

A. OTHER JUNCTIONS

B. SEMICONDUCTOR HETEROJUNCTIONS --

MOLECULES AT INTERFACES:

- **ORGANIC PHOTOVOLTAIC BULK HETEROJUNCTION**
 - **DYE-SENSITIZED SOLAR CELL**

March 20, 2014

The University of Toledo, Department of Physics and Astronomy
SSARE, PVIC

Principles and Varieties of Solar Energy (PHYS 4400)



p-n junction and semiconductor physics review

1. Poisson's equation:

$$\frac{\partial \bar{E}}{\partial x} = \frac{\rho}{\epsilon} = \frac{q}{\epsilon} (p(x) - n(x) - N_A^- + N_D^+)$$

2. Transport equations:

$$J_n = q\mu_n n(x)\bar{E} + qD_n \frac{dn(x)}{dx}$$

$$J_p = q\mu_p p(x)\bar{E} - qD_p \frac{dp(x)}{dx}$$

A note on units: looking at the Continuity equation(s) – units for dn/dt are $\text{cm}^{-3}\text{s}^{-1}$.
Units for $(1/q)(dJ/dx)$ work out to be:
 $(\text{C}^{-1})(\text{C s}^{-1} \text{cm}^{-2})(\text{cm}^{-1}) = \text{cm}^{-3}\text{s}^{-1}$.

3. Continuity equations:

General conditions

$$\frac{dn}{dt} = \frac{1}{q} \frac{\partial J_n}{\partial x} - (U - G)$$

$$\frac{dp}{dt} = \frac{1}{q} \frac{\partial J_p}{\partial x} + (U - G)$$

Under thermal equilibrium and steady state conditions

$$\frac{1}{q} \frac{\partial J_n}{\partial x} = (U - G)$$

$$\frac{1}{q} \frac{\partial J_p}{\partial x} = -(U - G)$$

where U and G are the recombination and generation rates in the particular material and depend on the details of the device and may also depend on distance.



p-n junction and semiconductor physics review

Poisson's Equation

$$\frac{d\hat{E}}{dx} = \frac{\rho}{\varepsilon} = \frac{q}{\varepsilon} (p - n + N_D^+ - N_A^-)$$

Straightforward definitions:

E is the electric field

ρ is the charge density

q is the magnitude of the electron charge

p is the concentration of free holes

n is the concentration of free electrons

N_D⁺ is the concentration of ionized donor atoms (recall that donors donate electrons, leaving them positively charged)

N_A⁻ is the concentration of ionized acceptor atoms (recall that acceptors accept electrons, leaving them negatively charged)



Semiconductor physics review

Density of States in Conduction and Valence Band (parabolic band approximation)

$$N_C(E) = \frac{m_n^{3/2} \sqrt{2}}{\pi^2 \hbar^3} \sqrt{E - E_C}$$

$$N_V(E) = \frac{m_p^{3/2} \sqrt{2}}{\pi^2 \hbar^3} \sqrt{E_V - E}$$

Look at units:
(note that $1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-2}$,
and $[h] = \text{m}^2\text{kg s}^{-1}$)

$$\frac{\text{kg}^{3/2} \text{J}^{1/2} \text{s}^3}{\text{m}^6 \text{kg}^3} = \frac{\text{kg}^{3/2} \text{kg}^{1/2} \text{s}^3 \text{m}}{\text{m}^6 \text{kg}^3 \text{s}} = \text{kg}^{-1} \text{s}^2 \text{m}^{-5} = \text{J}^{-1} \text{m}^{-3}$$

Fermi function (state occupation probability)

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$



Junctions

Reading assignment:

- Work Function: http://en.wikipedia.org/wiki/Work_function
- Electron Affinity (solid state physics): http://en.wikipedia.org/wiki/Electron_affinity
 - Vacuum Level: http://en.wikipedia.org/wiki/Vacuum_level
 - Fermi Energy: http://en.wikipedia.org/wiki/Fermi_energy
 - Fermi Level: http://en.wikipedia.org/wiki/Fermi_level

Work Function: potential required to remove the least tightly-bound electron:

$$\Phi_w = E_{vac} - E_F$$

Work function equals the electron affinity in metals.



Bases for effective fields at junctions

122

The Physics of Solar Cells

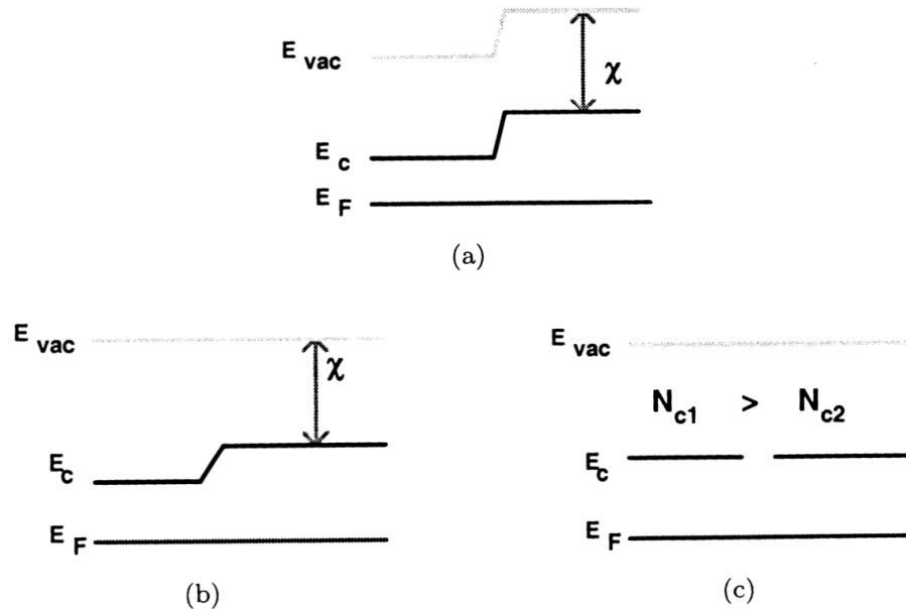


Fig. 5.2. Contributions to a built-in effective field for electrons. (See text for explanation.)

