The Opto-Electronic Physics that Broke the Efficiency Record in Solar Cells

Weizmann Inst. Alternative Energy Research Initiative
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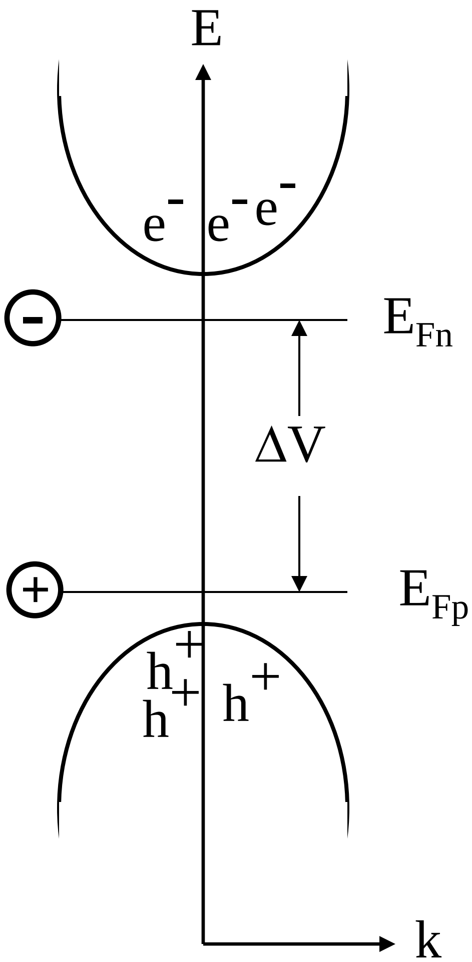
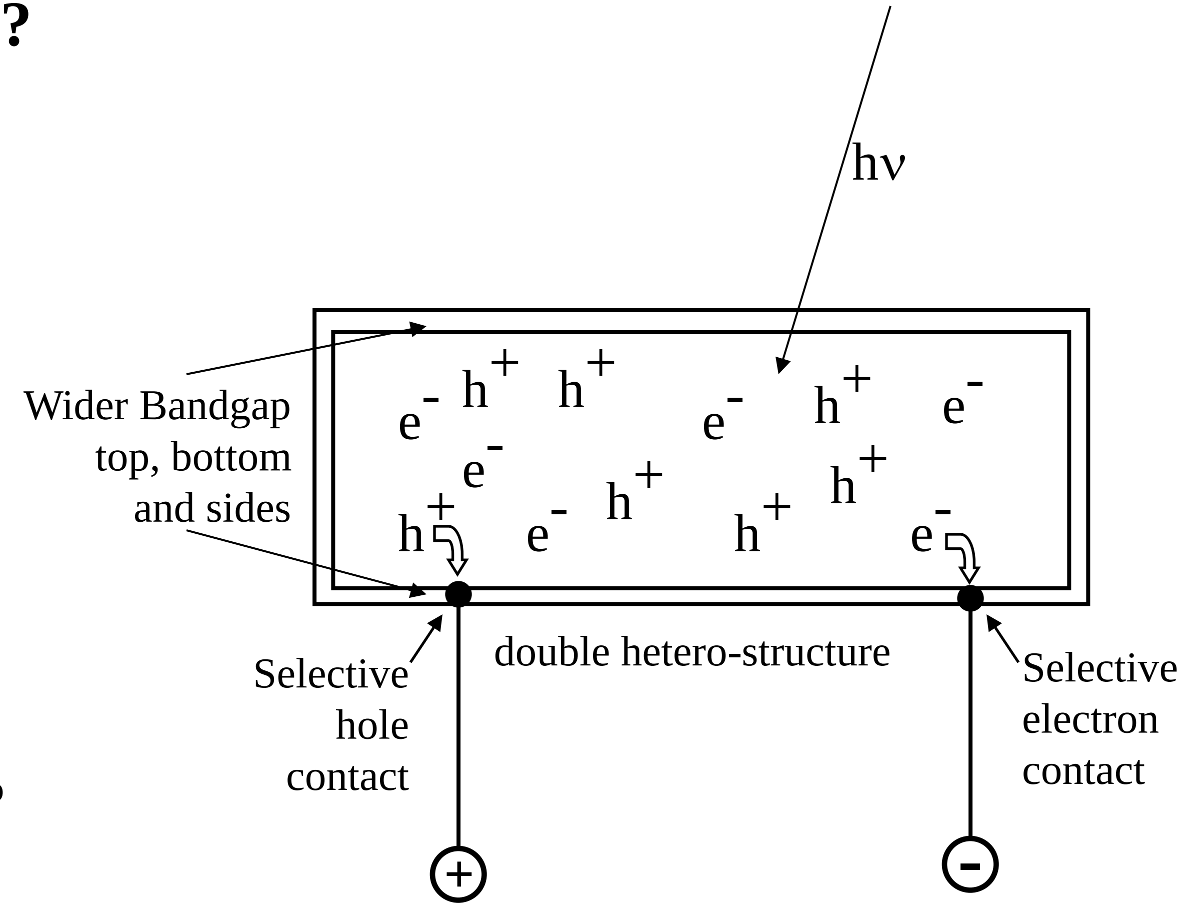
Miller et al, IEEE J. Photovoltaics, vol. 2, pp. 303-311 (2012)

1. Why the pn junction is merely optional in solar cells?
2. What determines the voltage of a solar cell?
3. What is the statistical mechanical approach to optics that is needed in solar cells?
4. Are photonic crystals of any help toward solar cells?
5. What are the top competing technologies?
6. What is the status of the industry today?

What is a Solar Cell?





Diffusion potential to contacts is typically <1mVolt.

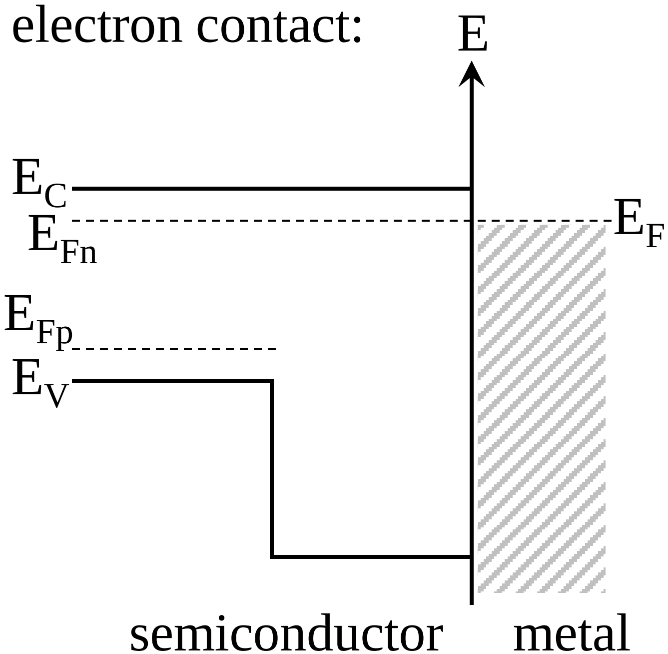
A Solar Cell does not require a p-n junction!

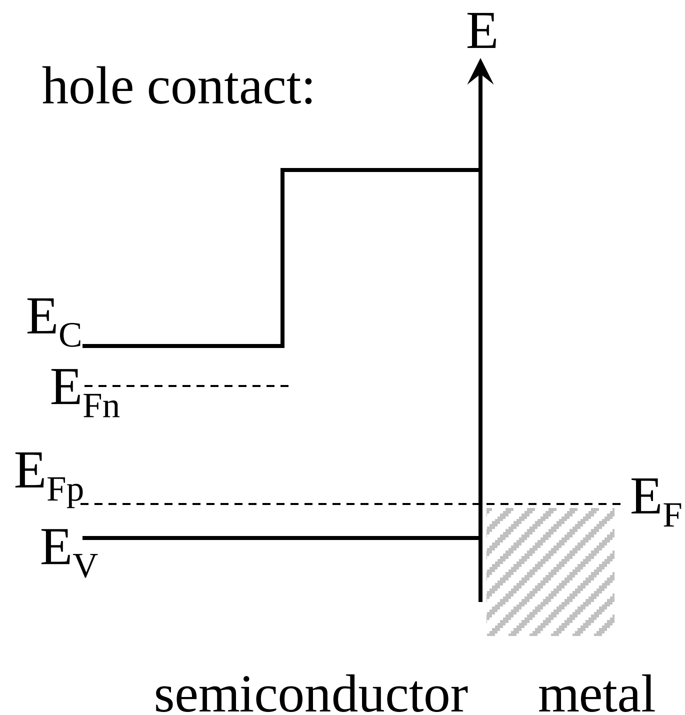
What is a Selective Contact?

It passes one type of carrier but not the other.

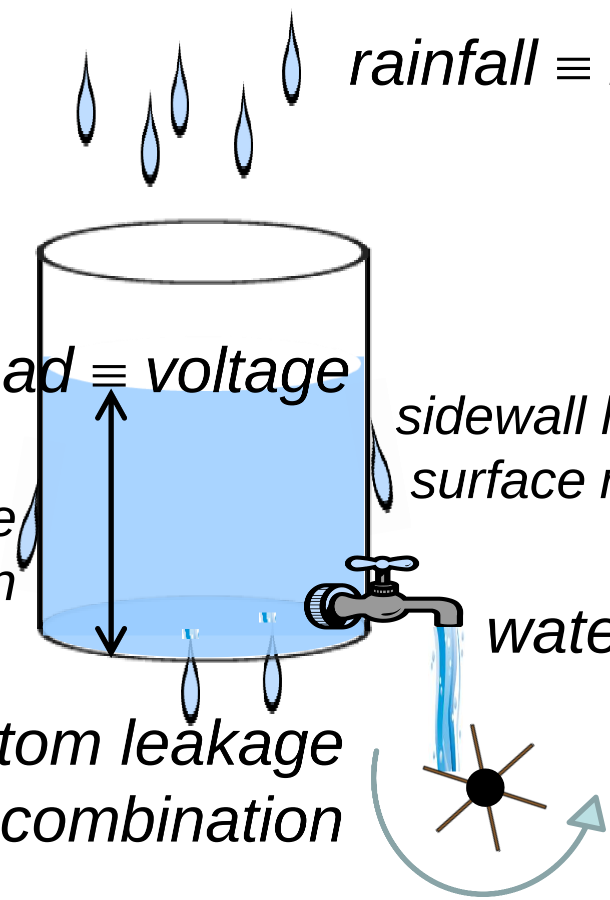
Most Ohmic electrical contacts barely work on even one type of carrier.
Therefore they are almost all selective.

The ideal type of selective contact is a hetero-contact:





Solar Cell as a Bucket feeding a Water Wheel



water wheel output ≡ solar cell power

There are three things to know about Solar Cells:

