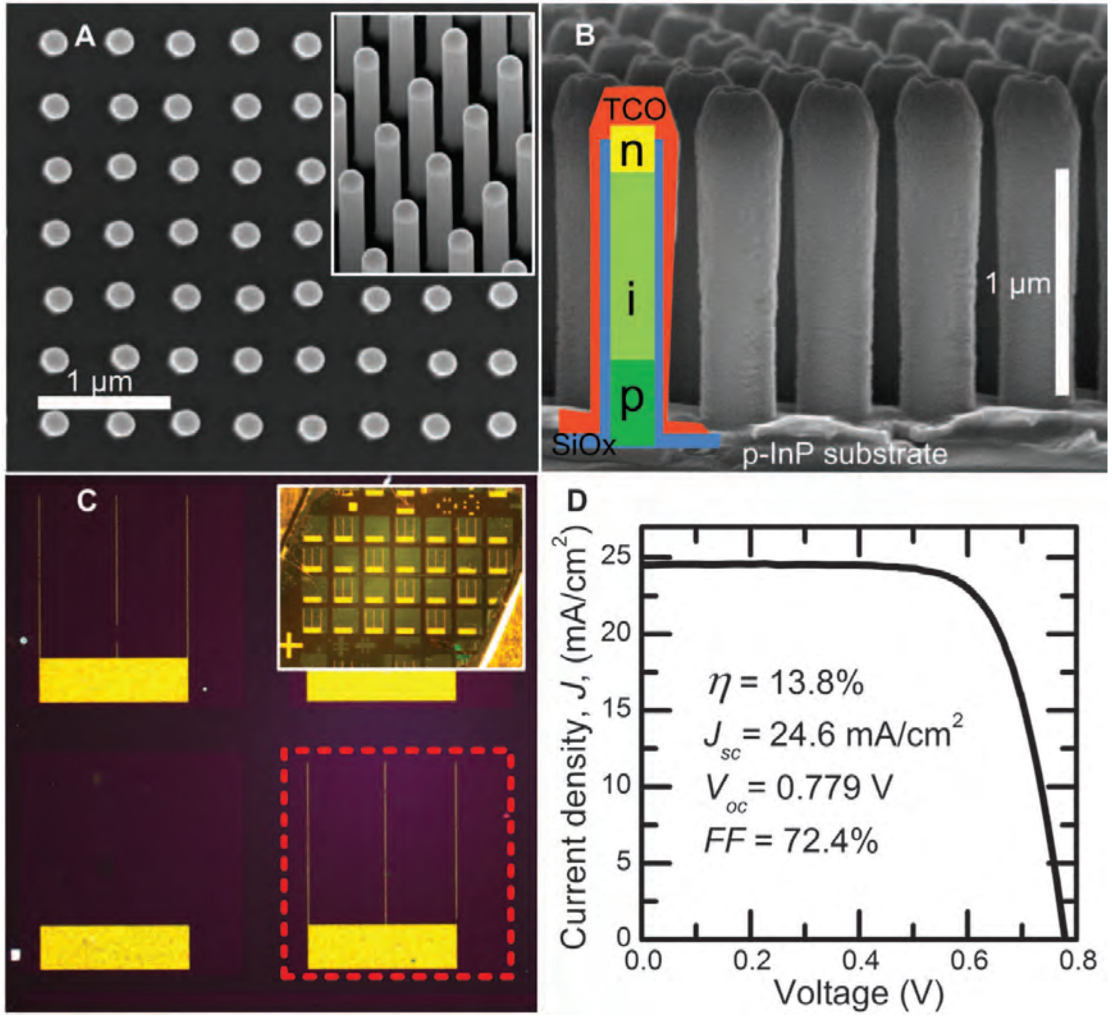
E.g. InAs, GaP, InP, GaN,…



P. M. Wu, N. Anttu *et al.*
Nano Letters 12, 4 (2012)

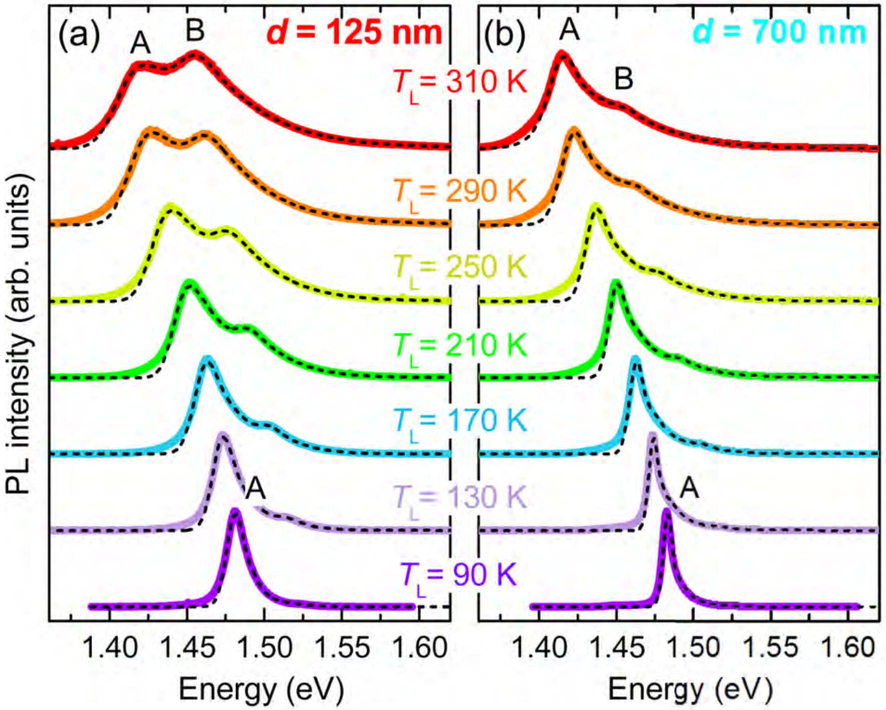