In (a) a difference in the work function has given rise to a gradient in the vacuum level and hence an electrostatic field, $\frac{1}{q}\nabla E_{vac}$.

In (b) a difference in the electron affinity due to a compositional gradient creates an effective field, $-\frac{1}{q}\nabla\chi$, seen as a gradient in the conduction band edge.

In (c) a field due to a gradient in the effective conduction band density of states, $-\frac{kT}{q}\ln\nabla N_c$, is driving electrons to the right. This term cannot be depicted on this diagram as it represents a gradient in the free energy rather than potential energy: carriers are driven thermodynamically in the direction of increasing availability of states.

Charge-separation mechanisms

- gradient in the vacuum level or work function
→ electrostatic field (e.g., doping level)
- gradient in electron affinity → effective field
- gradient in the band gap → effective field
- gradient in the band DOS → effective field

Metal-semiconductor junctions: Schottky-barrier

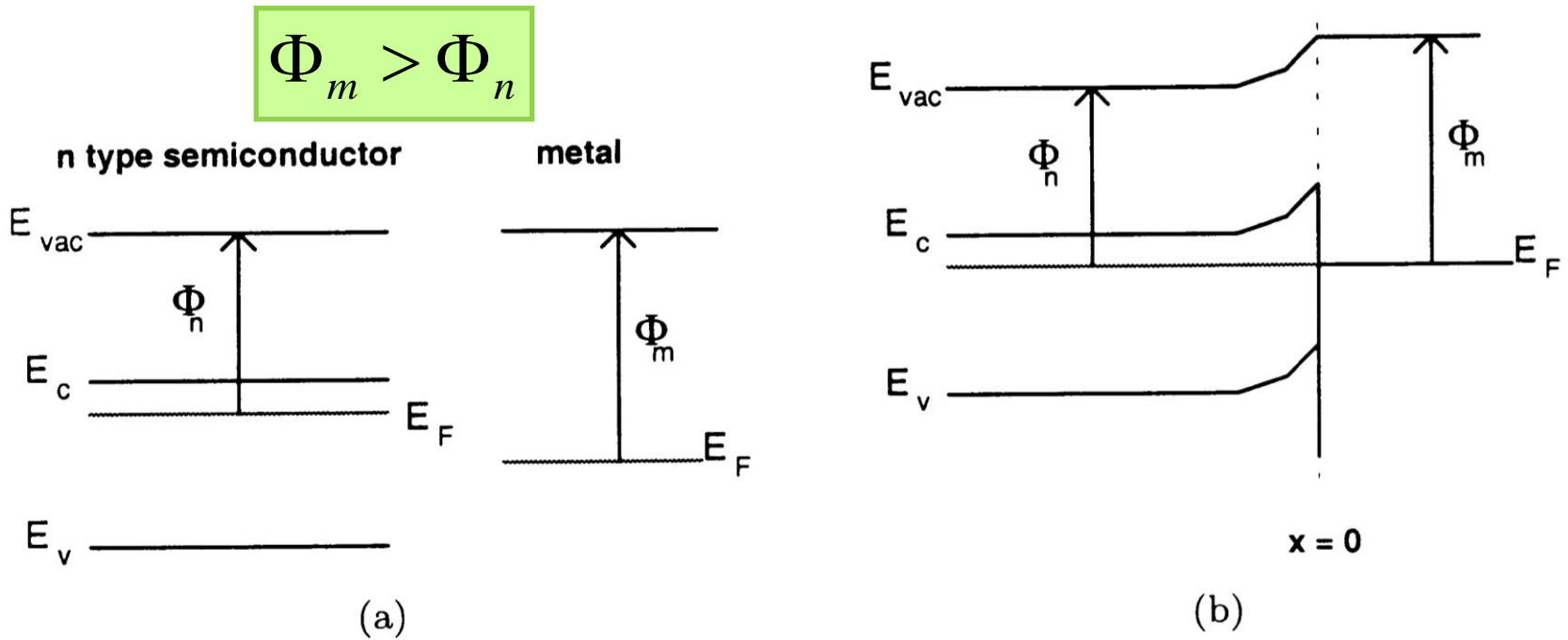


Fig. 5.4. (a) Band profiles of *n*-type semiconductor and metal in isolation. (b) Band profile of the semiconductor–metal junction in equilibrium.

- In contact: electrons flow from semiconductor to metal, resulting in a layer of positive fixed charge in the semiconductor, near the surface (and a negative image charge on the metal); Fermi levels equilibrate;
- Potential difference drops in the semiconductor (space charge, and/or depletion, region);
- Result is a lower resistance pathway for holes than for electrons



Metal-semiconductor junctions: Schottky-barrier (cont.)

