Solar Cell Materials and Device Characterization

April 3, 2012
The University of Toledo, Department of Physics and Astronomy
SSARE, PVIC

Principles and Varieties of Solar Energy (PHYS 4400)
and
Fundamentals of Solar Cells (PHYS 6980)
Requirements/conditions for constructing a valuable solar cell

A partial list...

• Absorb sunlight efficiently to optimize photogeneration of carriers
• Achieve charge separation, directing electron and holes to different contacts (e.g., use doped materials for p-n junction)
• Demonstrate strongly rectifying (diode) behavior
• Avoid excessive electron-hole recombination within the solar cell (maximize photocurrent)
• Maintain as much of the electric potential as possible (avoid resistive losses, and optimize energy band offsets)
• Resist/avoid degradation by air and water (sealing the modules is often essential) – i.e. achieve stability
• Do all of these things (a) with high yield, (b) inexpensively, and © at very large production levels
• What else?
Getting everything right...

$\eta \sim 33\%$

Max Efficiency (%)

Bandgap (eV)
So what’s required? Is this easy?

If I do most of the things right, will I get an “A” on my solar cell (will my solar cell convert sunlight efficiently if I do 9 or 10 things right)? Probably not... Good solar cells are not easy to make, in principle – you must understand many subtleties of the materials, interfaces, and chemical evolution through oxidation, diffusion, or other reactions.

What can go wrong?

Back to the list...
Absorb sunlight efficiently

What matters for absorption of sunlight to make a good solar cell?

High extinction coefficient, short absorption length, large absorption coefficient.

\[ I = I_0 e^{-\alpha x} \]
\[ I(\lambda) = I_0(\lambda)e^{-\alpha(\lambda)x} \]

Bandgap

Low reflection loss (can’t convert reflected photons).

How do we measure the parameters in **bold**?
Measuring the bandgap energy (T-dependence of resistivity)

Solid State Physics: Experiment #5
Measuring the Band-Gap of a Semiconductor

According to the band theory of solids, insulators and semiconductors are materials which possess a band-gap (i.e., a range of forbidden energy values) at the Fermi level. Thus, these materials have a completely filled energy band below the gap and an empty band above the gap. The width of this band-gap is what distinguishes insulators from semiconductors. In semiconductors the band-gap is small enough (<2 eV) that at finite temperatures thermal excitation of electrons across the gap, into the empty "conduction" band, is possible leading to a small but measurable conductivity. The band-gap in insulators is simply too large to have any appreciable concentration of charge carriers excited into the conduction band. The temperature dependence of the resistivity of a pure (i.e., intrinsic) semiconductor is given by

$$\rho_i = B(T) \exp(E_g/2k_BT)$$

where \(E_g\) is the width of the gap and the function \(B(T)\) is only very weakly dependent on temperature. To a good approximation we can take \(B(T)=\text{constant}\). Thus, we can easily measure the gap energy of a semiconductor material by measuring the resistance of a sample over a range

$$I = I_0 e^{-\alpha x}$$

$$I(\lambda) = I_0(\lambda) e^{-\alpha(\lambda)x}$$

Measuring the bandgap energy (optical absorption)

\[ I(\lambda) = I_0(\lambda)e^{-\alpha(\lambda)x} \rightarrow I(E) = I_0(E)e^{-\alpha(E)x} \]

**Direct-gap semiconductor**

\[ \alpha(E) = \alpha_0(E - E_g)^{\frac{1}{2}} \]

**Indirect-gap semiconductor**

\[ \alpha(E) \propto (E - E_g)^2 \]

**Indirect gap**: plotting \( \alpha \) vs \( E \) shows an \( E^2 \) dependence, so plotting \( \alpha^{1/2} \) shows a linear dependence.

**Direct gap**: Plotting \( \alpha \) vs \( E \) shows an \( E^{1/2} \) dependence, so plotting \( \alpha^2 \) shows a linear dependence.