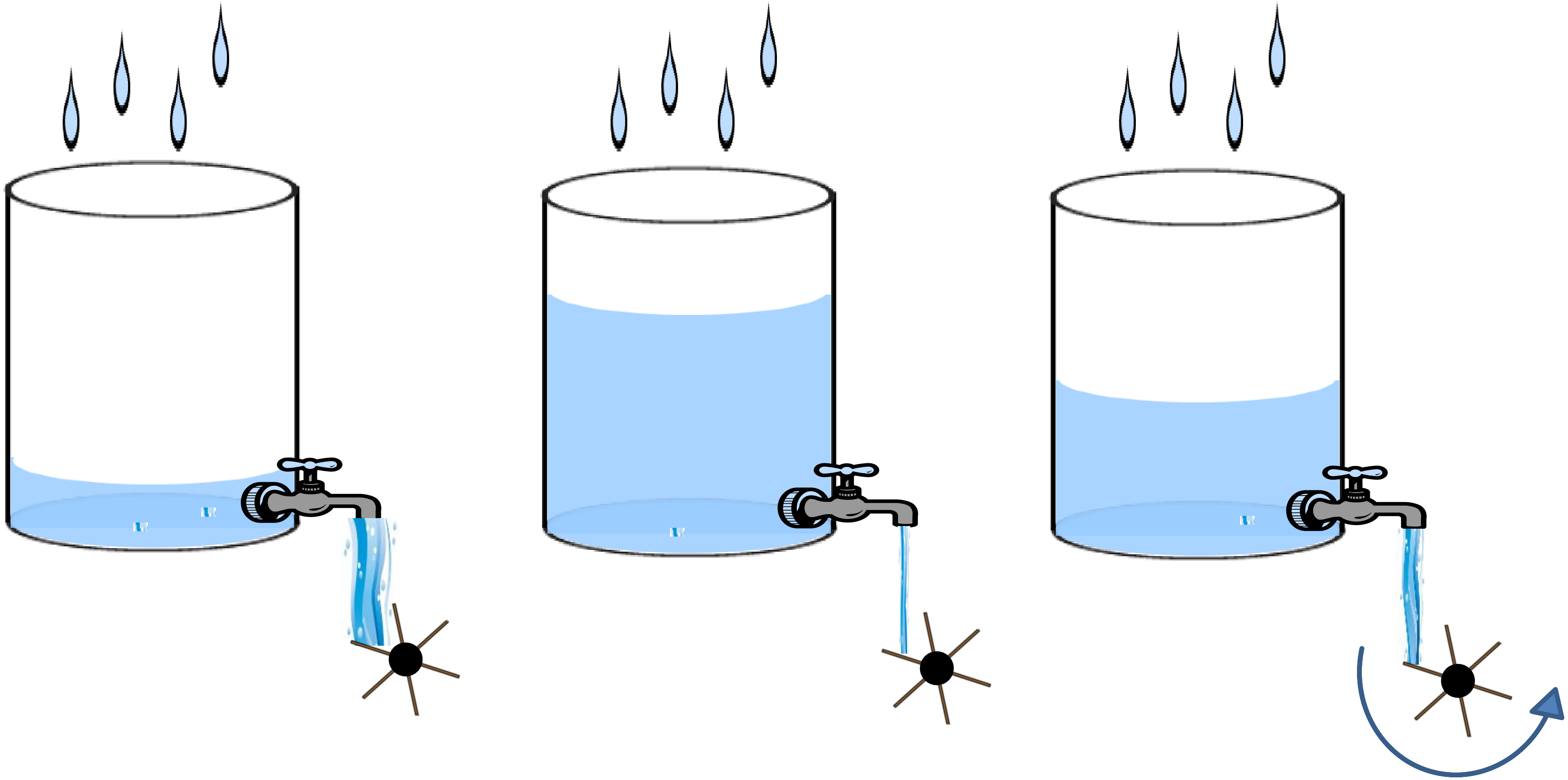
1. Fill Factor

2. Short Circuit Current

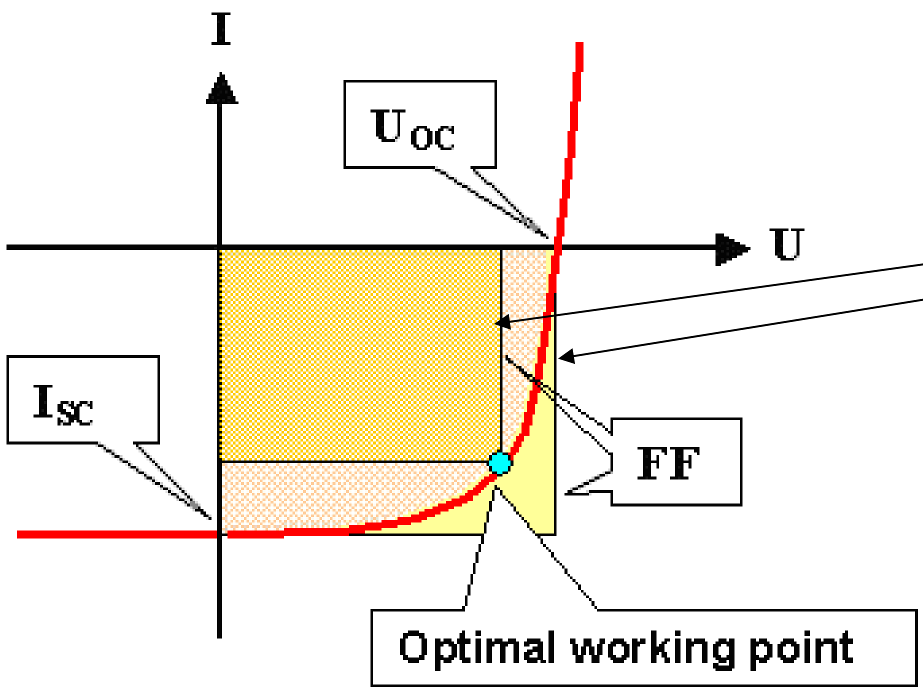
3. Open Circuit Voltage

Three possible valve conditions

Open valve Low-pressure, high-flow	Closed valve High-pressure, low-flow	Partially restricted valve Optimal pressure×flow



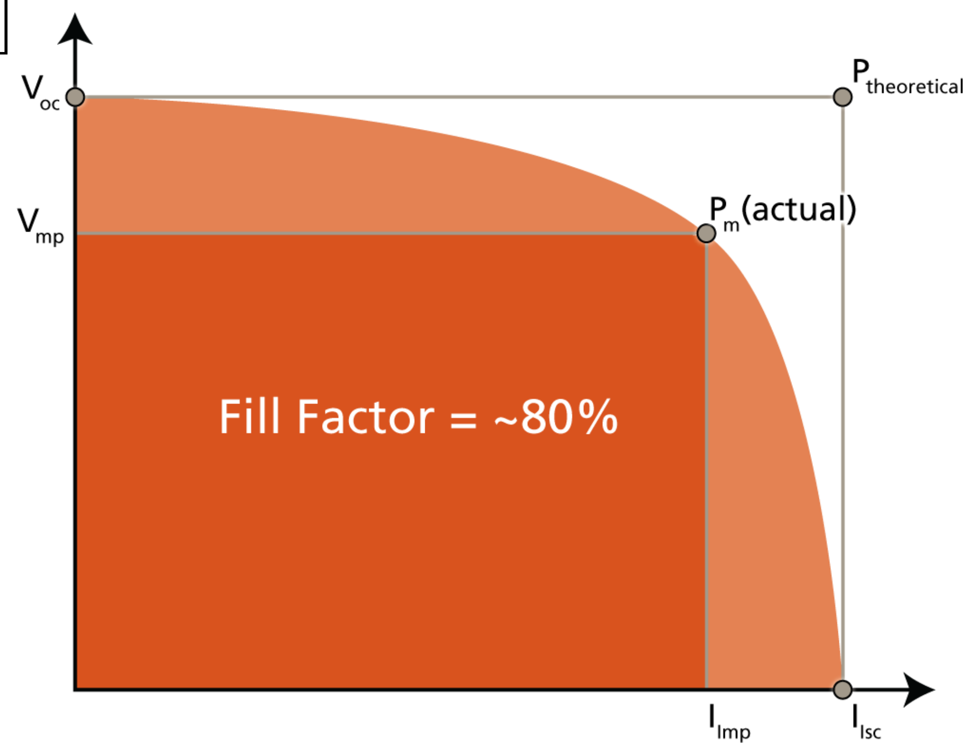
(Water wheel barely turns) (Water wheel doesn’t turn) (Max water wheel output)



Fill-Factor = ratio of these two rectangles

Fill-Factor is more a thermodynamic property, rather than a circuit property.

Ideal Fill-Factor ~ 89%

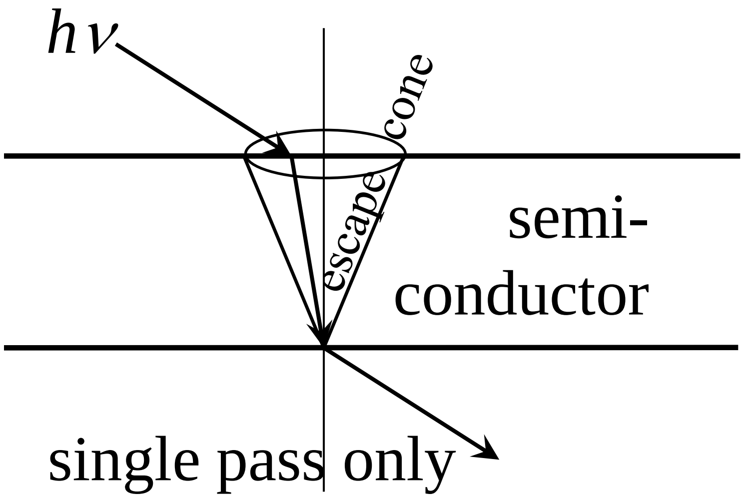


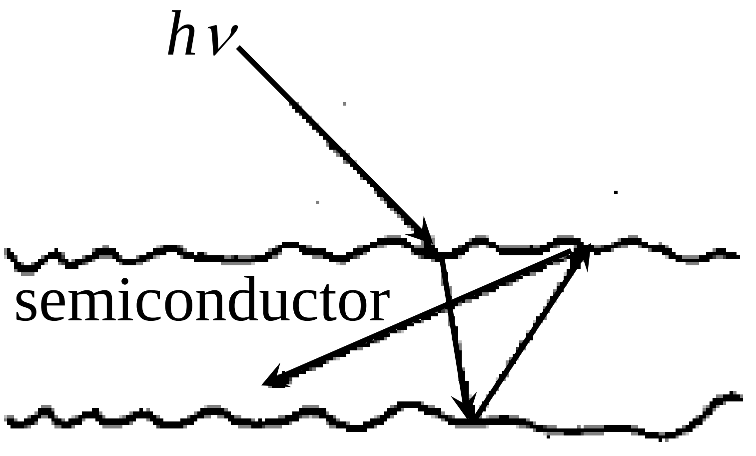
What is the current to expect?

Absorb all the incoming light, in as thin a layer as possible.

A direct bandgap uses less material than an indirect bandgap

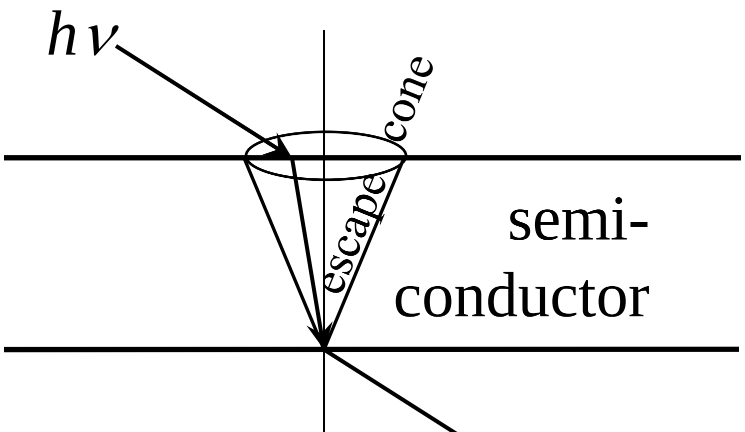
Solar Cell:



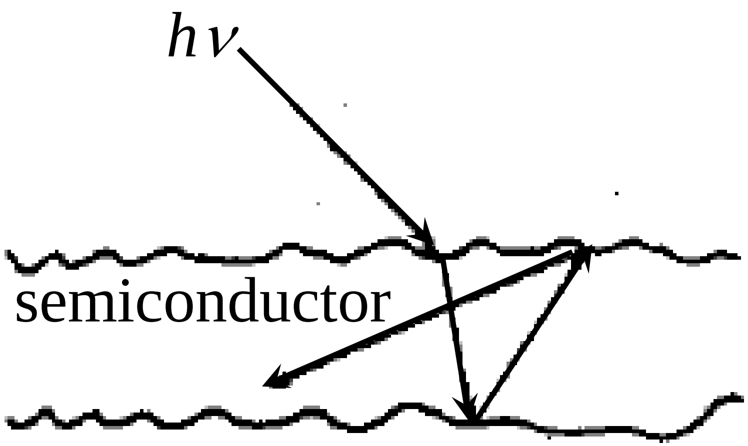


light trapping:
path length increased by $4n^2=50$
where n = refractive index

Solar Cell:

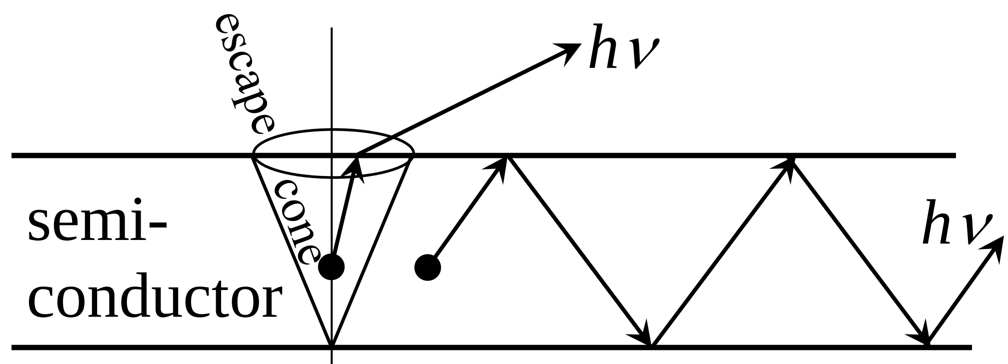


single pass only

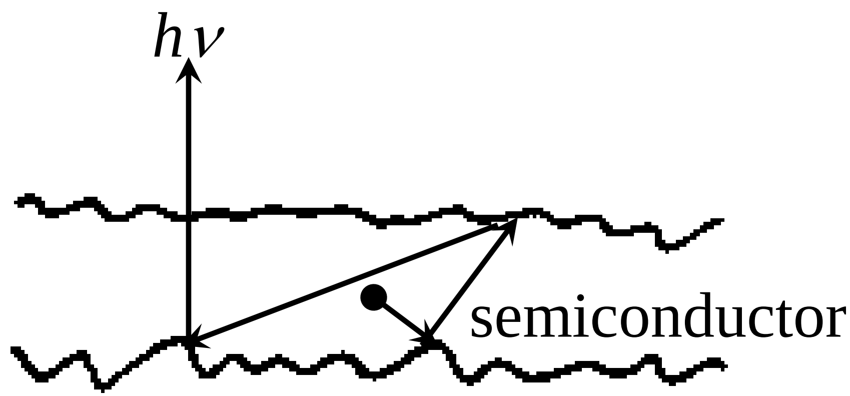


light trapping:
path length increased by $4n^2$=50
where n = refractive index

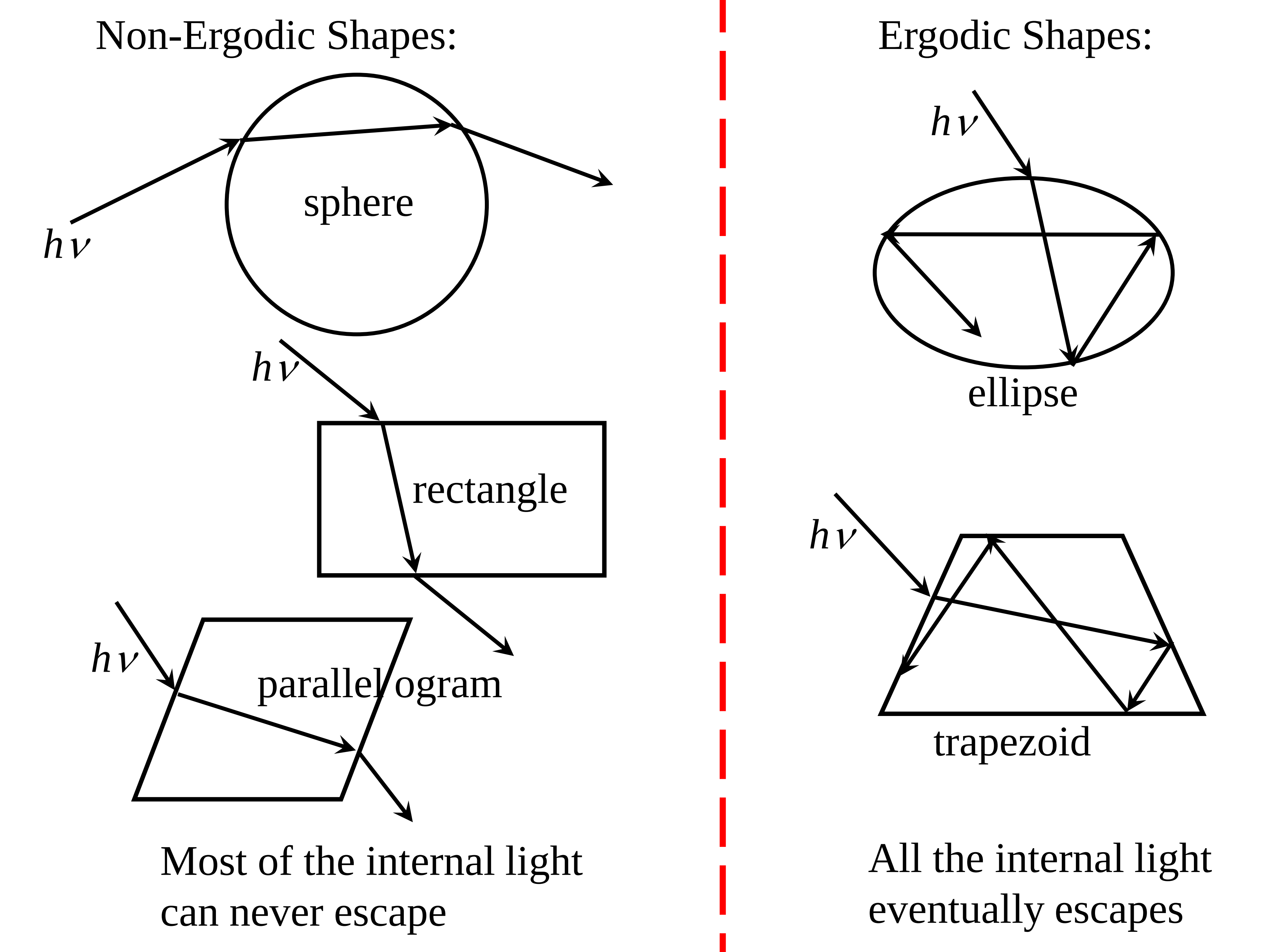
Light Emitting Diode:



only $1/4n^2$ = 1/50 = 2%
of the light escapes.



all the light eventually escapes.