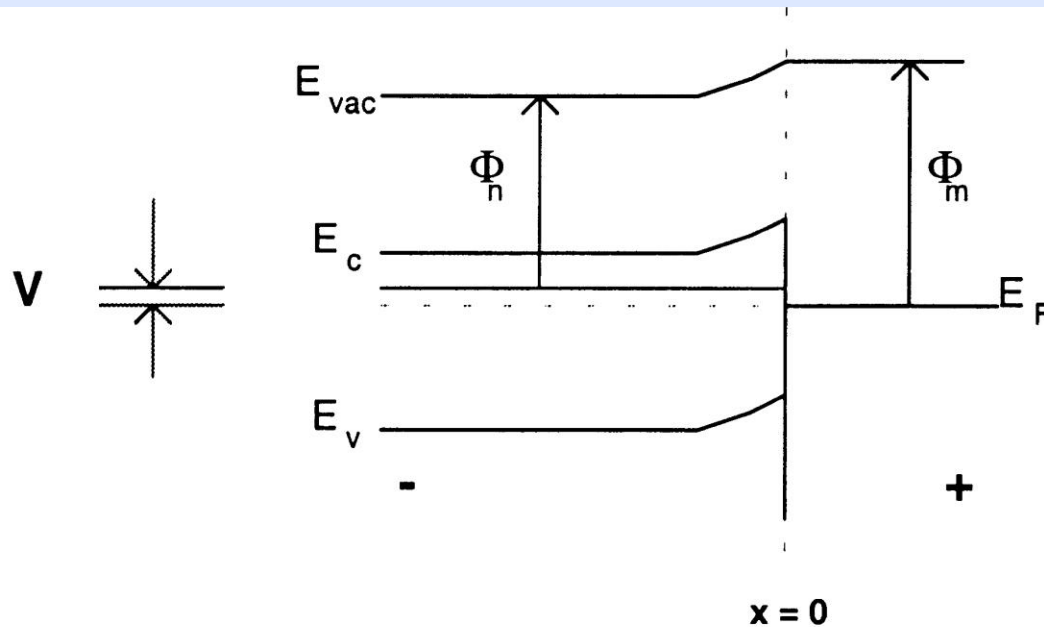


Fig. 5.5. Band profile of the semiconductor–metal junction under illumination at open circuit. The accumulation of photogenerated electrons in the n -type semiconductor raises the electron Fermi level and generates a photovoltage, V .

- Under illumination, holes flow to the right, and electrons accumulate in the semiconductor;
- Fermi level shifts up in the semiconductor (accumulation of electrons);
- Result is a photovoltage

Metal-semiconductor junctions: Schottky-barrier (cont.)

128

The Physics of Solar Cells

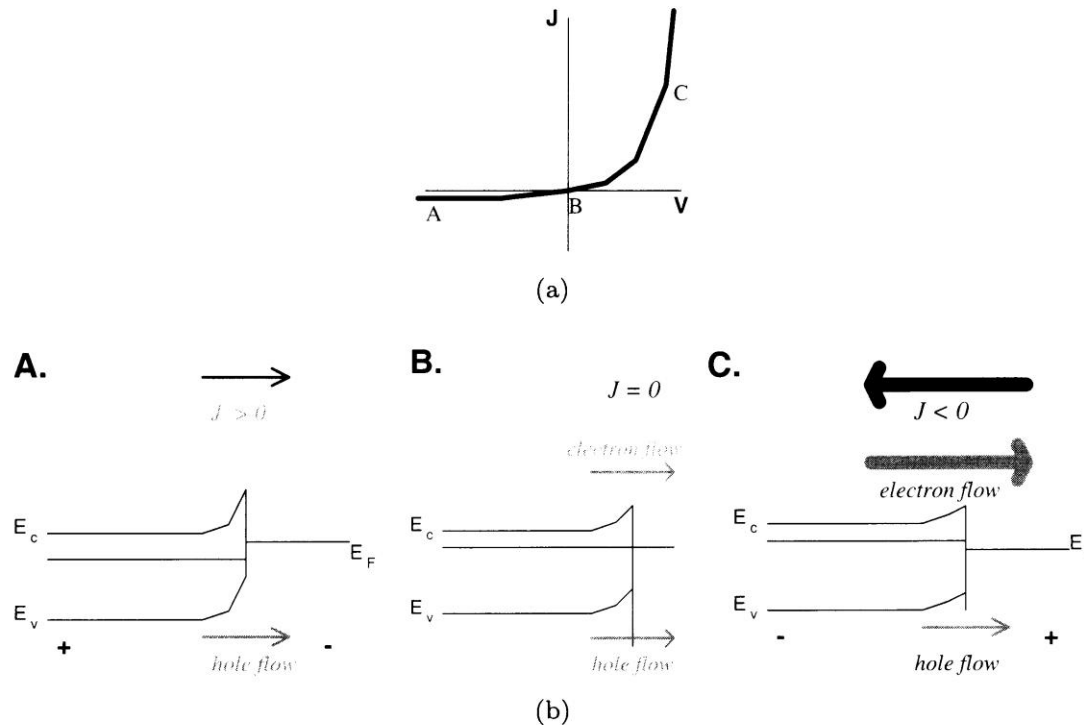


Fig. 5.6. (a) Schematic current–voltage characteristic of a Schottky barrier junction in the dark. A, B and C mark points on the curve where the device is at reverse bias, equilibrium and forward bias; (b) A: band profile of an *n*-type semiconductor–metal Schottky barrier at reverse bias. The only current is due to minority carrier (hole) drift across the depleted barrier region. B: band profile at equilibrium. The currents due to electron diffusion and hole drift cancel out. C: band profile at forward bias. The current due to electron diffusion is greatly increased as the barrier height is reduced, and the net current changes sign.

Metal-semiconductor junctions: Schottky-barrier (cont.)

