Photovoltaics in extreme conditions

Multi-temperature hot carrier solar cell: an issue or an opportunity?

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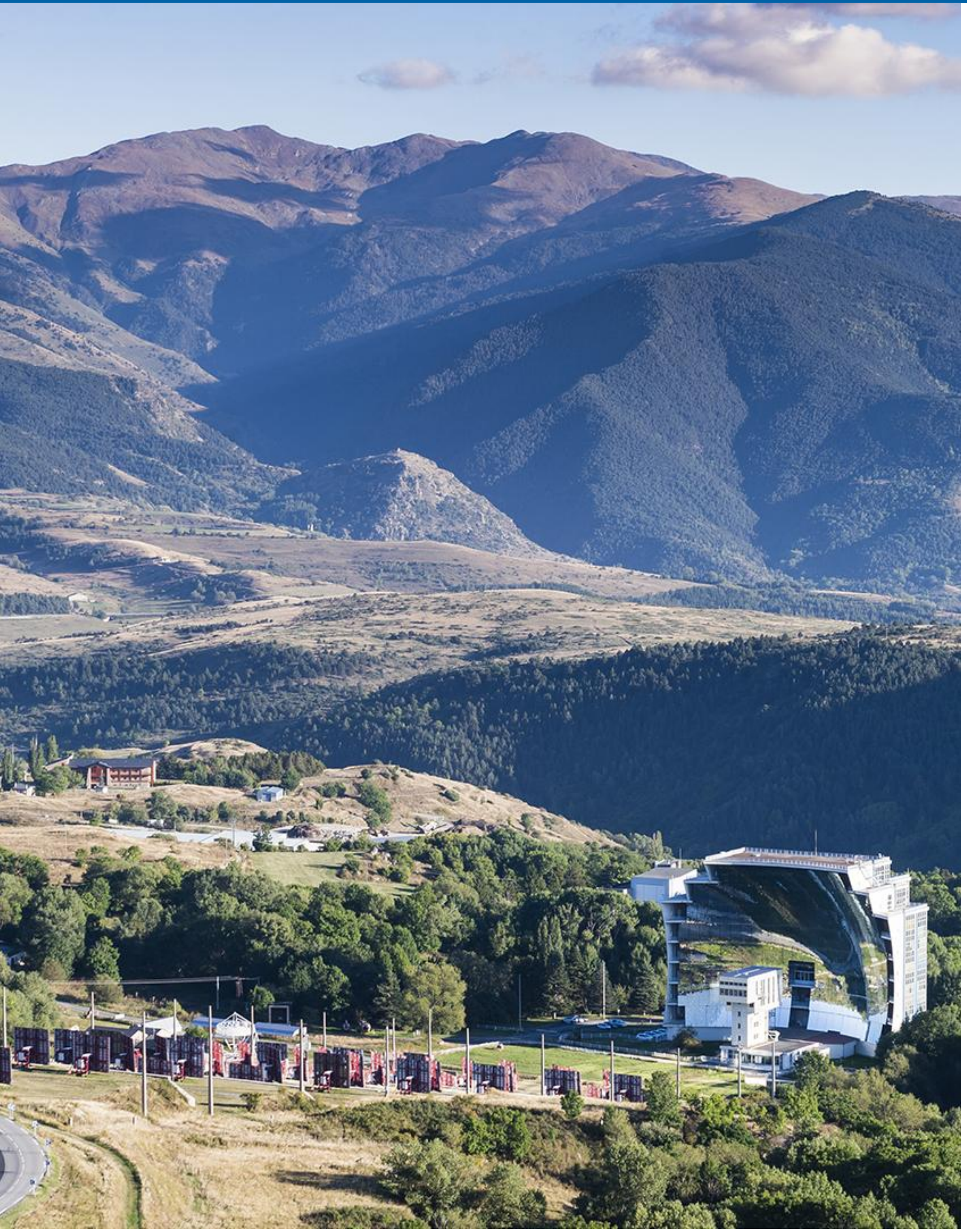
26/03/2025 RAURISERHOF

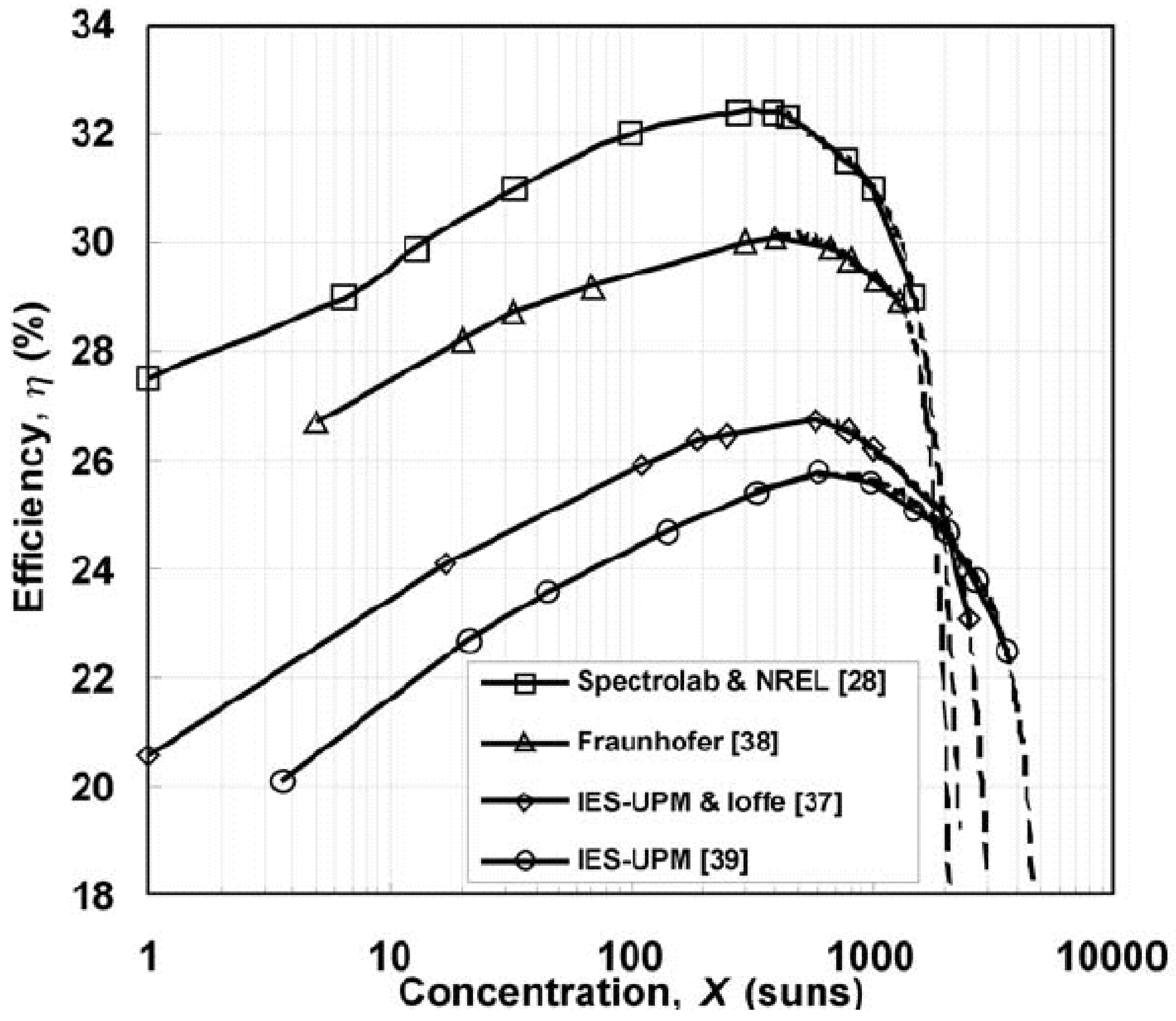
Outline



1. Solar cells under high concentration
2. Hot carriers : « More is different»
3. Electrons and holes

Devices under high concentration

Triple transport problem



Photons :

- Concentration optics

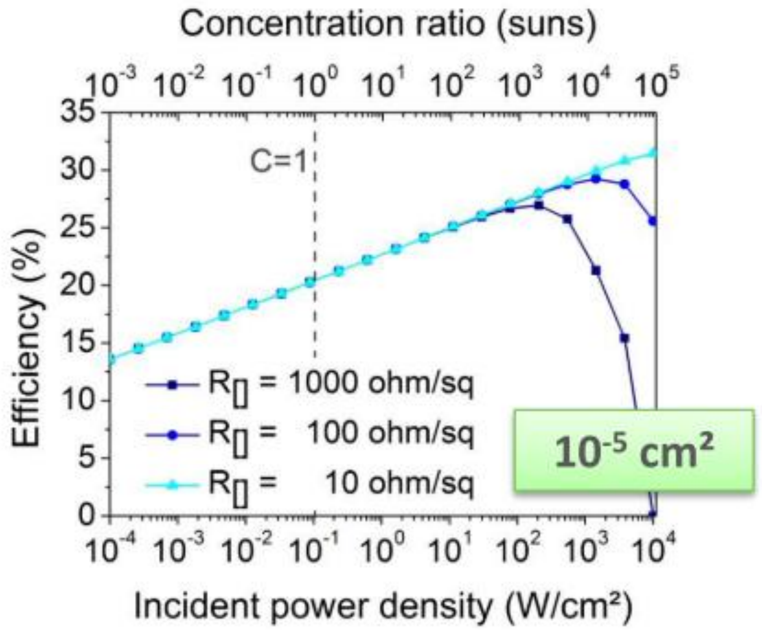
Electrons :

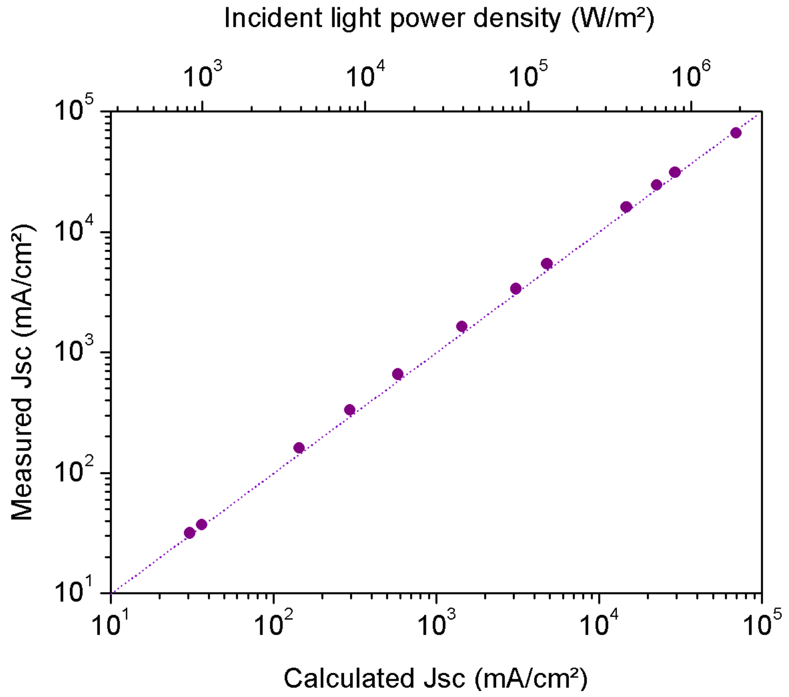
- Collection (~I^2 i.e. Conc.^{2})
- Series Resistance => $kT/q = R_s I^2$

Heat

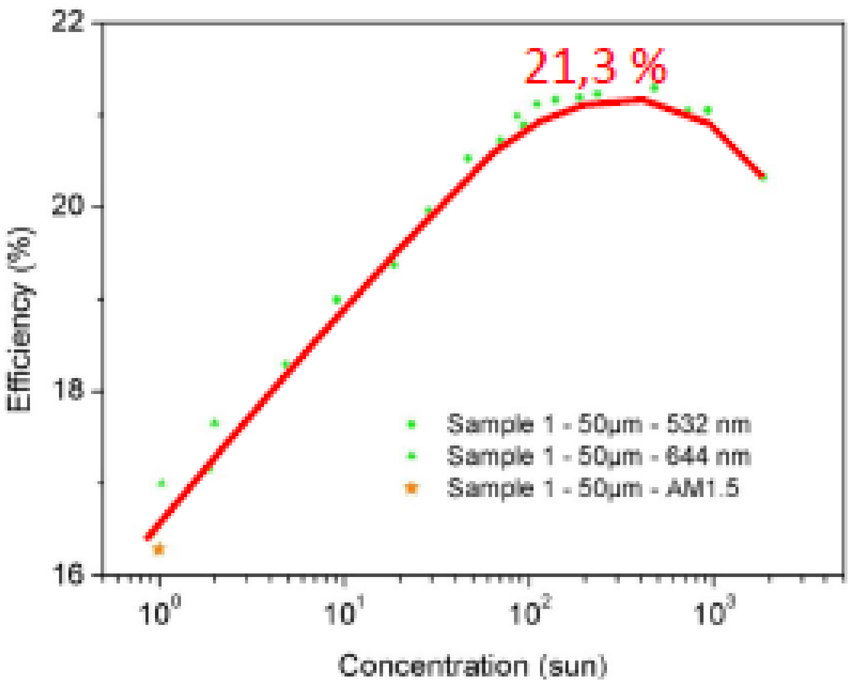
Solving the electron/heat transport issue

(1)



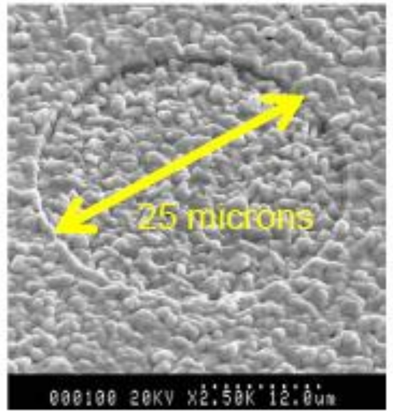


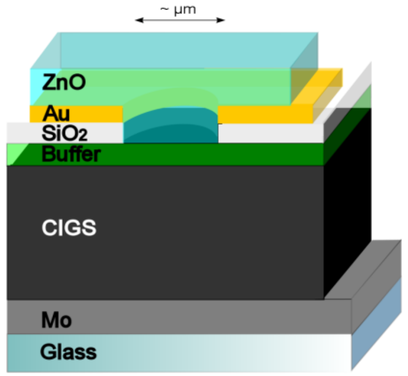
(2)

