Fundamental Limits in “nano” photovoltaics

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Solar energy conversion

Solar thermal

Solar chemical

Solar photovoltaic
Photons in, electrons out

- Photovoltaic energy conversion requires:
  - photon absorption across an energy gap
  - separation of photogenerated charges
  - asymmetric contacts to an external circuit
Photons in, electrons out

p type silicon

n type silicon
p type silicon

n type

efficiency
~ 15-20%

power rating
~ 100-200 W<p>Applications

CIS Tower, Manchester
0.4 MW (Solar Century)

Solar powered refrigeration
~100 W<p>

Blackfriars Bridge
~1.1 MW<p>
Power Conversion Efficiency =

\[ \frac{\text{Power converted into electrical work (J x V)}}{\text{Radiant Power received from the Sun}} \]
Efficiency from the Current density – Voltage (J-V) curve

- J(V) measured under Standard Test Conditions (AM1.5, 1000 Wm⁻², 25°C)
- Approximately:
  \[ J = -J_{sc} + J_0 \left( \exp \frac{qV}{nkT} - 1 \right) \]

Power conversion efficiency:
\[ \eta = \frac{J_{sc} V_{oc} FF}{P_{in}} \]
\[ FF = \frac{J_{mpp} V_{mpp}}{J_{sc} V_{oc}} \]
\[ P_{in} = \int \phi_{sun}(E)E \, dE \]

- Short circuit current density \( J_{sc} \)
- Open circuit voltage \( V_{oc} \)
- Fill factor FF
Future directions in solar photovoltaics

“Silicon + X”
Add a layer to silicon to improve performance

Crystalline Silicon

High efficiency designs
Stack different solar cells together in a multi-junction

“PV + X”
Integrate solar panels with other functions e.g.
Electricity / heat
PV / fuels
PV / storage

Low cost, low energy manufacture
Flexible, solution processible materials
• Photovoltaic energy conversion

• Limiting efficiency of solar cells

• Nanostructures in photovoltaics

• Routes to more work per photon

• Nanomaterials to approach the efficiency limit

• Nanomaterials to reduce costs
Detailed balance limit

(i) One electron hole pair per photon with $h\nu > E_g$,

(ii) Carriers relax to form separate Fermi distributions at lattice temperature $T_{ambient}$ with quasi Fermi levels separated by $\Delta\mu$.

(iii) All electrons extracted with same electrochemical potential $\Delta\mu = eV$

(iv) Only loss process is spontaneous emission
Solar cell absorbs visible light, emits IR light

\[ \Omega_{\text{emit}} >> \Omega_{\text{abs}} \]

Conventional solar cell

\[ \phi_{bb} [\text{cm}^{-2}\text{s}^{-1}\text{eV}^{-1}] \]

Ambient spectrum \( \phi_{\text{ambient}} \)

AM1.5G spectrum \( \phi_{\text{sun}} \)

\[ E [\text{eV}] \]

\[ 5760 \text{ K} \]

\[ x \times 2.16 \times 10^{-5} \]
Calculation of limiting efficiency

\[ \frac{J}{q} = -X\beta \int_{E_g}^{\infty} \phi_{sun}(E)\,dE - (1 - X\beta) \int_{E_g}^{\infty} \phi_{ambient}(E)\,dE + e^{\Delta\mu/kT} \int_{E_g}^{\infty} \phi_{ambient}(E)\,dE \]

\[ J = -J_{sc} + J_{0,rad} \left( \exp \frac{qV}{kT} - 1 \right) \]

\[ P = JV \]
Emission of sun and solar cell at open circuit

The same integrated photon flux goes from the sun to the solar cell as back.

Graph: courtesy Thomas Kirchartz
Practical and limiting efficiencies

In the ideal (detailed balance) case:
Energy is lost through transmission, relaxation and radiative recombination

Limiting efficiency depends only on the band gap (and the concentration factor of the light)
Practical and limiting efficiencies

In practice:
Energy is lost through transmission, reflection, relaxation, radiative and non-radiative recombination
Practical and limiting efficiencies

In the ideal (detailed balance) case:
Energy is lost through radiative recombination.

Part of the loss is due to the difference in angular range of absorbed and emitted light. Restricting the angular range of emission brings efficiency closer to the maximal concentration limit.

Absorbing substrate
Efficiency: 24.8 %
Spire Corp, IEEE Tr. Electron Dev. 37, 469 (1990)

Optical confinement in a thin-film structure
Efficiency: 28.8 %
Alta Devices, Prog. Photovoltaics 20, 606 (2012)
How bad are the assumptions?