Non-Ergodic Shapes:
Ergodic Shapes:
hν
sphere
hν
ellipse
hν
rectangle
hν
hν
parallel ogram
trapezoid
Most of the internal light
can never escape
All the internal light
eventually escapes

$$\text{Density of Optical Modes per Unit Volume in air} = \frac{8\pi \nu^2}{c^3}$$

$$\text{Density of Optical Modes per Unit Volume in semiconductor} = \frac{8\pi n^2 \nu^2}{c^3}$$

What is the ratio? …… n^2

There is a factor 2 from double pass

and

There is a factor 2 from $\cos\theta$ averaging

The net benefit is $4n^2$

Light Trapping;

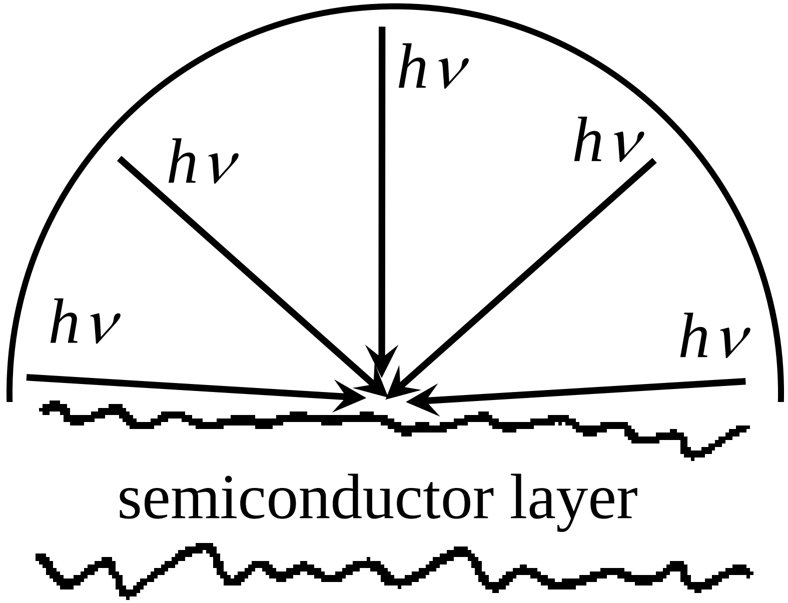
the Benefit:

a. $4n^2$ ~50 times thinner layer can be sufficient to absorb the sunlight saving semiconductor cost.

b. In a thinner cell, there is less series resistance, and a higher Fill Factor

c. The operating point voltage, (not just V_{oc}), increases by $kT \ln\{4n^2\} \sim 0.1$Volts.

Total Internal Reflection is completely compatible with an Anti-Reflection Coating.

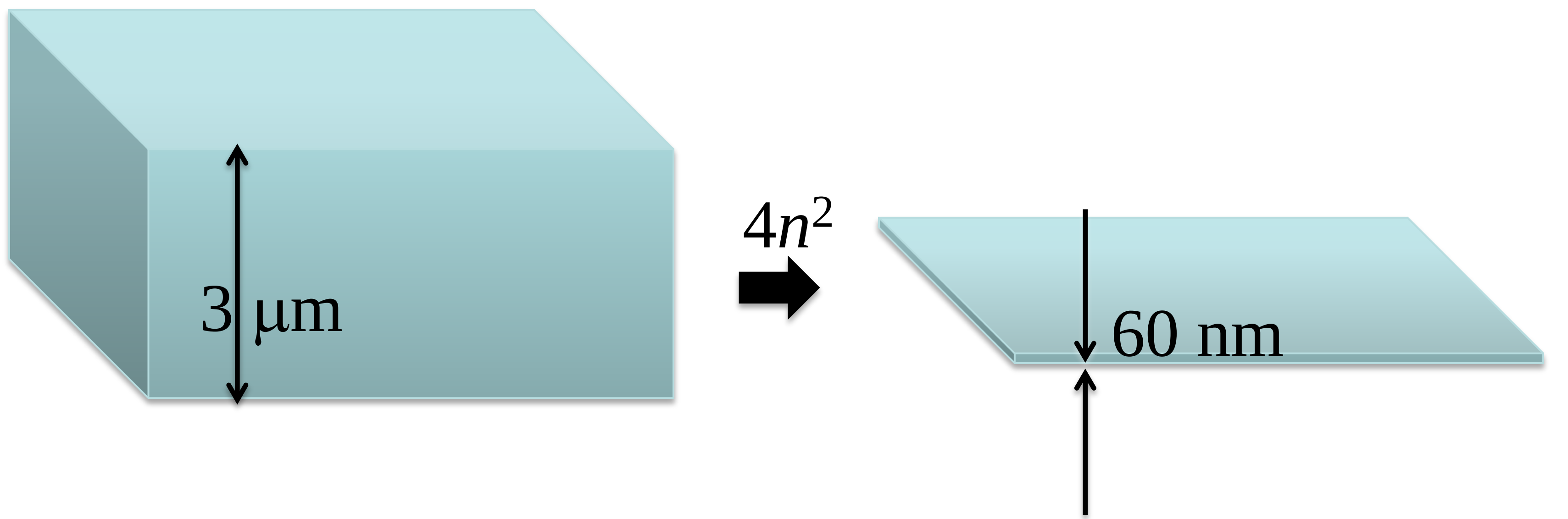


A randomly rough surface does approach
the statistical mechanical limit,
regardless what angle the light is coming in on.

Can a photonic crystal patterned surface do better
than a randomly rough surface?

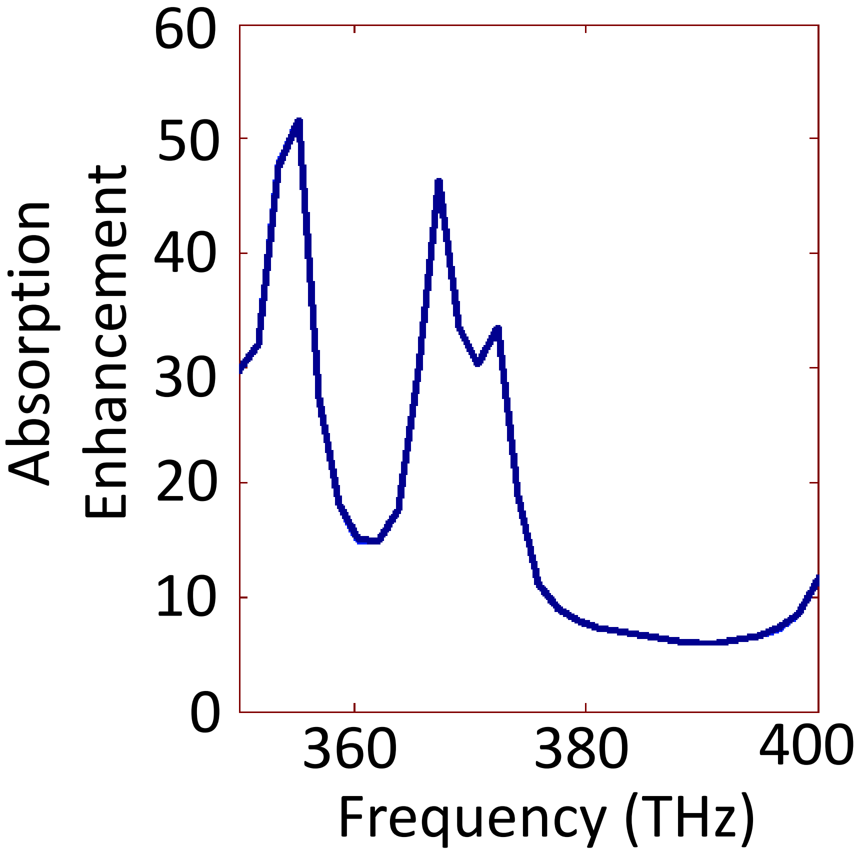
Solar cells are getting thinner.

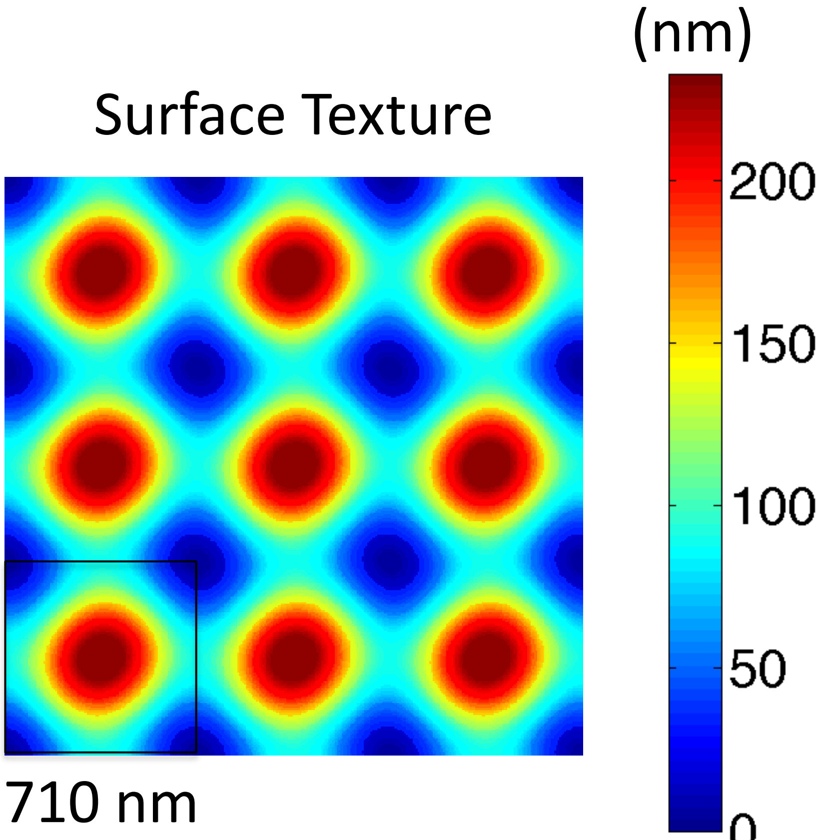
We would prefer that our solar cells should be much thinner, thinner than 1 wavelength.



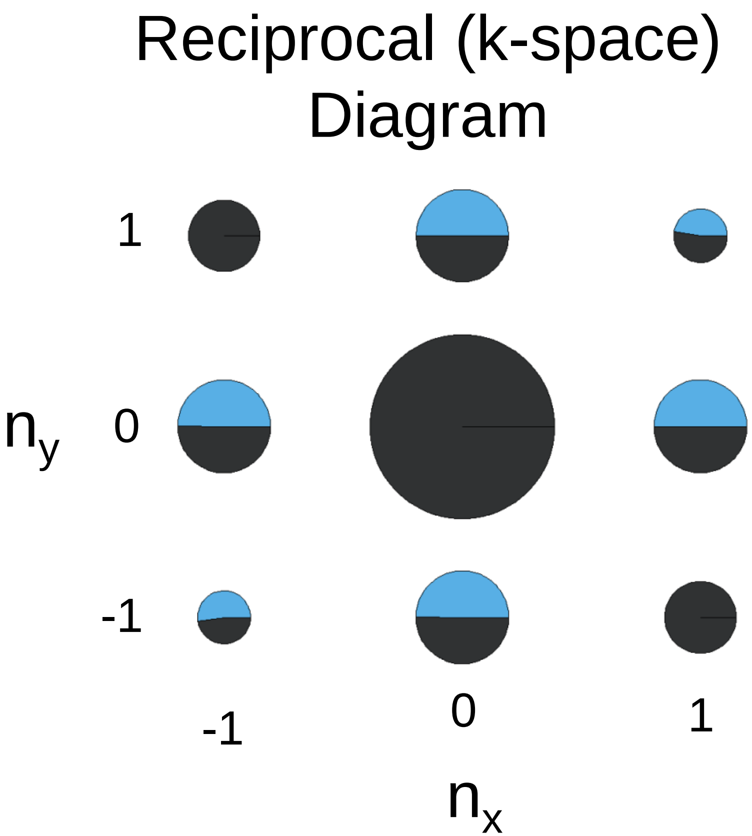
What is the meaning of random surface roughness in a film that is <1λ thick?