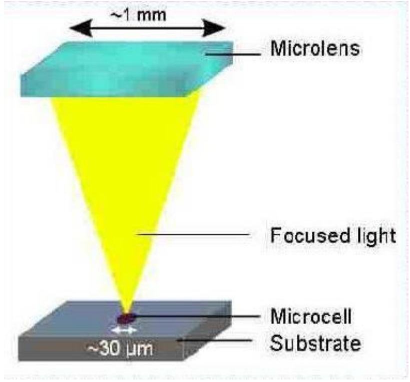


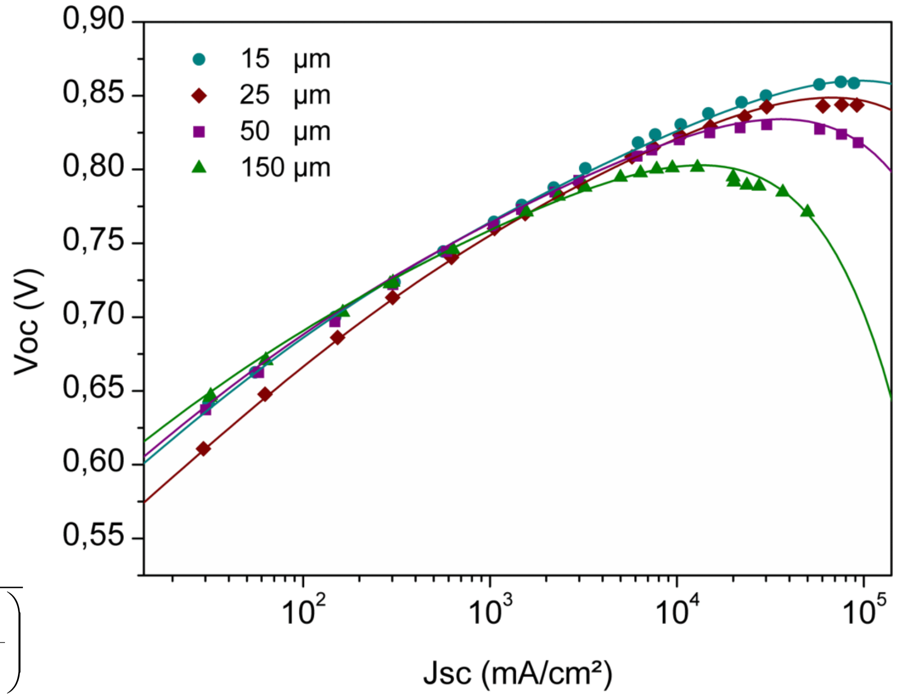
- **Adimensionnal analysis**

$$\alpha = R_{\square} a^2 C J_{ph}(1\ sun)\, q / AkT$$









High injection series resistance (3):

$$R_{s\,microcell} = R_c + R_{s\,abs} = R_c + \frac{R_{s0}}{1+\left(1+\frac{\mu_p}{\mu_n}\right)\times\left(\frac{L_n}{t}\right)^2\times\frac{q^2\times EQE\times R_{s0}\times P_{light}}{kT\times h\nu}}$$

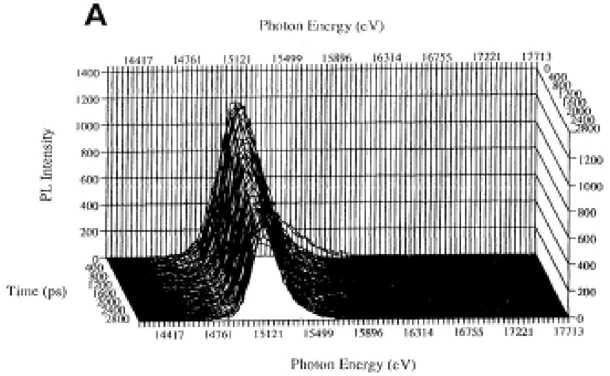
M. Paire et al: (1) J. Appl. Phys 2010; (2) Energy Environ. Sci., 2011; (3) Appl. Phys. Letters, 98, 264102 (2011)

More is different

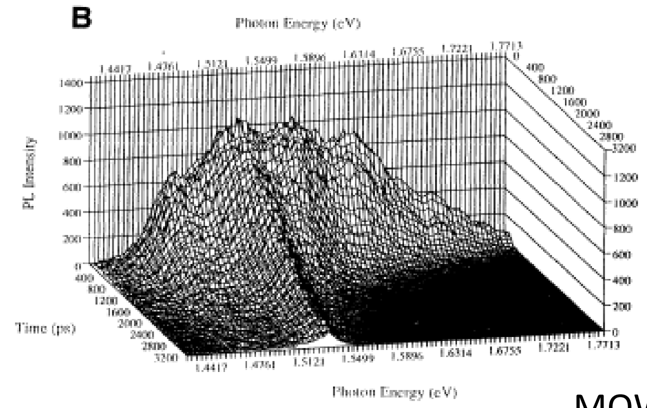
At very high power (mostly transient)

- Carrier cooling from interactions with LO phonons TR or CW [1-4]
- Nanostructured absorber can enhance the phonon bottleneck effect [1-4]
- Hot carrier confinement using claddings [2,3]

TR-PL characterizations from [1]



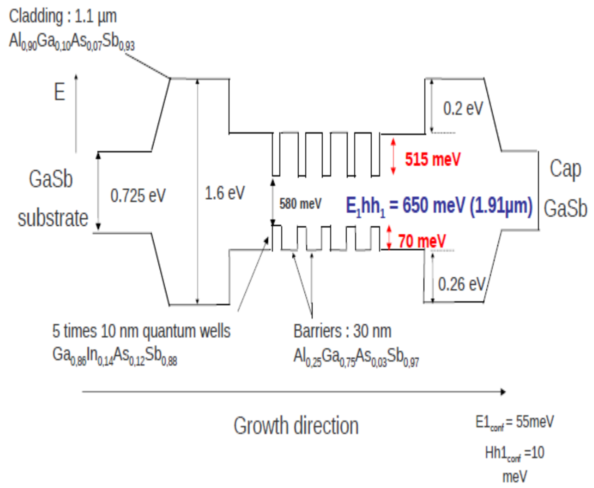
Bulk



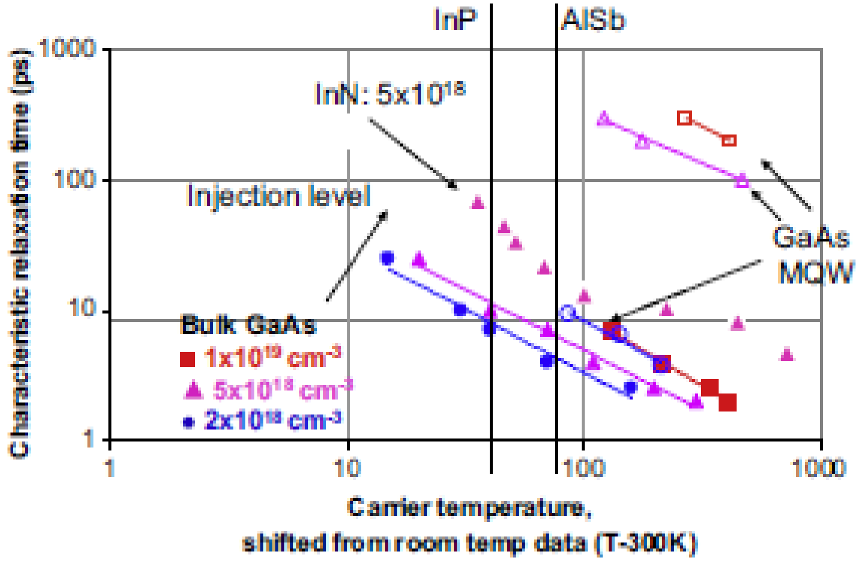
MQW

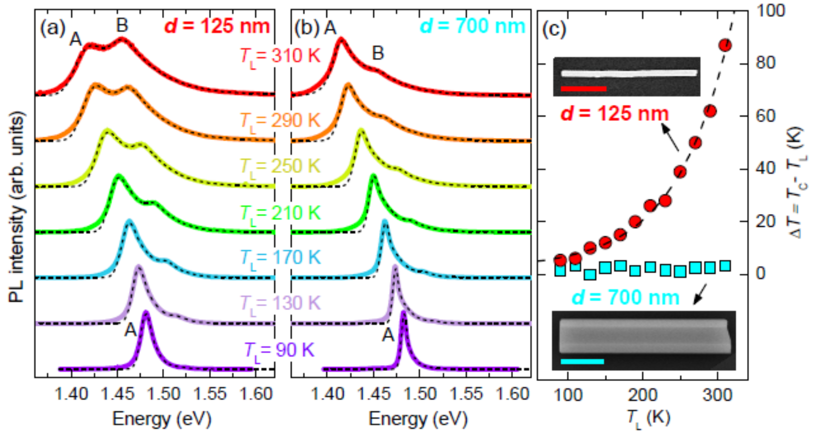
$$P_{th} = Q\,(T_H - T)$$

MQW with claddings from [2,3]

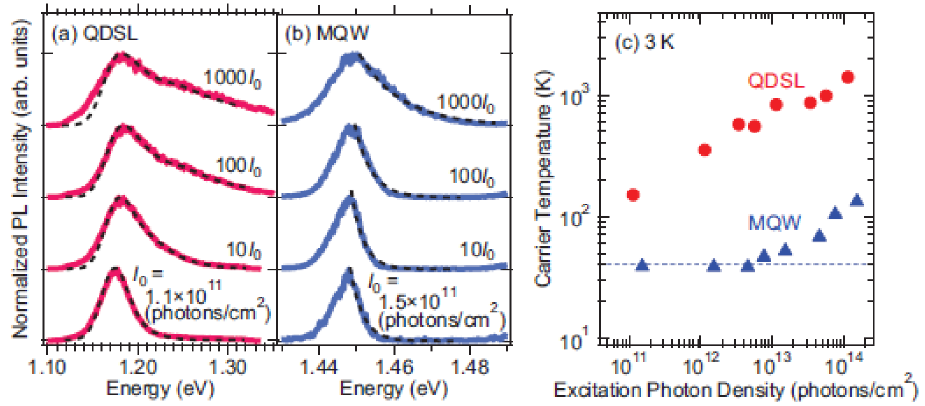


Bulk materials from [4]





Nanowires (Tedeschi et al, Nanolett. 2016)



QD and QW (Harada et al, PRB. 2016)

And in :
Perovskites
Graphene
Dichalcogenides
…..

[1] Y. Rosenwaks et al., Phys. Rev. B (1993)
[2] A. Lebris et al., Energy Environ. Sci., (2012)
[3] J. Rodiere et al., Appl. Phys Lett., (2015)
[4] JF Guillemoles et al. PVSEC 2005, & Conibeer et al., Solar Energy Materials & SolarCells (2015)

Hot carrier solar cell concept

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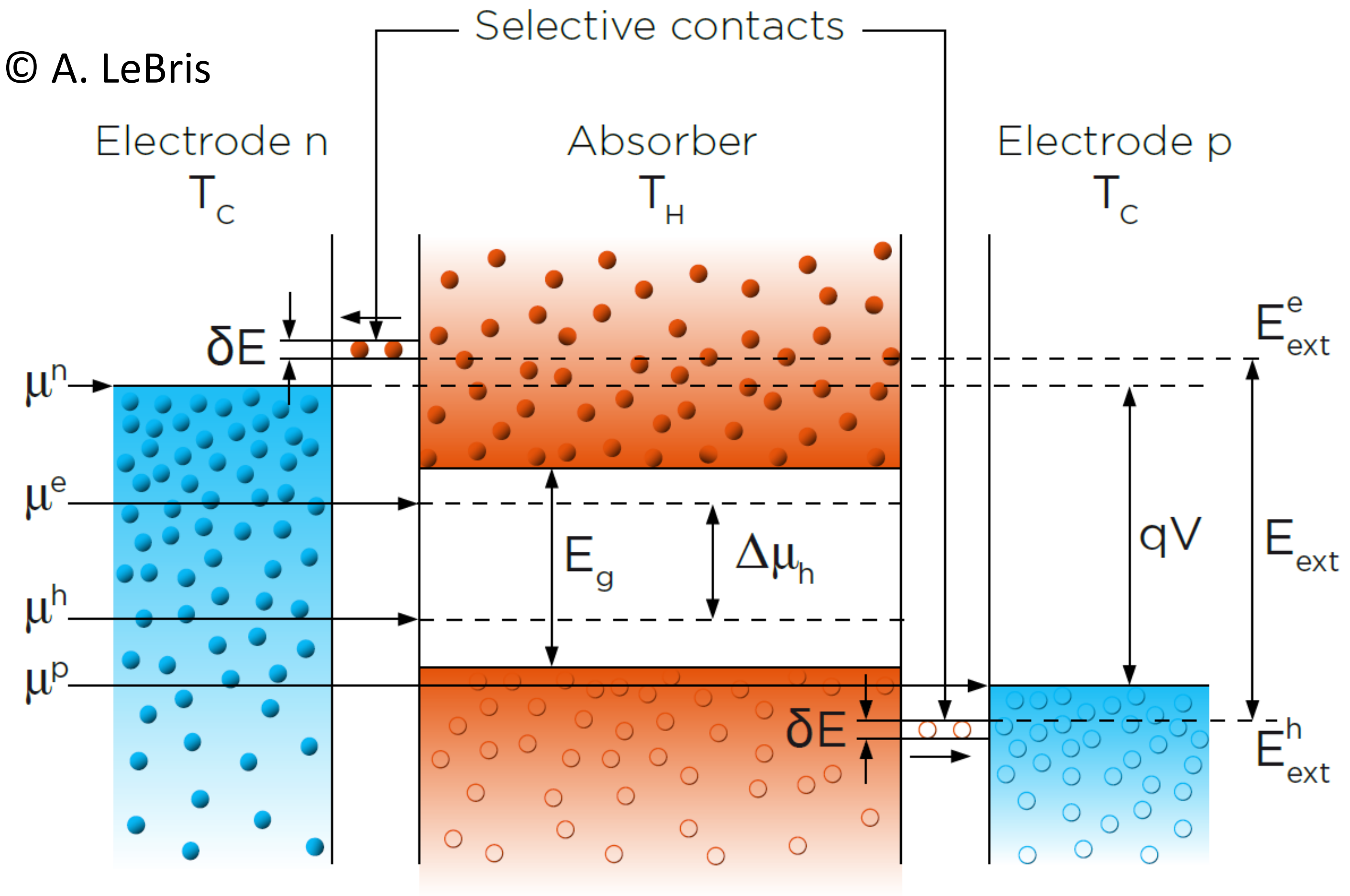


Extract carriers before full thermalization
Narrow width energy selective contacts

68% (1 sun)
86% (full)

Ross & Nozik, J. Appl. Phys (1982)
Würfel, Sol Mat (1997)

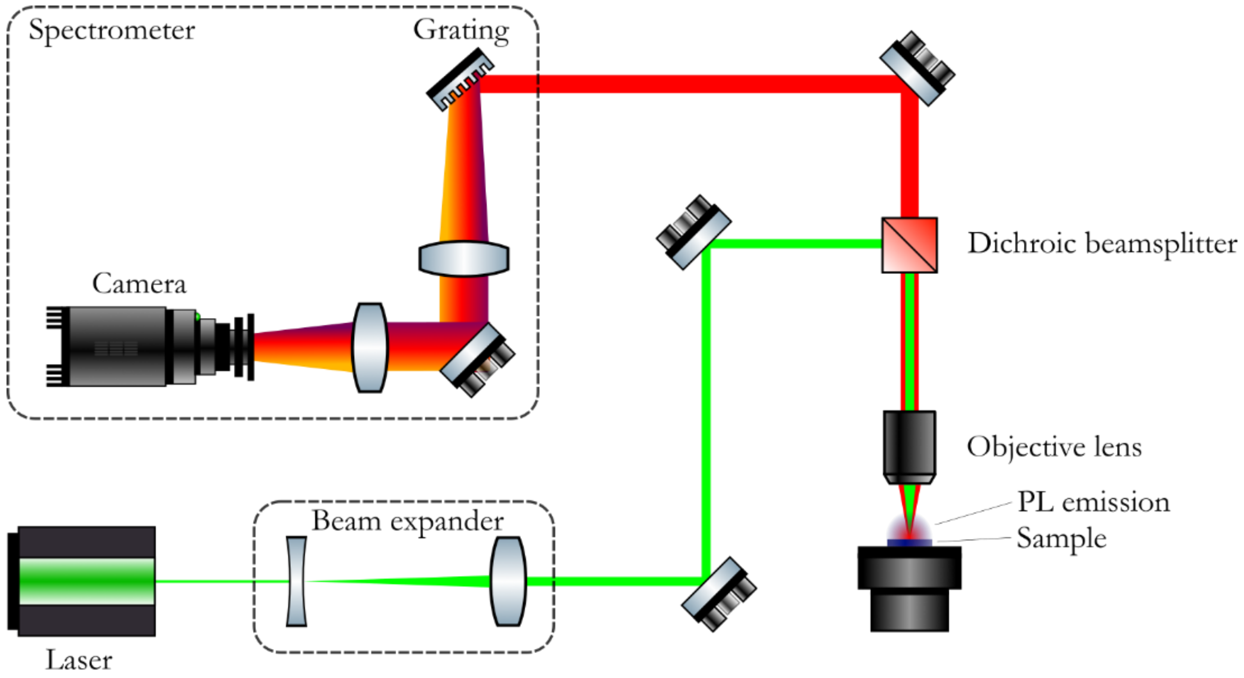
Hot carrier extraction occurs before full thermalisation

