Applied Physics of solar energy conversion

- Conventional solar cells, and how lazy thinking can slow you down
- Some new ideas
- Our work on semiconductor quantum dots
The big picture

• ~ $13 \times 10^{12}$ W (TW) energy production rate is currently used in the world.
• ~ 3 TW energy production rate is currently needed to maintain our quality of life in the US.
• Potential sources: fossil fuel, nuclear, geothermal, hydro, solar.
• Issues
  – hydro: we’re using it all now
  – fossil fuel: CO$_2$ release, limited supply, politics
  – nuclear: limited uranium, safety, waste, thermal pollution
  – geothermal: not enough energy
  – solar: new technologies needed, distributed source (large areas needed)
    • thermal, biomass, electric
How much solar energy is there?

• In the US:
  – \( \sim 10^{13} \text{ m}^2 \times 10^3 \text{W/m}^2 \times 2.4\text{hrs}/24\text{hrs} = 1000\text{TW} \) average
  – US highway area is almost 0.2% of the total land area
  – covering 0.2% of the US land area with 50% cells yields 1 TW
    • higher efficiency is important
  – to produce this area over a period of 20 years, we must manufacture 2000 km\(^2\)/year.
  – That’s a lot of stuff
    • PVC plastic wrap = \( 10^3 \text{m}^3/10^{-5}\text{m} = 10^8\text{m}^2 = 100\text{km}^2\) /year
Constraints on novel solar cells/panels

1) Due to the cost of the balance of systems, a solar cell of zero cost must exhibit efficiency greater than about 15% to be financially practical.
2) It must be deployable in large area.
3) It must have a useful lifetime greater than 10 years. 20 years is the goal.
A conventional solar cell
The p-n junction

- Doping a semiconductor with impurities produces regions with greater or lesser affinities for electrons.
- Touching these two types of materials together leads to band misalignments and different carrier densities on either side of the junction.
Photovoltaic idea

- When an electron-hole pair are excited near a p-n junction, they may separate in the field.
- If they have nowhere to go they will pile up on either side until the voltage opposes the built-in voltage due to the impurities.
Energy loss in a conventional p-n junction

1 e⁻ - h⁺ pair/photon; full hot carrier relaxation

\[ \eta_{\text{max}} = 32\% \]
(in radiative limit)

Basic Research Needs for Solar Energy Utilization 2005
Fundamental considerations
-The Shockley-Queisser limit

- Excess photon energy is transformed to heat during carrier relaxation
- Both carriers must diffuse to correct electrode
  - no recombination
  - principle of detailed balance
- Need to absorb as much light as possible in the active region
  - optimal thickness of active region depends on optical absorption, nonradiative processes, radiative losses, diffusion lengths for carriers
“Detailed Balance Limit of Efficiency of $p$-$n$ Junction Solar Cells”

• The sun is assumed to be a blackbody at 6000K.
• The solar cell is assumed to be a blackbody at 300K. (Cell is uniform in temperature throughout.)
• The active region is thick enough to absorb all light above the band gap.
• One photon gives rise to one electron-hole pair
• All recombination is via radiative processes (detailed balance).
• All photoexcited carrier pairs that do not recombine radiatively are extracted.
• All excited carriers relax to the band edge prior to extraction, relaxation is by creating phonons.
The solar spectrum as interpreted by the S-Q model

- The solar spectrum approximates a 6000K blackbody.
- Atmospheric absorption bands
- Carriers excited above a band edge can decay by phonon excitation (heating the lattice). Higher energy – more heat loss.
- Carriers below the gap are not absorbed
Detailed balance limit depends on bandgap

- Excitation energy above the bandgap is lost to heating.
- Excitation energy below the band gap is not absorbed.

Shockley, Queisser (1961)

- Optimum bandgap is $\sim1.2$ eV.
- Highest SQ efficiency is $\sim30\%$. 
A high efficiency Si solar cell

- Structured surface and multilayer coating maximize:
  - coupling of light into structure by interference
  - scattering of light into oblique angles for trapping weakly absorbed wavelengths

http://www.pv.unsw.edu.au/
An obvious extension of the Shockley-Queissser limit
Beating the Shockley-Queisser Limit: Stacked cells in the same detailed balance limit

- Proposal - A stack of cells with decreasing band gap, each one picking off a slice of the spectrum.
- Unconcentrated solar efficiency of ~65%.

Parrott, J Phys D (1979)
Making multijunction cells efficient requires many aspects to work simultaneously

- The current density in stacked junction cells must be matched.
- Materials compatibility
- Light of appropriate wavelength must couple in to each cell in the stack
- Typical best ~ two or three cells
- EXPENSIVE
History of Solar Cell Efficiency

Basic Research Needs for Solar Energy Utilization 2005
Rethinking the Shockley-Queisser limit
Beating the Shockley-Queisser limit in other ways—let’s check the assumptions

• A single absorbed photon gives rise to one electron hole pair.
  – Inverse Auger process can give rise to more than one e-h pair per absorbed photon.
  – Impact or avalanche ionization can lead to more than one pair per photon

• Photons below the band gap are not absorbed.
  – Nonlinear two photon absorption
  – “Intermediate band” absorption
Intermediate band solar cell (Luque et al, PRL 1997)

Intermediate band idea: An absorbing band that can accept electron excitations from the VB and then allow transitions to the CB.