InP-nanowire solar cell

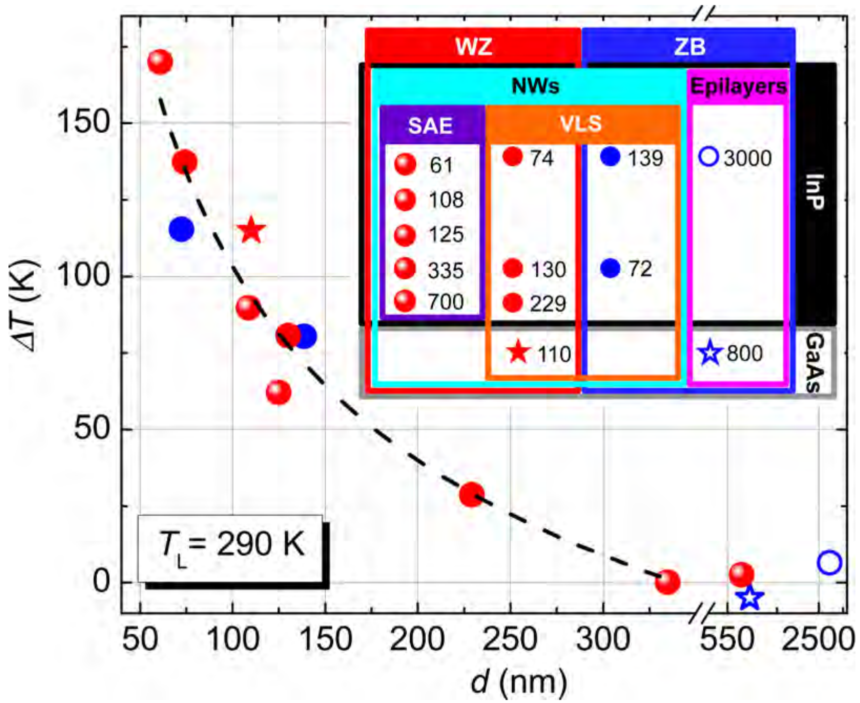
Use of photonic “antenna” effects enables 13.8% efficiency at about 12 % area coverage