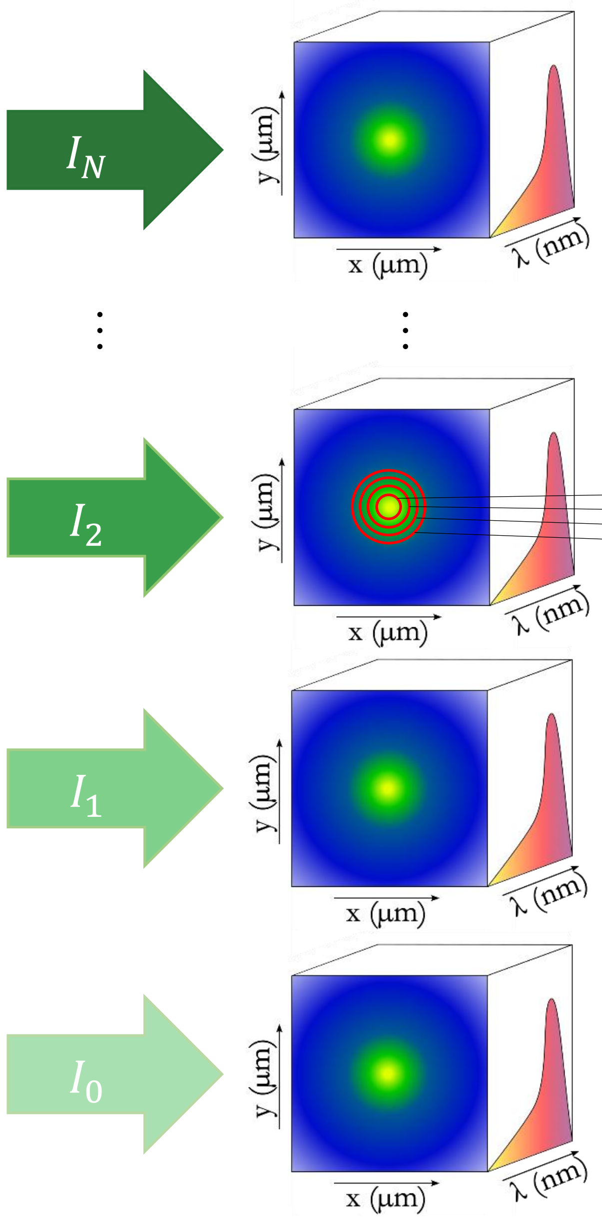
Selective energy contacts : gap does not limit Voc

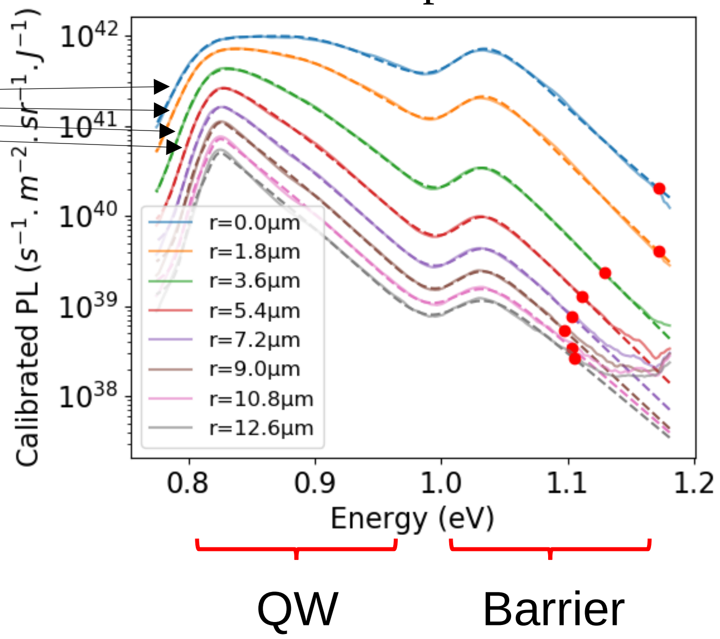
Photovoltaïque & thermoelectric device

Experimental setup:

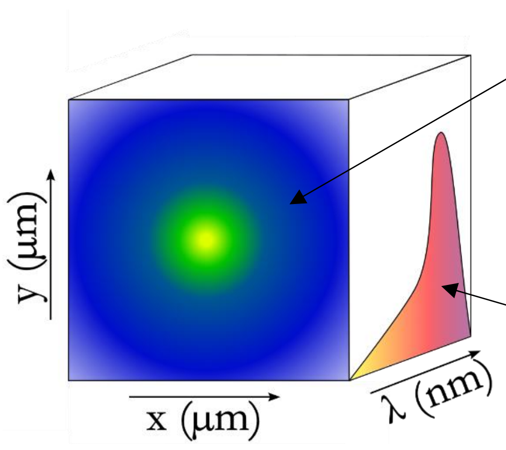
Hyperspectral imager + absolute calibration







Photoluminescence « cubes »:



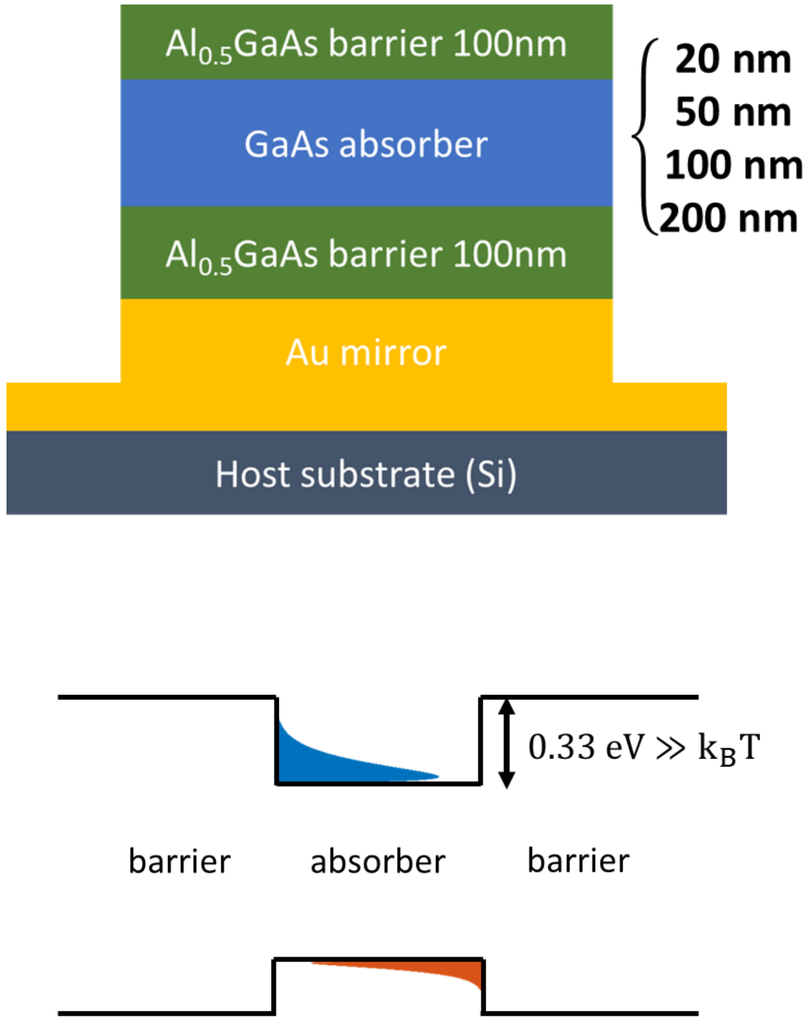
Spatial resolution
→ gradients

Spectral resolution and
photometric calibration → $T, \Delta\mu$

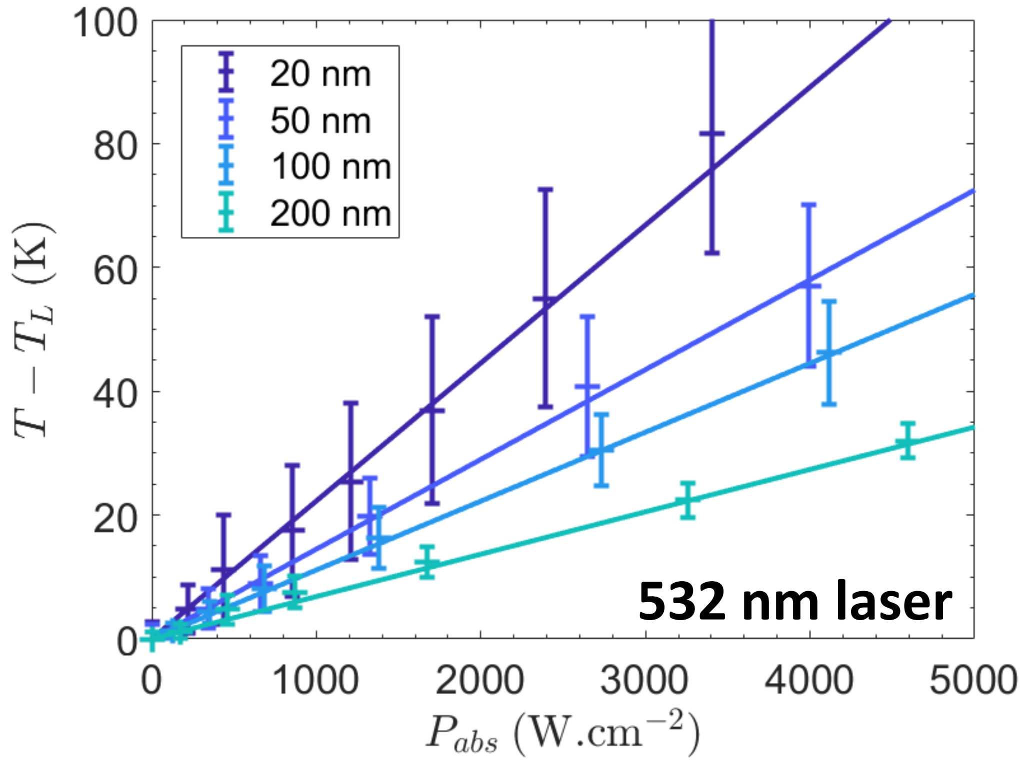
Generalized Planck Law:

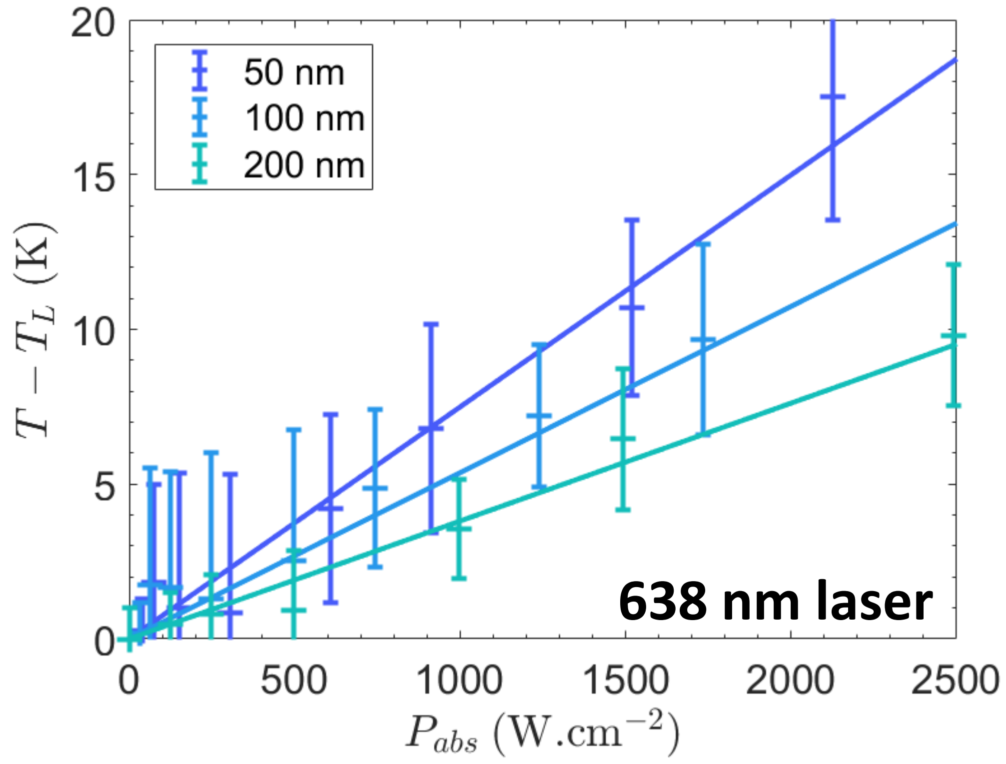
$$I_{PL}(E) = \frac{2}{h^3 c^2} E^2 \frac{A(E, \Delta\mu, T)}{\exp\left(\frac{E - \Delta\mu}{k_B T}\right) - 1}$$

Dependence on excitation wavelength and sample thickness



$$P_{th} = Q(T - T_L)$$



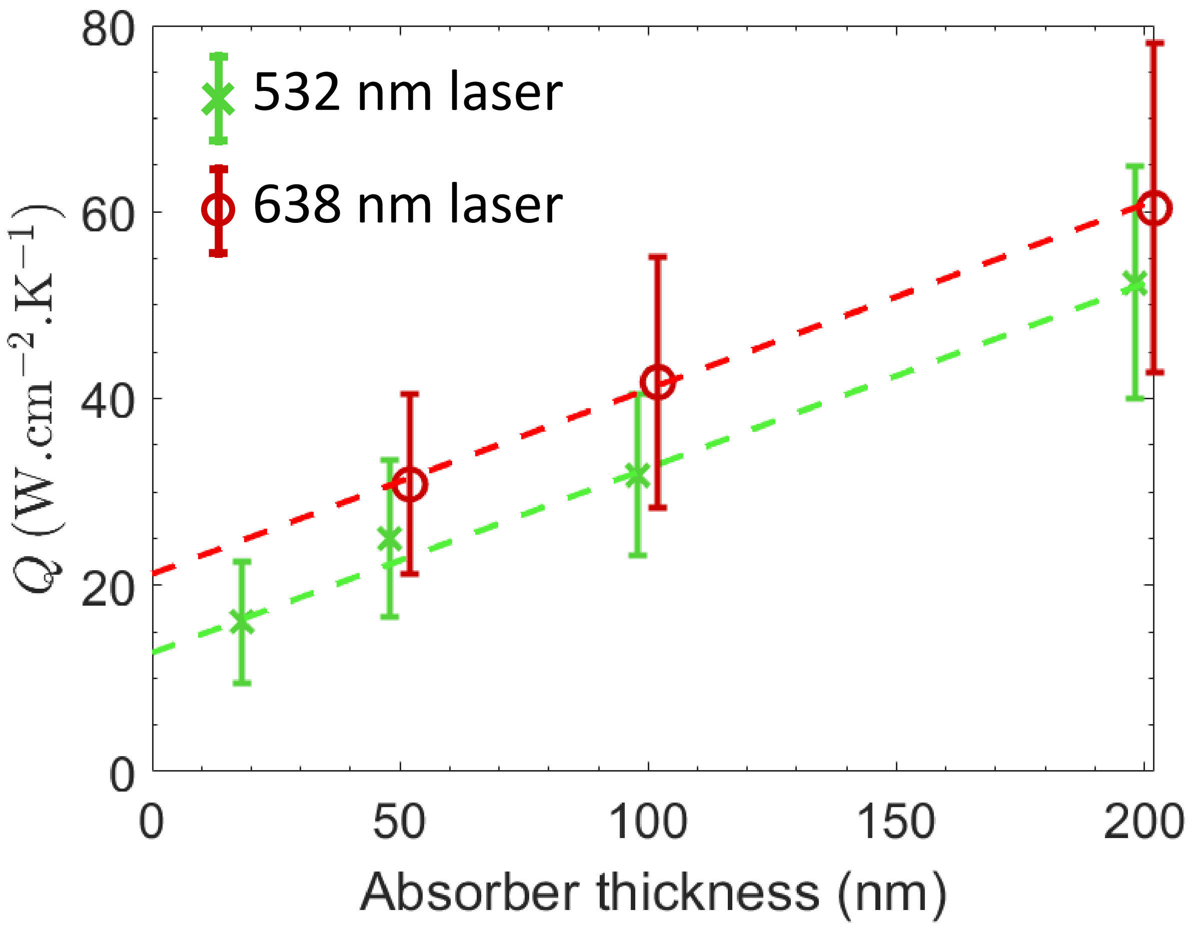


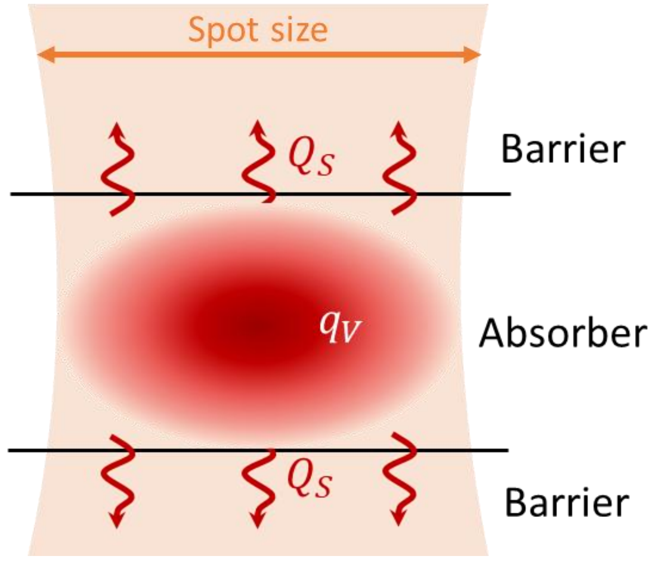
Temperature increase is proportional to absorbed power for all absorber thicknesses and laser wavelengths