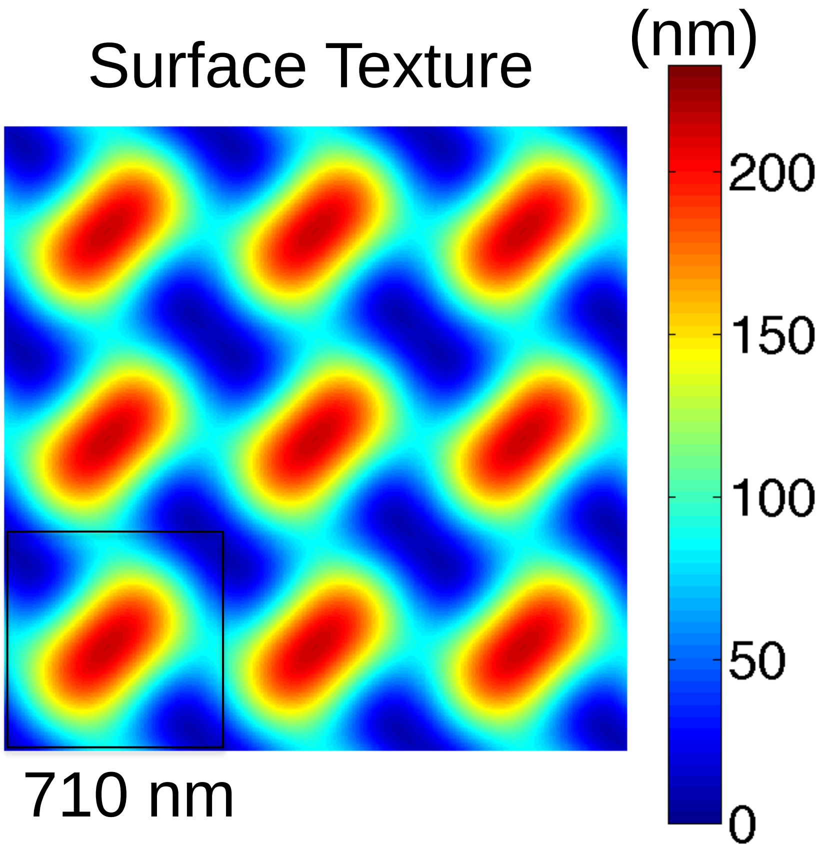
Spontaneous Symmetry Breaking

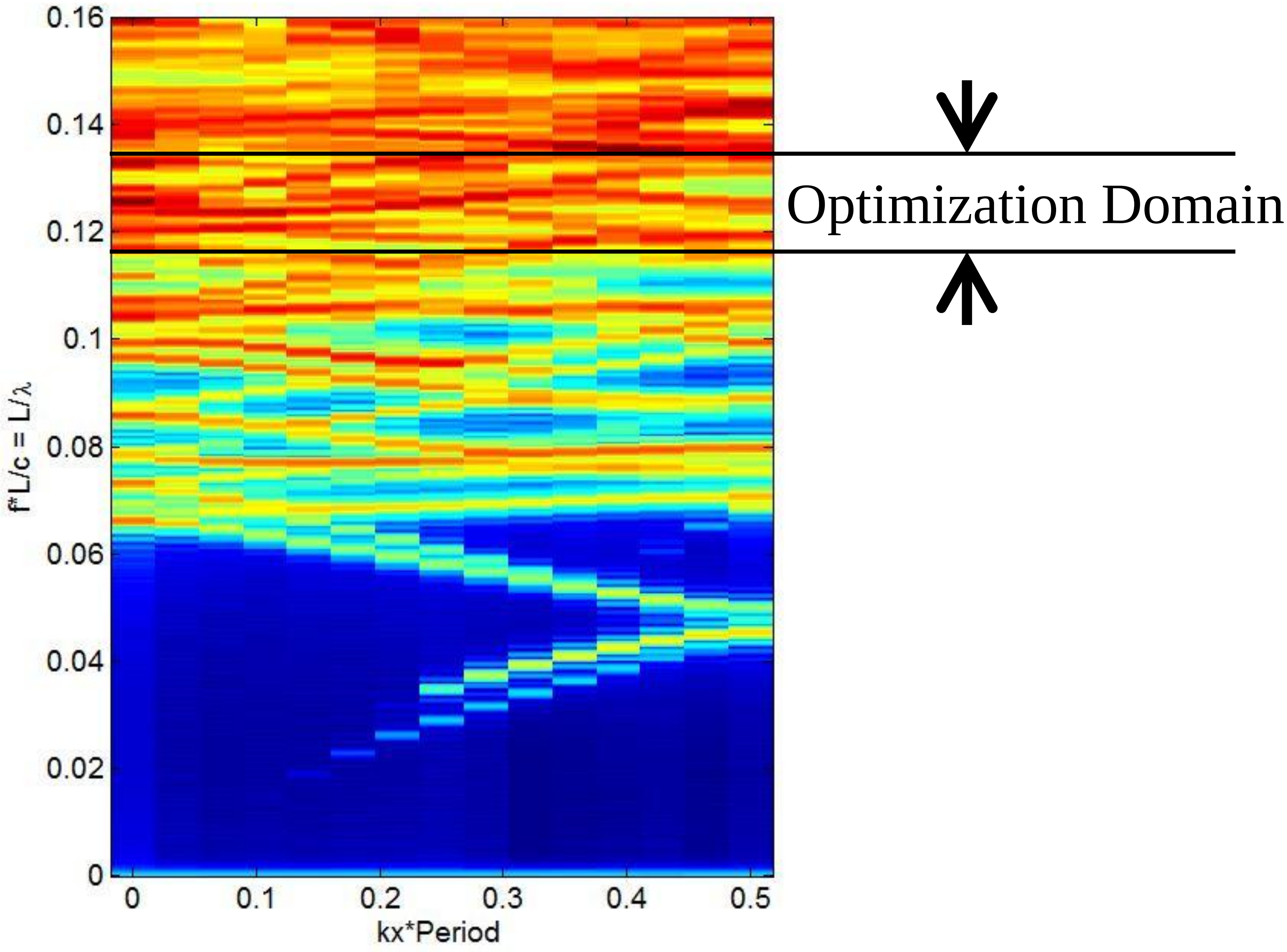




Spontaneous Symmetry Breaking

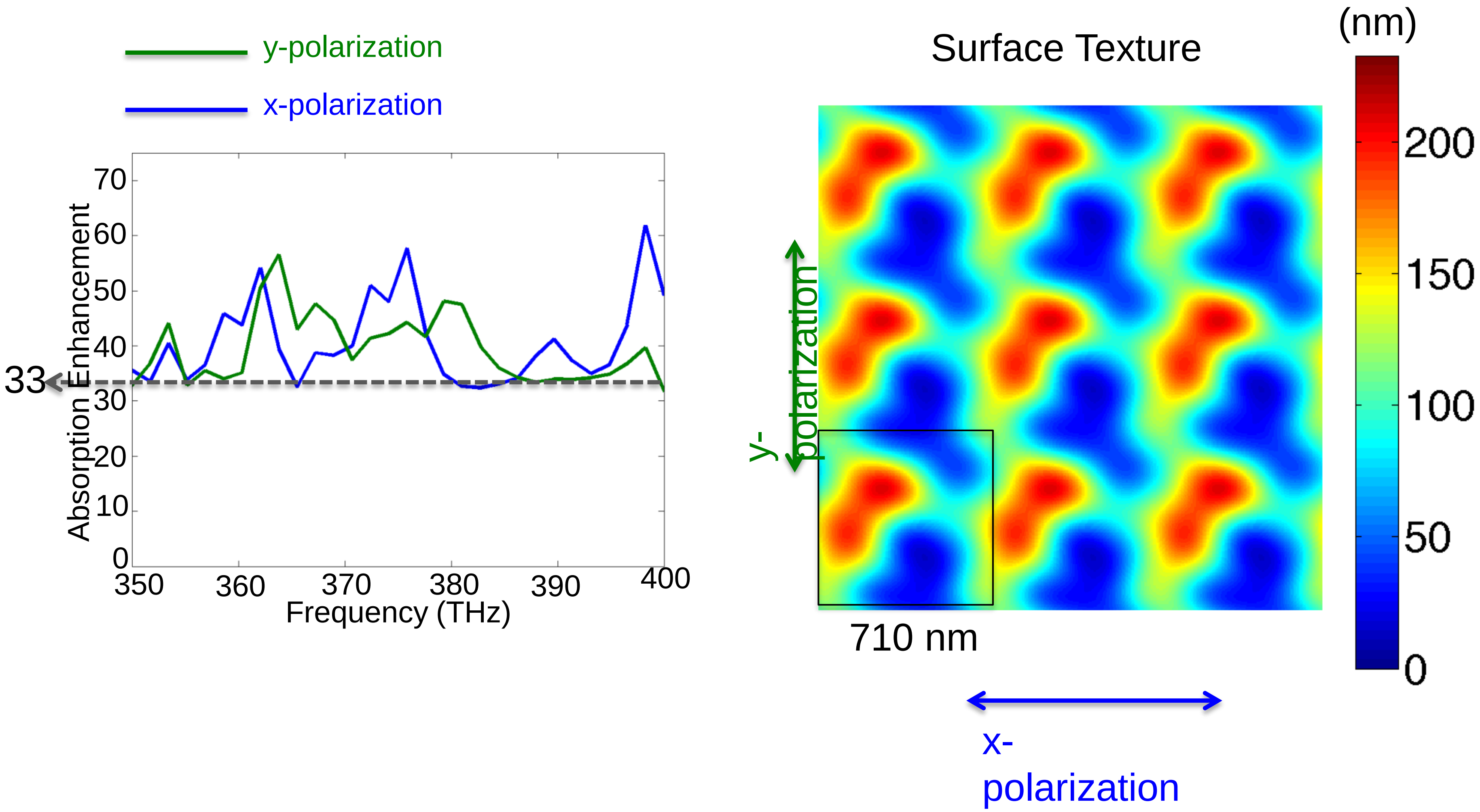




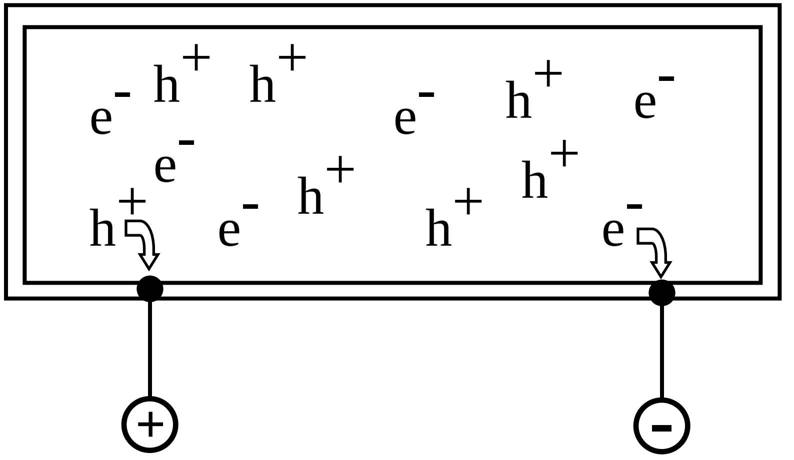


0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
f*L/c = L/λ
0
0.1
0.2
0.3
0.4
0.5
kx*Period
Optimization Domain

Final Texture: Iteration 143



What is the operating voltage?



To extract current, voltage at contacts must be slightly lower than Voc

But, operating voltage linked directly to Voc

$$V_{OP} \approx V_{OC} - \frac{kT}{q} \ln\left(\frac{qV_{OC}}{kT} \right)$$

We only need to understand the open-circuit voltage

What is the ideal voltage V_{oc} to expect, i.e. the Quasi-Fermi Level separation, chemical potential, or Free Energy?

$$\exp\left\{\frac{\text{Free Energy}}{\text{kT}}\right\} = \left\{\frac{\textit{excited state population in the light}}{\textit{excited state population in the dark}}\right\}$$

Boltzmann Factor

In molecules and quantum dots:

$$qV_{oc} = \text{Free energy} = \text{kT} \ln\left\{\frac{\text{excited state population in the light}}{\text{excited state population in the dark}}\right\}$$

In semiconductors with mobile electrons & holes:

$$\text{Free energy} = E_{Fc} - E_{Fv} = 2\text{kT} \ln\left\{\frac{\text{electron density in the light}}{\text{electron density in the dark}}\right\}$$

What is the voltage to expect, i.e. the Quasi-Fermi Level separation, chemical potential, or Free Energy?

Shockley-Queisser Limit (1961):

$$qV_{oc} = kT \ln\left\{\frac{\text{external Luminescent emission}}{\text{band} - \text{to} - \text{band emission in the dark}}\right\}$$

But in quasi-equilibrium:

$$qV_{oc} = kT \ln\left\{\frac{\text{incoming sunlight}}{\text{band} - \text{to} - \text{band emission in the dark}}\right\}$$

Yes photons have entropy, S

Photon Free Energy = $h\nu$ - TS
Photon Free Energy = $h\nu$ - kT lnW

$qV_{\mathbf{operating\ point}} =$

$$E_g - kT\{\underbrace{\overbrace{\ln(\pi/\Omega_s)}^{-0.28eV}}_{\text{Entropy due to loss of directivity information}} + \underbrace{\overbrace{\ln(4n^2)}^{-0.1eV}}_{\text{Entropy due to incomplete light trapping}} + \underbrace{\overbrace{\ln(qV_{op}/kT)}^{-0.1eV}}_{\text{Free energy loss due to power-point optimization}} \underbrace{\overbrace{-\ln(\eta)}^{0.0 \rightarrow -0.3eV}}_{\text{Free energy loss due to poor } \eta \equiv \text{ Quantum Efficiency}} \overbrace{\underbrace{-\ln\left(\frac{1.4T_s}{T} e^{-\frac{E_g}{kT_s}}\right)}_{\text{correction for Planck emission-bandwidth}}}^{+0.02eV}\}$$

where Ω_s is the solid angle subtended by the sun

nicest treatment:
R.T.Ross "Some Thermodynamics of PhotoChemical Systems", J. Chem. Phys. 46, 44590 (1967)

