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

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> Eli Yablonovitch UC Berkeley

Electrical Engineering & Computer Sciences Dept. & Lawrence Berkeley Nat'l Lab.

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

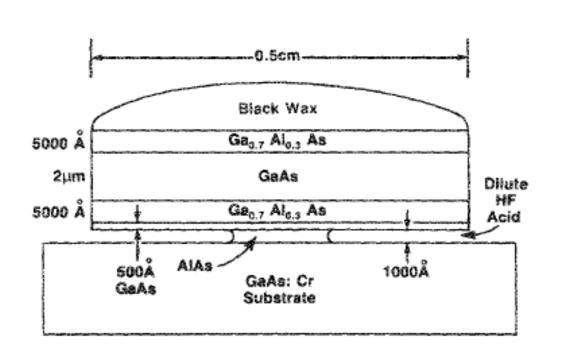


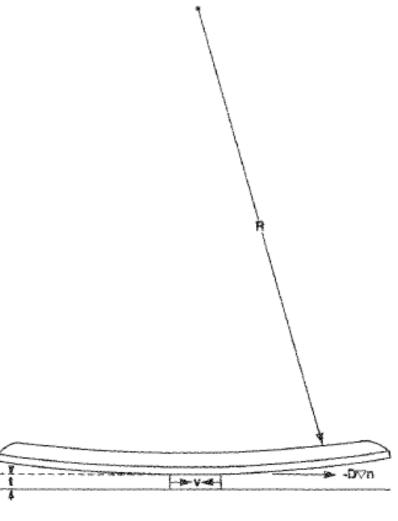
GaAs solar cells are the preferred technology, where cost is no objection: Space



Courtesy of JAXA

The Epitaxial Liftoff Process:





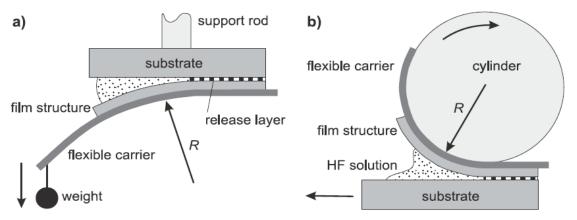


Fig. 1 Schematic representation of the ELO process. a) The weight induced ELO process, b) ELO with a stabilized radius of curvature by guiding the temporary flexible carrier over a cylinder surface.