J. Wallentin,.... , L. Samuelson
Science **339**, 1057 (2013)

High, achievable nonequilibrium carrier temperature in NWs



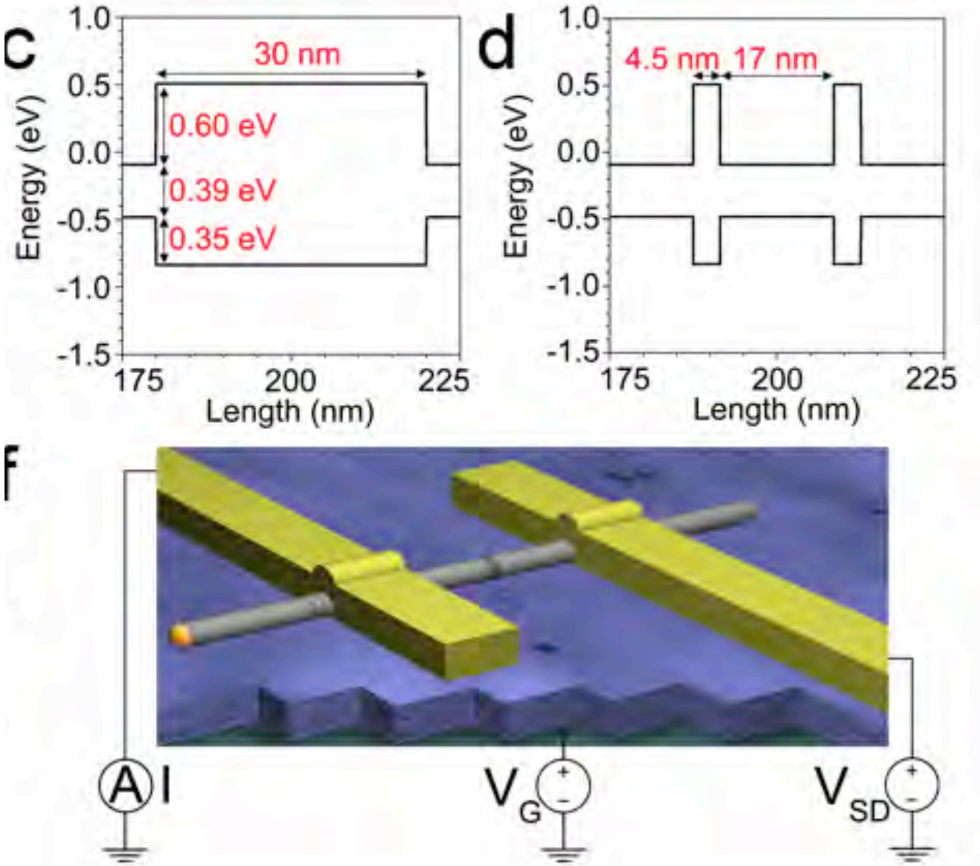


Steady-state PL measurements reveal “hot” carrier temperatures up to > 150 K above the lattice temperature for 50-nm thick nanowires

