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

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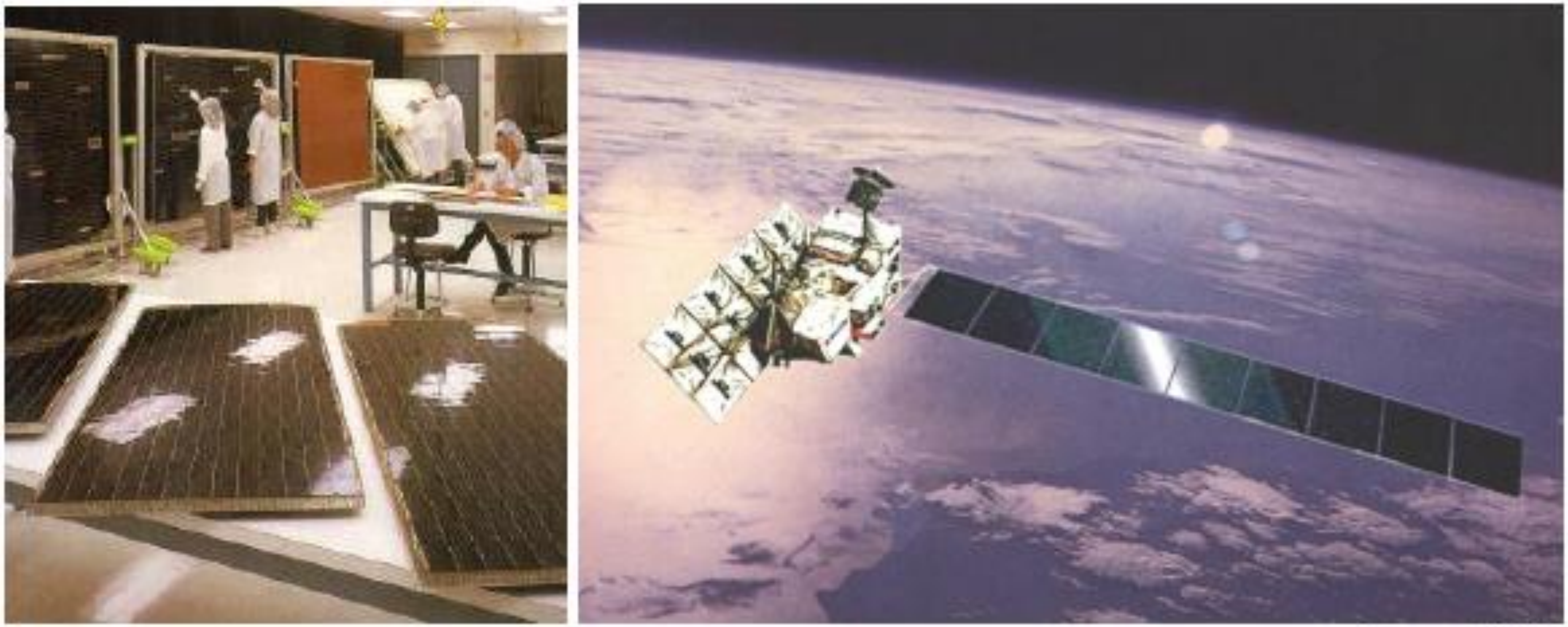
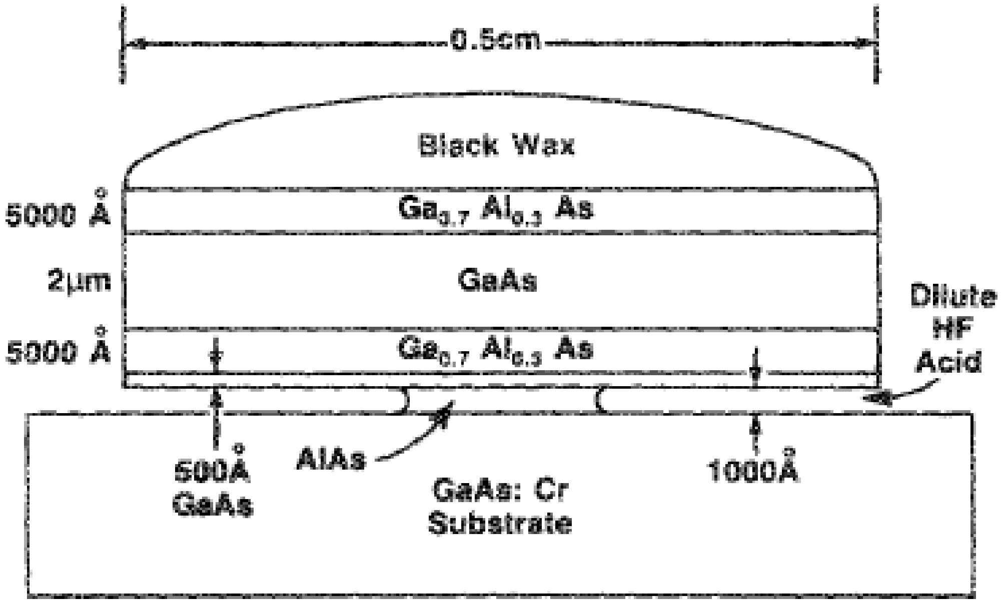
Miller et al, IEEE J. Photovoltaics, vol. 2, pp. 303-311 (2012)

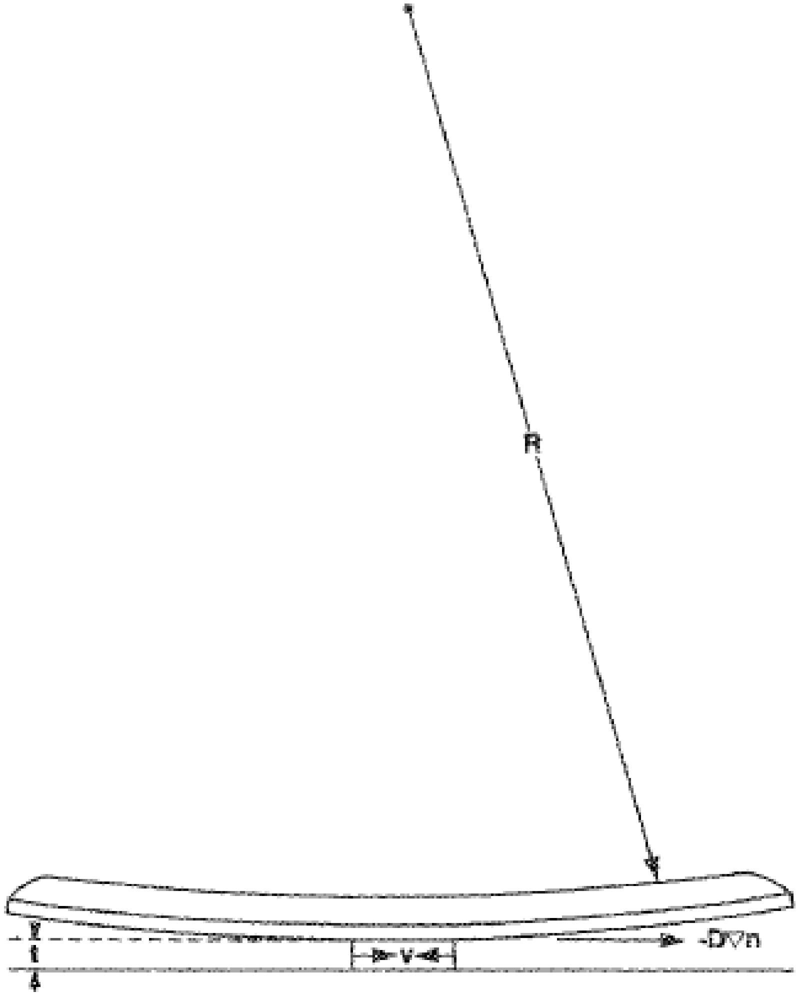
# GaAs solar cells are the preferred technology, where cost is no objection: Space