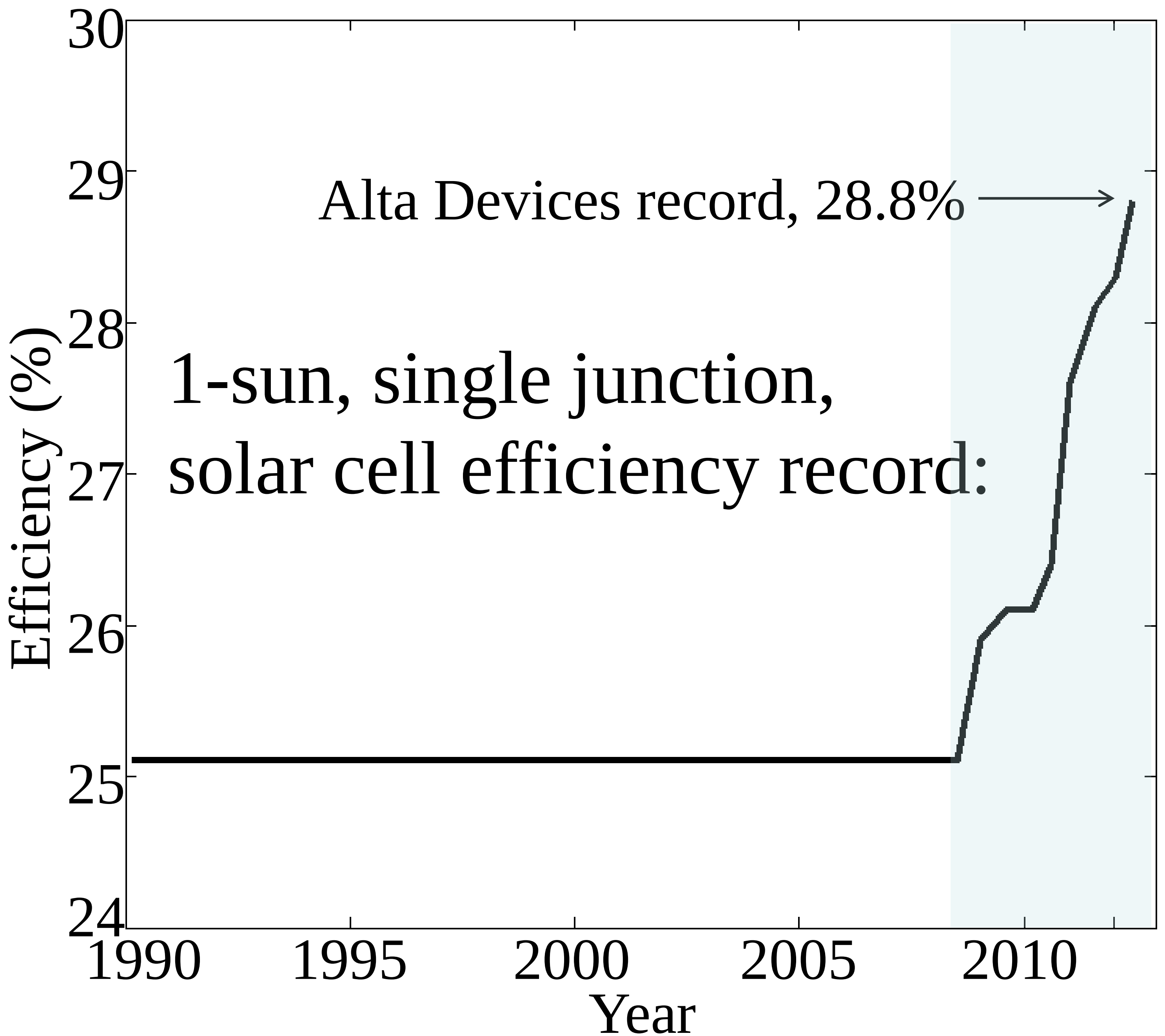
Small bandgaps are particularly vulnerable to entropy:

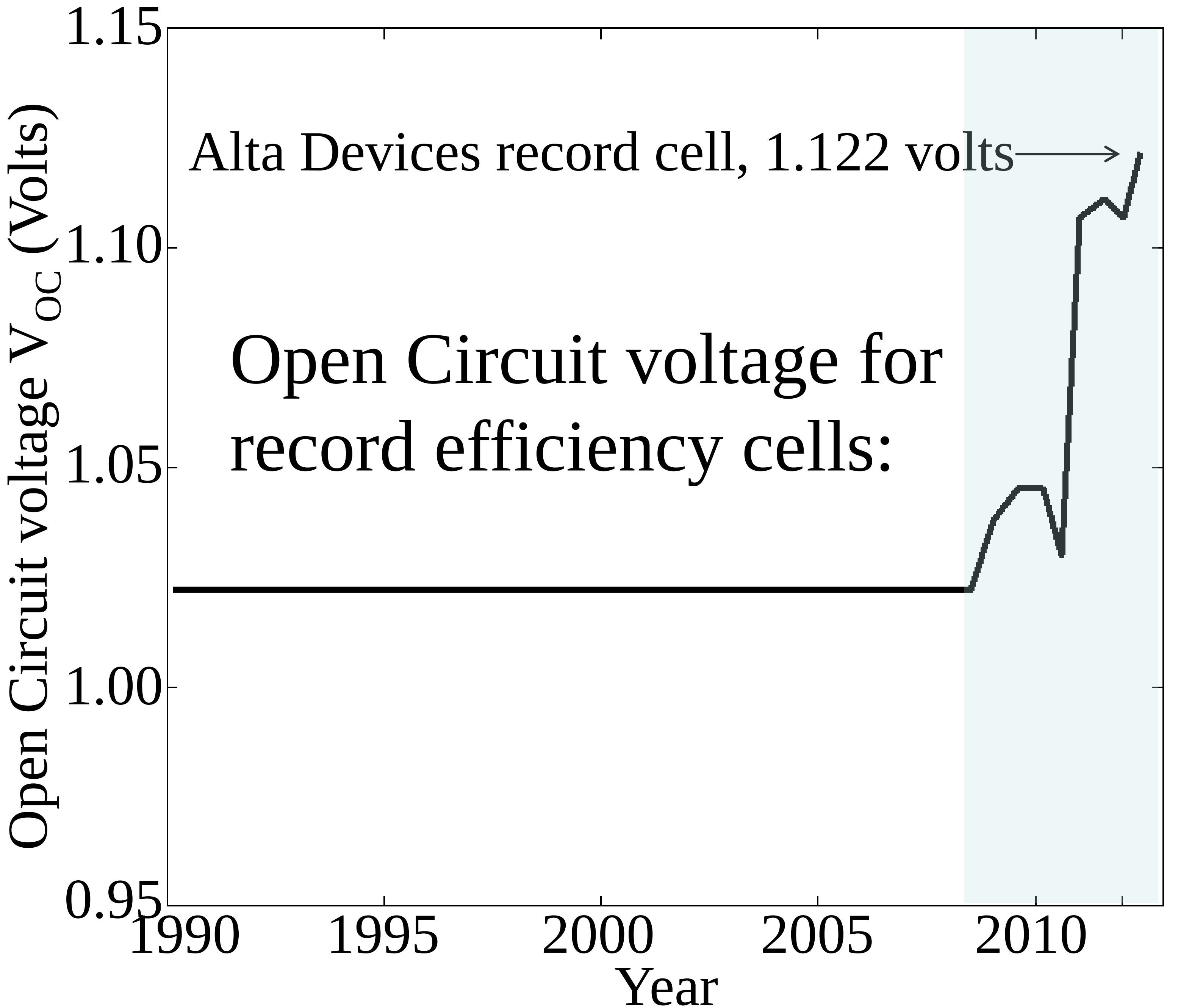
After you subtract off all the entropy terms, you don't have much Free Energy left.

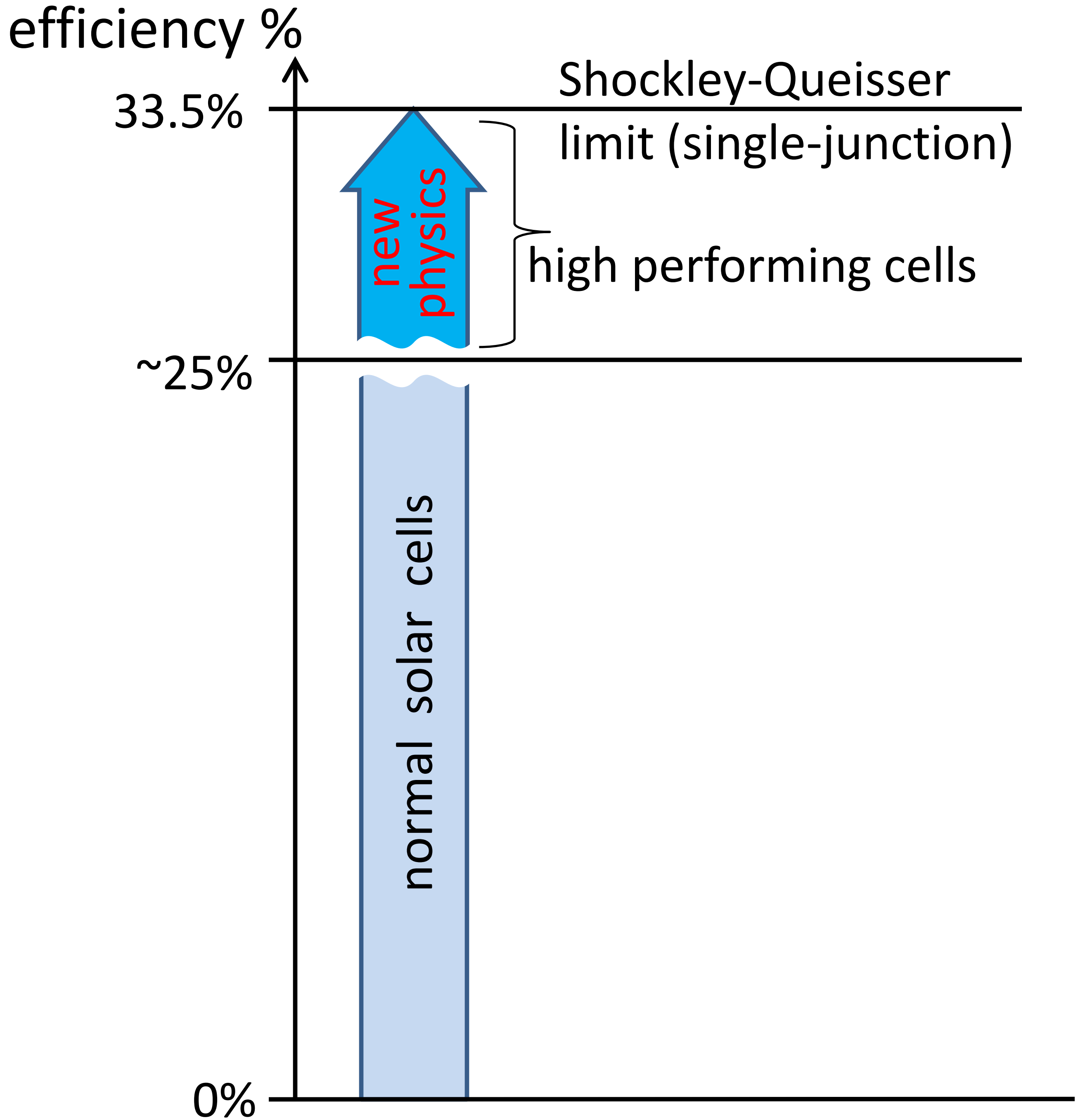
$$qV_{\textbf{operating point}}=1.1\text{eV} - 0.8\text{eV} = 0.3\text{eV}$$

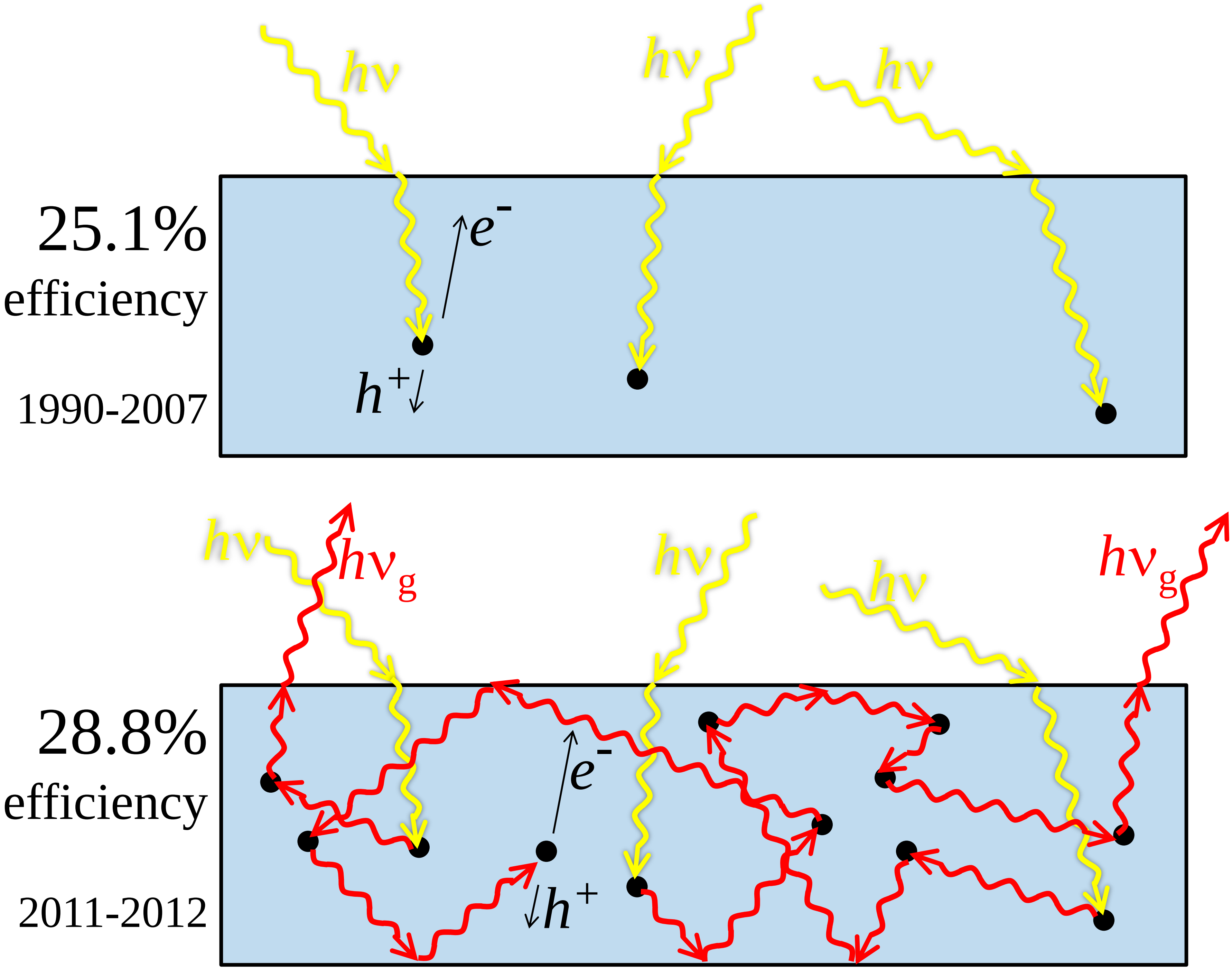
A lousy 0.3eV from all those big photons

In general we cannot afford to compromise with regard to quantum efficiency.