$$\Phi_m < \Phi_p$$

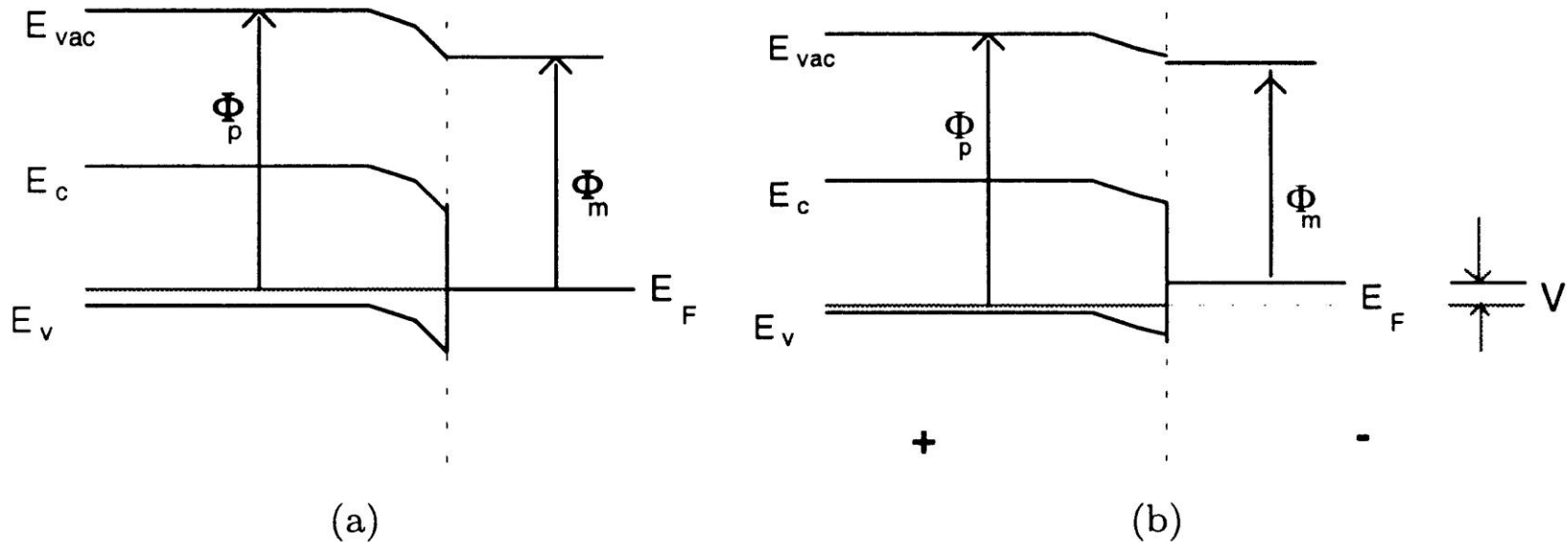


Fig. 5.7. Band profile of the *p*-type semiconductor–metal junction (a) at equilibrium and (b) under illumination at open circuit.

- In contact: holes flow from the semiconductor to the metal, resulting in a layer of negative fixed charge in the semiconductor near the surface (and a positive image charge on the metal); Fermi levels equilibrate;
- Potential difference drops in the semiconductor (space charge, and/or depletion, region);
- Result is a lower resistance pathway for electrons (to the metal) than for holes
- Under illumination, electrons flow into the metal from the semiconductor

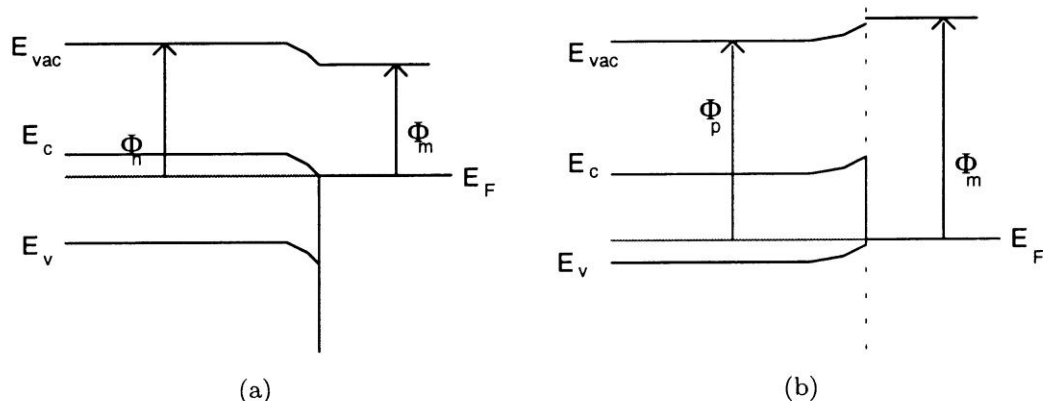


Metal-semiconductor junctions: Ohmic contact

$$\Phi_m < \Phi_n$$

130

The Physics of Solar Cells



$$\Phi_m > \Phi_p$$

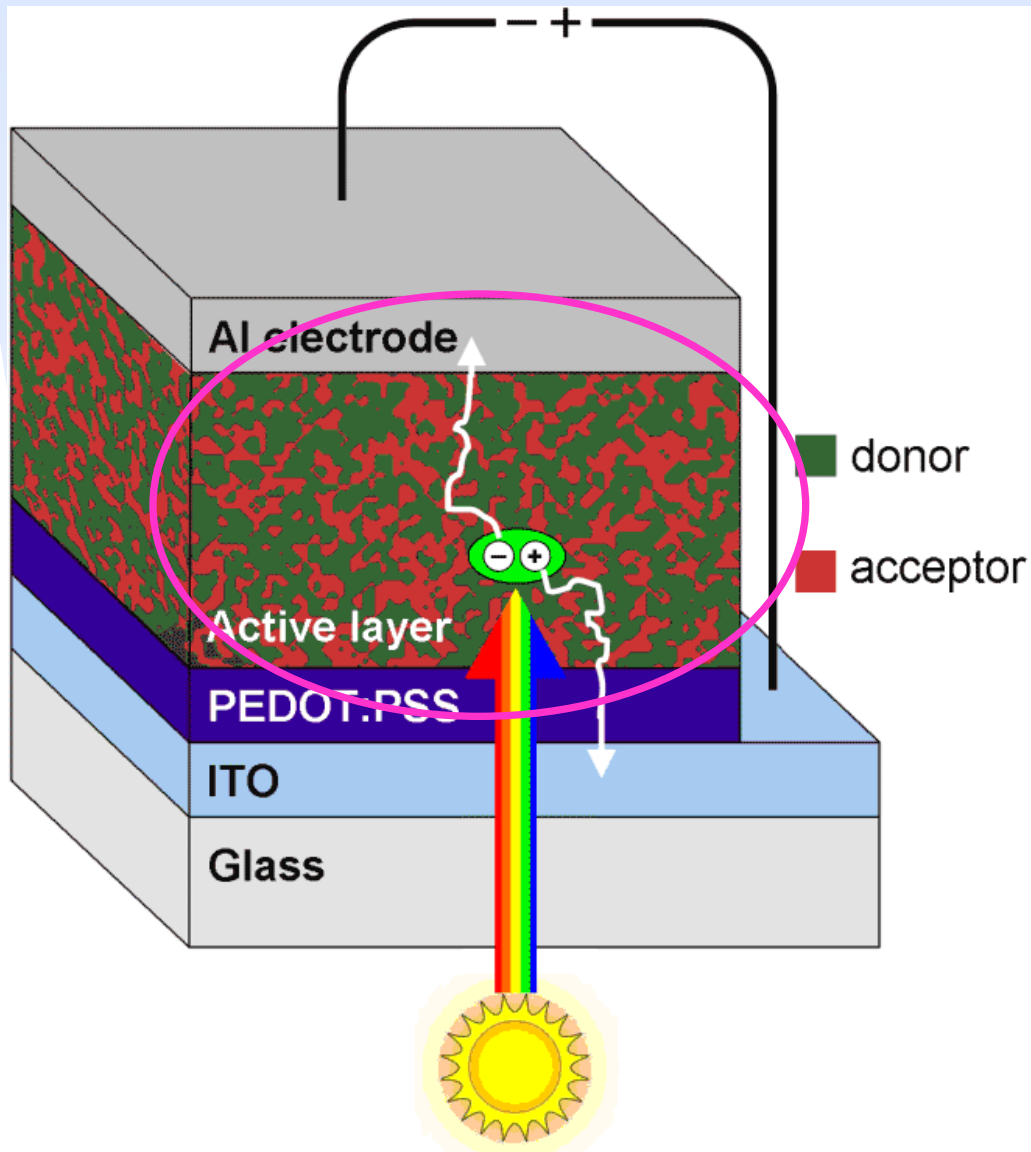
Fig. 5.8. Ohmic metal–semiconductor contacts for (a) an *n*-type semiconductor and (b) a *p*-type semiconductor. In each case the difference in work functions is supplied by the build up of majority carriers in an accumulation layer near the interface. An accumulation layer is generally narrow compared to a depletion layer because of the higher density of charges and stronger electric field.