Courtesy of JAXA

# The Epitaxial Liftoff Process:





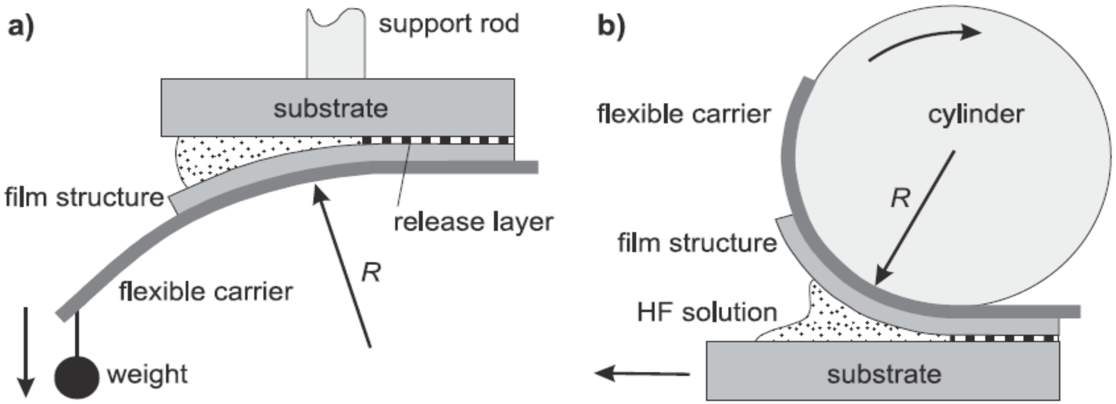


**Fig. 1** Schematic representation of the ELO process. a) The weight induced ELO process, b) ELO with a stabilized radius of curvature by guiding the temporary flexible carrier over a cylinder surface.

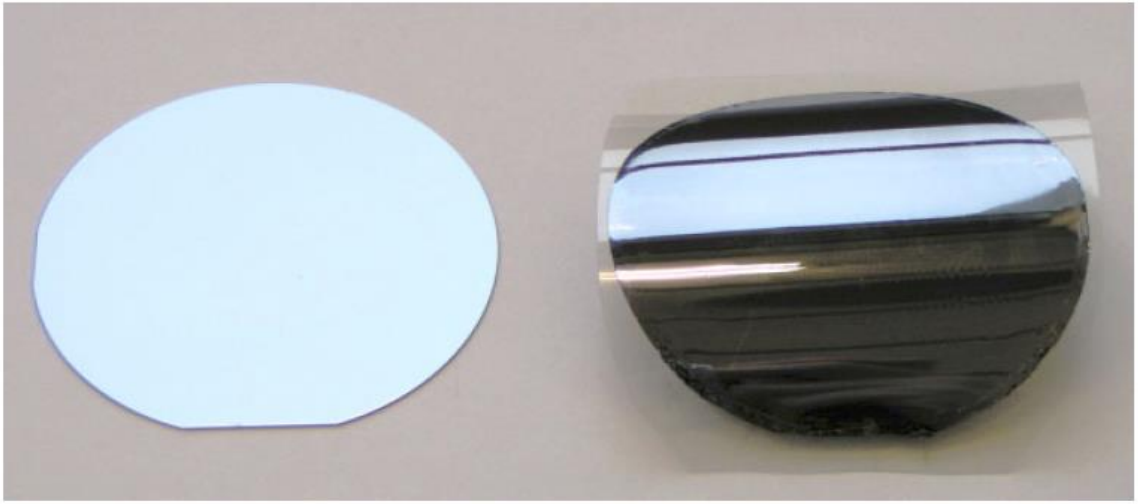


**Fig. 2** (online colour at: www.pss-a.com) 1 µm thick GaAs film of 2 inch in diameter on a flexible plastic carrier (right hand side) after epitaxial lift-off from its substrate (left hand side).

Courtesy of
Alta Devices,
Inc.

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A
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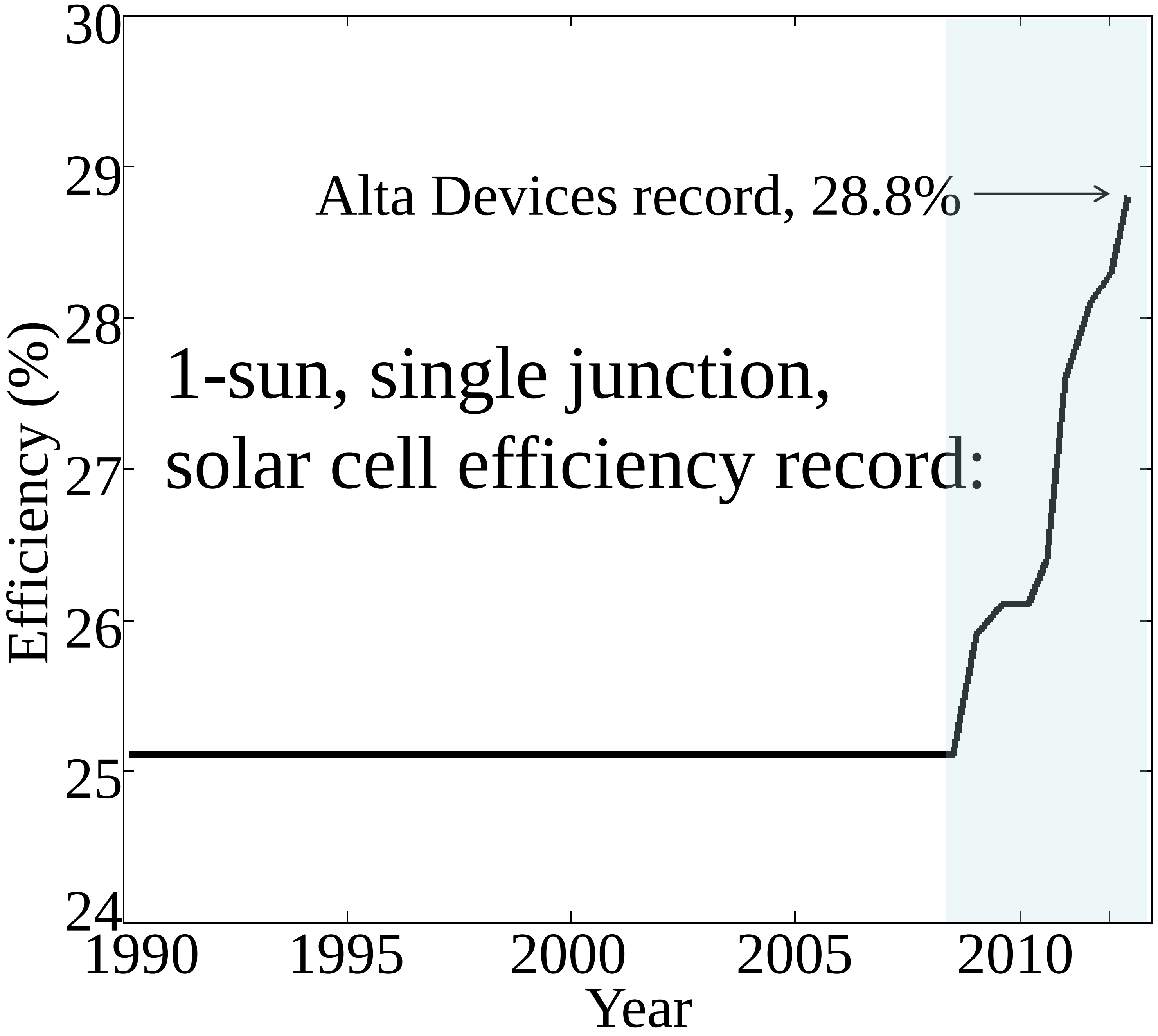
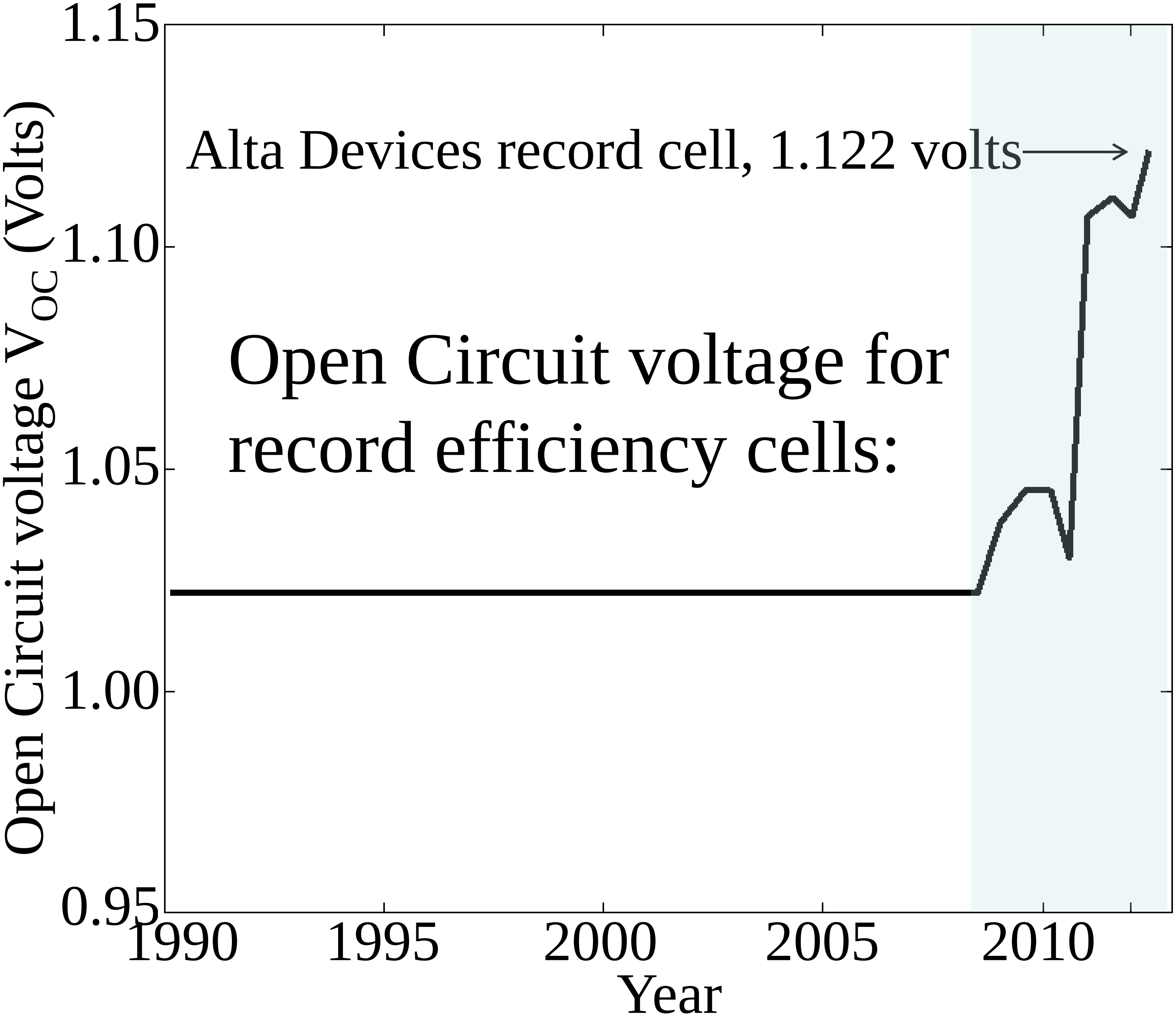
Company