Alta Devices record, 28.8%
1-sun, single junction,
solar cell efficiency record:
Efficiency (%)
30
29
28
27
26
25
24
1990
1995
2000
2005
2010
Year


Alta Devices record cell, 1.122 volts
Open Circuit voltage for
record efficiency cells:
Open Circuit voltage V_{OC} (Volts)
1.15
1.10
1.05
1.00
0.95
1990
1995
2000
2005
2010
Year


efficiency %
33.5%
~25%
0%
Shockley-Queisser
limit (single-junction)
high performing cells
new
physics
normal solar cells



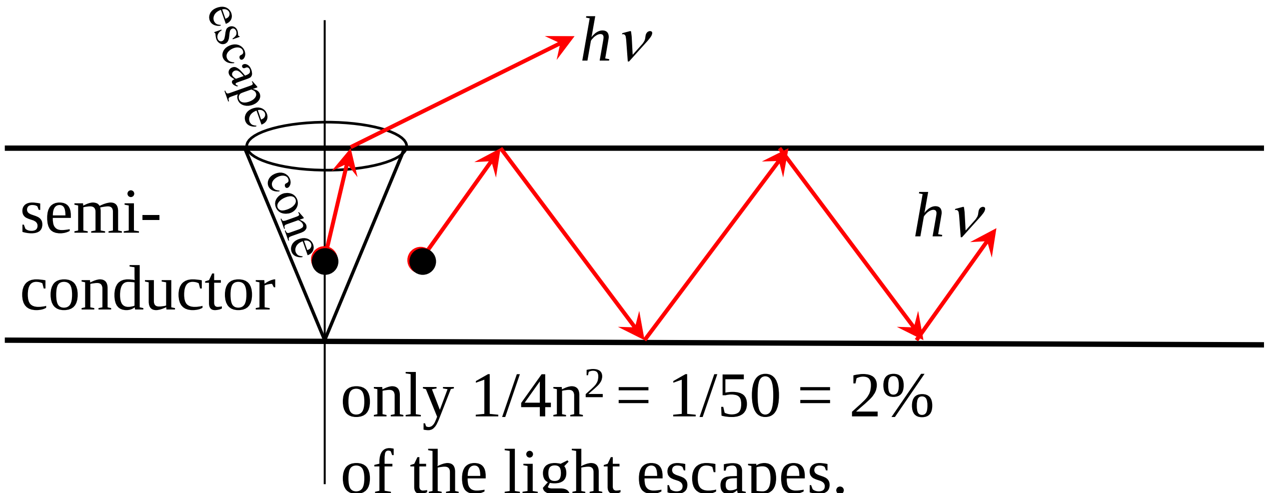
25.1%
efficiency
1990-2007
hν
hν
hν
e-
h+
28.8%
efficiency
2011-2012
hν
hν_g
hν
hν
hν_g
e-
h+

What if the material is not ideal, and the electrons and holes are lost to heat before they can luminesce?

$$qV_{oc} = qV_{oc\text{-}ideal} - kT|\ln\{\eta_{ext}\}|$$

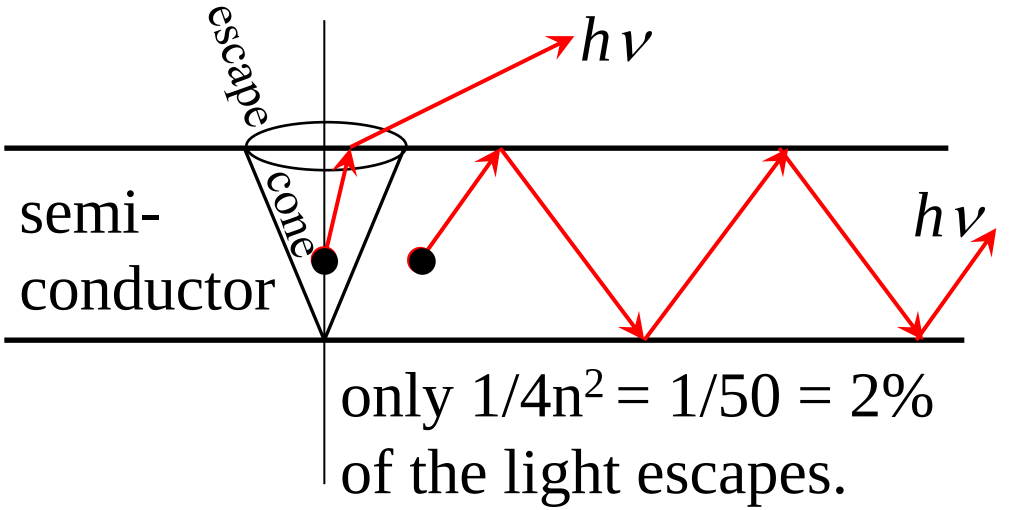
The external fluorescence yield η_{ext} is what matters!

Only external Luminescence can balance the incoming radiation.



You may need an internal efficiency of η_{int}=99%

just to get an external efficiency of η_{ext}=50%

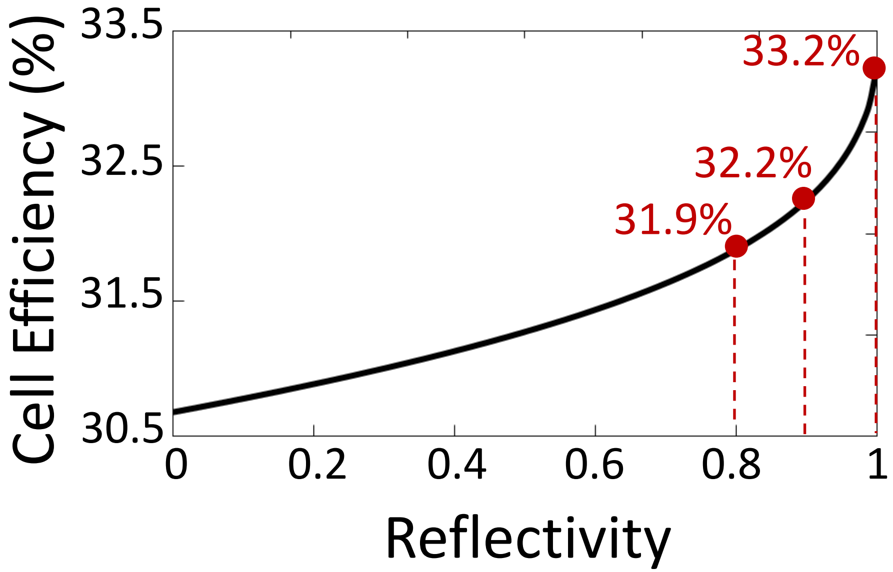


But this is really hard to do:

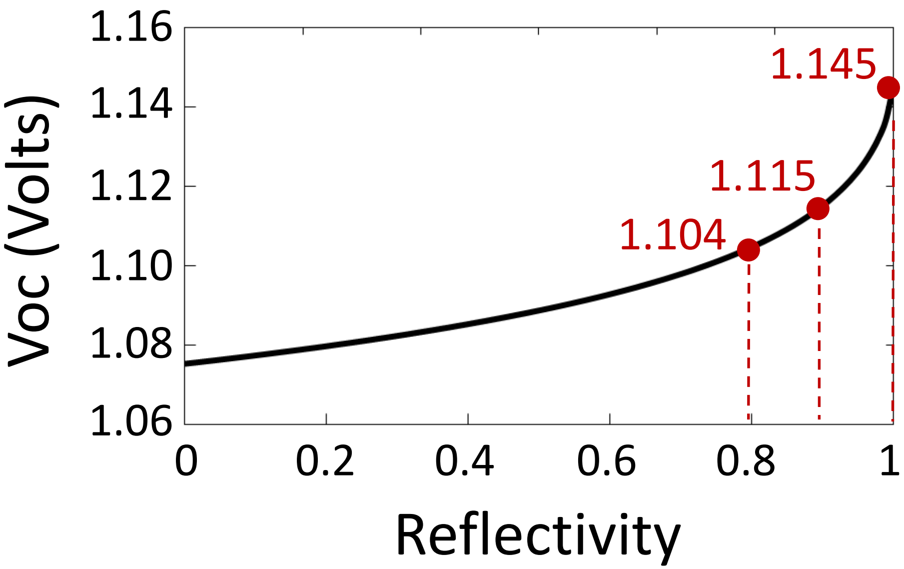
You may need an internal efficiency of η_{int}=99%

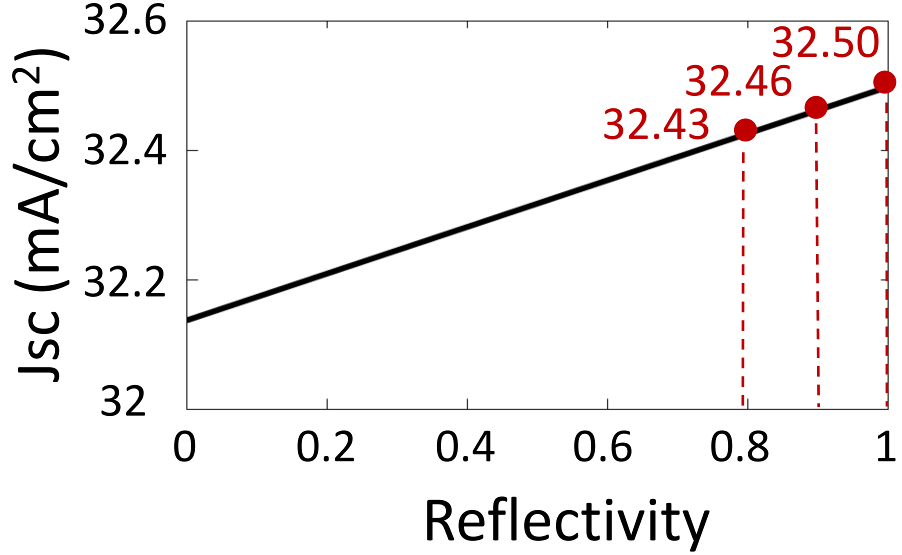
just to get an external efficiency of η_{ext}=50%

Efficiency vs. Rear Reflectivity, GaAs 3μm



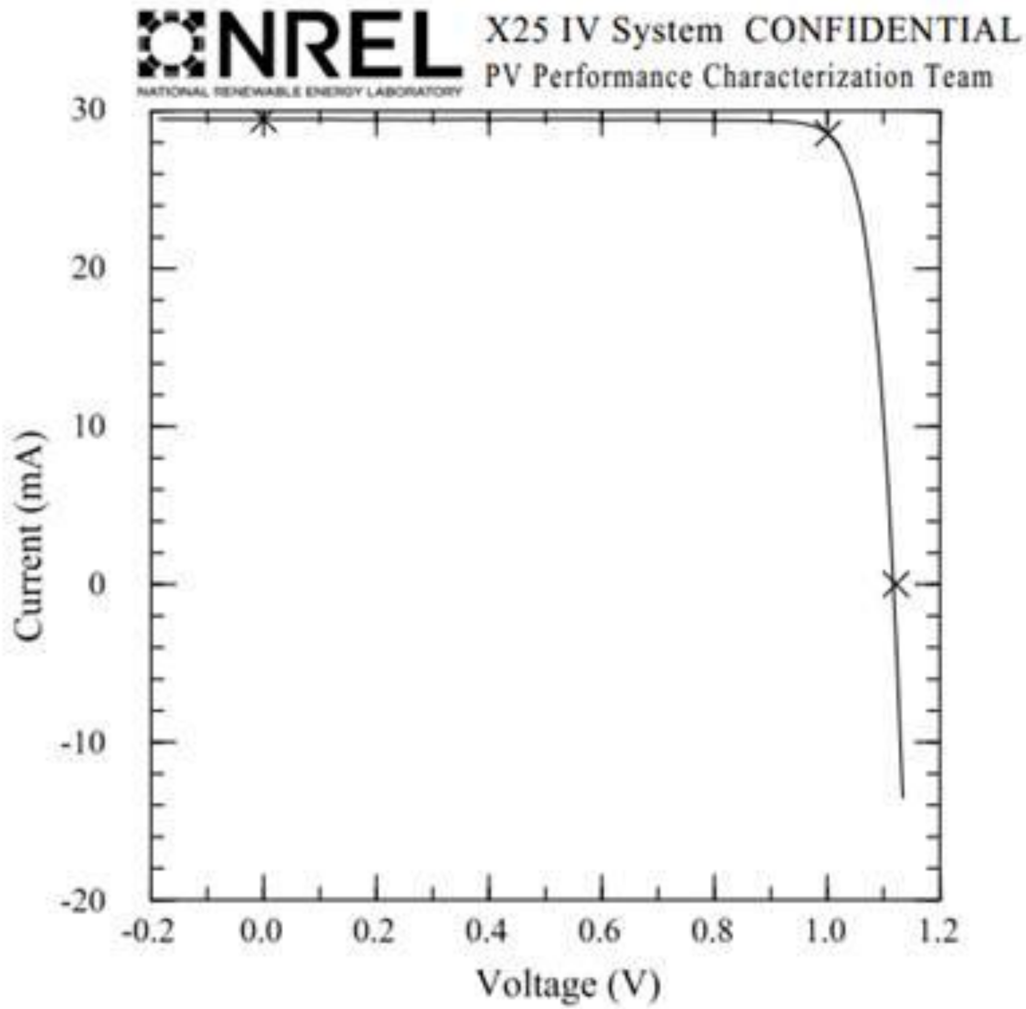
90% Rear Reflectivity Is Not Enough!