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See, for example,
http://engr.sjsu.edu/cme/MatELabs/MatE153/Ch7%20Optical%20Absorption.pdf,
or
http://engphys.mcmaster.ca/undergraduate/outlines/3pn4/LAB3P_N4-2%20Jan08.pdf
Measuring the bandgap energy (optical absorption)

\[ I(\lambda) = I_0(\lambda)e^{-\alpha(\lambda)x} \quad \Rightarrow \quad I(E) = I_0(E)e^{-\alpha(E)x} \]

**Direct-gap semiconductor**
\[ \alpha(E) = \alpha_0(E - E_g)^{1/2} \]

**Indirect-gap semiconductor**
\[ \alpha(E) \propto (E - E_g)^2 \]

Fe$_2$O$_3$, (haematite) – direct or indirect gap?

doi:10.1088/0268-1242/20/8/009

**Nanocrystalline haematite thin films by chemical solution spray**
J D Desai, H M Pathan, Sun-Ki Min, Kwang-Deog Jung and Oh-Shim Joo

.... energizing Ohio for the 21st Century
Measuring the bandgap of a thin film (optically)

Therefore, if a plot of $hv$ versus $\alpha^2$ forms a straight line, it can normally be inferred that there is a direct band gap, measurable by extrapolating the straight line to the $\alpha = 0$ axis. On the other hand, if a plot of $hv$ versus $\alpha^{1/2}$ forms a straight line, it can normally be inferred that there is an indirect band gap, measurable by extrapolating the straight line to the $\alpha = 0$ axis.

From http://en.wikipedia.org/wiki/Direct_and_indirect_band_gaps
“Linear optical properties of colloidal Si NCs studied in this report. (A) The absorption cross section for the NCs dispersed in hexane. Black lines show the computed cross section of the NCs based on an equivalent bulk Si volume. Part (B) displays the onset of the absorption in a Tauc plot showing the blue-shifted absorption onset. (C) PL spectra. (D) PL lifetime data measured at the peak of the emission wavelength (red line 3.8 nm, blue line 9.5 nm). The peak of the emission spectrum is taken as the effective bandgap for each of the NC samples, yielding bandgaps of 1.68 eV for the 3.8 nm NCs and 1.20 eV for the 9.5 nm NCs.”

*Multiple Exciton Generation in Colloidal Silicon Nanocrystals,*
Measuring bandgap (PL)

Photoluminescence (occurs at the bandgap for direct gap semiconductors)

Linear Absorption Spectrum

Global PL

TA @ 800 fs

Normalized A, I

Wavelength (nm)

450 500 550 600 650 700 750 800

0.0 0.5 1.0 1.5 2.0 2.5 3.0
Measuring bandgap (PL)

Photoluminescence (occurs at the bandgap for direct gap semiconductors)

Pushing the Band Gap Envelope: Mid-Infrared Emitting Colloidal PbSe Quantum Dots, J. AM. CHEM. SOC. 2004, 126, 11752-11753, Hollingsworth et al.

Bandgap can also be measured with:
• SPS – surface photovoltage spectroscopy
• Spectroscopic ellipsometry (?)
Optical characterization (transient absorption)

- **state filling**
  Electronic state occupation results in bleaching of interband transitions.

- **carrier-induced Stark effect**
  Photogenerated carriers create local fields within nanoparticle which modify transition energies.

\[
\frac{\Delta \alpha}{\alpha_0} = \frac{\ln T_0 - \ln T_{pumped}}{\ln T_0}
\]

\[
T_{pumped} = T_0 \left(1 + \frac{\Delta T}{T_0}\right)
\]

\[
T = 10^{-0.6} = e^{-\alpha_0 d}
\]
Optical characterization (transient absorption setup)

- Clark CPA-2001 Amplified Ti:sapphire (1 kHz, ~125 fs)
- Visible OPA
- IR OPA
- AgGaS₂
- Al₂O₃
- WL probe 440-950 nm
- Pump 290-2400 nm
- Sample
- Monochromator
- SRS Boxcar
- PC
- Delay 1.5 ns
- Delay 300 ps
- Mid-IR pump 3-12 µm
- 775 nm
Optical characterization (transient absorption setup)

~ 1 ps delay
\( \lambda_{\text{pump}} = 387 \text{ nm} \)
Achieve charge separation, directing electron and holes to different contacts (e.g., use doped materials for p-n junction)...

Prepare your materials and junctions to establish a built-in electric field. How?