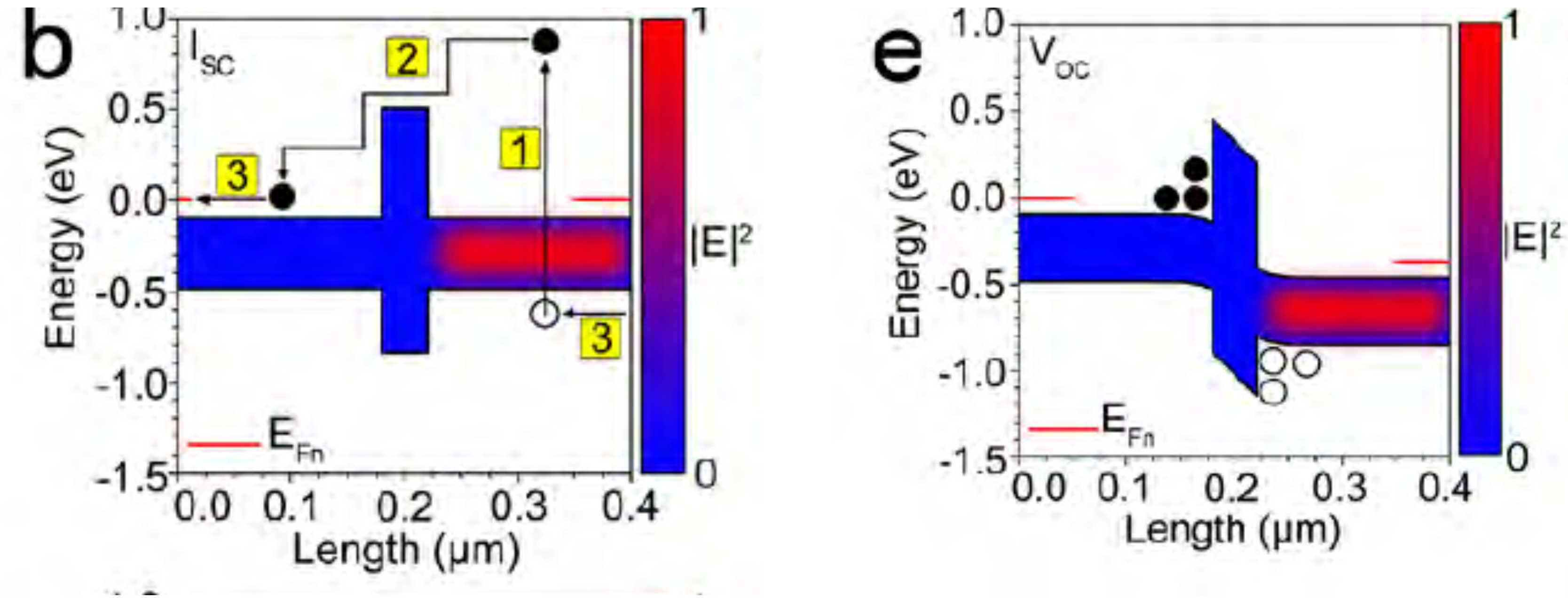
Tedeschi et al.
Long-Lived Hot Carriers in III–V Nanowires
Nano Letters **16**, 3058 (2016)