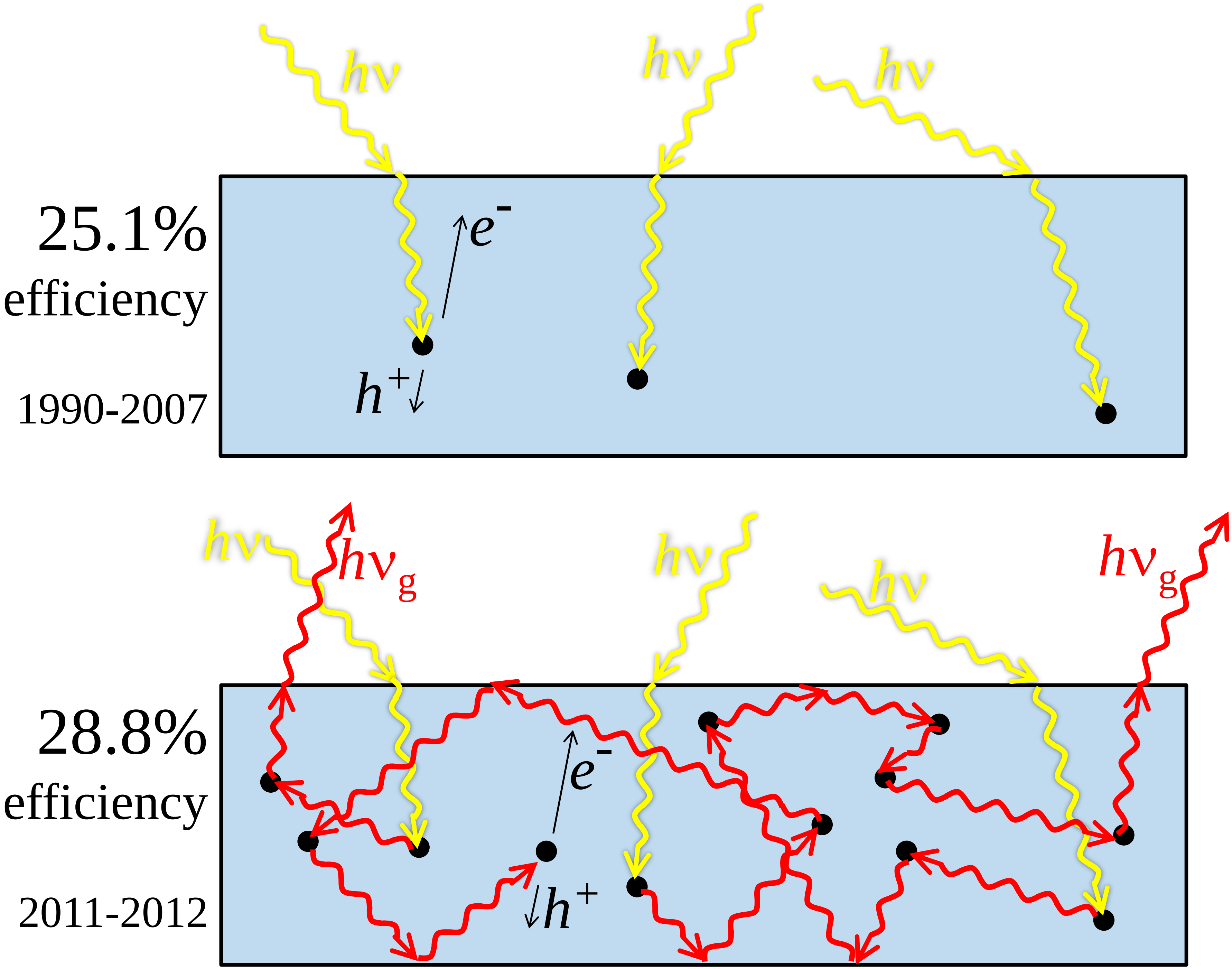
Latest 1 sun single-junction results from Alta Devices, Inc.

Expected to reach 34% dual junction, eventually.



V_{oc} = 1.1220 V
I_{sc} = 29.461 mA
J_{sc} = 29.677 mA/cm^2
Fill Factor = 86.50 %

I_{max} = 28.557 mA
V_{max} = 1.0013 V
P_{max} = 28.593 mW
Efficiency = 28.80 %



hν
hν
hν
25.1%
efficiency
1990-2007
e-
h+
hν
hνg
hν
hν
hνg
28.8%
efficiency
2011-2012
e-
h+

Counter-Intuitively, to approach the Shockley-Queisser Limit, you need to have good external fluorescence yield η_{ext} !!

Internal Fluorescence Yield η_{int} >> 90%
Rear reflectivity >> 90%

} Both needed for good η_{ext}

For solar cells at 25%,
good electron-hole transport is already a given.

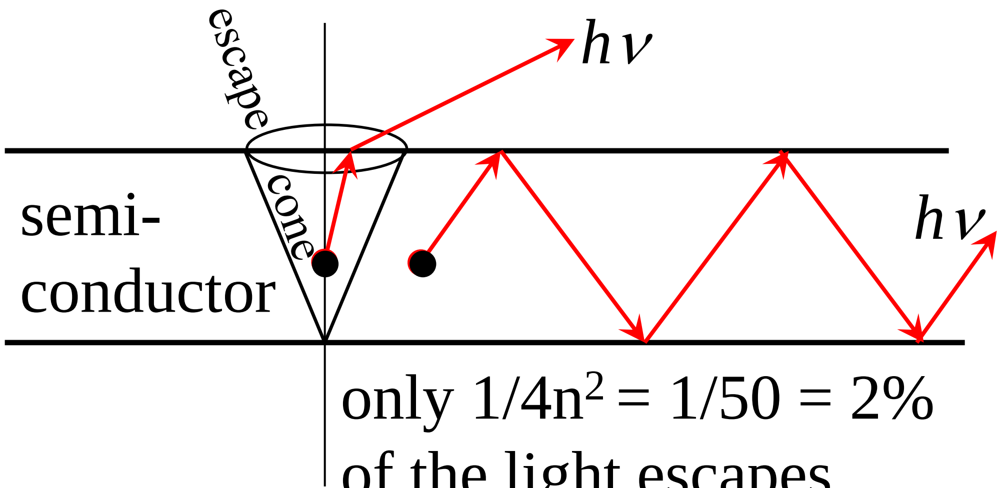
Further improvements of efficiency above 25% are all about the photon management!

A good solar cell has to be a good LED!

Counter-intuitively, the solar cell performs best when there is
maximum external fluorescence yield η_{ext}.

Miller et al, IEEE J. Photovoltaics, vol. 2, pp. 303-311 (2012)

Why the record-setting Voltage?



only $1/4n^2 = 1/50 = 2\%$ of the light escapes.

Another way to look at this,

1. the recycled photons are not lost,
2. the carrier lifetime increases,
3. increasing carrier density
4. Increasing V_{oc}

This Photon-Recycling explanation is incomplete!
Good external luminescence can be achieved with texturing and no-photon-recycling.

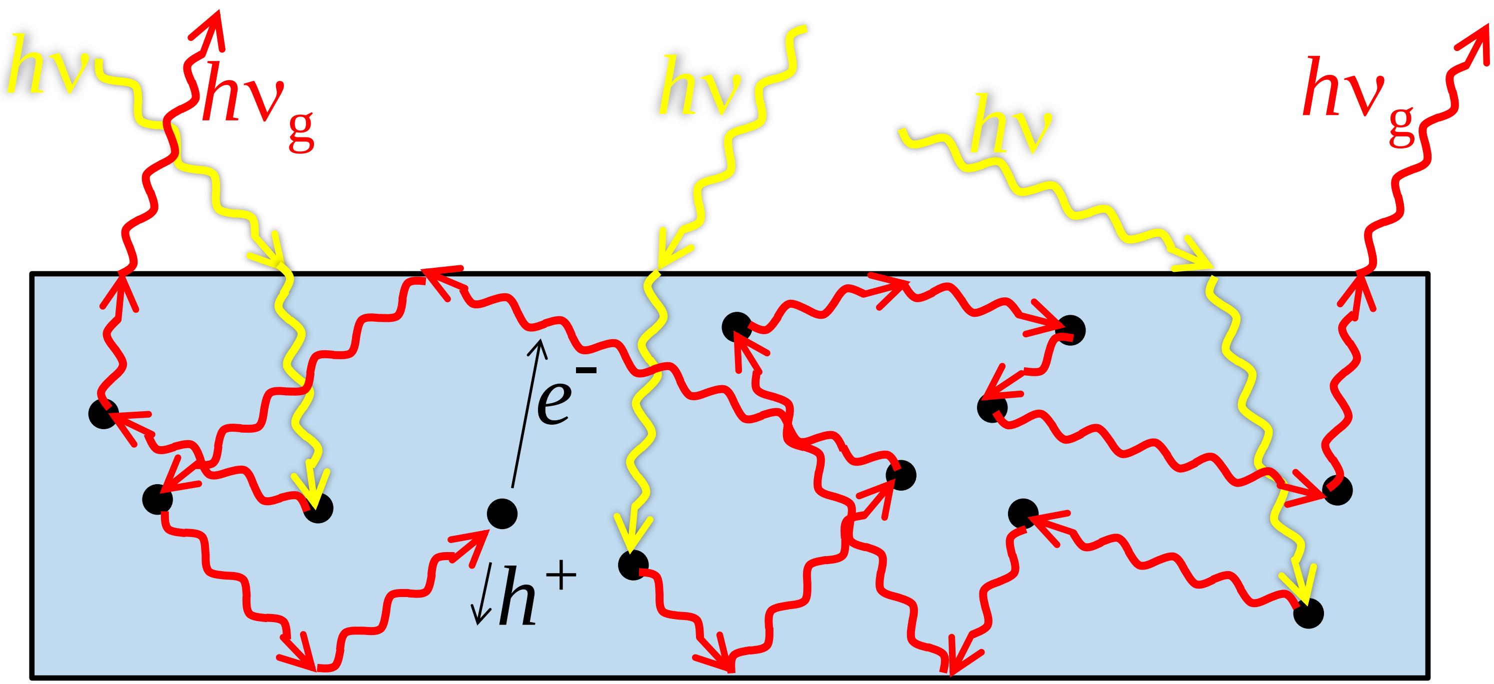
Paradox:
Why is external luminescence is good for solar cell efficiency?
Reason #1; ~~Non-radiative Recombination:~~

Good external luminescence is a gauge of low internal non-radiative recombination processes.
Non-radiative recombination would certainly impair the solar cell efficiency.

Paradox:

Why is external luminescence is good for solar cell efficiency?

Reason #2; External emission of photons into free space is unavoidable. All other losses can, in principle, be eliminated. Total losses are at their very least, when external emission is the only loss mechanism, which leads to the highest efficiency.



Paradox:
Why is external luminescence is good for solar cell efficiency?
Reason #3; The LED and solar cell are reciprocal devices. A good solar cell makes a good LED

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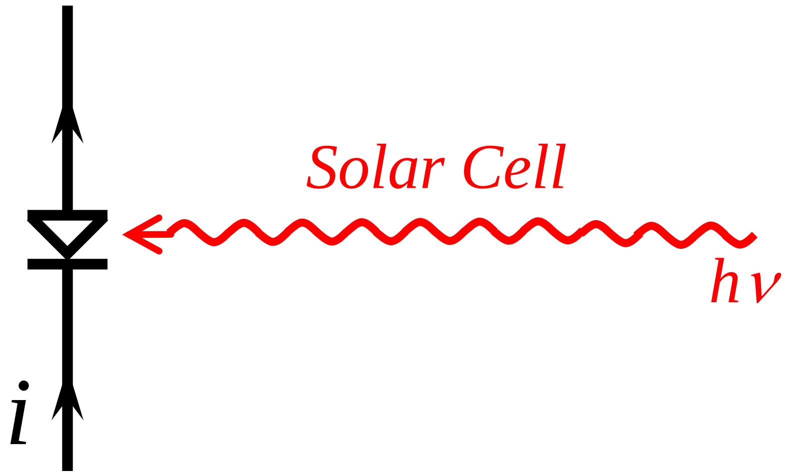
Why is external luminescence is good for solar cell efficiency?

Reason #3; The LED and solar cell are reciprocal devices. A good solar cell makes a good LED



Paradox: Why is external luminescence is good for solar cell efficiency?
Reason #4; Luminescence IS Voltage:

External luminescence is sometimes used as a type of **contactless voltmeter**, indicating the separation of quasi-Fermi levels in the solar material.
At quasi-equilibrium:

$$\text{Luminescence} = (\text{Black Body}) \times exp\{qV/kT\}$$

(This is sometimes employed as a contactless, quality-control-metric, in solar cell manufacturing plants.)

This viewpoint is tautological:
Good external luminescence actually is good voltage, and therefore good efficiency.

What if the material is not ideal, and the electrons and holes are lost to heat before they can luminesce?

$$qV_{oc} = qV_{oc\text{-}ideal} - kT|\ln\{\eta_{ext}\}|$$

The external fluorescence yield η_{ext} is what matters!

Only external Luminescence can balance the incoming radiation.

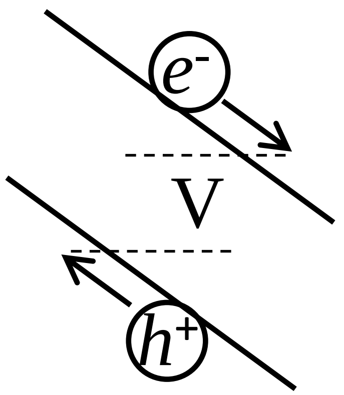
Objections to: "Good luminescence IS good voltage"

1. My solar cell doesn't luminesce at all!

   answer: Undoubtedly the voltage is very low,
   but there is always some small luminescence.