1-sun, single junction,
solar cell efficiency record:



Open Circuit voltage for record efficiency cells:

Alta Devices record cell, 1.122 volts

# 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:

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

In semiconductors with mobile electrons & holes:

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

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

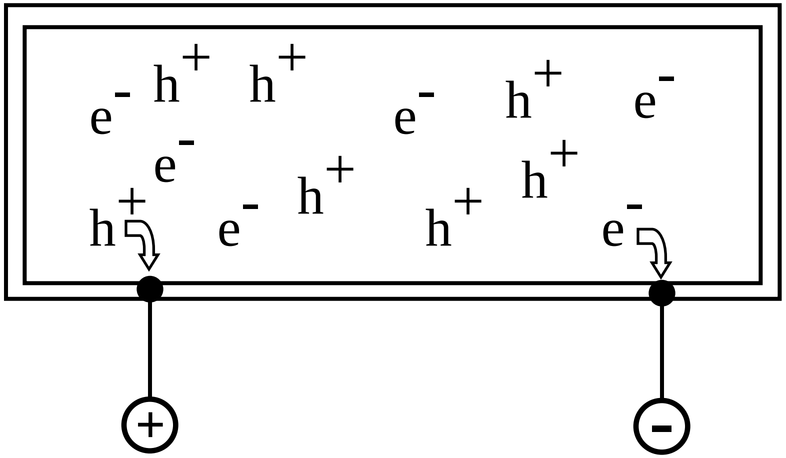
Shockley-Queisser Limit (1961):

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

But in quasi-equilibrium:

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

# 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

# Yes photons have entropy, S

Photon Free Energy = $h\nu - TS$

Photon Free Energy = $h\nu - kT \ln W$

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

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

where $\Omega_s$ is the solid angle subtended by the sun

nicest treatment:

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

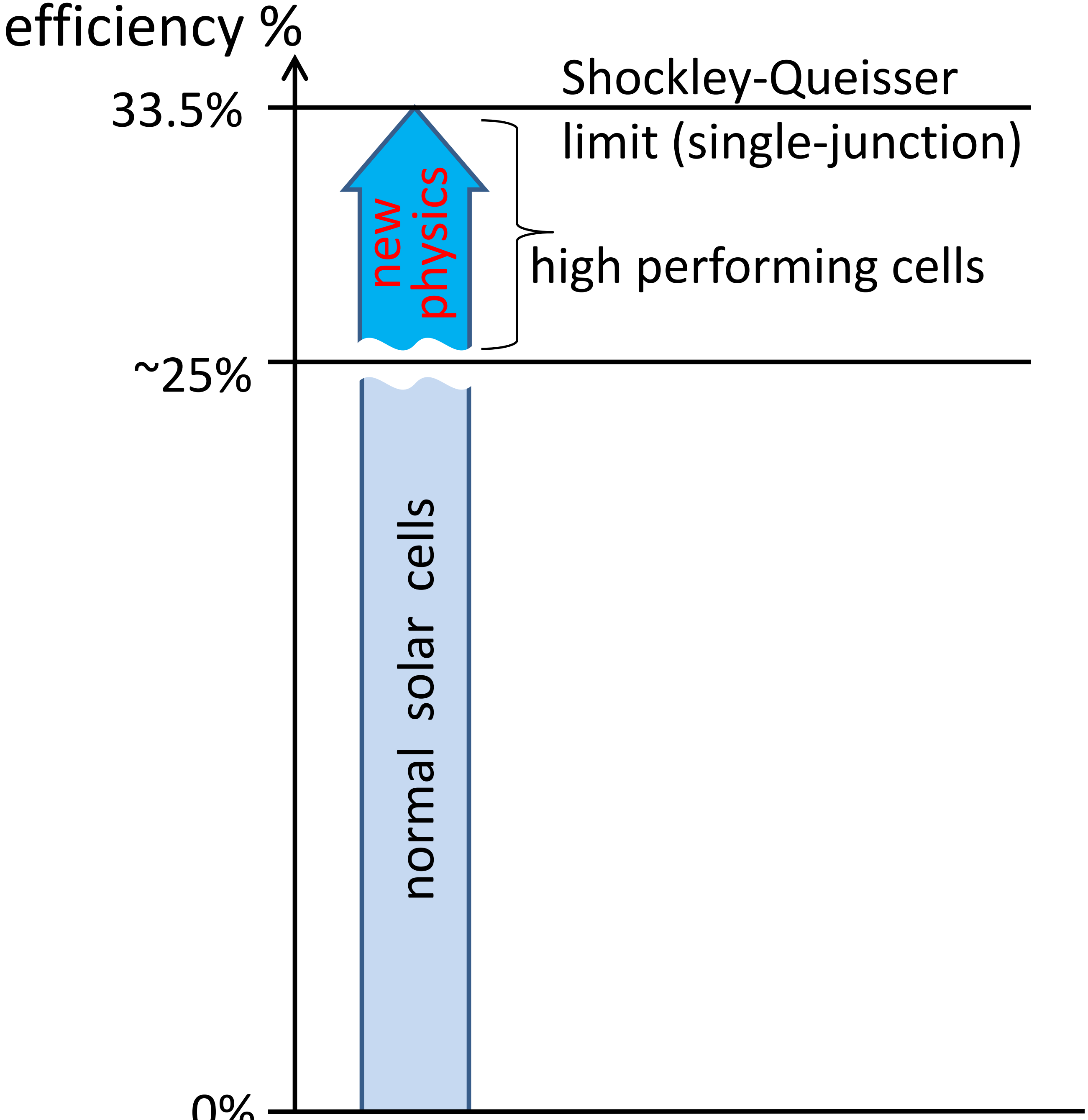
Small bandgaps are particularly vulnerable to entropy:

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.



efficiency %

33.5%

Shockley-Queisser limit (single-junction)

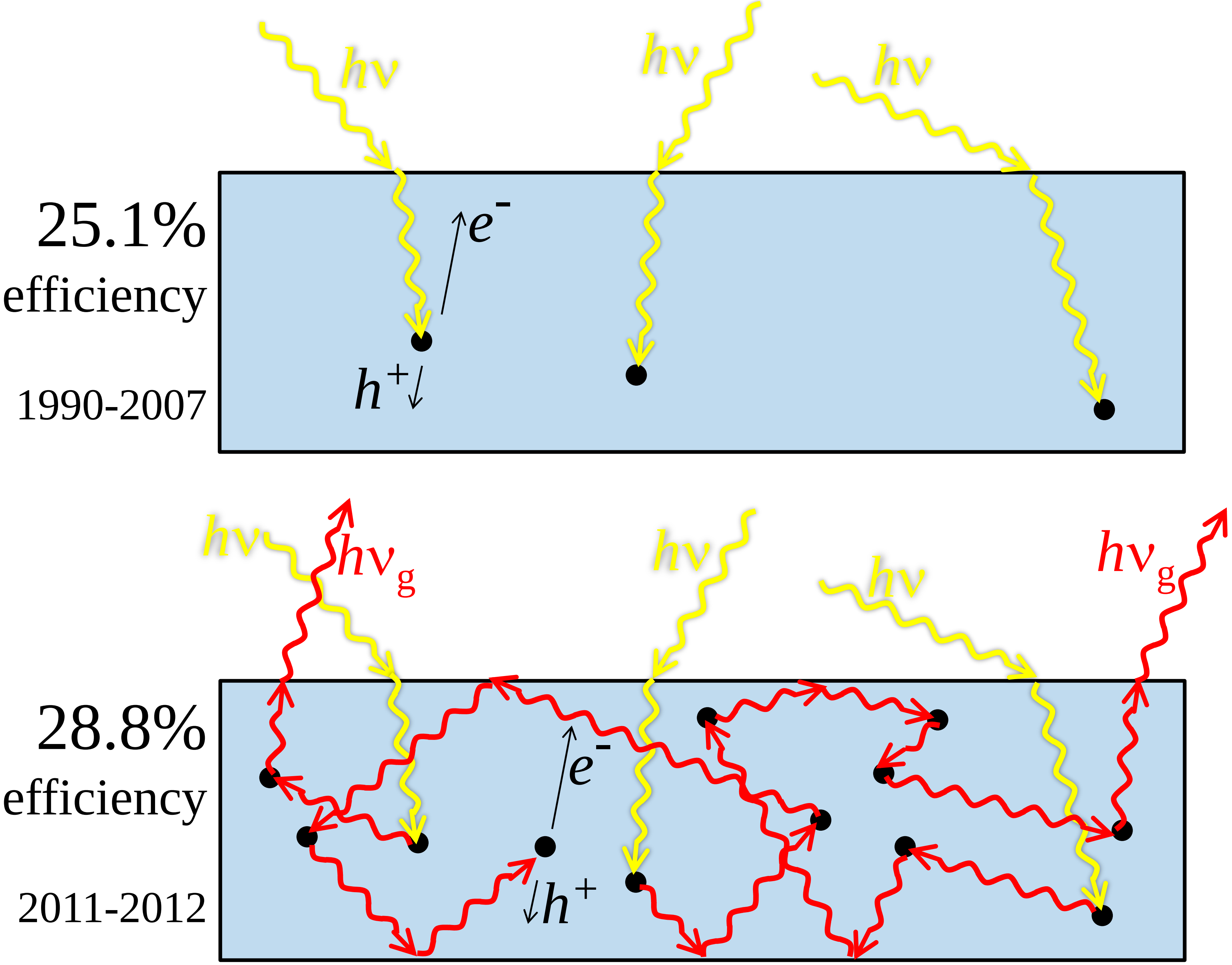
new physics

high performing cells

~25%

normal solar cells

0%

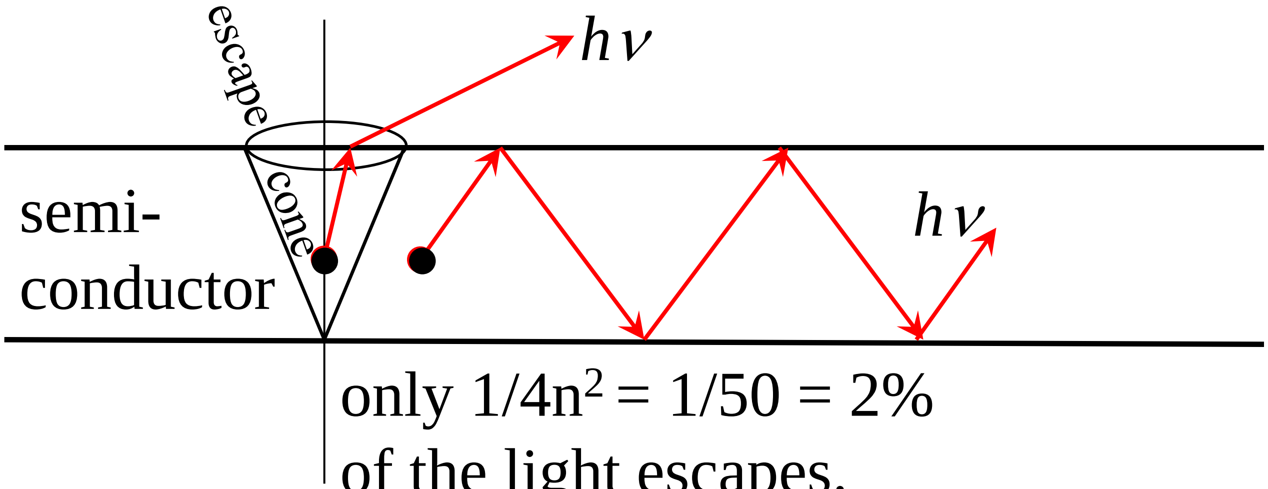

25.1%
efficiency
1990-2007
$h\nu$
$h\nu$
$h\nu$
$e^-$
$h^+$
28.8%
efficiency
2011-2012
$h\nu$
$h\nu_g$
$h\nu$
$h\nu$
$h\nu_g$
$e^-$
$h^+$

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

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

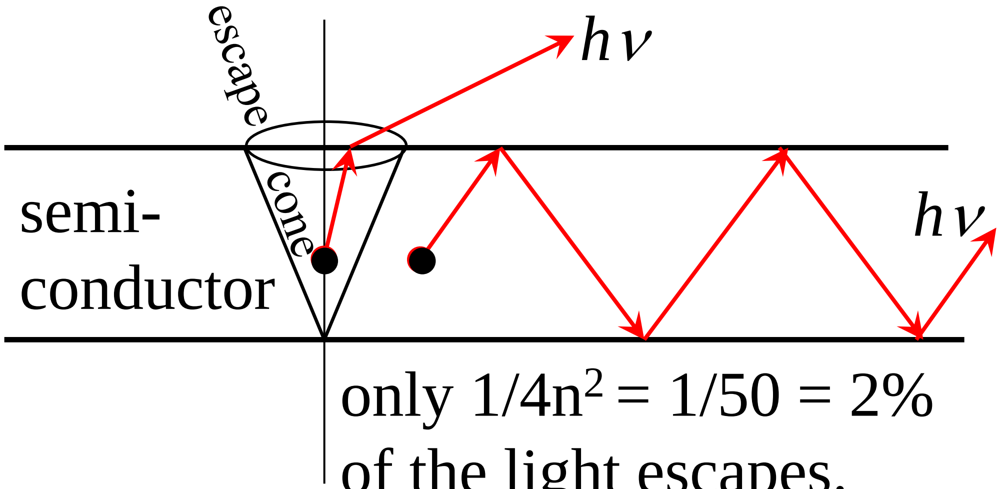
The external fluorescence yield $\eta_{ext}$ is what matters!

