Photon *Extraction*: the key physics for approaching solar cell efficiency limits

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Slides/Codes/Relevant Papers: math.mit.edu/~odmiller/publications

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Value of High Photovoltaic Efficiency

Efficiency and Cost of Electricity (COE) inversely related:

\[
\text{COE} \propto \frac{(\text{Cost}_{\text{module}} + \text{Cost}_{\text{BOS}})}{\text{Insolation} \times \text{Efficiency}} \times \text{Finance} + \text{Operating}
\]

Factors that impact COE:

- Location: decides the available input energy
- Efficiency: decides the portion that can be converted to electricity
Which PV technology? Ask Shockley-Queisser

- Canonical method for fundamental limits
  - solar cell = absorber
  - absorber = emitter
  - internals = black-box (equilibrate rates through surface)
  - constant quasi-Fermi level separation (thermalization)

Shockley & Queisser

Single-Junction
Intermediate-Band
Multi-Carrier
Multi-Junction

< 33.5%
< 65%
< 45%
< 50%

Many more: concentrating, hot-carrier, spectrum-splitting, nanowires, etc.
Fundamental limits should be…

**General**
(few parameters)

**Robust**
A real system will never be perfect. But **small imperfections** in material/optics should yield **small losses in performance**.

Shockley-Queisser

Absolutely.
In simplest case, bandgap only

No!
By hiding internals, important photon dynamics are obscured

Two consequences:
(a) For technology selection, **need a “modified” SQ**
(b) To approach SQ: explicitly design for photon **extraction**
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Open-Circuit Voltage
Determines Operating-Point 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.

Any bad things that can happen, will happen. Can’t extract the charges before, say, non-radiative recombination.
Photon Extraction $\rightarrow V_{OC}$

- Basic solar cell definition: absorbs sunlight
- Thermodynamics: absorber = emitter
  - Equilibrium: $R_{em}(\theta, \omega) = R_{abs}(\theta, \omega)$
  - Non-eq: $\int R_{em}(\theta, \omega) \, d\omega d\Omega = \int R_{abs}(\theta, \omega) \, d\omega d\Omega$

Emission (through front) is not a loss mechanism!

Any alternate path for photons:
  (a) represents loss
  (b) reduces effective carrier lifetimes

$qV_{OC} = qV_{OC-ideal} - kT|\ln \eta_{ext}|$
The Voltage Penalty: $kT |\ln \eta_{\text{ext}}|$

- Mathematically formulated by Ross, 1967

$$qV_{OC} = qV_{OC-Ideal} - kT |\ln \eta_{\text{ext}}|$$

Generalized:
Rao, PRB 76, 085303 (2007)
Kirchartz & Rau, PSSA 205, 2737 (2008)

- So what?

$\eta_{\text{ext}}$ depends very non-linearly on internal parameters!
Why do many solar cells have small $V_{OC}$?

*Photon extraction is hard! (Ask LED designers)*

Diagram showing solar radiation, outside escape cone, absorbed by contact, heat, and non-ideal reflectivity.

For a typical high-index material:

- $\sim 50$ re-absorption/re-emission events
- $\sim 50$ bounces off the rear mirror

...before escape

Consequently:

- A 99% internal radiative efficiency
- Or a 99% reflective back mirror
- $\eta_{ext} \approx 50%$

Only half of the photons escape!
Many material systems have fundamental limits to $\eta_{int}$:

- **GaAs**: $\eta_{int} < 99.7\%$
- **c-Si**: $\eta_{int} < 20\%$
- **a-Si**: $\eta_{int} < 10^{-4}$
Single-Junction Efficiency Records: 1990-2013

Efficiency (%) vs. Bandgap (eV)

- **GaAs**
  - 33.5% (Theory)
  - 26.4% (Previous Record 2010) \(V_{oc} = 1.03\)V
  - 25.1% (Record 1990-2007)
  - 25.0% (Best Si 1999-)

Bandgap (eV) from 0.8 to 1.6
Single-Junction Efficiency Records: 1990-2013

- GaAs
- 33.5% Theory

- ~30%
- 28.8% Alta Devices

- 25.0% Best Si (1999-)

- 25.1% Record (1990-2007)

- 26.4% Previous Record (2010)

- $V_{oc} = 1.12V$ (2012)
- $V_{oc} = 1.03V$
Efficiency vs. Rear Mirror Reflectivity

GaAs 3μm

90% Rear Reflectivity Is Not Enough!
M. A. Green, “Radiative Efficiency of state-of-the-art photovoltaic cells”

**2010 GaAs (ISE)**

- $J_{sc}$: $29.8 \, mA/cm^2$
- $V_{oc}$: 1.030 V
- $FF$: 86.0%
- $Eff$: 26.4%

**2013 GaAs (Alta)**

- $J_{sc}$: $29.7 \, mA/cm^2$
- $V_{oc}$: 1.122 V
- $FF$: 86.5%
- $Eff$: 28.8%

**World’s most efficient solar cell beams fluorescent light**

Courtesy of Alta Devices
Clarification: enhanced extraction ≠ photon recycling

Photon recycling is one way to achieve light extraction, and thereby high Voc.

However, there are ways to improve light extraction without enhancing photon recycling. For example: surface texturing. Voc increases.

Light extraction is the general parameter that determines Voc, not photon recycling.

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Application to many solar technologies

GaAs Single-Junction

Multi-Junction

Photon up-conversion

Photon down-conversion

Sunlight

Solar cell

Converter

3Eg

2Eg

Eg

0
Multiple-exciton generation: Shockley-Queisser
Robustness analysis: multi-exciton generation

The **absolute** voltage penalty \( \Delta V_{oc} = kT \ln \eta_{ext} \) is independent of bandgap.

The **relative** voltage penalty \( \frac{\Delta V_{oc}}{V_{oc}} \sim \frac{\Delta V_{oc}}{E_g} \) is much worse for small \( E_g \).

- Depends on exact assumptions – geometry, refractive index
- **Illustrates how important it is to look at robustness, photon dynamics**
Sub-wavelength solar cells: a new wrinkle

New physics: emission partially de-coupled from absorption
emission can occur into near-field (plasmons, quenching, etc.)
Modeling emission: fluctuation-dissipation theorem

\[ qV_{OC} = kT \ln \left( \frac{R_{abs,Sun}}{R_{em,300K}} \right) \]

\[ R_{em,300K} = \int_0^n \frac{d\omega}{\hbar \omega} \langle S(r, \omega) \rangle \cdot \hat{n} \]

\[ \langle P(r, \omega) \cdot P(r', \omega) \rangle_S = \frac{\hbar}{e^{\hbar \omega/kT} - 1} \epsilon_I(r, \omega) \delta(r - r') \]
Example system: air-Si-Au thin film

Emission into plasmon modes:
- reduces extraction through the front
- reduces carrier lifetimes
- reduces $V_{OC}$

Here, plane waves don’t couple to plasmons $\rightarrow$ no absorption effect ($J_{SC}$ unaffected)

This is ONLY an emission/$V_{OC}$ effect!
• **Photon extraction**: driver behind record 28.8% efficiency
  – Power output = current * voltage
  – voltage = extraction (difficult!)
  – There are significant returns to:
    > 90% material quality
    > 90% rear mirror reflectivity
  – New considerations at nano-scale

• **Technology selection**: Shockley-Queisser is fragile
  – Adding a single parameter, $\eta_{int}$, enables robustness analysis
  – Can be applied everywhere SQ can be applied

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