We can draw the following conclusions from the above discussion:

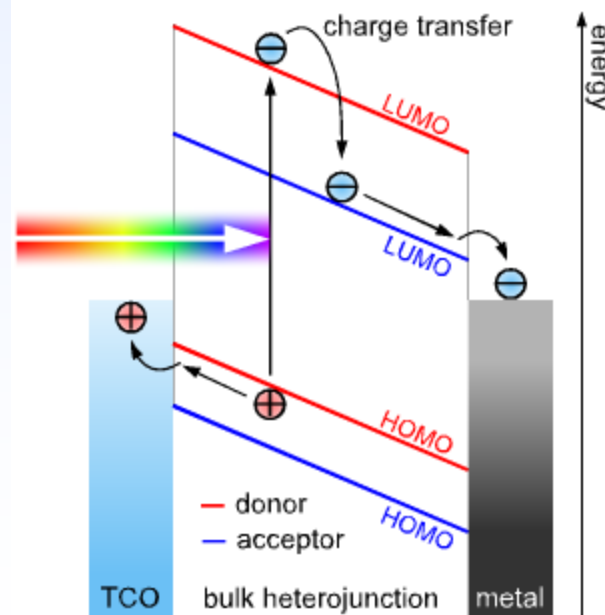
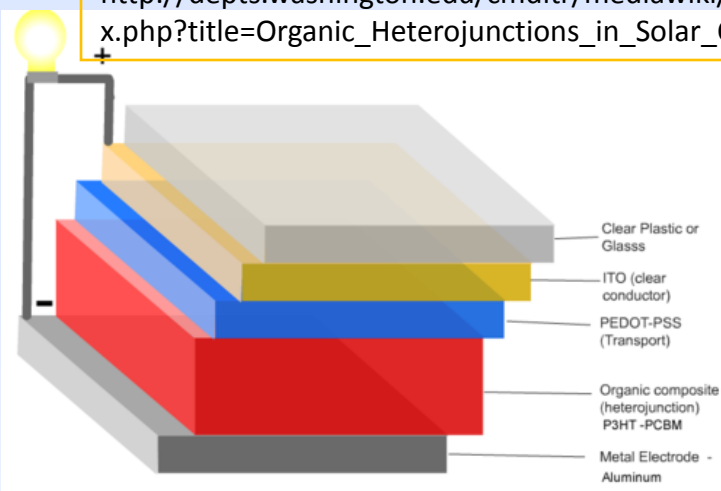
- a charge separating field is established at the interface between two materials of different work function
- the junction will develop a photovoltage provided that it presents a barrier to majority carrier currents
- the photovoltage is related to the difference in work functions

- Note that at Ohmic contact provides a low resistance pathway for majority carrier from the semiconductor to the metal