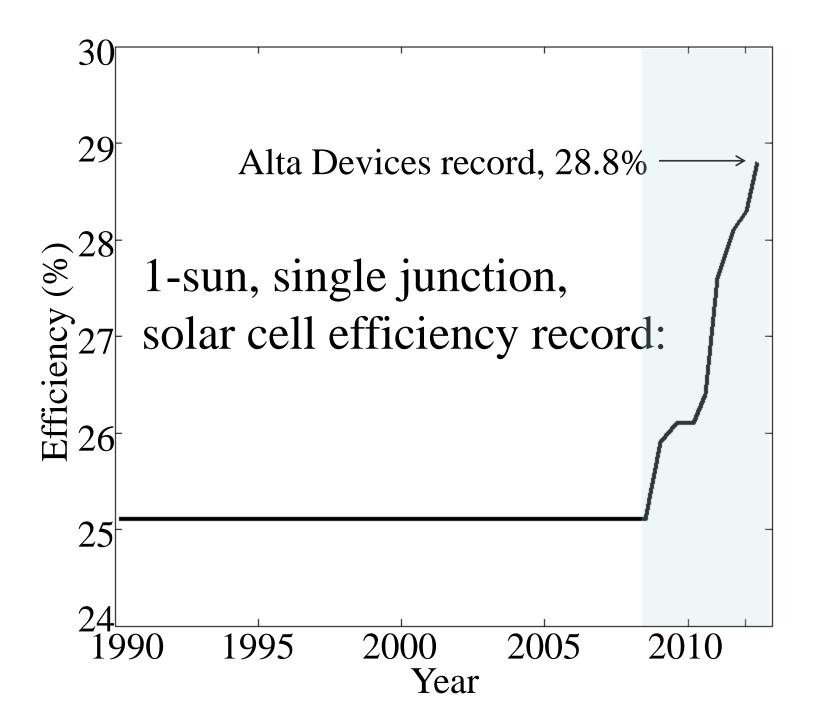


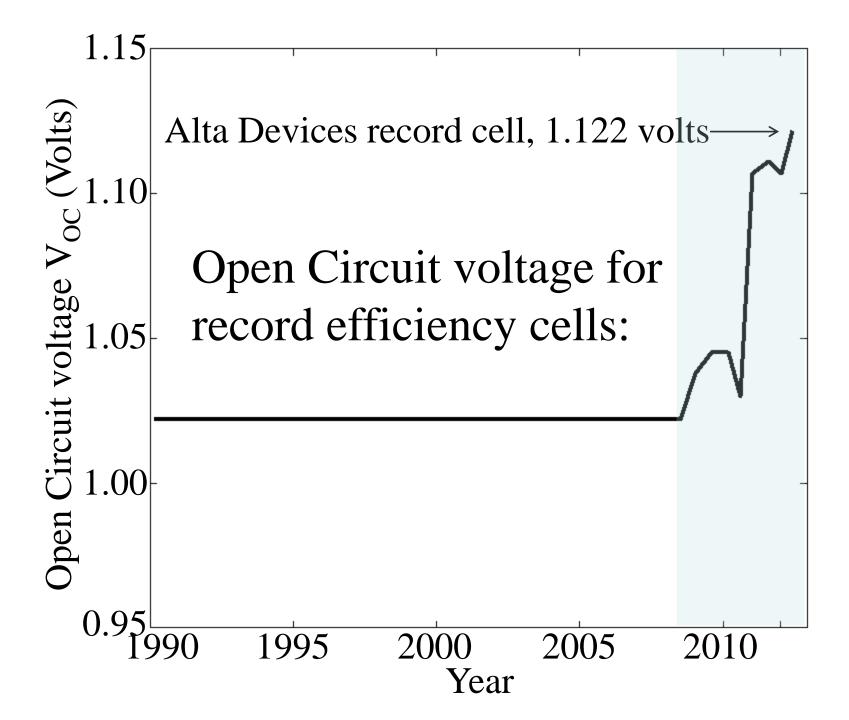
Fig. 2 (online colour at: www.pss-a.com) $1 \mu m$ thick GaAs film of 2 inch in diameter on a flexible plastic carrier (right hand side) after epitaxial lift-off from its substrate (left hand side).



GaAs
Courtesy of
Alta Devices,
Inc.







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

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

In molecules and quantum dots:

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

In semiconductors with mobile electrons & holes:

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

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

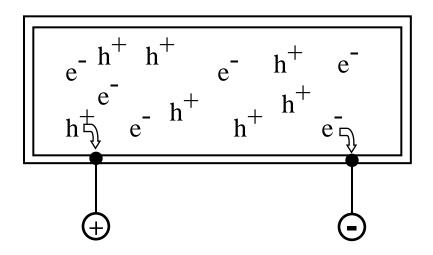
Shockley-Queisser Limit (1961):

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

But in quasi-equilibrium:

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

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 lnW

$$\begin{aligned} qV_{\substack{\text{operating} \\ \text{point}}} = \\ E_g - kT\{ln(\pi/\Omega_s) + \underbrace{ln(4n^2)}_{-0.1eV} + \underbrace{ln(qV_{op}/kT)}_{-0.1eV} \underbrace{-0.3eV}_{-0.3eV} \underbrace{+0.02eV}_{+0.02eV} \\ E_g - kT\{ln(\pi/\Omega_s) + \underbrace{ln(4n^2)}_{-0.1eV} + \underbrace{ln(qV_{op}/kT)}_{-0.1eV} \underbrace{-ln(\eta)}_{-0.1eV} \underbrace{-ln(\eta)}_{-0.3eV} \underbrace{-ln(\eta)}_{-0.3eV$$

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)

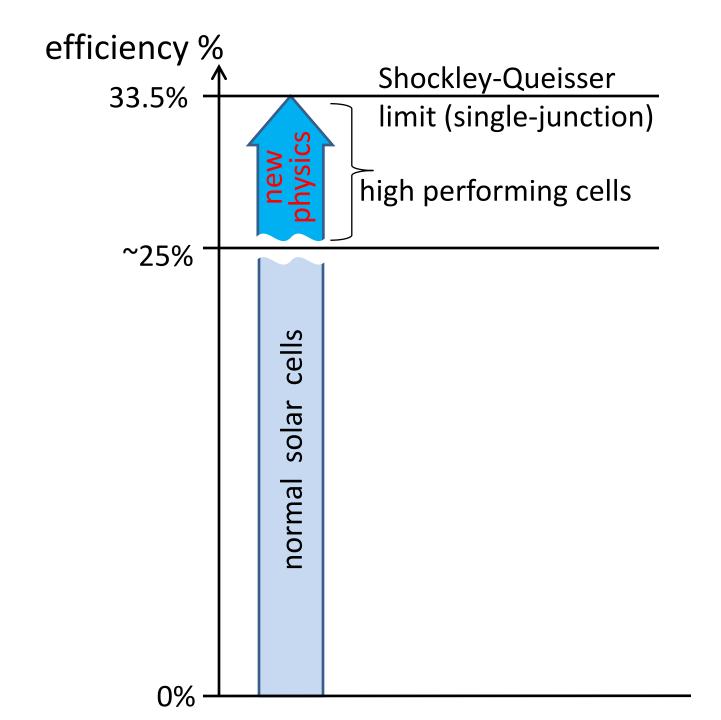
Small bandgaps are particularly vulnerable to entropy:

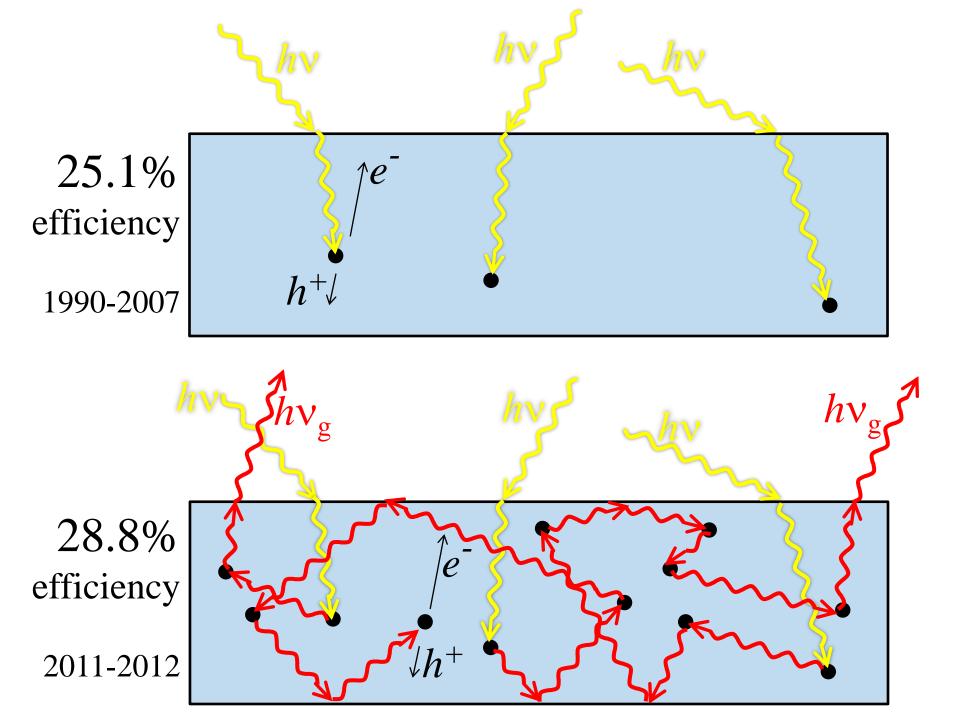
After you subtract off all the entropy terms, you don't have much Free Energy left.

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

A lousy 0.3eV from all those big photons

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





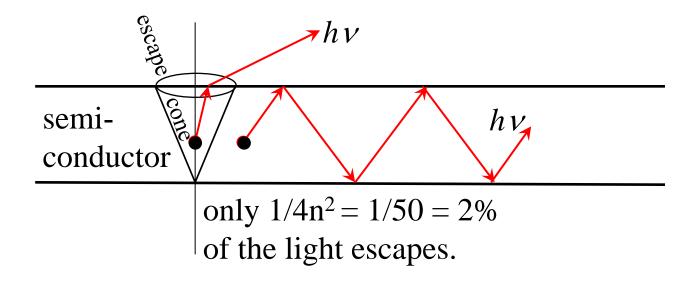
What if the material is not ideal, and the electrons and holes are lost to heat before they can luminesce?

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

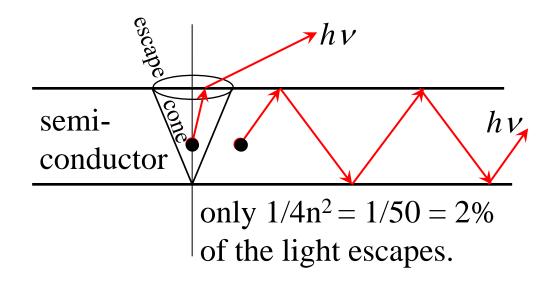
Only external Luminescence can balance the incoming radiation.

fluorescence yield η_{ext} is what matters!