Thermalisation

$$P_{th} = Q(T - T_L)$$

Q: Thermalization coefficient $(\mathrm{W.cm^{-2}.K^{-1}})$





$$Q = d * q_V + 2Q_s$$

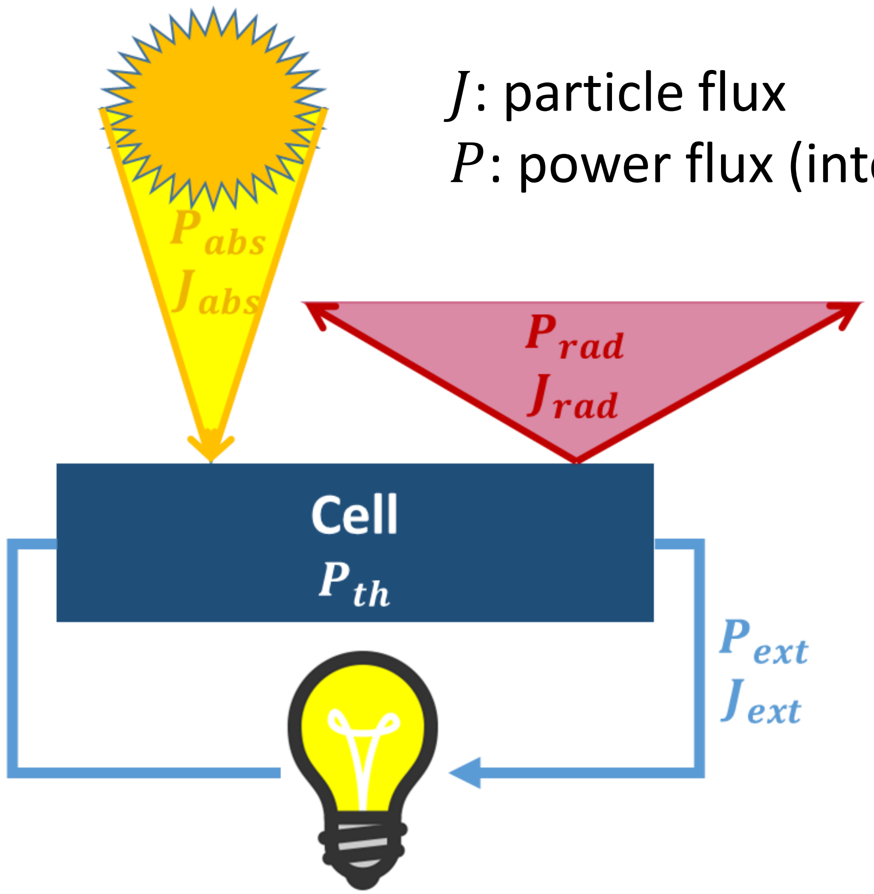
q_V: **volume thermalization coefficient**

Q_S: **surface thermalization coefficient**

	532 nm laser	638 nm laser
q_V $(\mathrm{W\,cm^{-2}\,K^{-1}\,nm^{-1}})$	$\boxed{0.20 \pm 0.07}$	$\boxed{0.20 \pm 0.13}$
Q_S $(\mathrm{W\,cm^{-2}\,K^{-1}})$	6.4 ± 3.2	10.8 ± 6.9

Identification of surface and volume contributions to thermalization
An empirical model for thermalization (validated by theory)

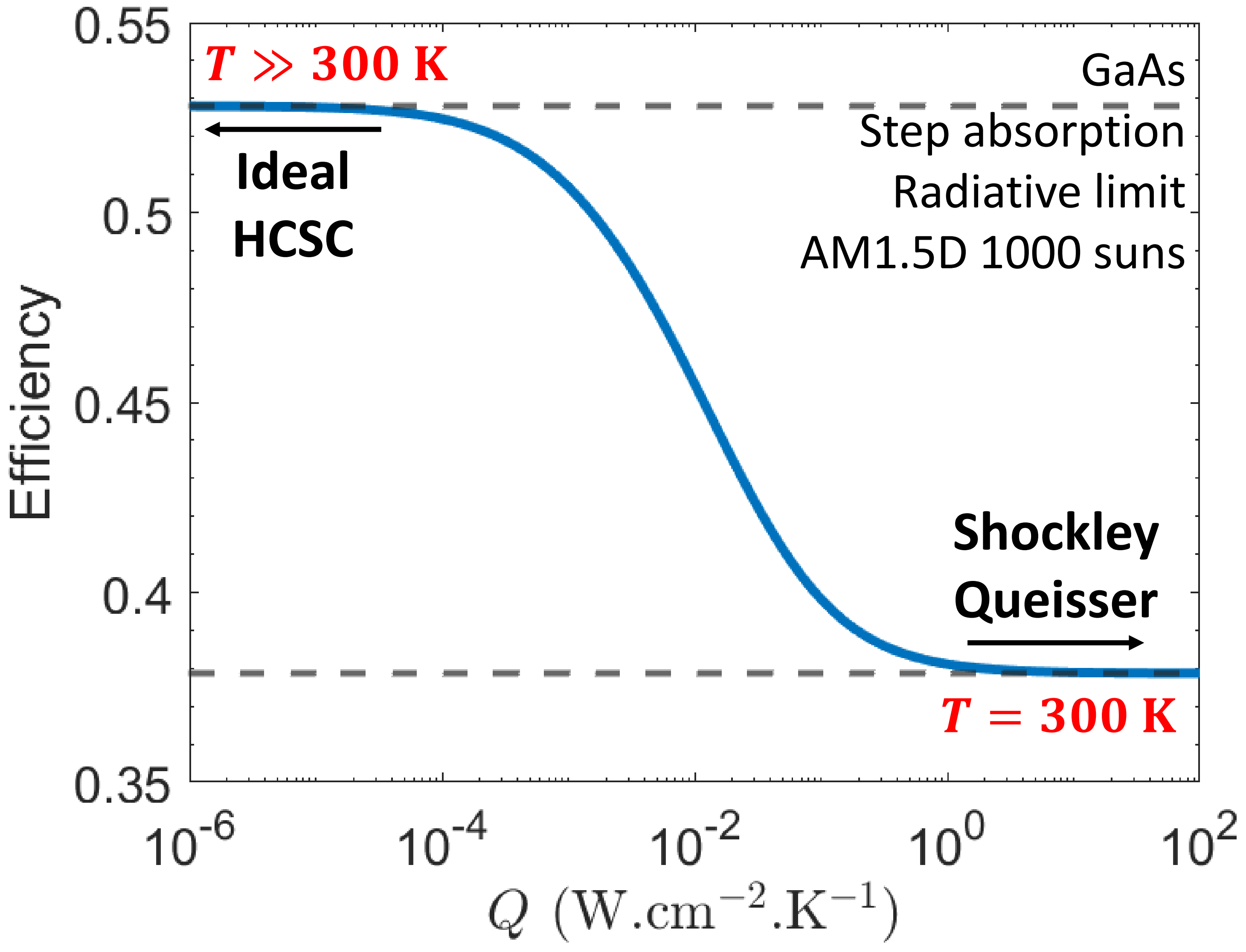
M. Giteau *et al.*, *J. Appl. Phys*, **128**, 193102 (2020).



J: particle flux
P: power flux (intensity)

$$\begin{cases} J_{ext} = J_{abs} - J_{rad} \\ P_{ext} = P_{abs} - P_{rad} - \boldsymbol{P_{th}} \end{cases}$$

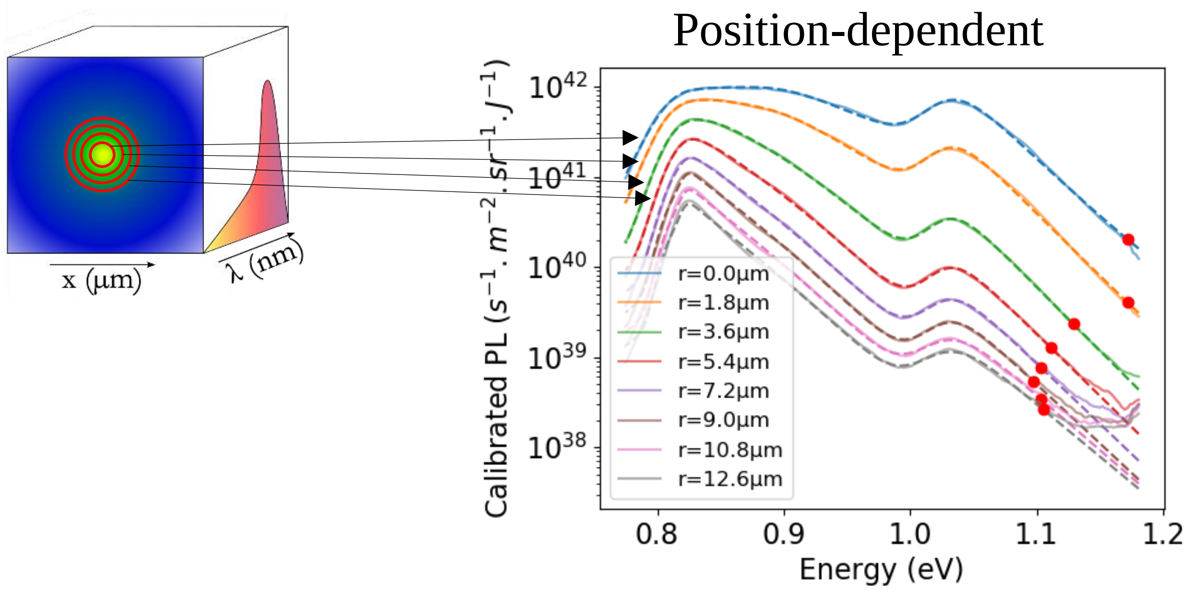
$$\boldsymbol{P_{th} = Q(T - T_L)}$$

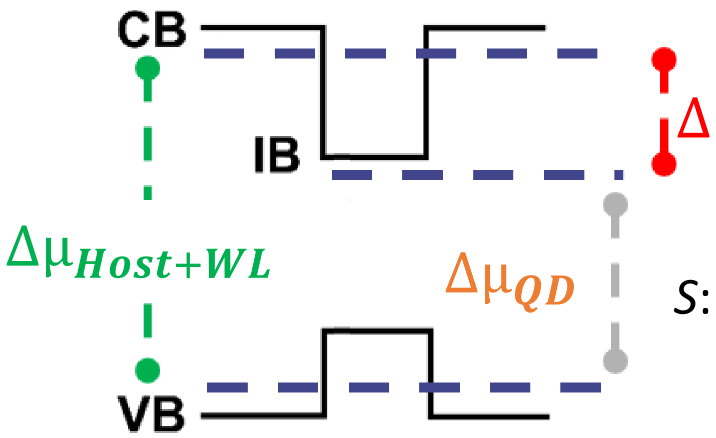


Q is a useful indicator for thermalization

JF Guillemoles et al. PVSEC 2005
LeBris et al, JPV 2012
M. Giteau et al., J. Appl. Phys, 128, 193102 (2020)

Carrier extraction and thermoelectric effect

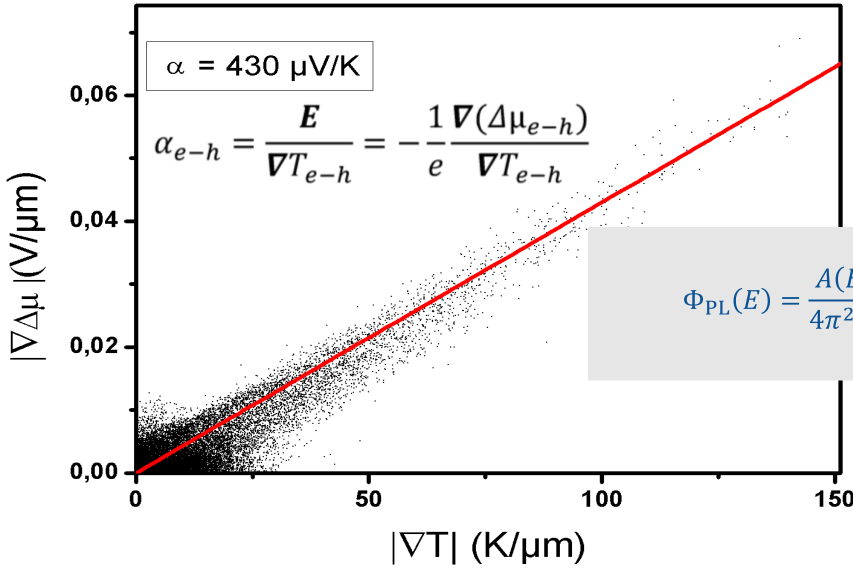




(S~500 µV/K)

S: Seebeck coeff

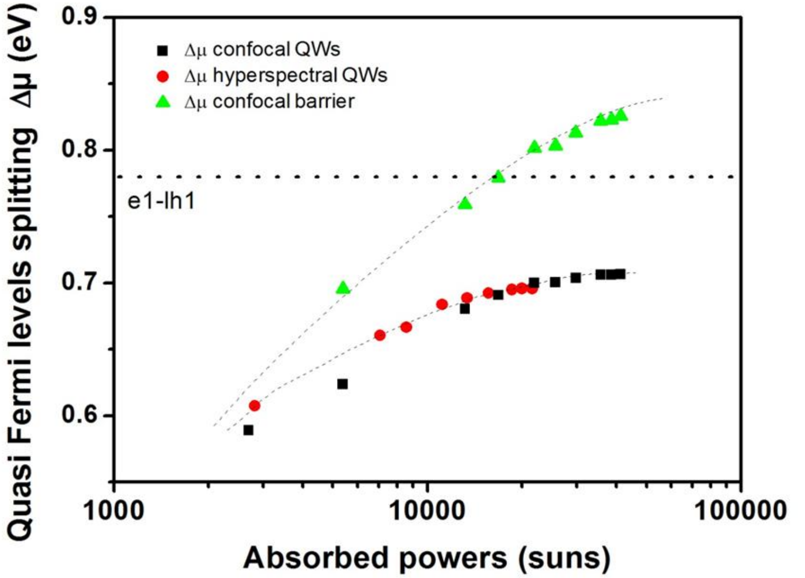
J. Rodière et al, APL **106** (2015) 183901