Organic PV: Bulk heterojunction

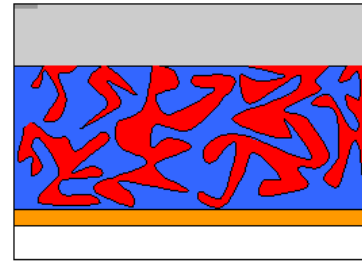
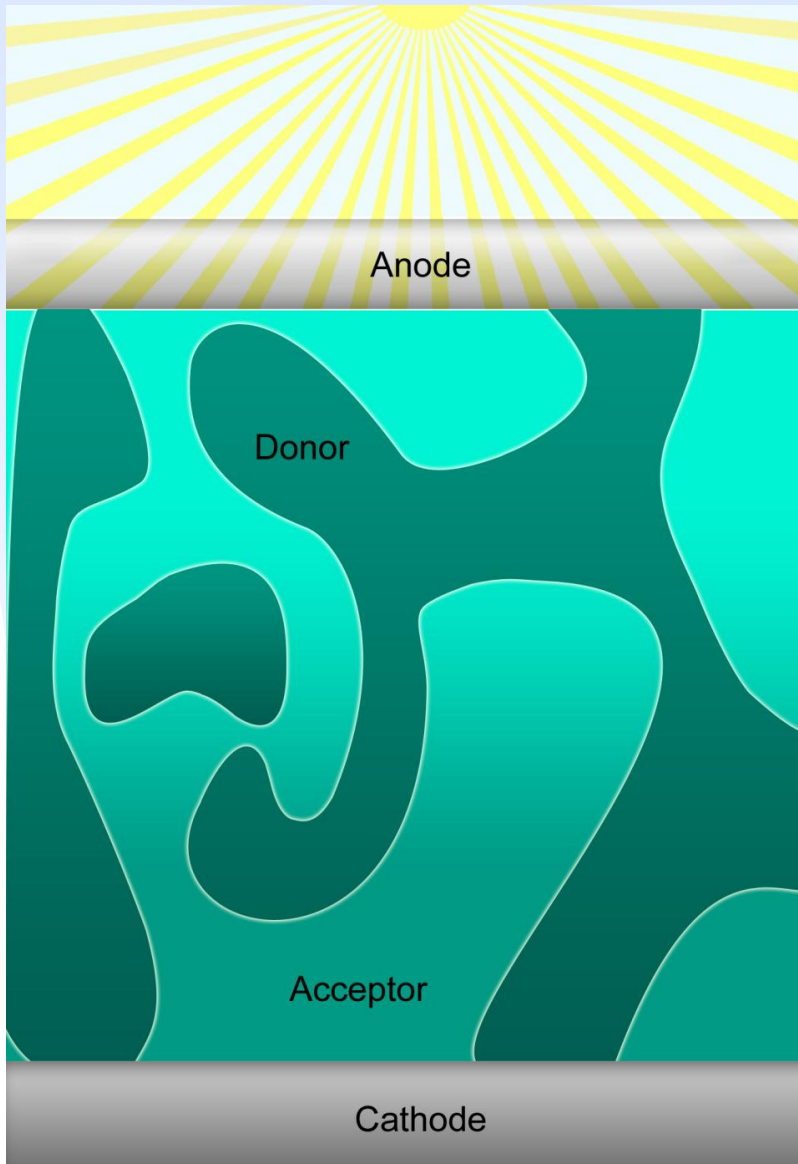


http://depts.washington.edu/cmditr/mediawiki/index.php?title=Organic_Heterojunctions_in_Solar_Cells

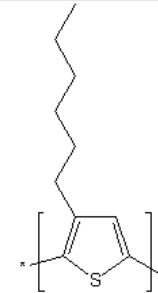


http://www-ssrl.slac.stanford.edu/sites/default/files/science-highlights/images/2011/January/Verploegen--fig1_0.png

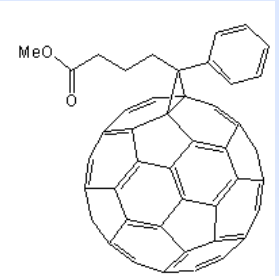
Organic PV: simplified BH structure



Bulk Heterojunction by Mixture

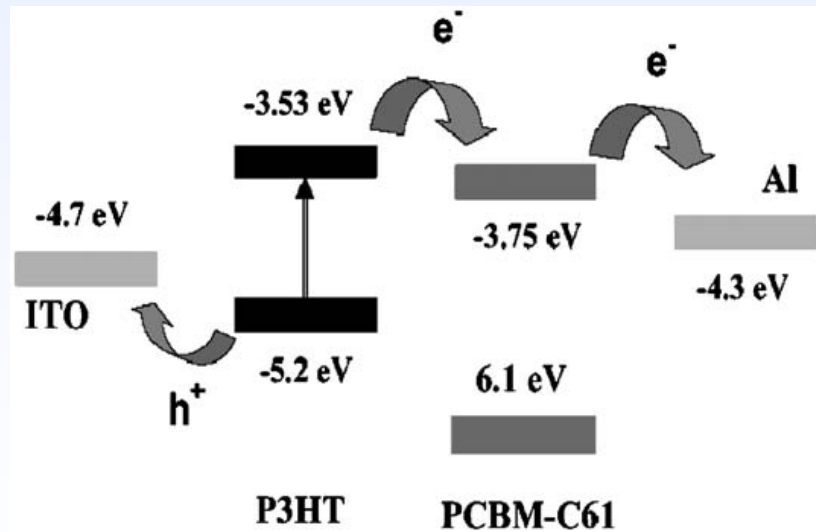


P3HT



PCBM

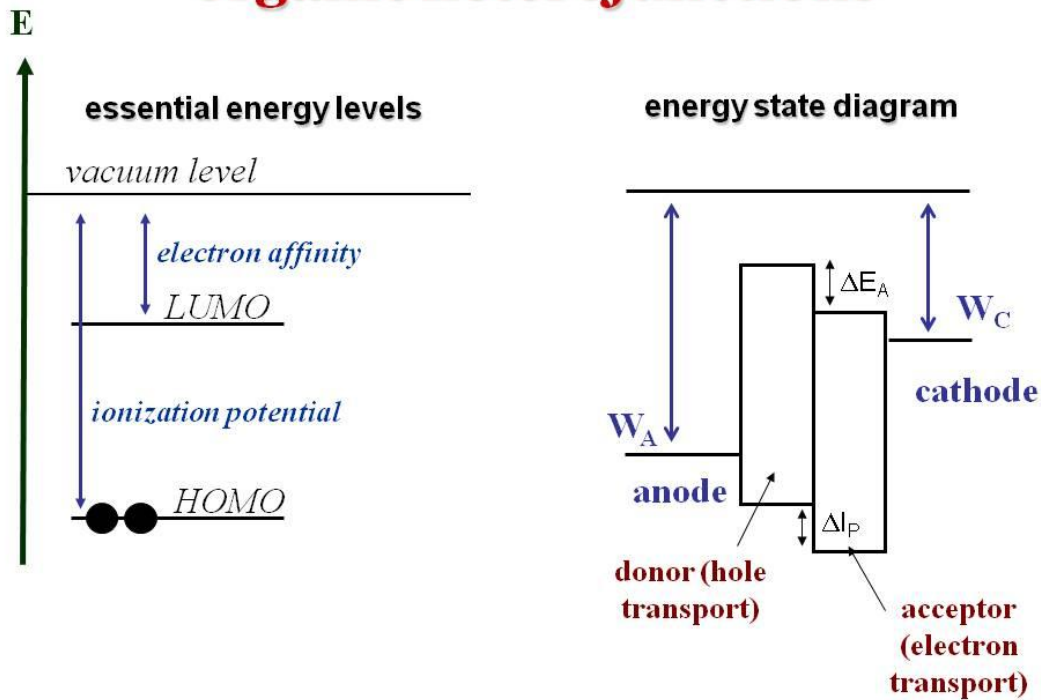
<http://www.light.t.u-tokyo.ac.jp/english/photovoltaic/Introduction.html>