The external



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

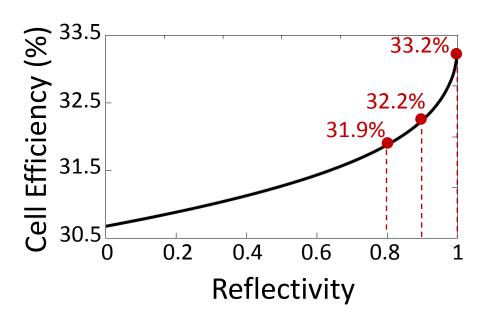


But this is really hard to do:

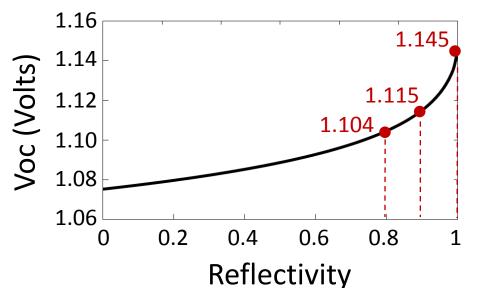
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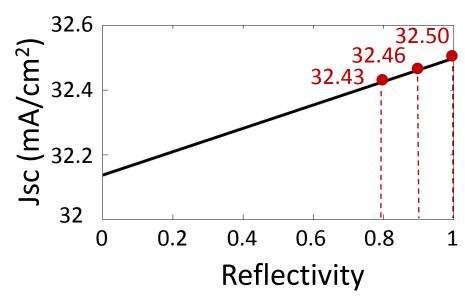
Efficiency vs. Rear Reflectivity,

GaAs 3µm



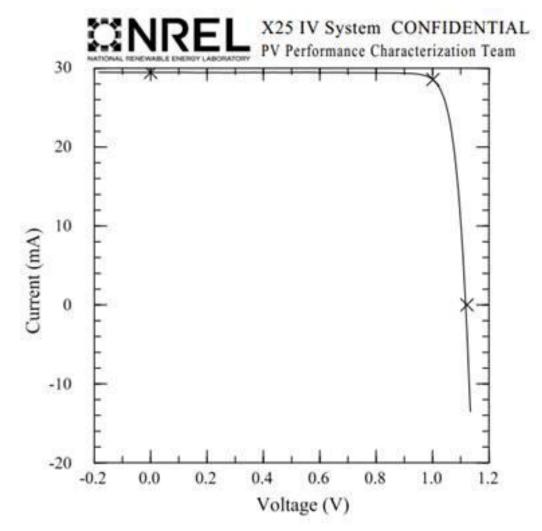
90%
Rear
Reflectivity
Is Not
Enough!





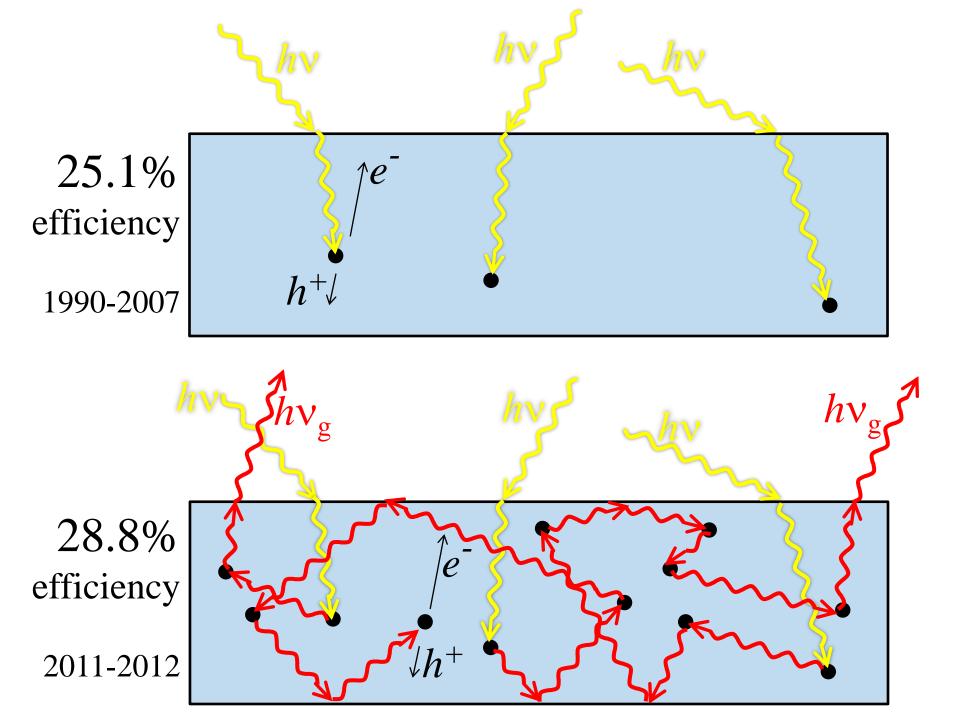
Latest 1 sun single-junction results from Alta Devices, Inc.