2. I need to separate the electron and hole as quickly as possible.
   There is little time for radiative recombination.

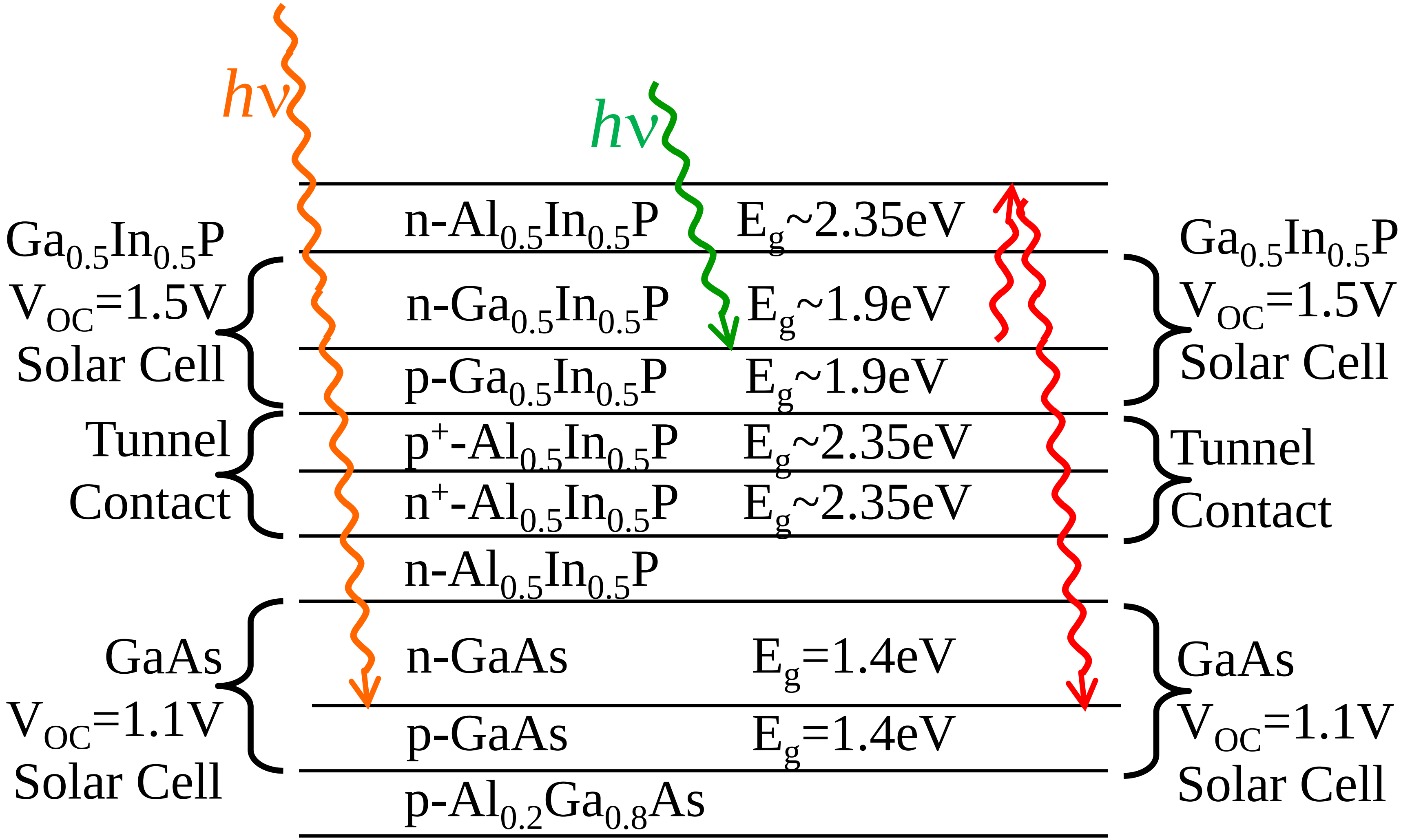
   answer: That built-in electric field is costing
   voltage, which means less luminescence.



3. I need to suppress fluorescence occurring before the electron and hole have separated, which would cost current.

   answer: The suppressed fluorescence is an indicator that
   voltage was sacrificed for current.
   The carrier extraction needs improvement.

Dual Junction Series-Connected Tandem Solar Cell



All Lattice-Matched η~34% efficiency should be possible.

Latest 1 sun dual-junction results from Alta Devices, Inc.

Expected to reach 34% dual junction, eventually.

Alta Devices

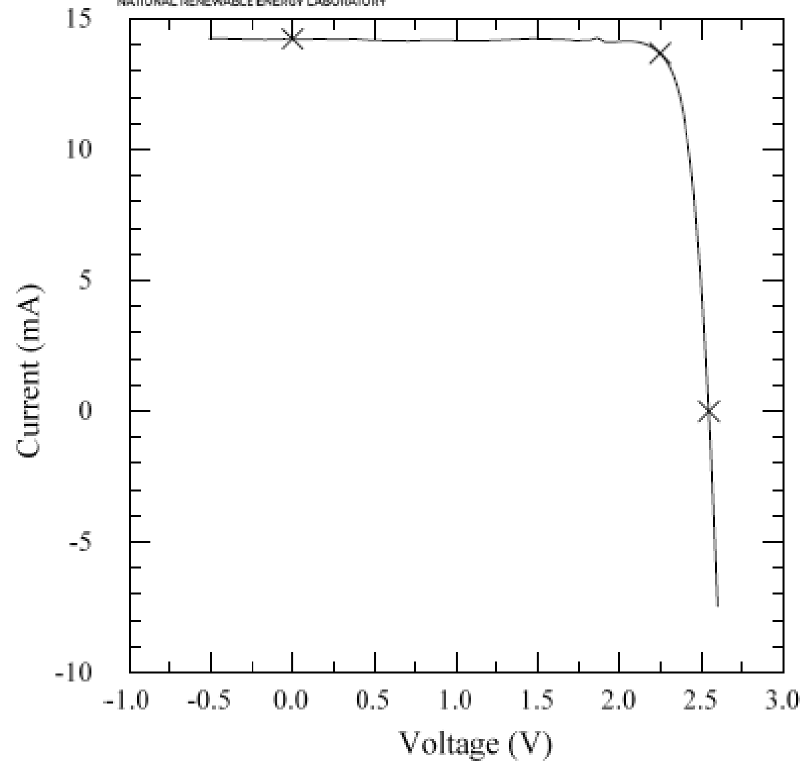
GaInP/GaAs Tandem Cell

Device ID: AD13609-F-G2
4:41 PM 2/1/2013
Spectrum: ASTM G173 global

Device temperature: 25.0 ± 1.0 °C
Device area: 0.999 cm^2
Irradiance: 1000.0 W/m^2

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

OSMSS IV System CONFIDENTIAL
PV Performance Characterization Team

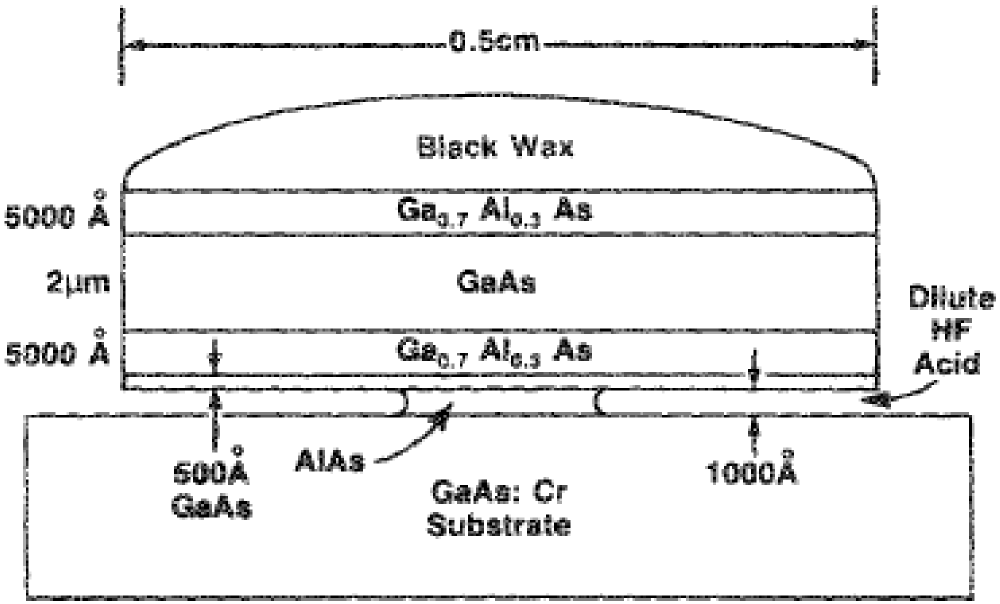


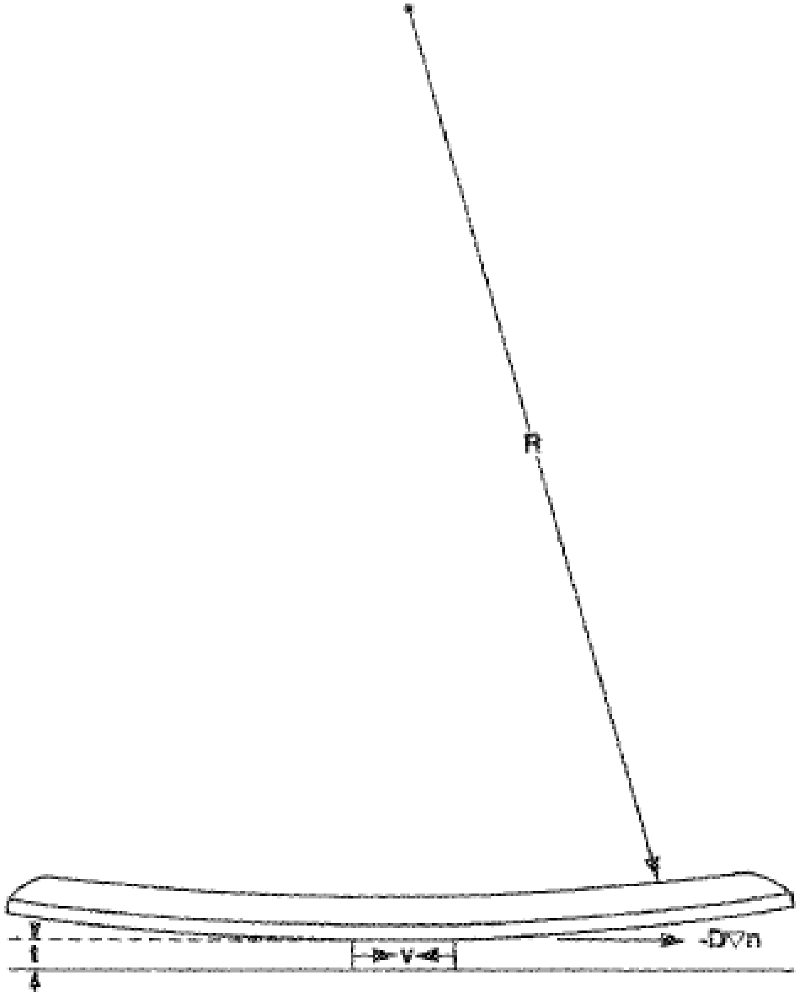
V_{oc} = 2.5468 V
I_{sc} = 14.247 mA
J_{sc} = 14.255 mA/cm^2
Fill Factor = 84.7 %

I_{max} = 13.681 mA
V_{max} = 2.2477 V
P_{max} = 30.752 mW
Efficiency = 30.77 %

Luminescent coupling corrected bottom QE

The Epitaxial Liftoff Process:





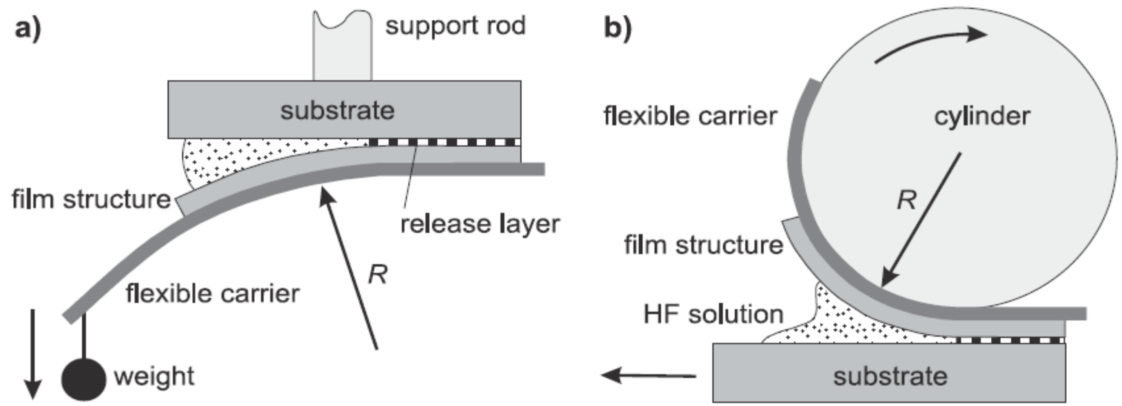


Fig. 1 Schematic representation of the ELO process. a) The weight induced ELO process, b) ELO with a stabilized radius of curvature by guiding the temporary flexible carrier over a cylinder surface.

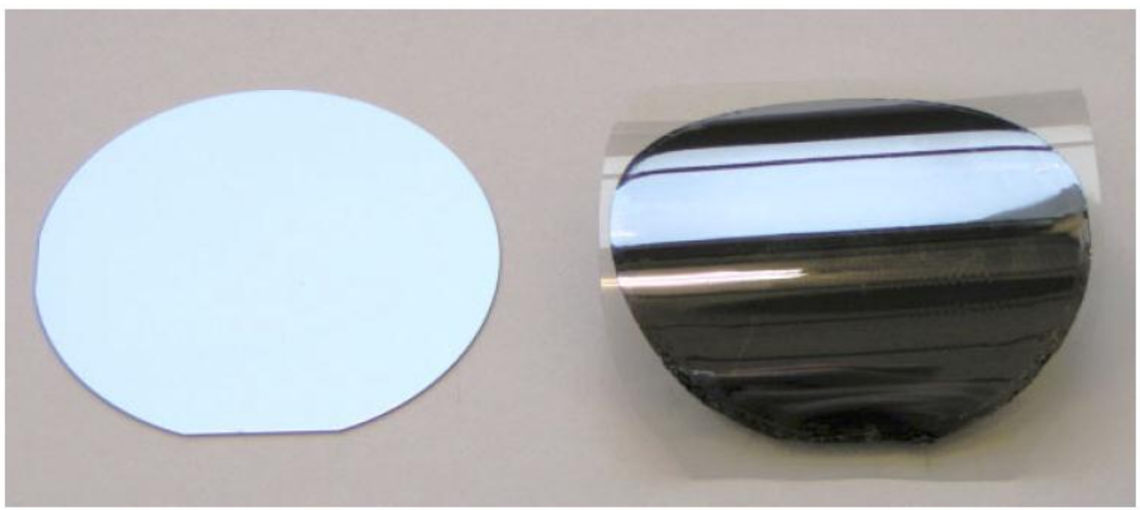


Fig. 2 (online colour at: www.pss-a.com) 1 µm thick GaAs film of 2 inch in diameter on a flexible plastic carrier (right hand side) after epitaxial lift-off from its substrate (left hand side).

GaAs
Courtesy of Alta Devices, Inc.

What is happening in the solar economy?

c-Si η ~ 15%-23% in production
90% market share

60GW/year annual production capacity in China

World-wide demand ~30GW/year

~28GW/year idle-capacity in China (moth-balled)

Price war!

The current world price has settled at $0.61/Watt!!

This is very important information. It's the variable cost of producing c-Si panels, does not cover fixed investment costs.

New technologies have been shut down,
including poly-$CuInGaSe_2$, poly-CdTe, concentrators, etc.
Companies are being kept alive by old fixed price contracts.