Only external Luminescence can balance the incoming radiation.



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

You may need an internal efficiency of $\eta_{int}$=99%
just to get an external efficiency of $\eta_{ext}$=50%



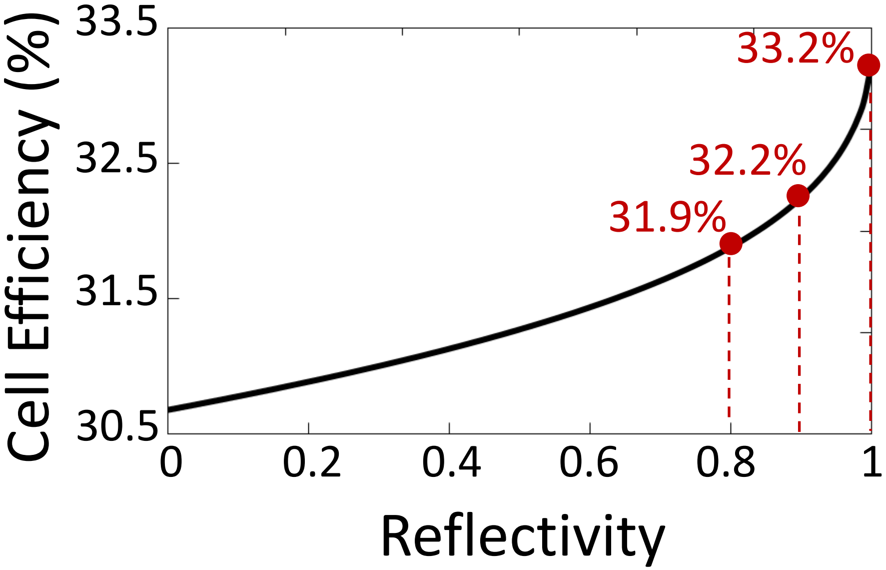
only $1/4n^2$ = 1/50 = 2%
of the light escapes.

But this is really hard to do:

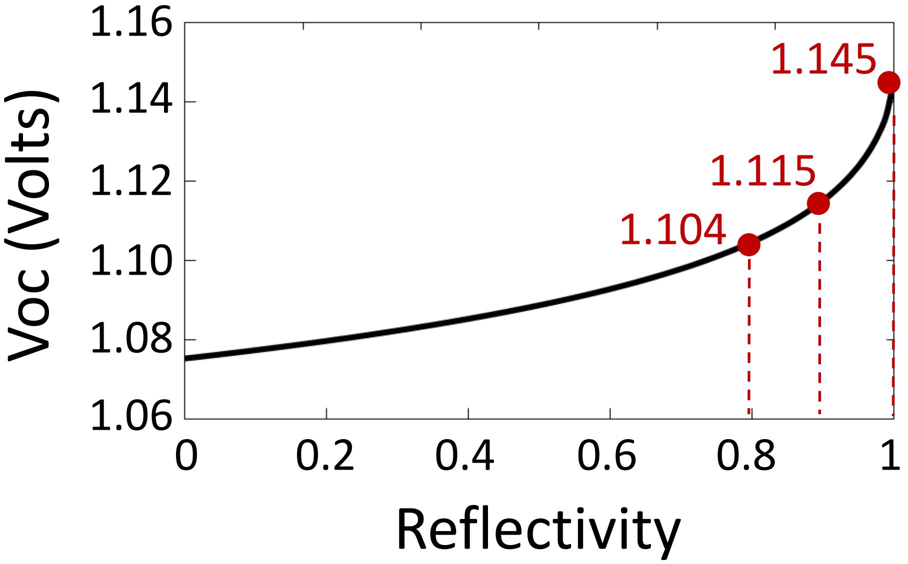
You may need an internal efficiency of $\eta_{int}=99\%$

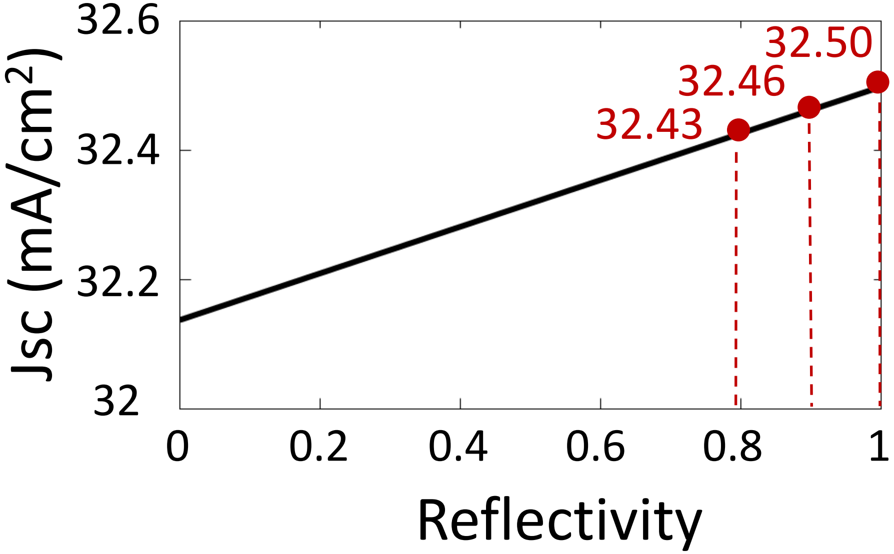
just to get an external efficiency of $\eta_{ext}=50\%$

# Efficiency vs. Rear Reflectivity, GaAs 3μm



90%
Rear
Reflectivity
Is Not
Enough!

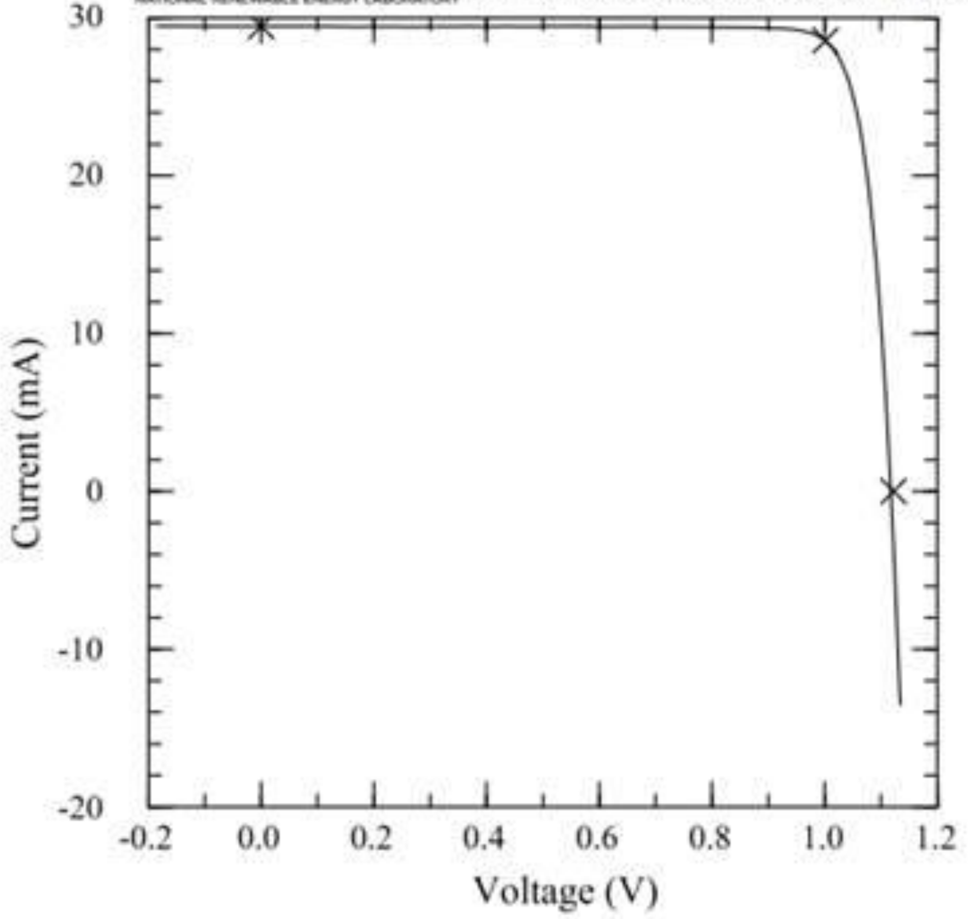




1 sun results from Alta Devices, Inc.