Device

CBE grown InAs/InP/InAs nanowire

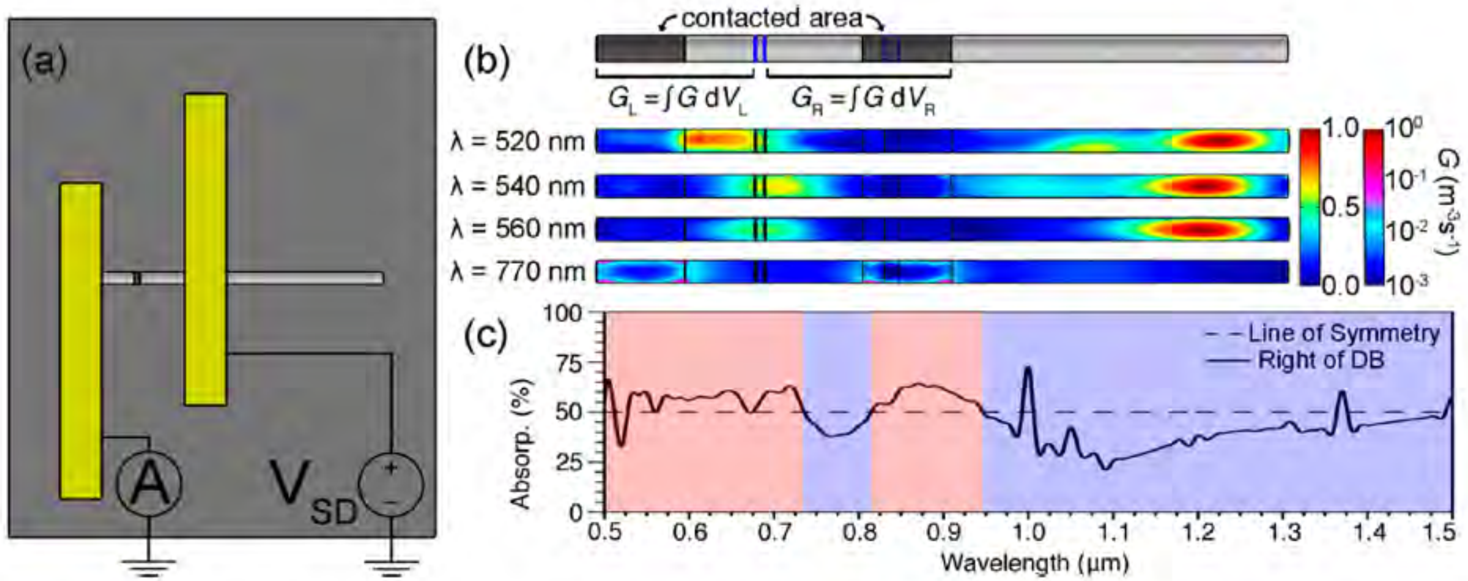


Operation principle

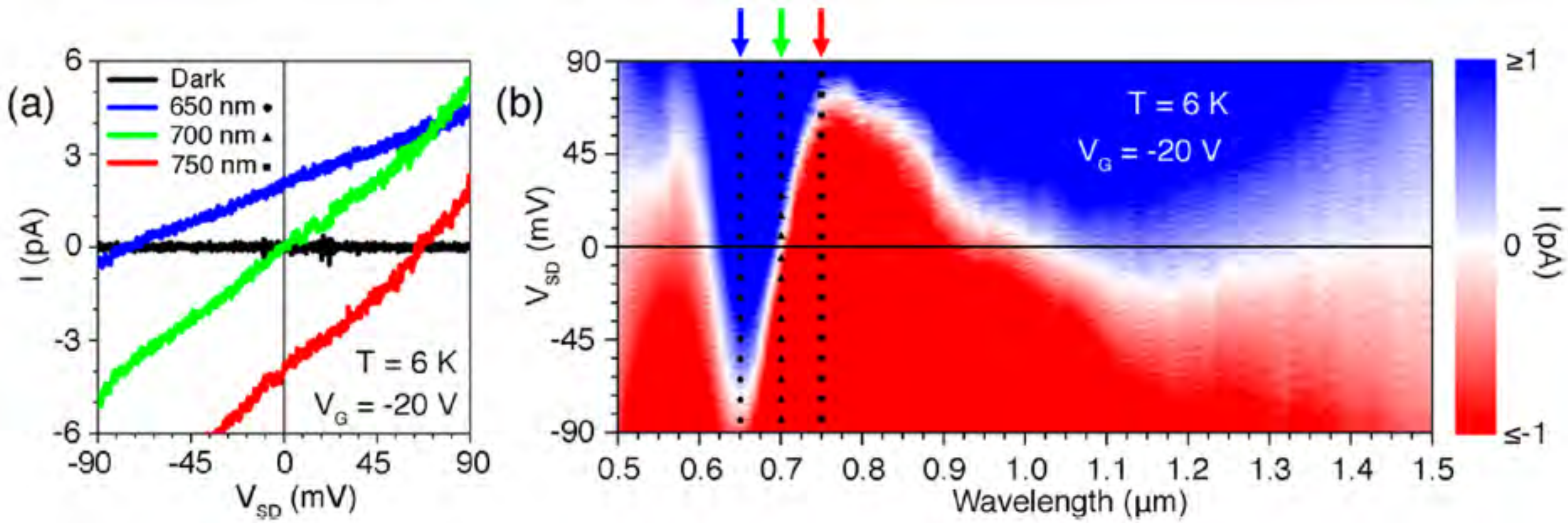


Wavelength-sensitivity (Double-barrier device)

Model



Experiment



S. Limpert et al, Nano Lett. **17**, 4055 (2017)

Photovoltaic power production (without pn-junction!)