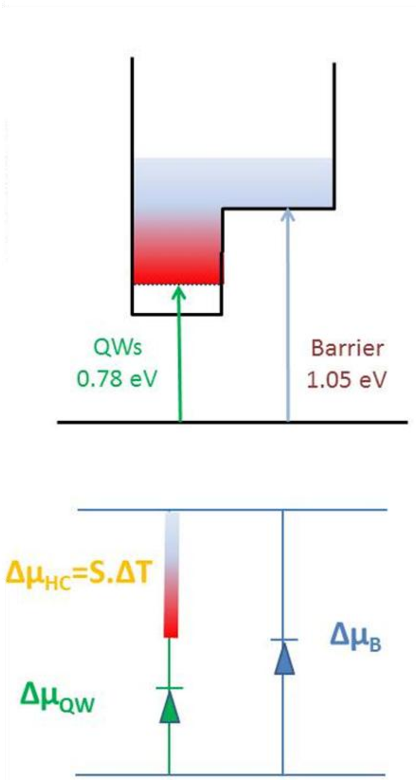


$$\Phi_{\mathrm{PL}}(E) = \frac{A(E)E^2}{4\pi^2\hbar^3 c_0^2}\frac{1}{\exp\left(\frac{E-\Delta\mu}{kT}\right)-1}$$

F. Gibelli et al, Phys Rev Applied, 2016

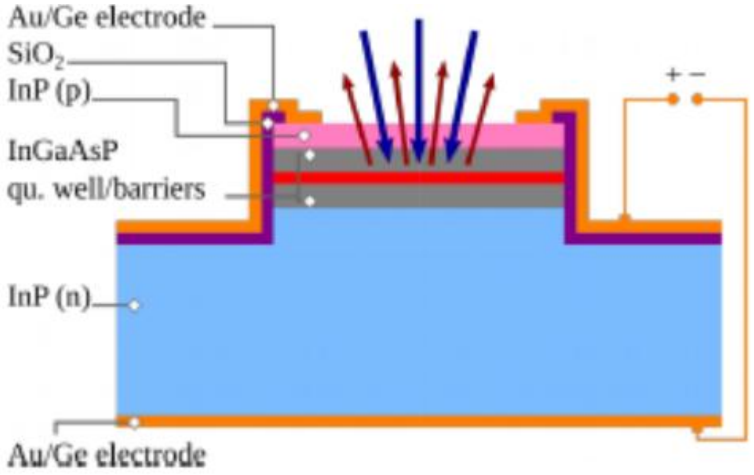
T. Vezin et al. PRA, 2024





IPVF
UMR 9006
Joint Research Unit

Experiments

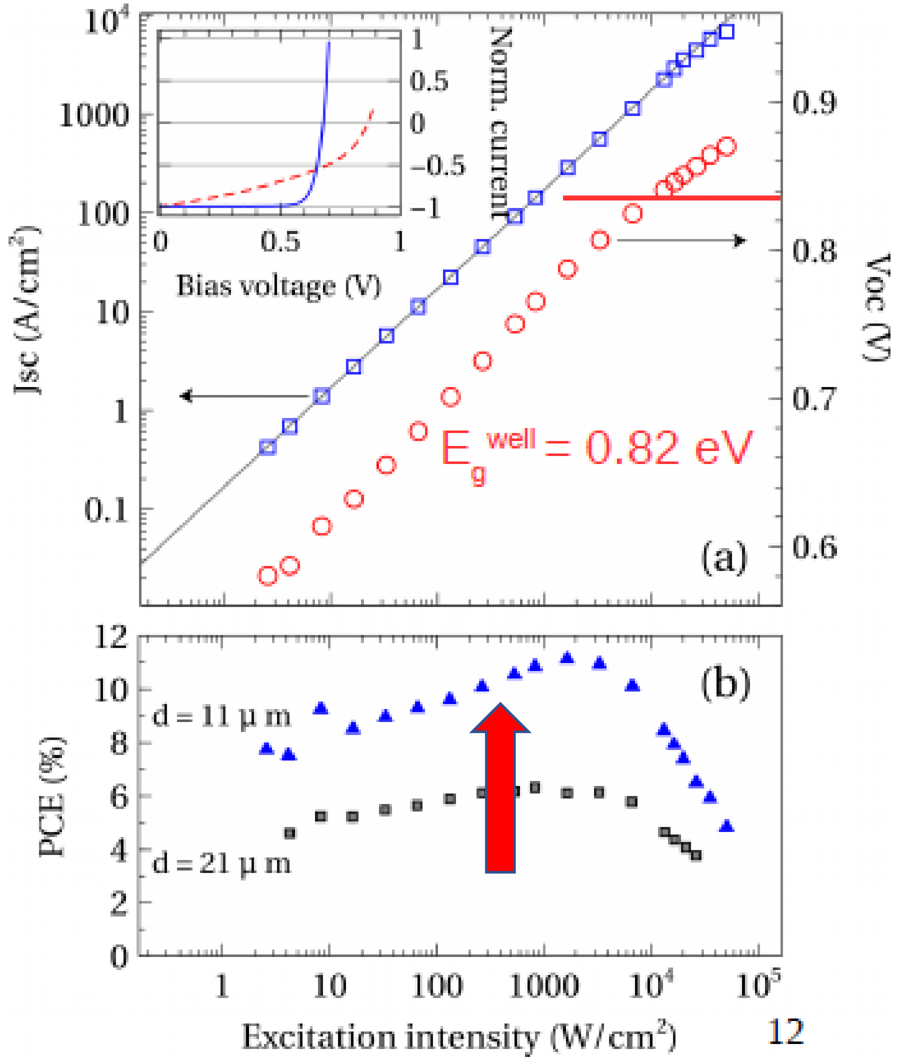


Thermalisation slowed down in nanostructures and under high power

⇒ Ultrathin devices

Solar cells MPP at 15000 suns and carrier **temperature 600K**

Still extracting at 100 000 suns



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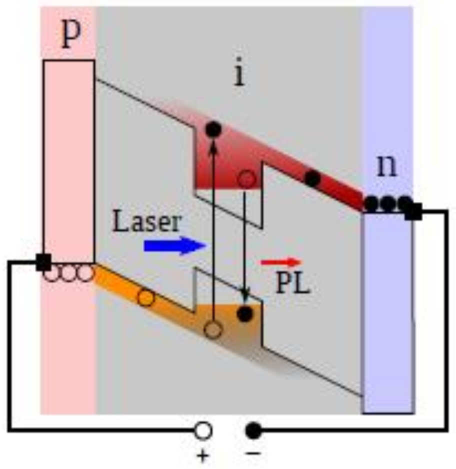
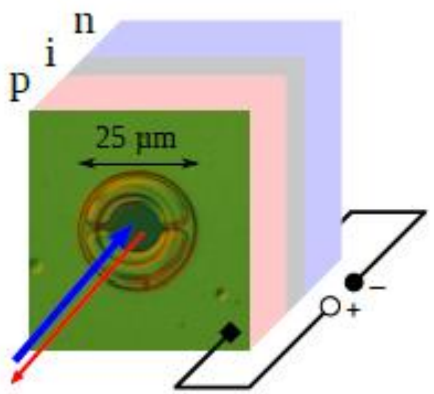
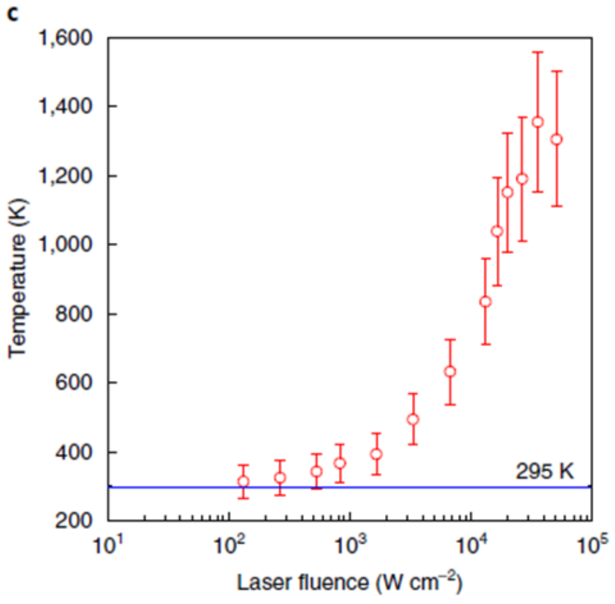






ARTICLES
https://doi.org/10.1038/s41560-018-0106-3
nature energy

Quantitative experimental assessment of hot carrier-enhanced solar cells at room temperature

Dac-Trung Nguyen[1], Laurent Lombez[1,2*], François Gibelli[1,2], Solène Boyer-Richard[3], Alain Le Corre[3], Olivier Durand[3] and Jean-François Guillemoles[1,2]

Myriam Paire et al., Energy Environ. Sci., 2011
A. Lebris et al., Energy Environ. Sci., 2012
Trung Dac Nguyen et al, Nat Energy 2018

IPVF UMR 9006 Joint Research Unit

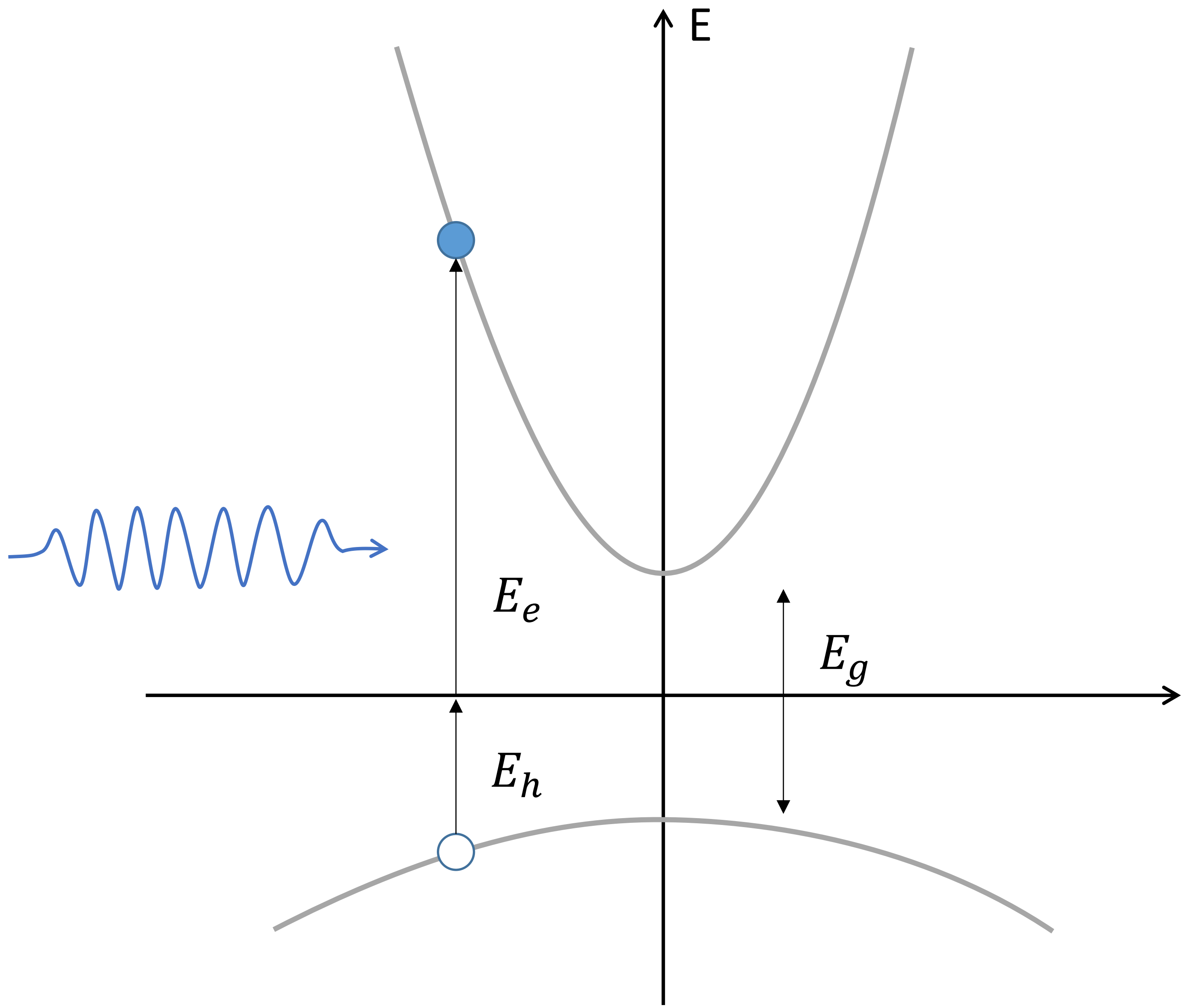
Foton CNRS UMR 6082

Wafer growth and device fabrication
Soline Richard-Boyer, Olivier Durand
OHM team – FOTON laboratory, Rennes.

Electrons and holes

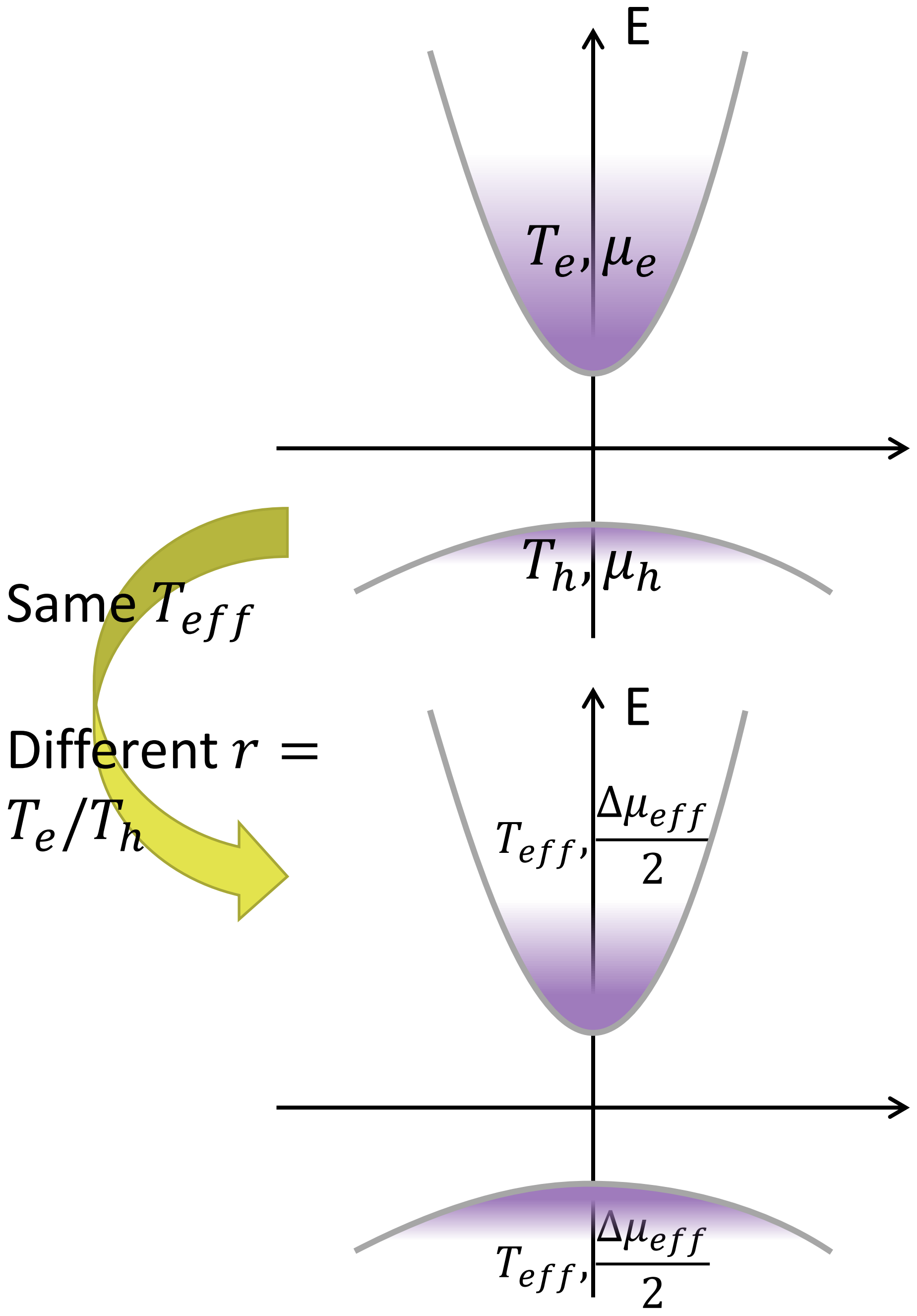
Asymetry of electrons and holes

$(m_e \ll m_h)$



[1] M. Asche and O. Sarbei, *Physica Status Solidi b*, 1984 (Theory)