(i) One electron hole pair per photon with $h\nu > E_g$,
   Overestimate current by 10-20% 

(ii) Carriers relax to form separate Fermi distributions at lattice temperature $T_{ambient}$ with quasi Fermi levels separated by $\Delta \mu$.
   ~ OK

(iii) All electrons extracted with same electrochemical potential $\Delta \mu = qV$
   Overestimate $eV_{oc}$ by $O(0.1 \text{ eV})$

(iv) Only loss process is spontaneous emission
   Overestimate $qV_{oc}$ by several 0.1 eV
   Overestimate fill factor
Assumptions in the Shockley Queisser limit

- Multijunctions
- Up-conversion
- Intermediate gap solar cell

- Impact ionization
- Singlet fission
- Down conversion

- Hot carrier solar cell

- Step-function $A(E)$
- one e/h pair
- Thermalization
- Radiative recombination
- Selectivity

- Below band gap emission
- Reflection losses
- Transparency

- Parasitic absorption
- Incomplete charge collection

- $T_{cell} > T_{amb}$ (Cell heats up)

- Auger, defect, interface & surface recombination

- Resistive losses

Slide: courtesy Thomas Kirchartz
Outline

• Photovoltaic energy conversion

• Limiting efficiency of solar cells

• Nanostructures in photovoltaics

• Routes to more work per photon

• Nanomaterials to approach the efficiency limit

• Nanomaterials to reduce costs
First International conference on “Nanostructures in Photovoltaics”
Max Planck institute for Complex Systems
Dresden, 2001
Photovoltaic “nano”-materials

Quantum well

Dye

Conjugated molecule

Nanocrystal

2D transition metal chalcogenide

Conjugated polymer
Properties of nanomaterials for use in photovoltaics

- Control of the electronic density of states
- Control of the phonon density of states
- Anisotropy in electronic and optical properties
- Access new spectral ranges
- Manipulate the optical response

How can nanomaterials help PV efficiency?
- **Surpass** the SQ efficiency limit (?)
- **Approach** the SQ efficiency limit with imperfect materials
- **Reduce the cost** of reaching a given efficiency
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Routes to more work per photon

1. More band gaps

2. Spectral conversion

3. Slow carrier cooling

Power spectrum from black body sun at 5760K

Optimum cell converts 31% of power

Lost by thermalisation

Lost by transmission
Route 1. Higher efficiency via multiple band gaps

- Multi-junction structures or spectral splitting
This works, but multijunction III-V structures are expensive to grow.

- Limiting efficiency around 46% for a monolithic four-junction cell under concentration.
Using nanostructures to achieve multiple band gaps

- Quantum well structures could be used to achieve target band gaps for monolithic multi-junctions on selected substrates

- Strained layer quantum well solar cell: effectively a single junction device
Route 2. Reshaping the spectrum by up and down-conversion

Optimum cell converts 31% of power

Power spectrum from black body sun at 5760K

Lost by thermalisation

Lost by transmission

Singlet fission (image: NREL)

Tim Schmidt, U. Sydney
Singlet fission as a downconversion strategy

- Singlet fission: high energy singlet excitons converted efficiently into triplet pairs in some molecular materials
  - Separate triplets into e – h pairs OR
  - Convert into IR luminescence by energy transfer to nanoparticles
- Goal of an optical coating on silicon

![Graph showing photoluminescence spectra](https://example.com/graph.png)
Reducing the photon entropy loss

- Approach the ‘ultimate’ efficiency by restricting the angular range of emission to match the range of absorption.
- May be possible by engineering the optical modes of semiconductor nanowires

Route 3: More work per photon by slowed cooling

- Generation
- Equilibration
- Cooling
- Recombination

\[ \frac{3}{2} kT \]

0.00 0.50 1.00 1.50 2.00 2.50 3.00 3.50 4.00
Photon Energy (eV)

Irradiance (W m\(^{-2}\) eV\(^{-1}\))

Optimum cell converts 31% of power

Power spectrum from black body sun at 5760K

Lost by thermalisation

Lost by transmission

Optimum cell converts 31% of power
Reduced thermalisation in solar cells

- Eliminating thermalisation of charge carriers with environment could increase efficiency to 85% but not physically achievable

- Approaches that have been studied:
  - Multiple exciton generation
  - Slow cooling via “phonon bottleneck”

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Nanostructures to improve charge collection

- Radial nanowire solar cells can outperform planar junctions only when diffusion length << absorption depth
- Helps to approach limiting efficiency in poor quality semiconductors

- Comparable to the use of ‘bulk heterojunctions’ in molecular photovoltaics

Nanostructures to reduce light reflection

- Array of low geometrical cross section nanowires results in low refractive index and weak reflection
- Exploit forward Mie scattering into high index substrate to reduce reflection
Nanostructures to improve the radiative efficiency

- Nanowires can show optical cross section > 10x geometrical
- If recombination is proportional to bulk volume can enhance generation relative to non-radiative recombination
Use of Plasmonics in Photovoltaics

a) Internal Scattering
b) Field Enhancement
c) Surface Plasmon Polariton Propagation
Use of Plasmonics in Photovoltaics

- Design of nanostructures for plasmonic enhancement depends strongly on accurate knowledge of the dielectric function of the metal used!

See poster by Phoebe Pearce at this meeting
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Printable photovoltaics

1990- Dye sensitised

2001- Organic (polymer:C60)

2007- Organic tandem

2010- Particle slurry CZTS

2012- Perovskite

Other new materials and new processes ...
Summary

- Photovoltaic energy conversion efficiency is limited to 33% in unconcentrated sunlight.

- To approach this efficiency need to maximise radiative efficiency; to surpass it we need to reduce losses to light transmission and charge carrier thermalisation.

- Nanostructures have capability to modify the electronic and optical density of states.

- Several approaches proposed to achieving more work per photon:
  - Upconversion, downconversion, multiple gaps, slowed cooling.
  - Only multi-junctions are currently practically useful.

- Most effective uses of nanostructures to raise efficiency are in manipulating light absorption and emission to approach the theoretical limit.

Thank you for your attention! Questions?