Expected to reach 29.8% single junction, and 34% dual junction, eventually.

NREL
X25 IV System CONFIDENTIAL
PV Performance Characterization Team



$V_{oc}$ = 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 %

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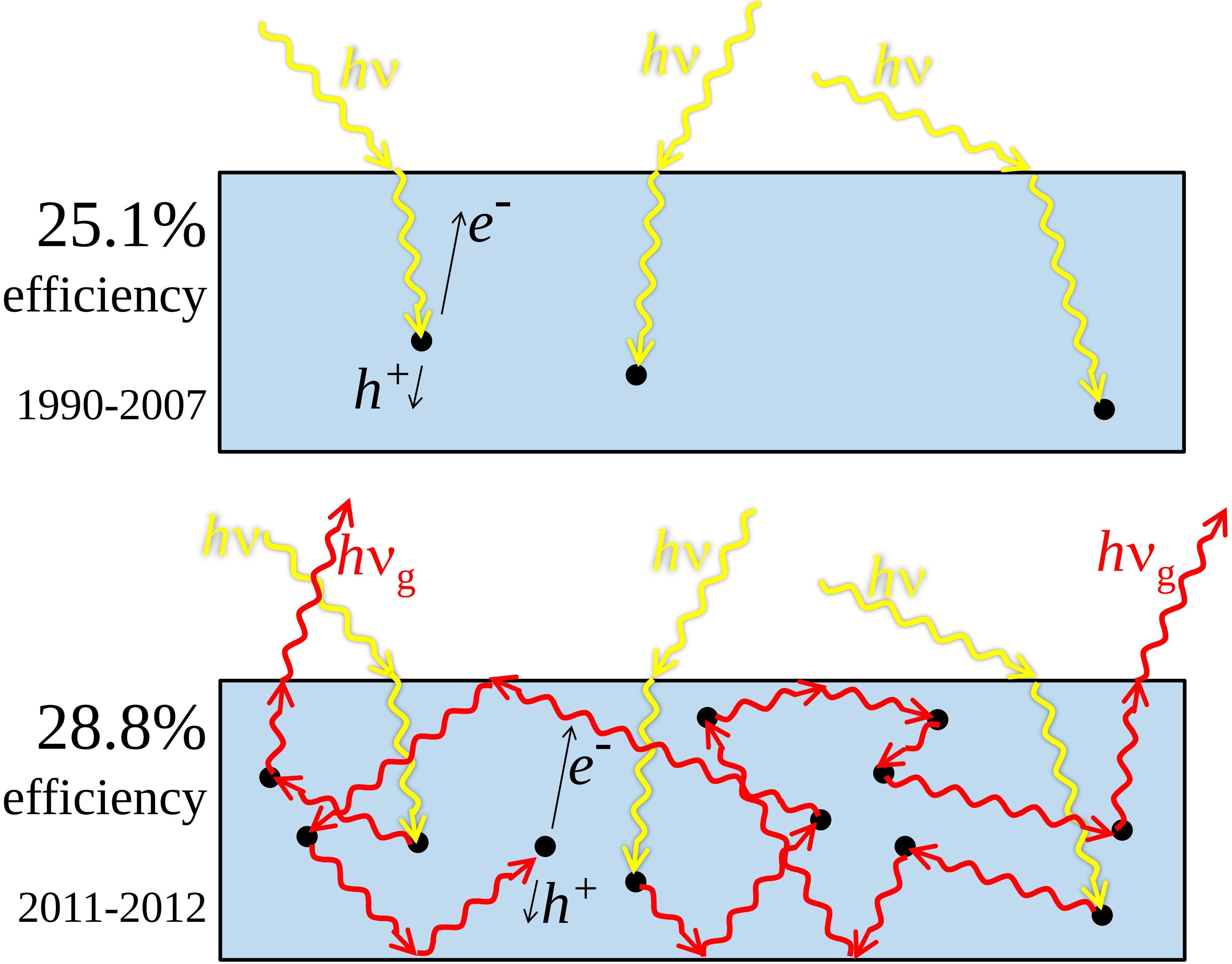

hν
hν
hν
25.1%
efficiency
1990-2007
$e^-$
$h^+$
hν
$hν_g$
hν
hν
$hν_g$
28.8%
efficiency
2011-2012
$e^-$
$h^+$

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

$$\left.\begin{array}{r}\text{Internal Fluorescence Yield } \eta_{int} >> 90\% \\ \text{Rear reflectivity } >> 90\%\end{array}\right\} \begin{array}{l}\text{Both} \\ \text{needed for} \\ \text{good } \eta_{ext}\end{array}$$

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!

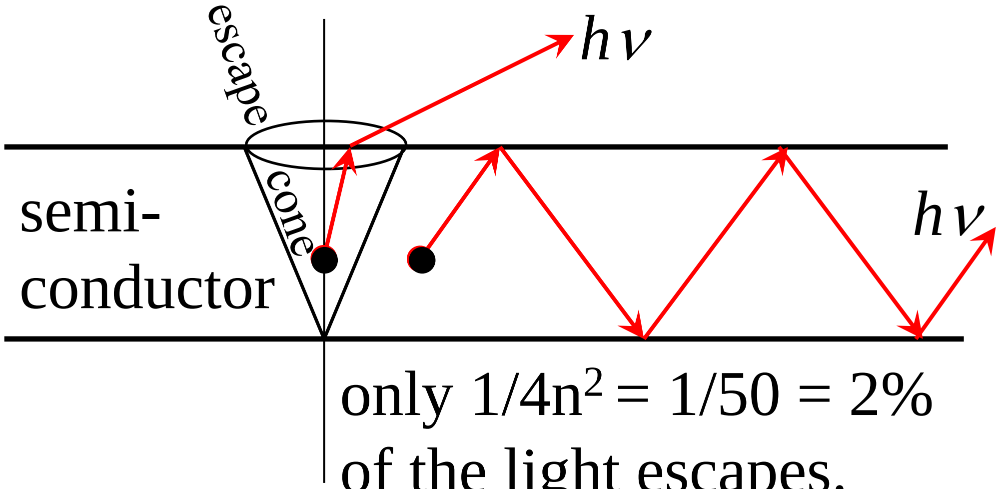
A good solar cell has to be a good LED!

Counter-intuitively:

1. Thin-film cells are more efficient than the best wafer cells.
2. Solar cells perform best when there is maximum external fluorescence yield $\eta_{ext}$.

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 #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.