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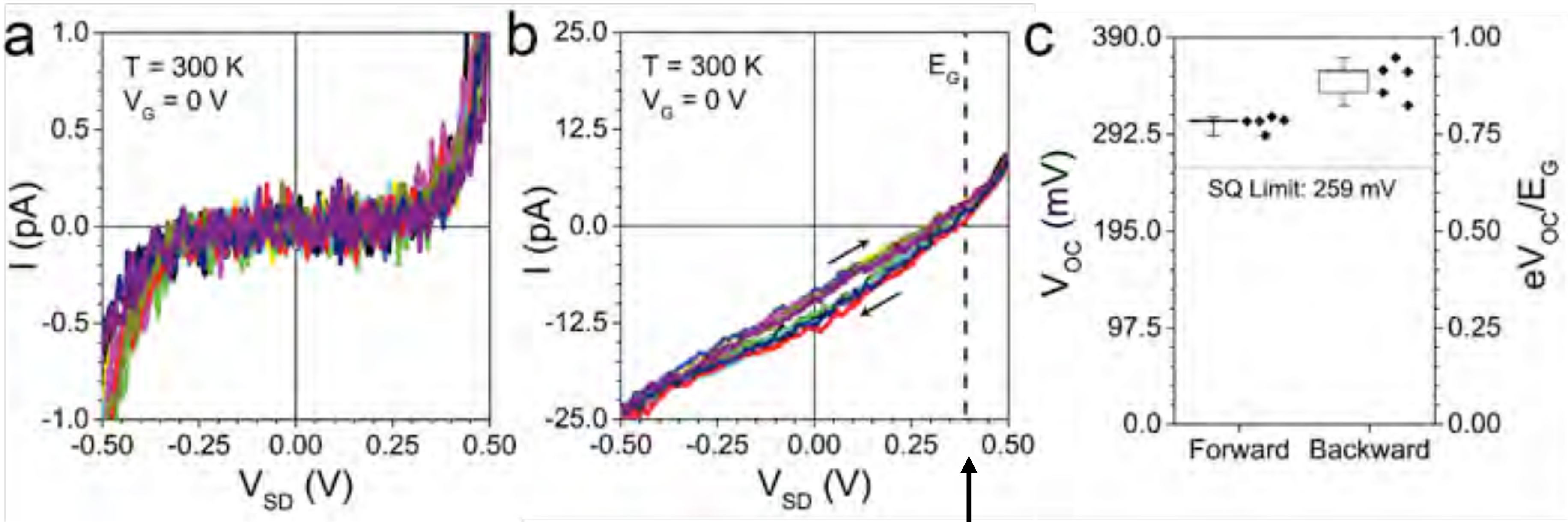
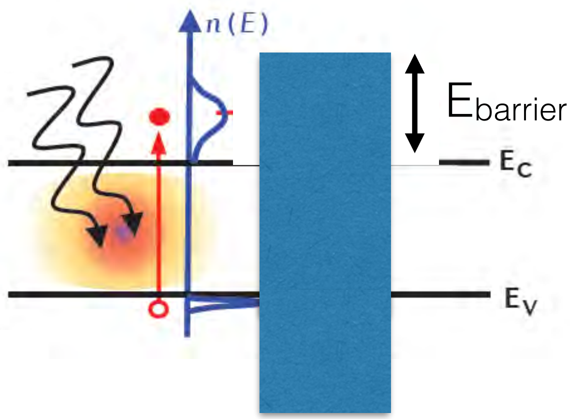
Single-barrier (thermionic) device



E_g of WZ InAs
≈ 0.39 eV

S. Limpert et al, Nano Lett. **17**, 4055 (2017)

Thermionic interpretation



Thermionic interpretation:

$V_{oc} = (k/e)\,(2 + E_{barrier}/kT)\,\Delta T_{carrier}$

$V_{oc} \approx 0.35$ V is consistent with $\Delta T_{carrier} \approx 170$ K

Since ΔT in this interpretation is the carrier temperature, phonon-mediated heat flow is irrelevant to the efficiency analysis.