**Homojunction:** (junction between two layers of the same material, which can differ by doping, structure, etc. but show the same dominant elemental makeup) -- must vary the chemical potential of the material (Fermi level) across the interface between n-type and p-type.
Achieve charge separation

Achieve charge separation, directing electron and holes to different contacts (e.g., use doped materials for p-n junction)...

Prepare your materials and junctions to establish a built-in electric field. How?

**Heterojunction:** (junction between two different semiconductor materials) -- must create an energy band structure that promotes charge separation – a combination of energy band offsets and doping.

How do we measure the dopant type and density?
Measuring dopant type and density

**Hall Effect:** The Lorentz force, \( F = -qv \times B \), deflects carriers to the left and right as they pass through a material under the influence of a magnetic field. The induced voltage lateral to the current flow direction provides information about the Hall coefficient, which can then be related to the carrier density and mobility:

\[
R_H = \frac{E_y}{J_x B_z}
\]

\[
\mu = \frac{R_H}{\rho} \quad n = \frac{1}{eR_H}
\]

Preston and Dietz, (Expt. 17; pp 303-315)
Measuring dopant type and density (Mott Schottky)

\[ C = \frac{Q}{V} = \frac{\varepsilon A}{W_d} \]

Mott-Schottky: measuring in depletion, not in accumulation. Changing the depletion width by applied voltage; when the capacitance reaches a maximum \(\to\) flat band potential.

\[ W = \left[ \frac{2K_s\varepsilon_0}{q} \left( \frac{N_A + N_D}{N_A N_D} \right) (V_{bi} - V) \right]^{\frac{1}{2}} \]

Hot Probe Test to determine Carrier Type

Seebeck Effect

• In 1821, Thomas Seebeck discovered that an electric current would flow continuously in a closed circuit made up of two dissimilar metals if the junctions of the metals were maintained at two different temperatures.
• When a metal wire is connected between two different temperatures, an additional number of electrons are excited at the hot end versus the cold end.
• Electrons drift from the hot end to the cold, and
• A thermal emf develops to oppose the drift
• If the material is uniform, the magnitude of the voltage developed depends only on the temperature difference.
• The Hot Probe is the trivial case……i.e., no junctions.
Hot Probe Test to determine Carrier Type

All you need is a soldering iron, and an ammeter!

http://ecee.colorado.edu/~bart/book/hotprobe.htm
<table>
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<th>Intrinsic</th>
<th>n-type</th>
<th>p-type</th>
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<td>generated free electrons</td>
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Number of free electrons equals number of positively charged donor ions

Number of free holes equals number of Negatively charged acceptor cores

After Hamers
Hot Probe Test to determine Carrier Type

Distribution of OCCUPIED C.B. levels:

\[
\begin{array}{c}
\text{N(E)} \\
\hline
\text{1} & \text{1} & \text{1} \\
\text{1} & \text{1} & \text{1} \\
\text{1} & \text{1} & \text{1} \\
\end{array}
\]

Hot

Cold

These are not in equilibrium!

After Hamers

... energizing Ohio for the 26th Century
Hot Probe Test to determine Carrier Type

Seebeck effect, n-type semiconductor

Fick’s Law of Diffusion:

\[
J = -D \frac{\partial c}{\partial x}
\]

Electrons diffuse from region of high Concentration to region of lower concentration

Seebeck effect, n-type semiconductor

“Cold” side becomes slightly negatively charged
Hot side becomes positively charged

After Hamers
Another way to look at what is happening:

Fermi energy remains constant throughout the material. The variation in free carrier density then changes the positions of the CB and VB as a function of temperature (position).

“As the effective density of states decreases with decreasing temperature, one finds that the conduction band energy decreases with decreasing temperature yielding an electric field which causes the electrons to flow from the high to the low temperature. The same reasoning reveals that holes in a p-type semiconductor will also flow from the higher to the lower temperature.”

\[
J = \mu_n n \left( \frac{\partial E_F}{\partial x} - q \mathcal{P} \frac{\partial T}{\partial x} \right)
\]

\[
q \mathcal{P} = -k \left( \frac{5}{2} - \frac{T}{\mu_n} \frac{\partial \mu_n}{\partial T} + \ln \frac{N_C}{n} \right)
\]

http://ecee.colorado.edu/~bart/book/hotprobe.htm