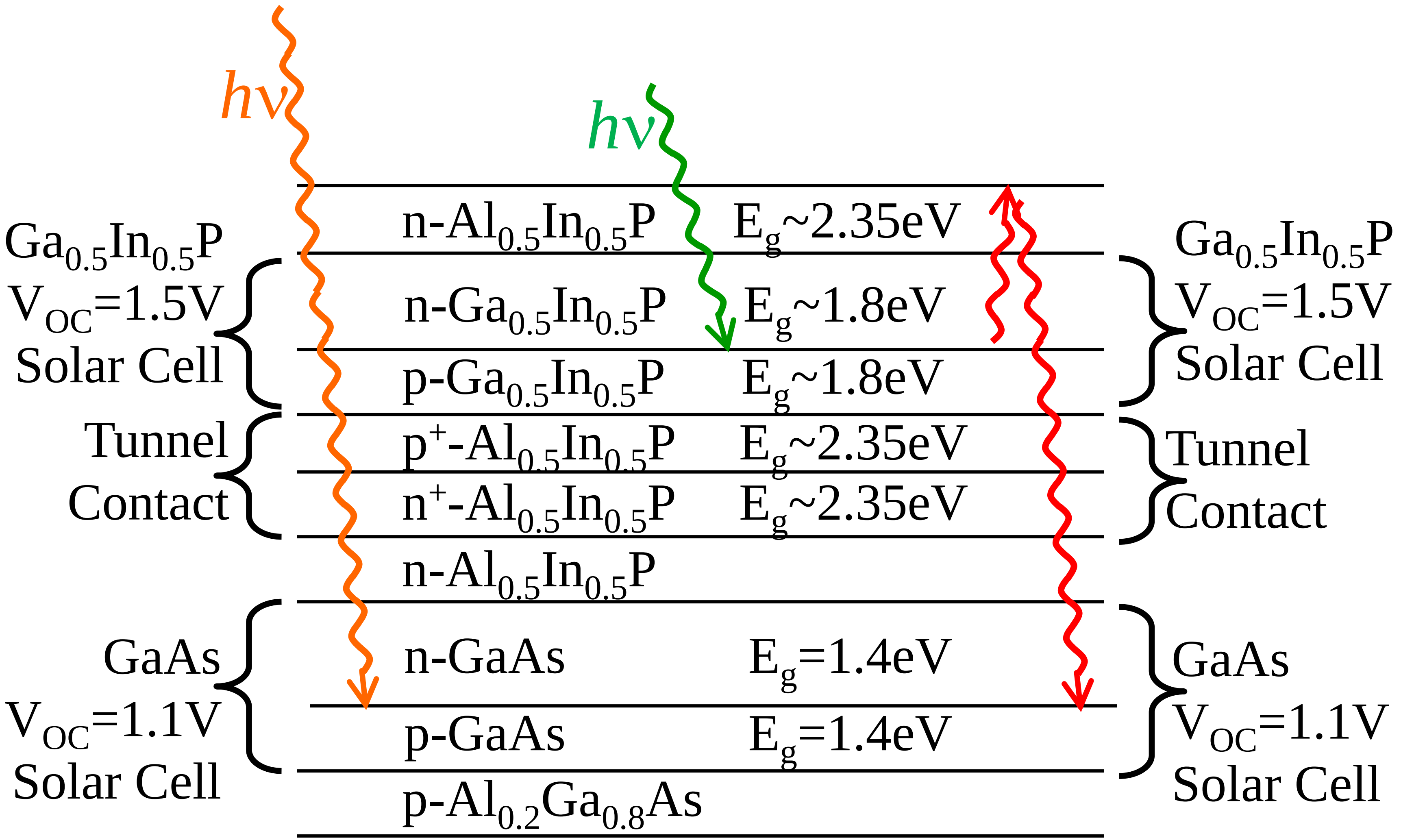
What if the material is not ideal, and the electrons and holes are lost to heat before they can luminesce?

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

The external fluorescence yield $\eta_{ext}$ is what matters!

Only external Luminescence can balance the incoming radiation.

# Dual Junction Series-Connected Tandem Solar Cell



$h\nu$

$h\nu$

| | |
|---|---|
| n-$Al_{0.5}In_{0.5}P$ | $E_g$~2.35eV |
| n-$Ga_{0.5}In_{0.5}P$ | $E_g$~1.8eV |
| p-$Ga_{0.5}In_{0.5}P$ | $E_g$~1.8eV |
| $p^+$-$Al_{0.5}In_{0.5}P$ | $E_g$~2.35eV |
| $n^+$-$Al_{0.5}In_{0.5}P$ | $E_g$~2.35eV |
| n-$Al_{0.5}In_{0.5}P$ | |
| n-GaAs | $E_g$=1.4eV |
| p-GaAs | $E_g$=1.4eV |
| p-$Al_{0.2}Ga_{0.8}As$ | |