Controlling the light-absorption hot spot

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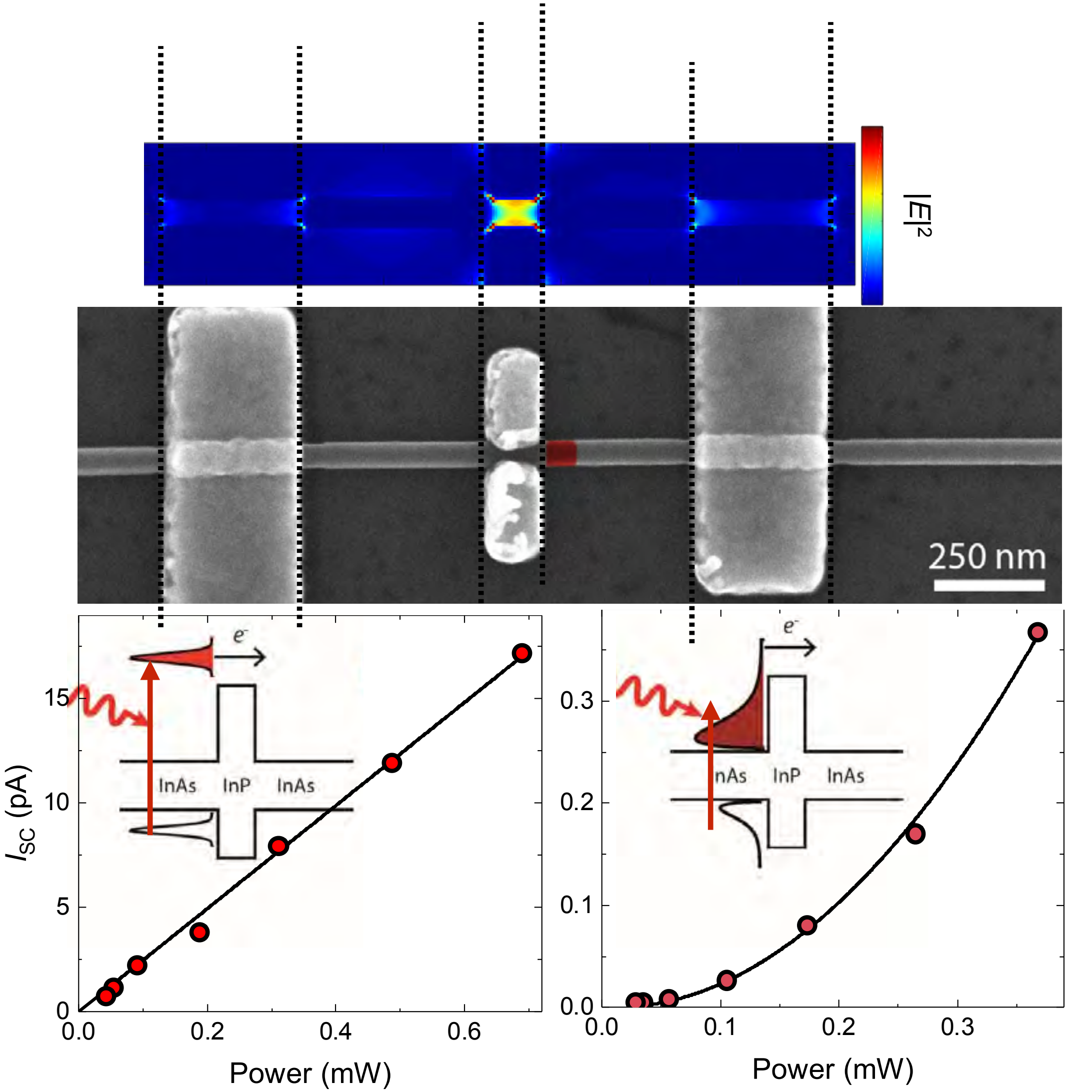
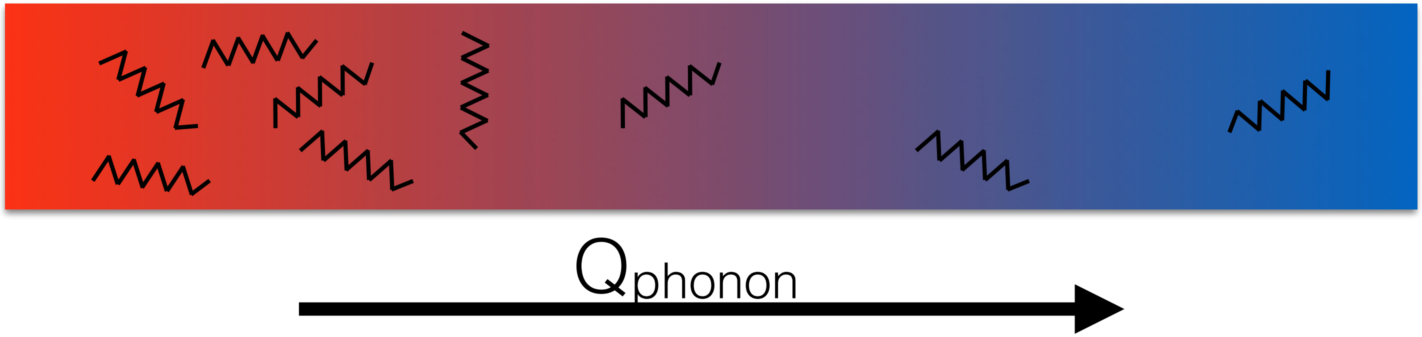