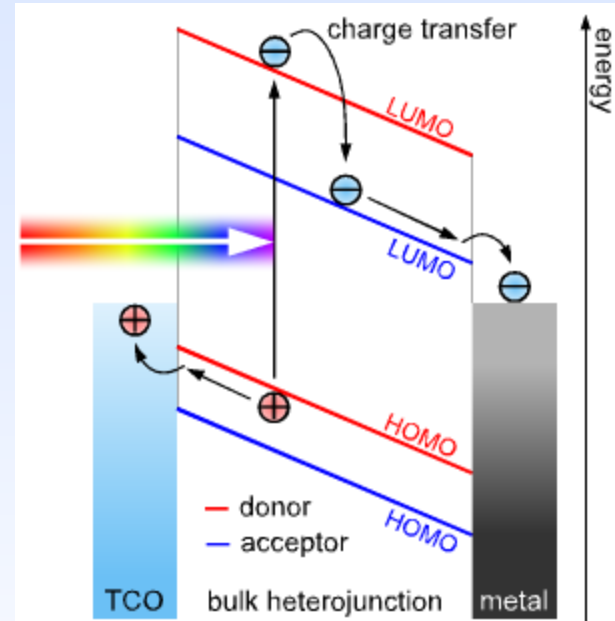
M. Al-Ibrahima et al., Solar Energy Materials & Solar Cells 85 (2005) 13–20

<http://www.cfn.uni-karlsruhe.de/?id=221>

organic heterojunctions

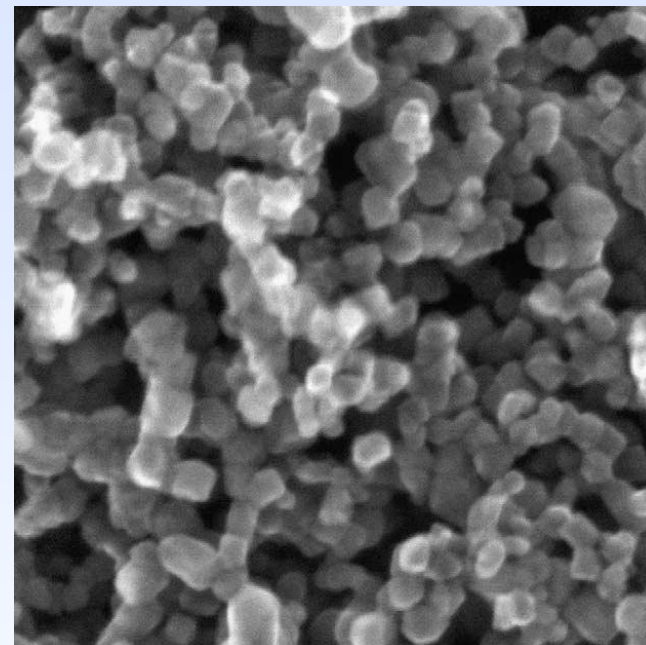
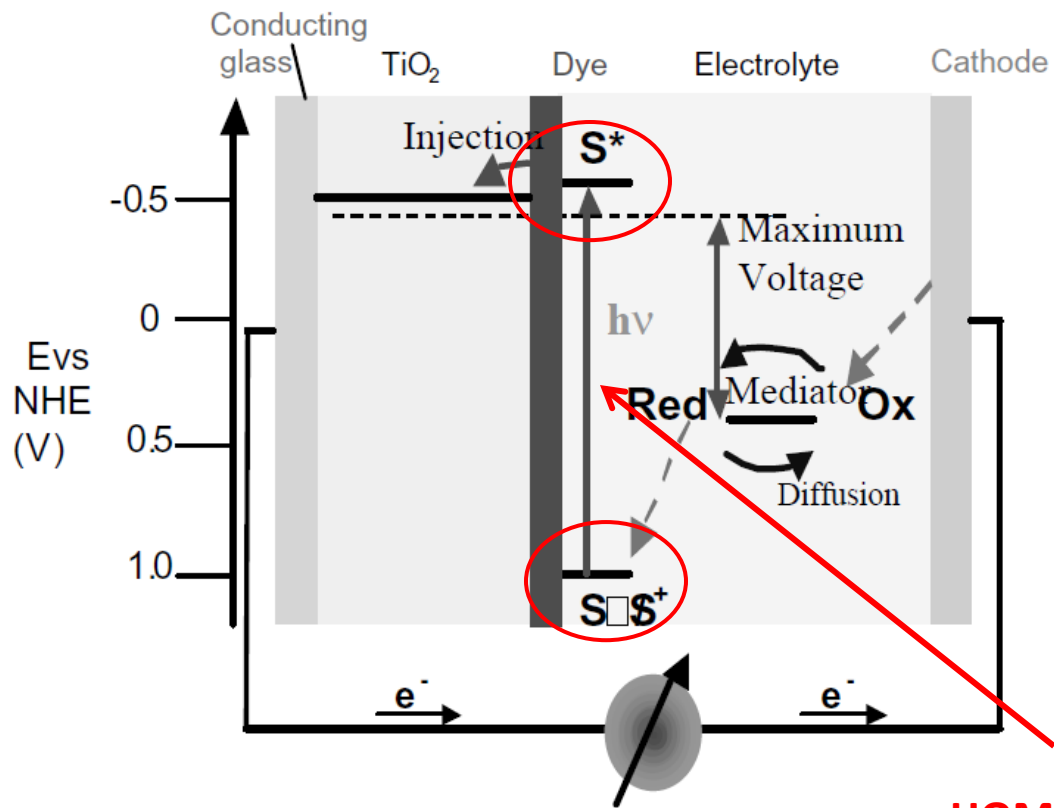