[2] C. Bradley et al., *Solid-State Electronics*, 1989 (PAS)



Two-temperature generalized Planck law [1]:

$$\phi_{PL}(E) = \frac{2}{h^2 c^3} A(E) \frac{E^2}{\exp\left(\frac{E - \boldsymbol{\Delta\mu_{eff}}}{k_B \boldsymbol{T_{eff}}}\right) - 1}$$

with

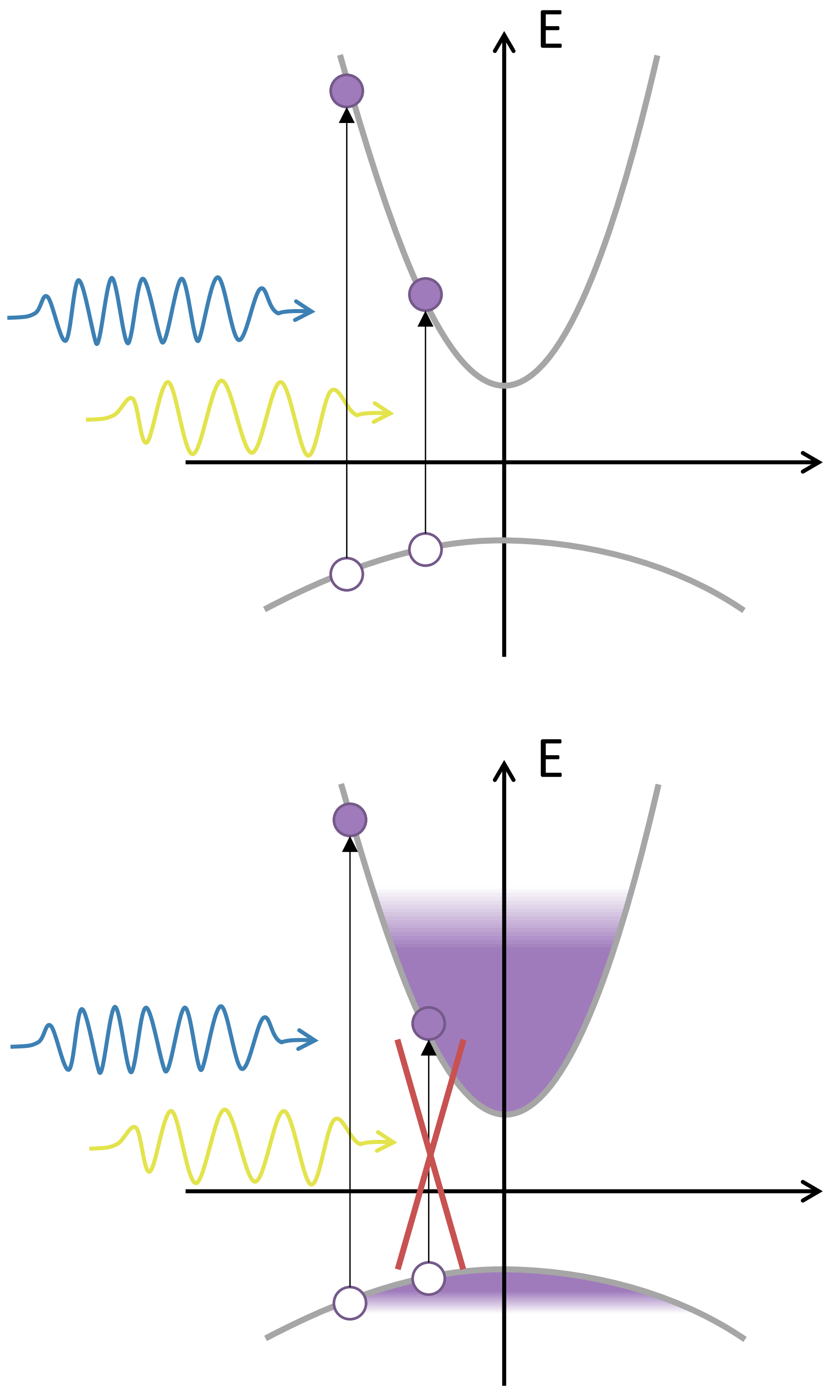
$$\begin{cases} \frac{1}{T_{eff}} = \frac{1-\xi}{T_e} + \frac{\xi}{T_h} \\ \frac{\Delta\mu_{eff}}{T_{eff}} = \frac{\mu_e}{T_e} + \frac{\mu_h}{T_h} - E_g\left(\frac{1}{2} - \xi\right)\left(\frac{1}{T_h} - \frac{1}{T_e}\right) \end{cases}$$

$$\left(\xi = \frac{m_e}{m_e + m_h}\right)$$

Emission high energy slope does not give a hint on individual carrier temperatures

[1] F. Gibelli et al., *Physica B: Condensed Matter*, 2016
NB: Pan APL 1986

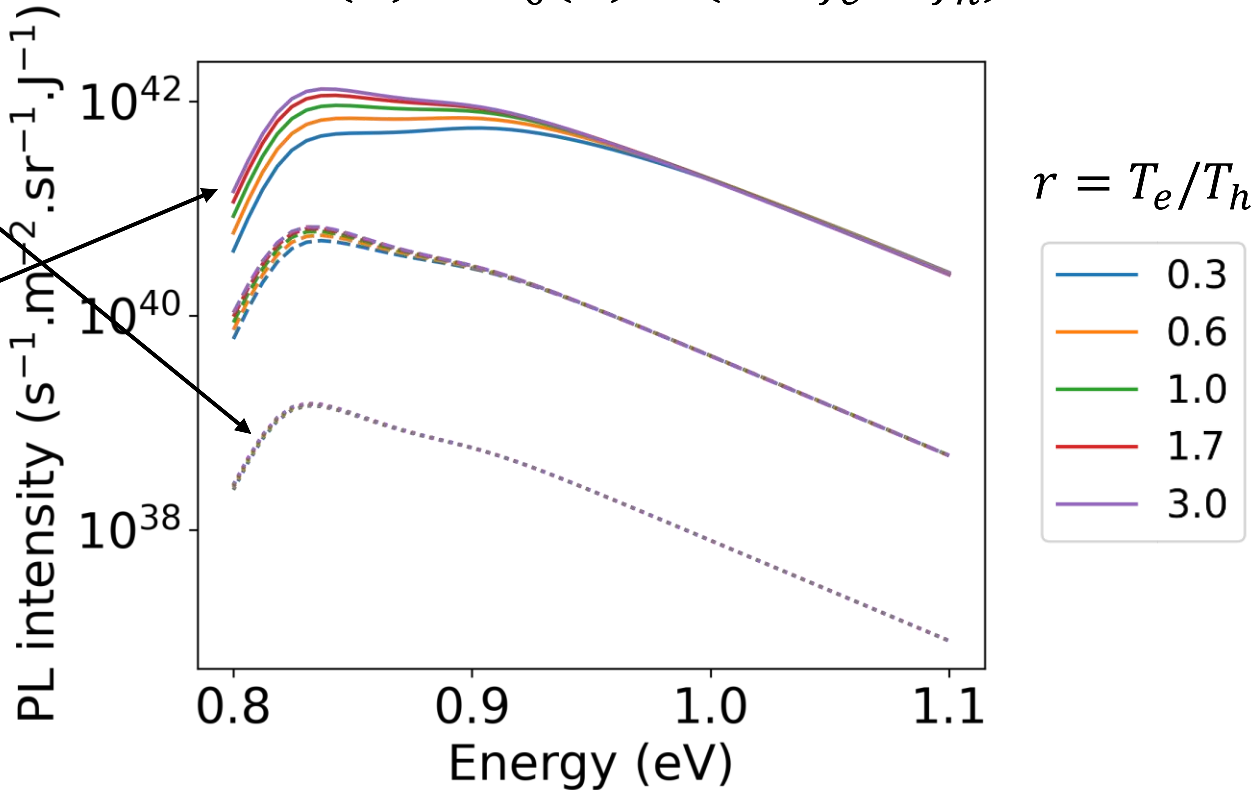
Absorptivity and band-filling



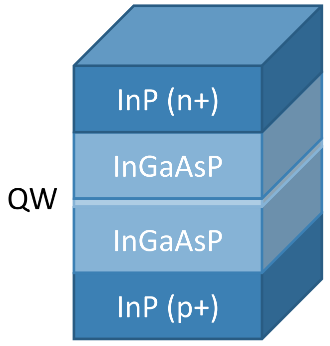
$$\phi_{PL}(E) = \frac{2}{h^2 c^3} \boldsymbol{A(E)} \frac{E^2}{exp\left(\frac{E - \Delta\mu_{eff}}{k_B T_{eff}}\right) - 1}$$

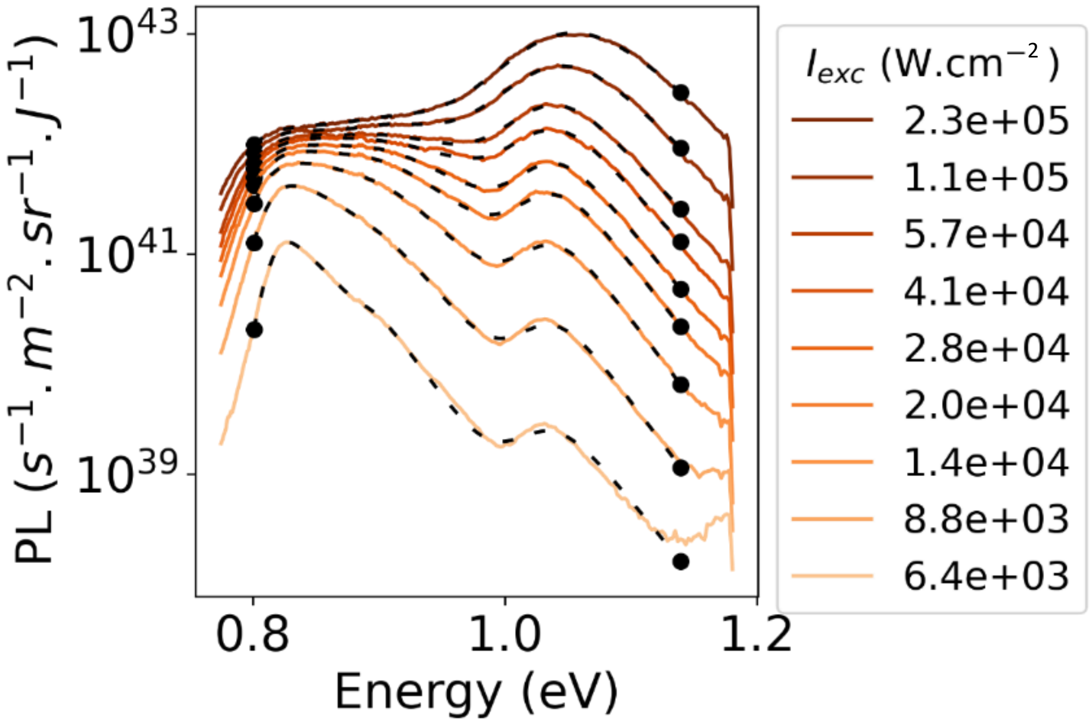
The absorptivity $A(E)$ depends on carrier populations through the **band-filling effect**

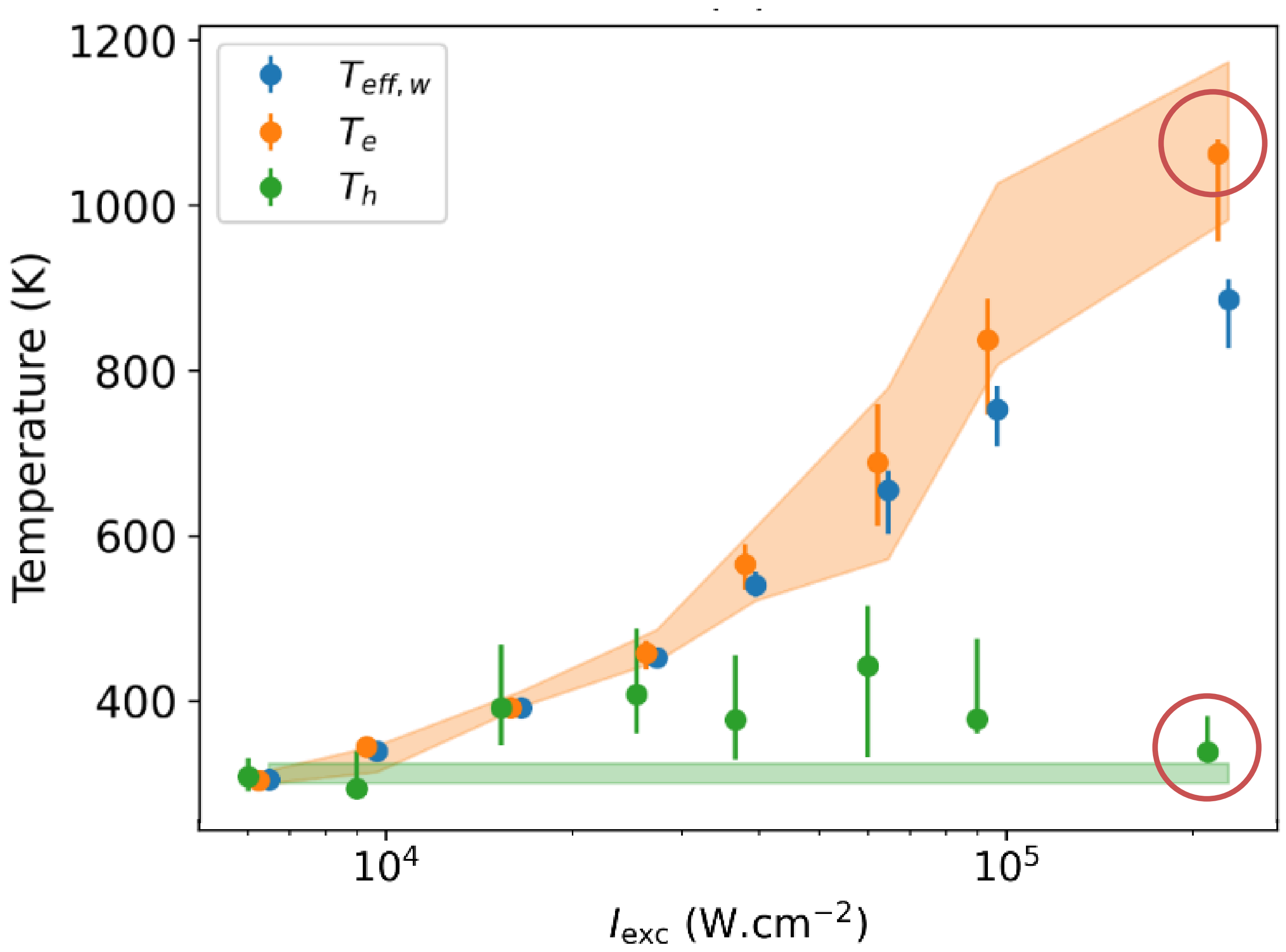
$$A(E) \simeq A_0(E) \times (1 - f_e - f_h)$$



The band-filling effect depends **on the temperature mismatch r**



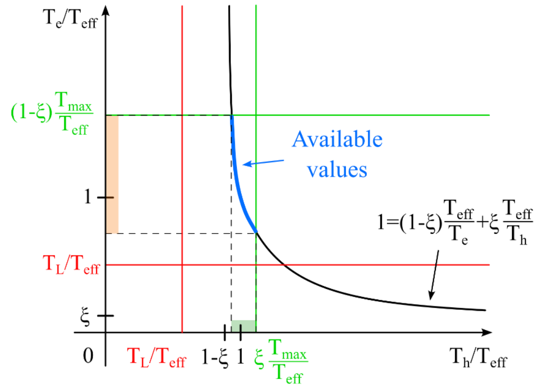




PHYSICAL REVIEW B **110**, 125207 (2024)

Direct determination of electron and hole temperatures from continuous-wave photoluminescence measurements

Thomas Vezin,[1,*] Nathan Roubinowitz,[1] Laurent Lombez,[2] Jean-François Guillemoles,[1] and Daniel Suchet[1]



- **Electrons are much hotter than holes (1000K vs 300K)**

- Holes are hotter than expected, which indicates electron-hole interaction (Auger ?)