Computed ideal conversion efficiency for single gap, two gap, and intermediate band structures based on single photon/single exciton model. (Luque et al. 1997)
Semiconductor Quantum Dots
A nanoparticle or cluster is frequently just like a piece of a larger crystal.

A TEM image of a CdSe nanocrystal.
States in a nutshell

(a) CdSe Bulk Semiconductor

(b) CdSe Quantum Dot (QD)

(c) $E_{g}(QD) = E_{g} + \frac{\hbar^{2}a^{2}}{2m_{eh}R^{2}}$

$m_{eh} = \frac{m_{e}m_{h}}{m_{e} + m_{h}}$

$m_{e} =$ effective electron mass
$m_{h} =$ effective hole mass

(d) $E_{g}(bulk) \rightarrow E_{g}(QD) \rightarrow Photon\ energy$

Absorption Coefficient (cm$^{-1}$)

Energy (eV)
Impact ionization in PbSe

**History**

- Schaller and Klimov (2004) demonstrate that the quantum yield of excitons per photon is ~120%!!!
- This means that the inverse Auger process is significant.
Multiple exciton generation in PbSe

- Ellingson et al. (Nozik) 2005 – The yield of excitons exceeds 100% by a lot!
Seven Excitons at a Cost of One: Redefining the Limits for Conversion Efficiency of Photons into Charge Carriers

Nanoletters 6, Feb 2006

Richard D. Schaller, Milan Sykora, Jeffrey M. Pietryga, and Victor I. Klimov*

Chemistry Division, C-PCS, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Received November 17, 2005; Revised Manuscript Received December 19, 2005
The situation now

• Two approaches to efficient solar cells have been proposed that “break” the Shockley-Queisser limits.

• Intermediate state cells allow two low energy photons to add up to one exciton. - ~63% efficiency limit at one sun.
  – Cells have been demonstrated but no records have been broken.

• Multiple exciton generation can give rise to 75% efficient conversion.
  – Only the Auger principle has been demonstrated.
Quantum dot work at Rensselaer:

Some examples
PbS Quantum Dots in Glass

P. Rao - partially funded by Evident Technologies, Troy NY
cw Absorption and Photoluminescence Spectra
R = 3 nm radius

- 50 mW red-shift between absorption and emission – could be trap, dark exciton, or Stokes shift
- excitation within lowest absorption peak decreases the width of the emission band slightly
- PL efficiency ~ 4%, long lifetime~10^{-5} s
The cw photomodulation spectrum

- The PM spectrum overlaps the first absorption peak
- Circles: PM spectrum at room T with excitation at ~2.4 eV
- Solid line: fit to first absorption peak (size distribution)
- The shape and position of the spectrum is consistent with bleaching by filling of either the HOMO or the LUMO state (or both).
Photoluminescence measurements from last summer
Photoluminescence from this summer
CdSSe quantum dots in glass

• A series of glass hosts with CdS_{0.5}Se_{0.5} nanoparticles.
• The particle size is varied from <0.5 nm radius (left) to ~5 nm radius (right).
• The particle volume fraction is ~10^{-3}.

Absorption spectra of CdS_{0.5}Se_{0.5}
r=1.7 nm to r=6.3 nm
(Stokes, 1996)

Quantum shift in lowest excited state
with size (Persans, 1996)
Quantum Dot Plans at Rensselaer

• Study decay pathways for highly excited carrier pairs in PbS/PbSe quantum dots
  – efficiency of multiexciton generation
  – effect of surface treatments/ligands
  – decay dynamics

• Study separation of carriers in PbS/PbSe quantum dots in organic hosts
  – time resolved transport (terahertz fields)
  – effect of ligands
  – effect of host materials
Lots of work to be done

- (MEG) How to ensure that competing processes are minimized?
  - absorption into the wrong state, no impact ionization
  - Auger recombination after decay
  - phonon mediated decay
- (MEG) How do we get the excitation out of the particles???
- Need to find appropriate host matrices.
- Have we found the best quantum dot materials? (How did we choose these?)
Current undergraduates in Quantum Dot Research

- Josh Katz, Eric Hofman – modulation spectroscopy of optical absorption in quantum dots
- Matt Weed – electromodulation spectroscopy of CuInGaSe solar cell interfaces
- Eric Chan, Craig Hays, Alex Pickle – photoluminescence spectroscopy of PbS quantum dots
- Tim Schiftner – quantum theory of electronic states of PbS dots
- Nathaniel Berry*, Nick Scaptura+ – time-resolved photoluminescence from PbS quantum dots
  - *Schenendahowa HS, *Columbia HS
Other recent collaborators and projects

• Quantum dots: Evident Technologies, Applied Nanoworks
• CuInGaSe Solar Cells: DayStar Technologies
• Photoconductivity in “black silicon”: Watervliet Arsenal
• Optics of organics formed on Titan: Prof. Ferris, Dr. B Tran
• Optical interconnects: Profs. Gutmann and J. Lu
• Optical scattering from steel corrosion layers (in reactors): Lockheed Martin
• X-ray reflection characterization of thin films: GE