<http://depts.washington.edu/cmditr/mediawiki/images/8/84/Organicheterojunctions.JPG>



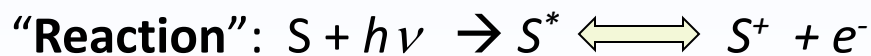
<http://www.physik.uni-wuerzburg.de/EP6/research-oe.html>

Dye-sensitized TiO₂ solar cell



~25 nm nano-porous TiO₂ electrode

HOMO-LUMO transition



Dye-sensitized TiO₂ solar cell

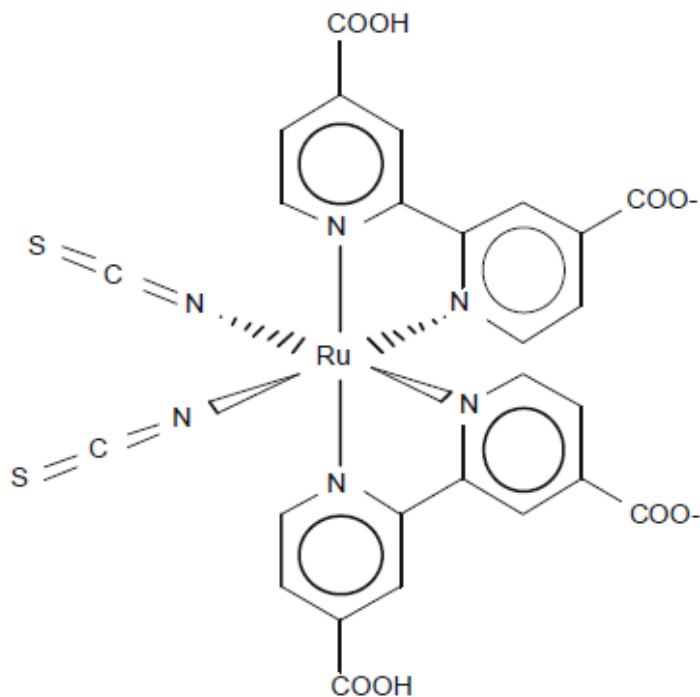
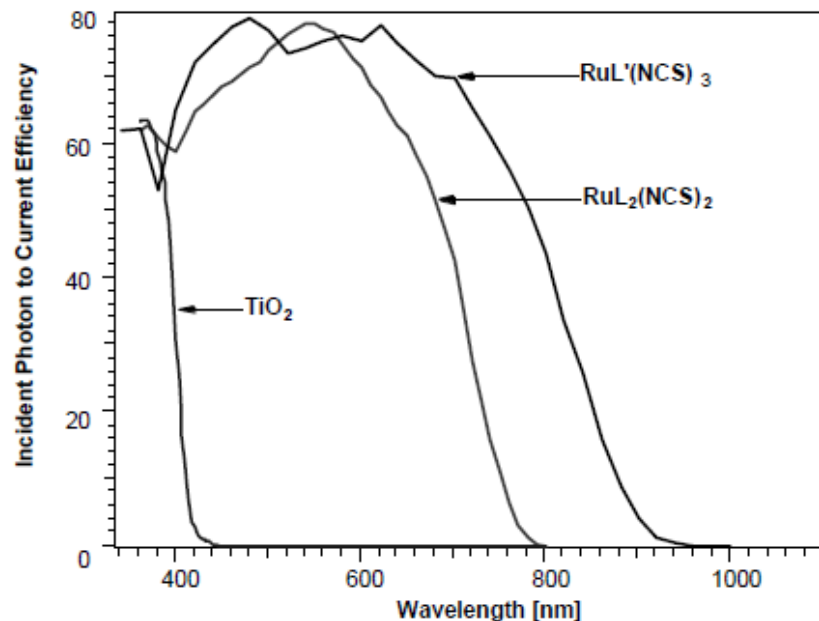


Fig. 4. Chemical structure of the N3 ruthenium complex used as a charge transfer sensitizer in dye-sensitized solar cells.



L = 4, 4'-COOH-2,2'-bipyridine

L' = 4,4',4'' -COOH-2,2':6',2''-terpyridine

Fig. 5. Photocurrent action spectra obtained with the N3 (ligand L) and the black dye (ligand L') as sensitizer. The photocurrent response of a bare TiO₂ films is also shown for comparison. Detailed experimental

Binding of dye (monolayer) to TiO₂ through carboxylate groups; photon absorption results in metal-to-ligand charge transfer (MLCT) and rapid injection (<20 fs) of the e⁻ into the TiO₂ CB.

Bid on a PV project, using different technologies

Analysis of the LCOE for a rooftop PV system, including a summary of the materials science of the technology

1. Thin film silicon (Abril)
2. CdTe (Jeff)
3. c-Si (Ryan)



Projects (preliminary information)

Issues to be considered:

- Materials science: describe the key properties of the materials used to make the solar PV modules. What are the values for efficiency, stability over time, performance vs. module temperature, power:weight ratio (W_p /kg), module size, and toxicity concerns.
- Rooftop area: 600 square feet at a slope of 30° limited area.
- Cost factors: cost per W_p of modules; cost of inverter, total system capacity (W_p at STC), racking and labor costs.
- Calculation of the LCOE: based on all costs incurred (include M&O) and all energy produced (include your projected electricity costs and any SREC value).



Projects (preliminary information): expected output

PowerPoint presentation:

- 20 min. plus 5 min Q&A
- Completely referenced, with appropriate figures
- Original content/work (new ideas and ways of presenting data and results)
- Presentations on April 22