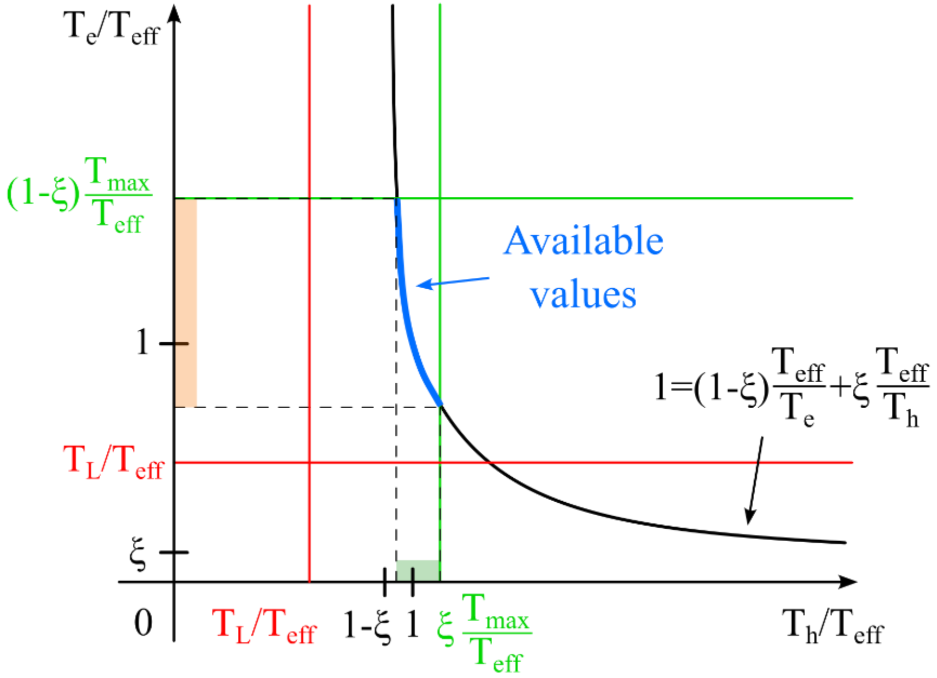
Fit 2T: Physical constraints

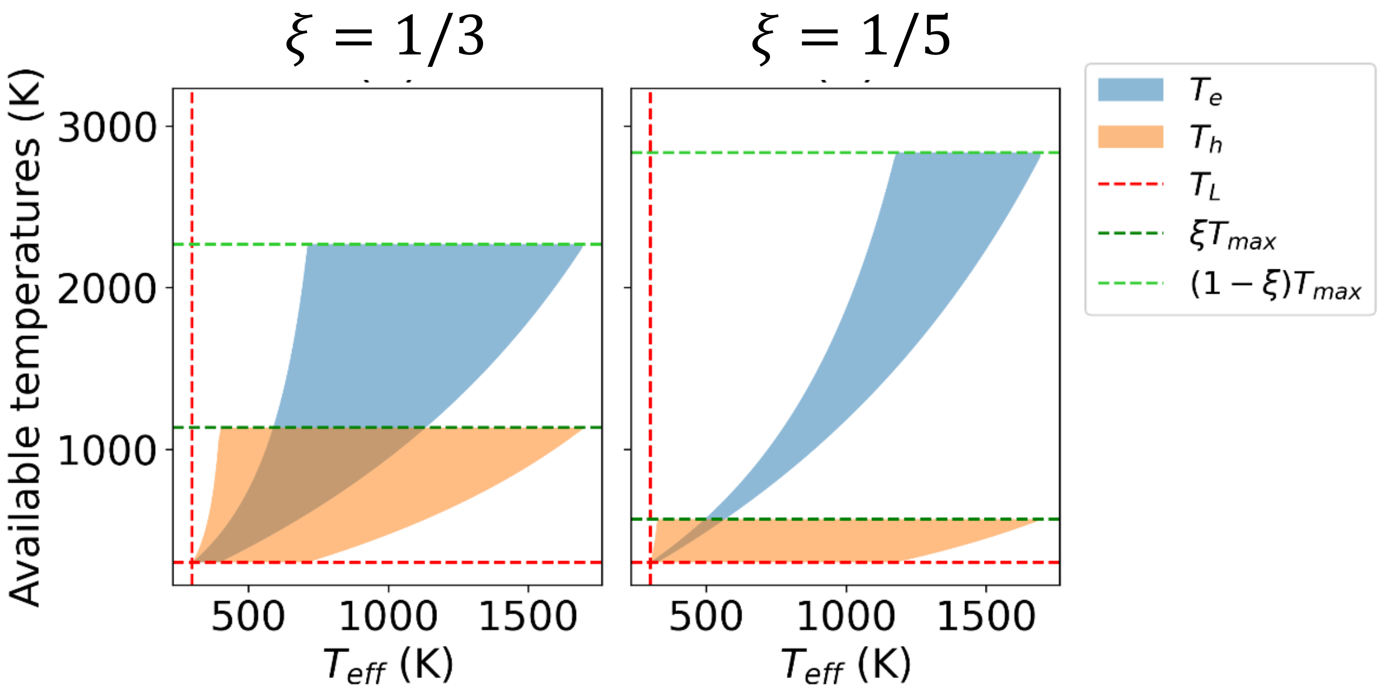
In the absence of electron-hole interactions,

$$\begin{cases} T_L \le T_e \le (1-\xi)T_{max} \\ T_L \le T_h \le \xi T_{max} \end{cases} \quad [1]$$

$$+$$

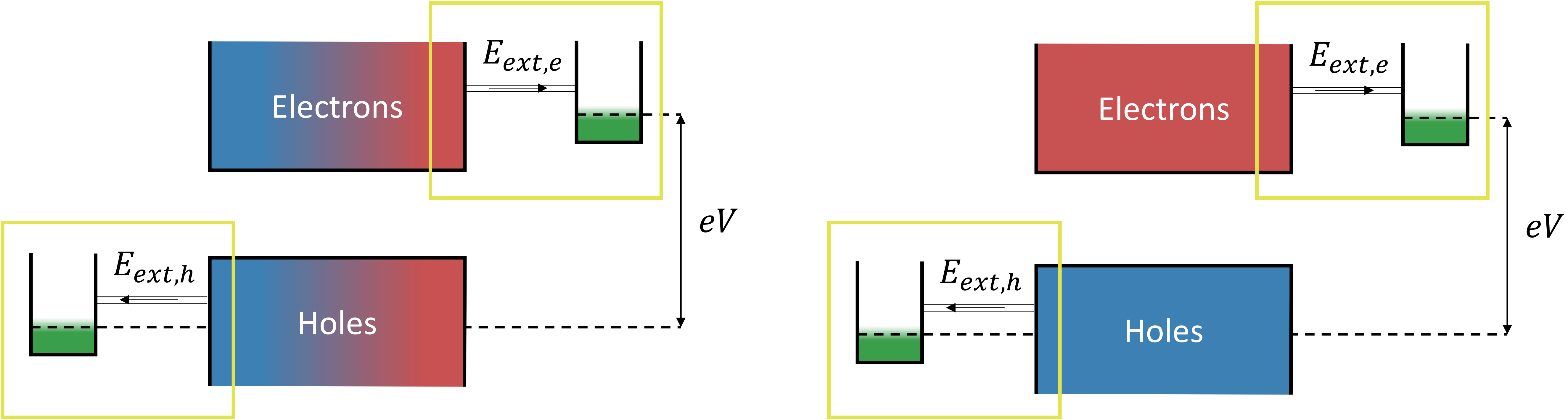
$$\frac{1}{T_{eff}} = \frac{1-\xi}{T_e} + \frac{\xi}{T_h}$$





[1] F. Gibelli et al., *Physica B: Condensed Matter*, 2016.

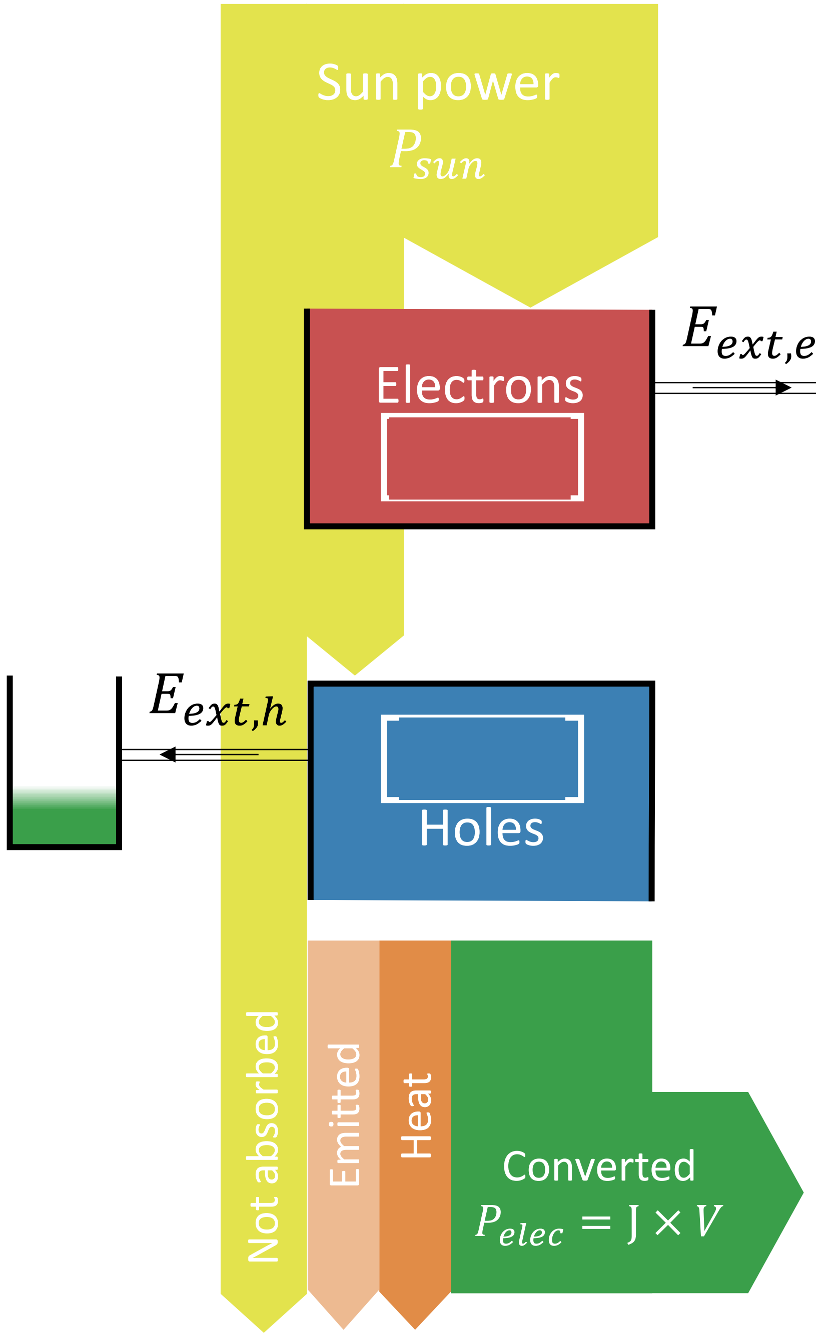
Voltage of a 2T hot-carrier solar cell



Perfectly selective contacts + isentropic (reversible) extraction [1]

$$eV = E_{ext,e}\left(1-\frac{T_L}{T_e}\right)+\mu_e\frac{T_L}{T_e}+E_{ext,h}\left(1-\frac{T_L}{T_h}\right)+\mu_h\frac{T_L}{T_h}$$

Detailed balance model for two-temperature hot-carrier solar cells



Ideal absorptivity: $P_{abs,e} = \int_{E_g}^{\infty} E_e(E)\phi_{sun}(E)dE$

2T GPL: $P_{rad,e} = \frac{2\pi}{h^3c^2}\int_{E_g}^{\infty} \frac{E_e(E)E^2}{\exp\left(\frac{E-\Delta\mu_{eff}}{k_B T_{eff}}\right)-1}dE$

Phenomenological: $P_{th,e} = Q_e(T_e - T_L)$

4 parameters $(\boldsymbol{T_e, \mu_e, T_h, \mu_h})$ ⇔ 4 equations

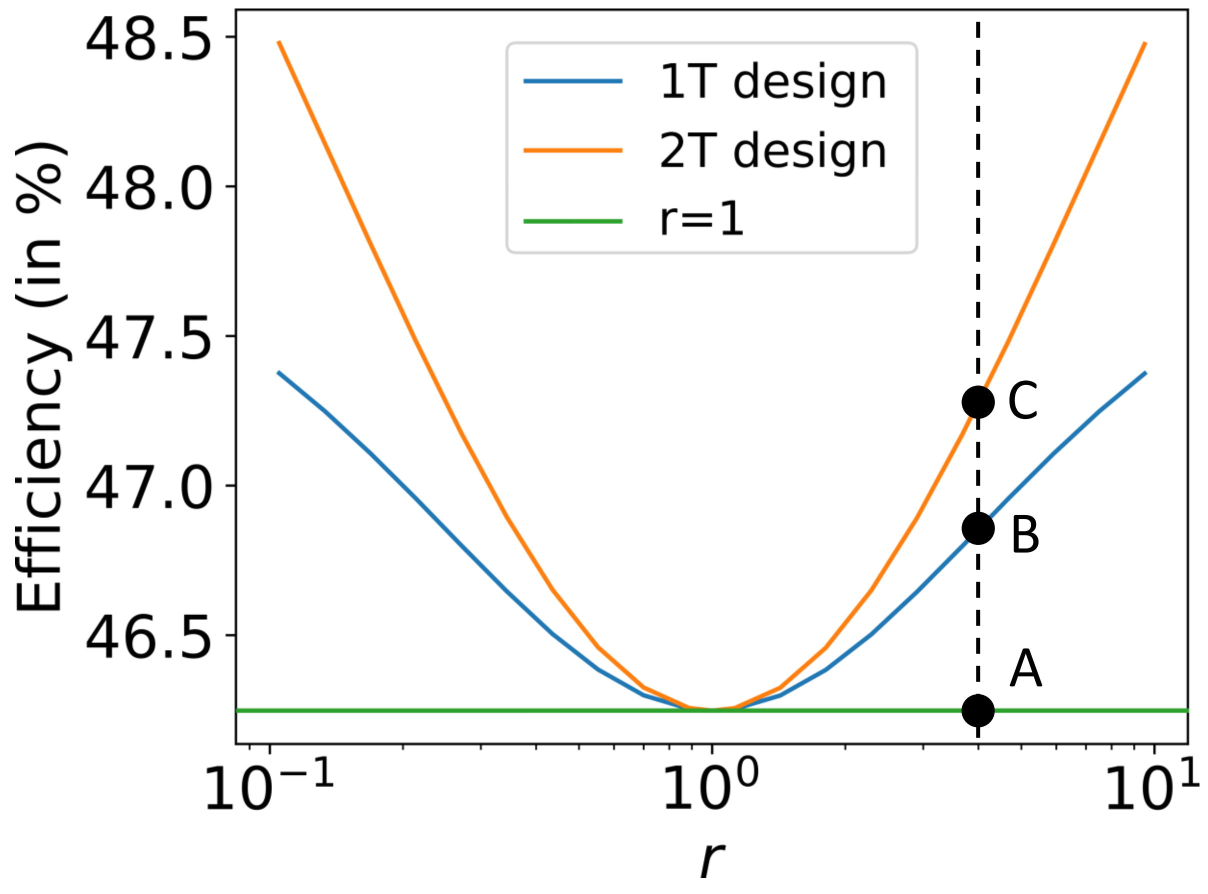
	Electrons	Holes
Particle balance	1	2
Power balance	3	4