$Ga_{0.5}In_{0.5}P$
$V_{OC}$=1.5V
Solar Cell

Tunnel
Contact

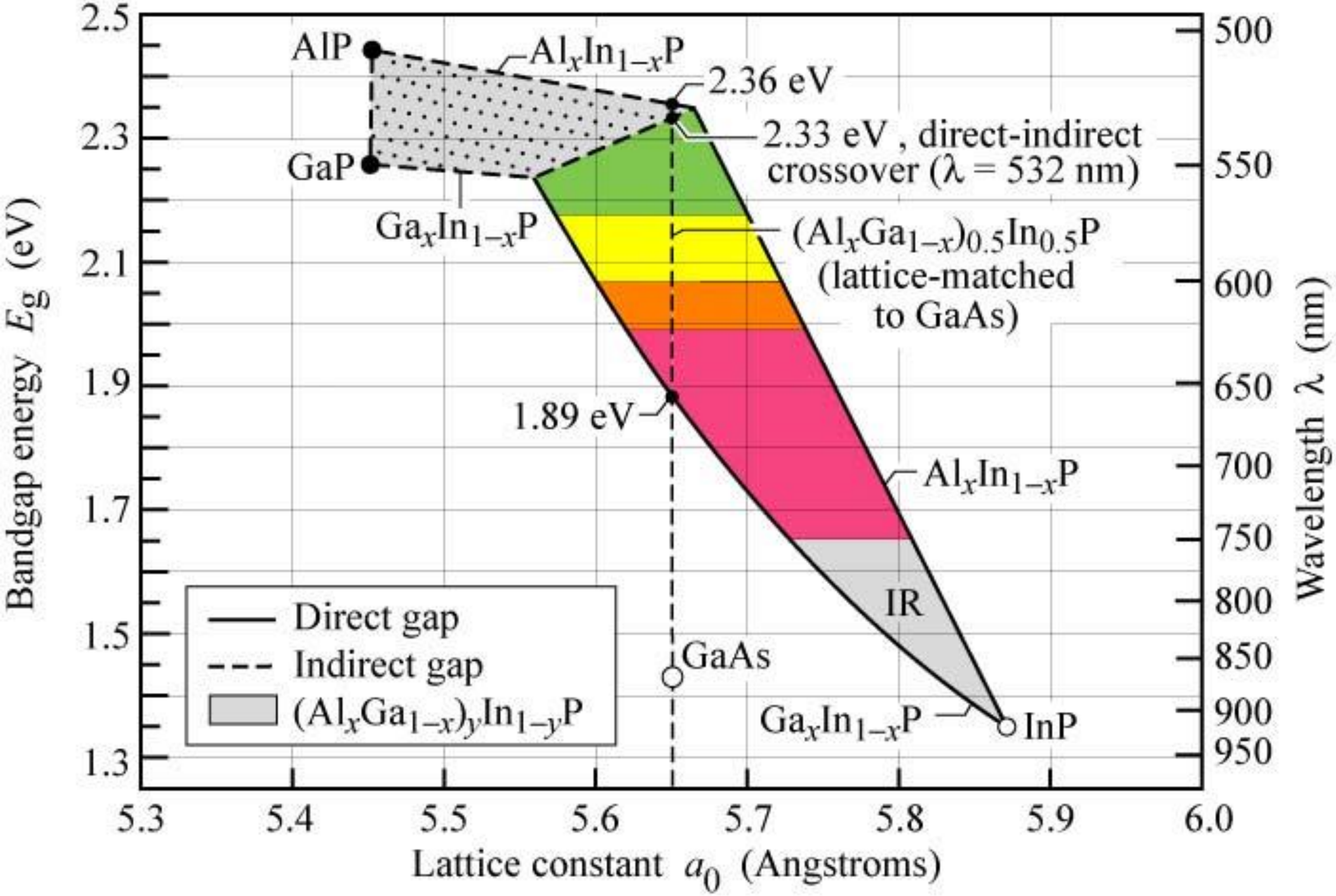
GaAs
$V_{OC}$=1.1V
Solar Cell

$Ga_{0.5}In_{0.5}P$
$V_{OC}$=1.5V
Solar Cell

Tunnel
Contact

GaAs
$V_{OC}$=1.1V
Solar Cell

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



AlP
$E_g = 2.45$ eV
$a_0 = 5.4510$ Å

GaP
$E_g = 2.26$ eV
$a_0 = 5.4512$ Å

InP
$E_g = 1.35$ eV
$a_0 = 5.8686$ Å

GaAs
$E_g = 1.424$ eV
$a_0 = 5.6533$ Å

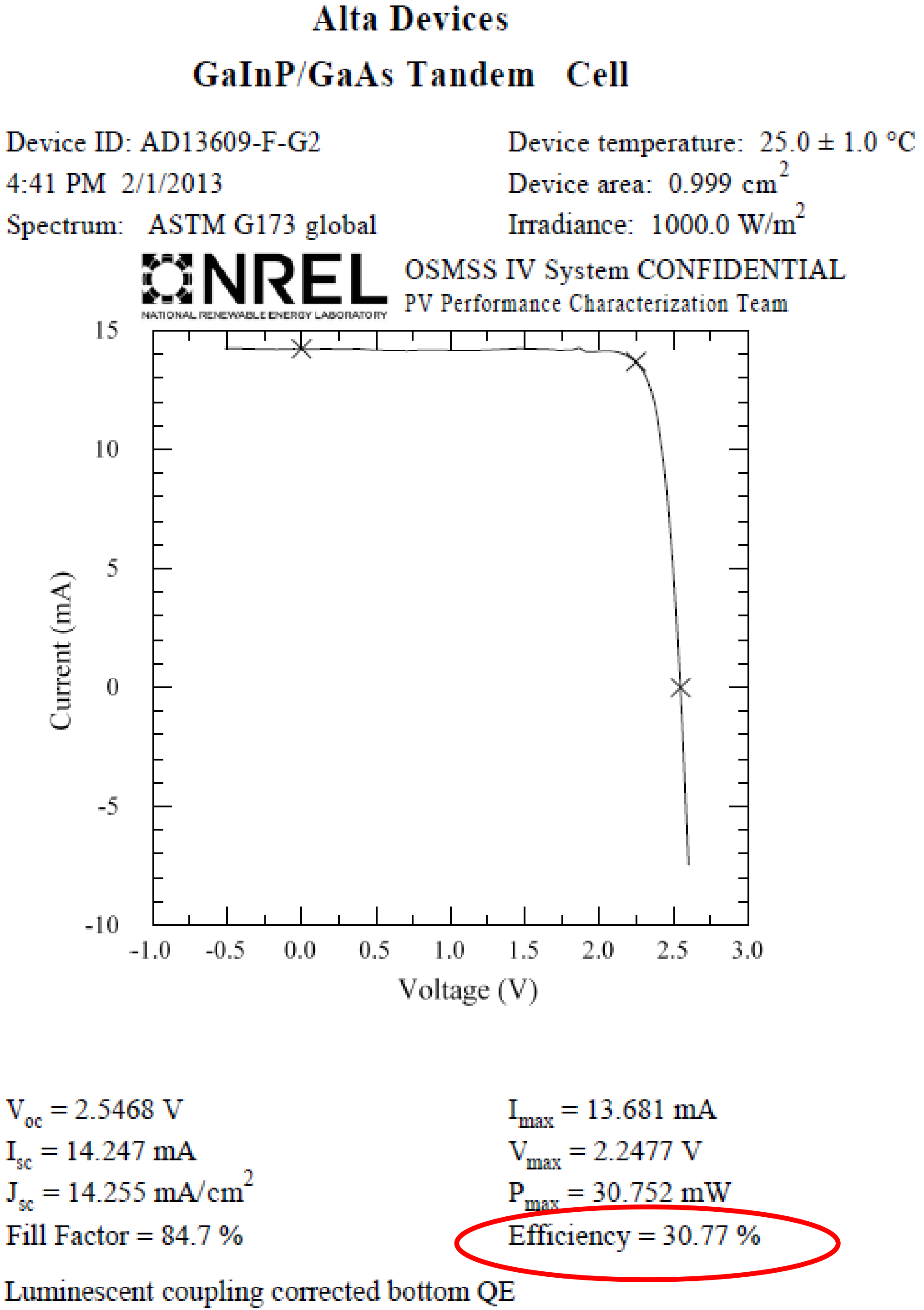
Fig. 12.9. Bandgap energy and corresponding wavelength versus lattice constant of $(Al_xGa_{1-x})_yIn_{1-y}P$ at 300 K. The dashed vertical line shows $(Al_xGa_{1-x})_{0.5}In_{0.5}P$ lattice matched to GaAs (adopted from Chen *et al*., 1997).

Dual-junction 1 sun results from Alta Devices, Inc.

ALTADEVICES
A
Hanergy
Company

NREL has demonstrated >31.1% efficiency in the same system.

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

# What is happening in the solar economy?

c-Si $\eta \sim$ 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.

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Company

California Utility Commission Mandates

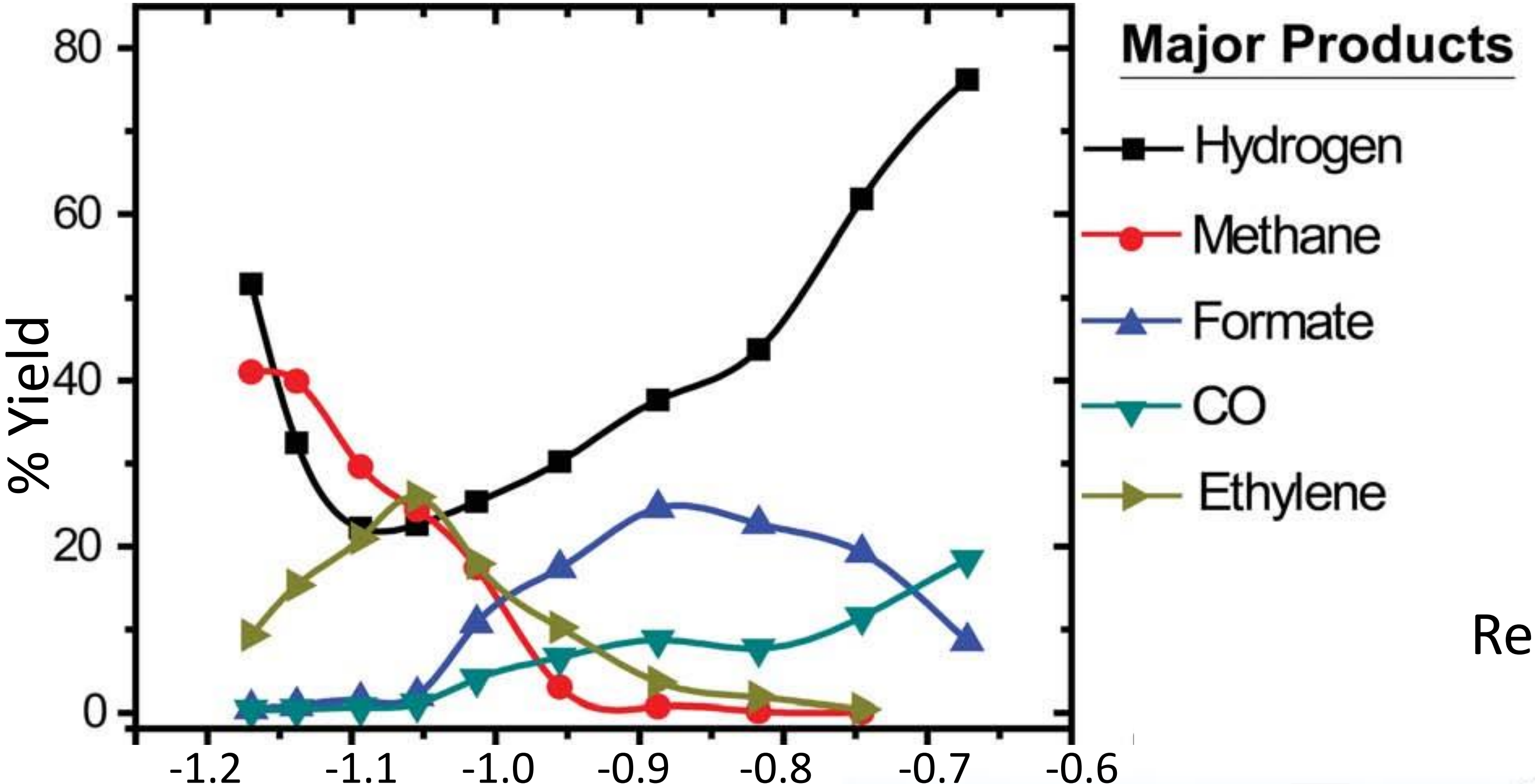
were 5 years too early.

Mandates Subsidized the outdated Silicon Technology

65 years old

Time for a cheaper and more efficient technology.

# Produce Liquid Fuel: Electrolyze Club Soda Producing Methane, Methanol, Formic Acid, Ethylene…



Requires <15¢/Watt

K.P. Kuhl, E.R. Cave, N. David, T.F. Jaramillo. “New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces,” Energy & Environmental Science. pp. 7050-7059 (2012)