I-Ju Chen

I-Ju Chen et al.
in preparation

Why can this work? Isn't thermoelectric energy conversion inefficient?

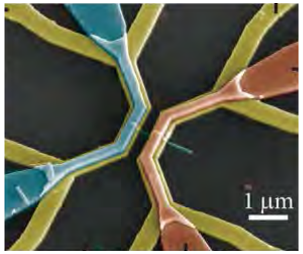
Standard thermoelectrics:
Heat source heats phonons, who then heat electrons.
Phonon-mediated heat flow is a major energy loss.



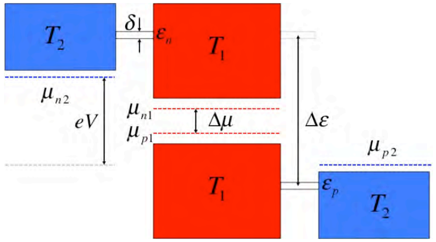
Hot carrier solar cell / Photothermoelectrics:
Photons heat **carriers**. In the best case scenario, carriers are separated before they heat the phonons, **eliminating phonon-mediated heat flow**

Summary

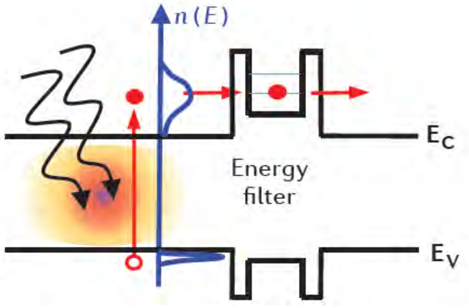
- Quantum dot heat engines realised with > 70% of Carnot efficiency



- There is no fundamental limit to the efficiency of an ideal hot-carrier solar cell other than the Carnot limit (even though there are many potential practical limitations).



- Nanowires are promising candidates for hot-carrier cells because
  - photonic or plasmonic hot spots;
  - high carrier temperatures under steady-state illumination;
  - heterostructures can be used for thermionic power generation;



- Power conversion with high V_{OC} observed

Acknowledgments

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Artis Svilans

Martin Josefsson

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Theory: **Steven Limpert**, N. Anttu, **M. Josefsson**, M. Leijnse

Collaboration: Stephen Bremner, UNSW, Sydney

Vetenskapsrådet

Swedish Energy Agency

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