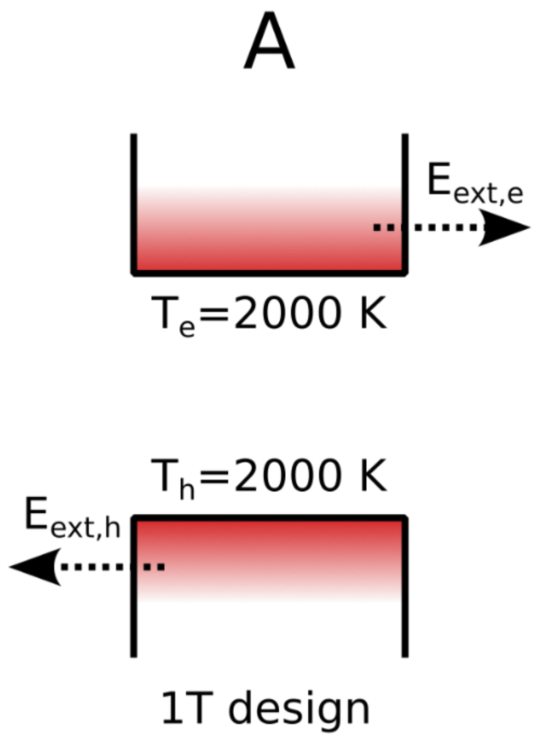
T. Vezin, N. Roubinowitz, J.F. Guillemoles, D. Suchet, "Hot electrons and cold holes: operation, efficiency and design of a two-temperature hot-carrier solar cell", *JPEPV*, 2024 **(in print)**.

Influence of the 2T effect on the efficiency

For an absorber with $E_g = 1$ eV, $\xi = 1/3$, and no thermalization.

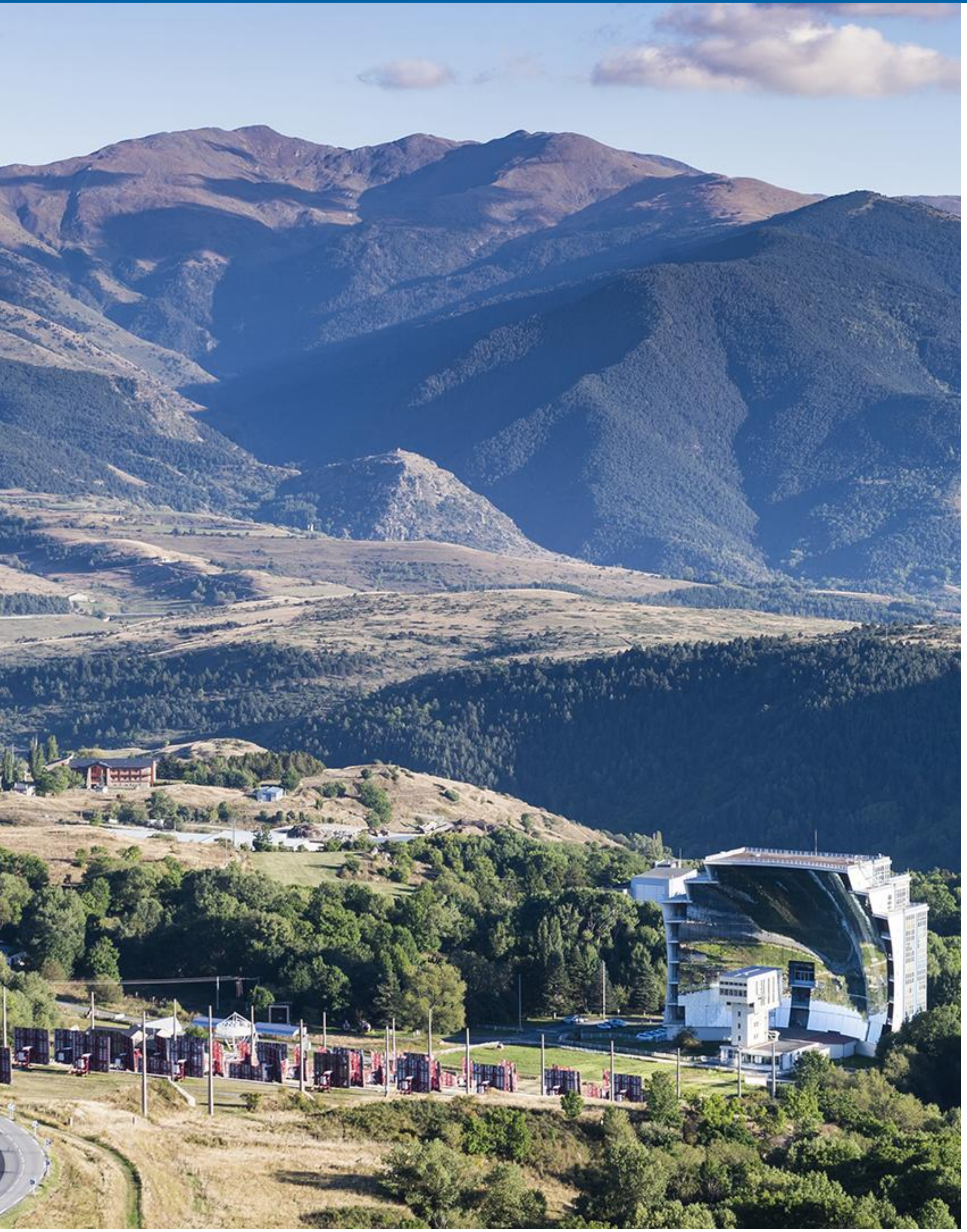
We consider an absorber with $T_{eff} = 2000$ K, and vary $r = T_e/T_h$. $(E_g = 1$ eV, $m_e = m_h)$





- The efficiency **increases slightly** when $T_e \neq T_h$.
- Knowing precisely T_e and T_h leads to small efficiency boost. $\boldsymbol{T_{eff}}$ **is more relevant.**

T. Vezin, N. Roubinowitz, J.F. Guillemoles, D. Suchet, "Hot electrons and cold holes: operation, efficiency and design of a two-temperature hot-carrier solar cell", *JPEPV*, 2024 **(in print)**.



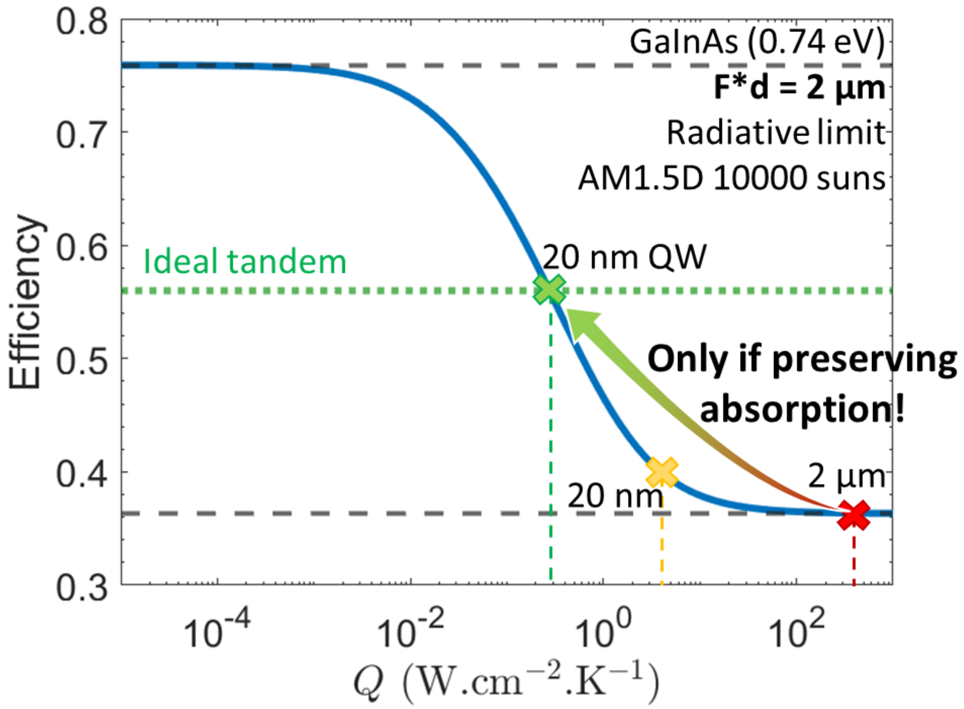
Hot carriers:

More (concentration) is different: hot carriers

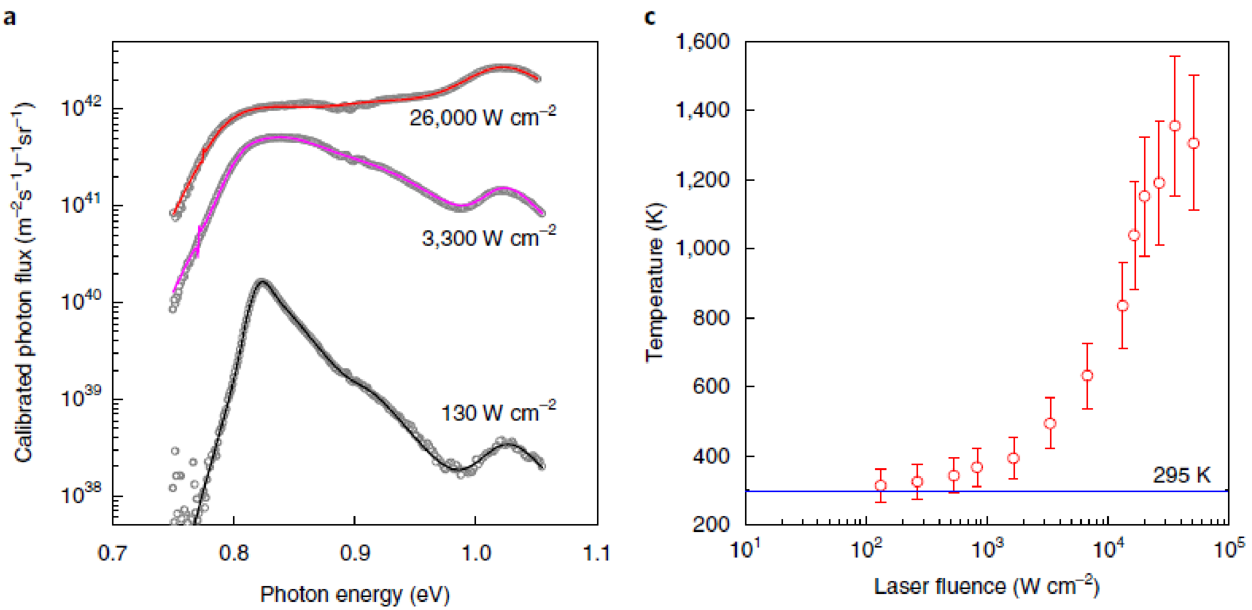
Thermalisation rates at the verge of efficiency increase

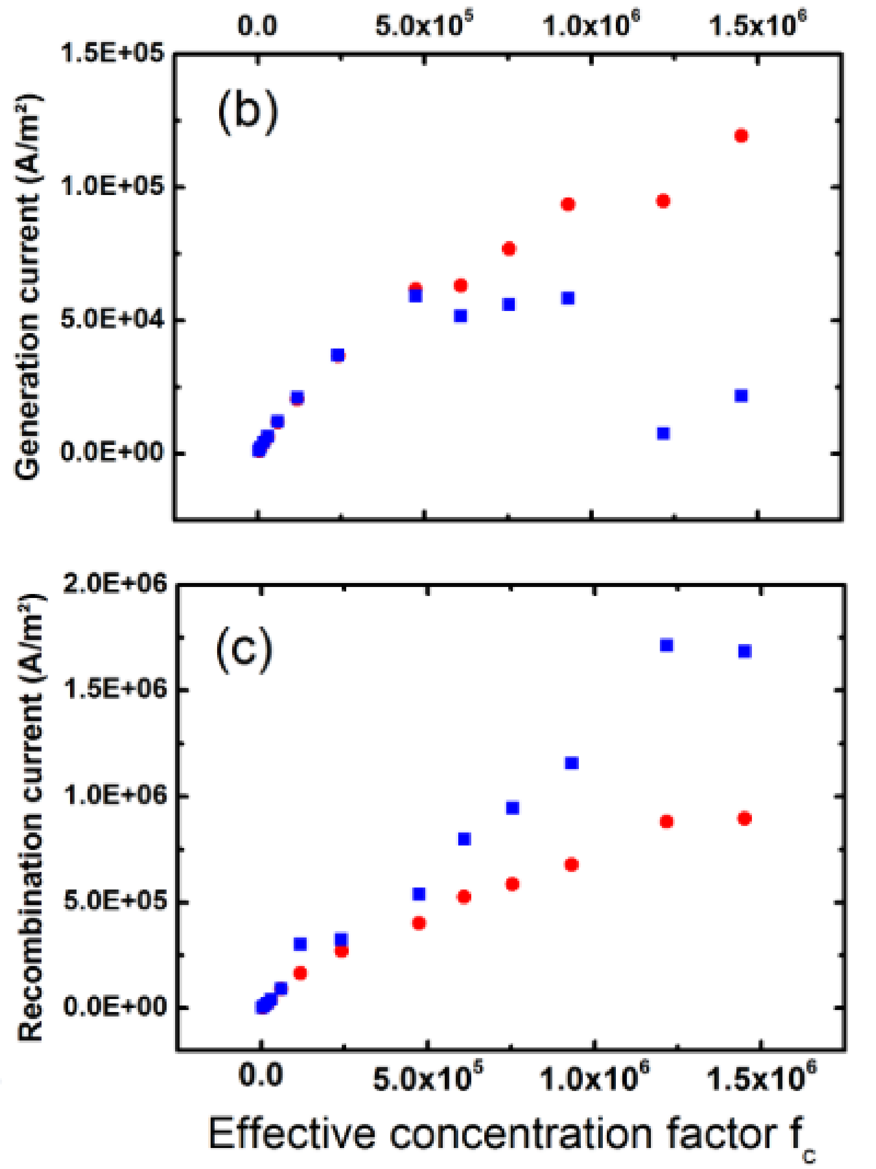
Device design is mostly dependent on effective temperature and chemical potential

(Electrons and holes with different temperatures could actually be better)



Generation-recombination gain





MPP **15000** suns and carrier **temperature 600K**

Hot carrier regime: more generation (less band filling), less recombination

ARTICLES
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Quantitative experimental assessment of hot carrier-enhanced solar cells at room temperature

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