Expected to reach 34% dual junction, eventually.



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

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



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

Internal Fluorescence Yield
$$\eta_{int} >> 90\%$$
 Rear reflectivity $>> 90\%$ 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!

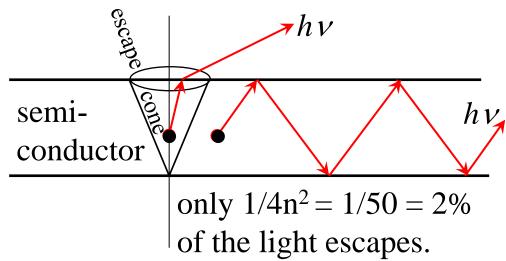
A good solar cell has to be a good LED!

Counter-intuitively:

- 1. Thin-film cells are more efficient than the best wafer cells.
- 2. Solar cells perform 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?



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:

Luminescence = (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?

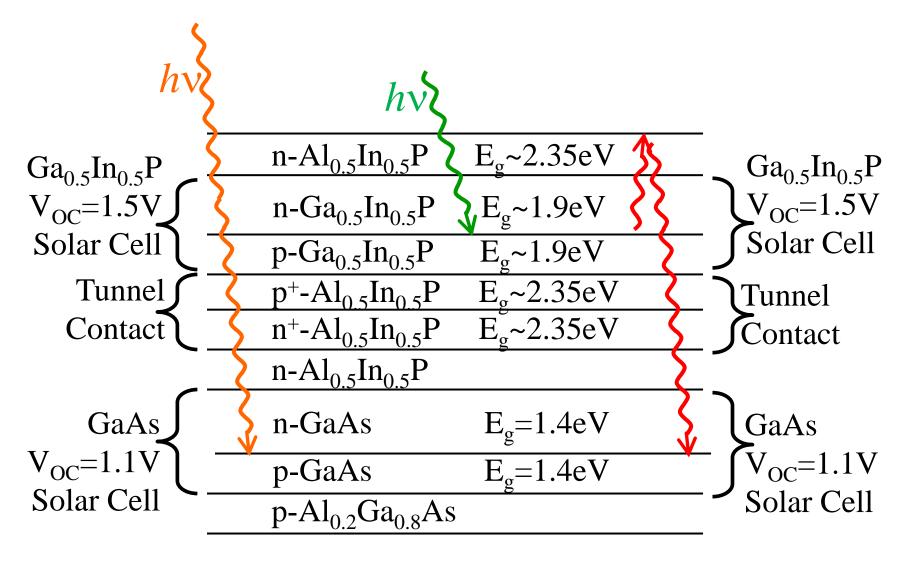
$$qV_{oc} = qV_{oc\text{-ideal}} - kT|ln\{\eta_{ext}\}|$$

Only external Luminescence can balance the incoming radiation.

fluorescence yield η_{ext} is what matters!

The external

Dual Junction Series-Connected Tandem Solar Cell



All Lattice-Matched $\eta \sim 34\%$ efficiency should be possible.

Alta Devices

GaInP/GaAs Tandem Cell

Device ID: AD13609-F-G2

-5

-10

-1.0

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

Expected to reach 34% dual junction, eventually.

2.0

2.5

3.0

Device temperature: 25.0 ± 1.0 °C

$$\begin{split} V_{oc} &= 2.5468 \text{ V} & I_{max} = 13.681 \text{ mA} \\ I_{sc} &= 14.247 \text{ mA} & V_{max} = 2.2477 \text{ V} \\ J_{sc} &= 14.255 \text{ mA/cm}^2 & P_{max} = 30.752 \text{ mW} \\ Fill Factor &= 84.7 \% & Efficiency = 30.77 \% \end{split}$$

0.5

1.0

Voltage (V)

1.5

Luminescent coupling corrected bottom QE

-0.5

0.0

Conclusions:

1. Thin-Film GaAs of ~28% efficiency is in the process of scale-up for solar panels.

2. Opto-electronics can provide the motive power for automobiles.

3. The automotive power market is 10× bigger than the panel electricity market.