# A. *Other Junctions*

# B. *Semiconductor Heterojunctions --*

# *Molecules at Interfaces*:

- **Organic Photovoltaic Bulk Heterojunction**
- **Dye-Sensitized Solar Cell**

February 9 and 14, 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)

# p-n junction and semiconductor physics review

1. **Poisson's equation:**

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

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 $cm^{-3}s^{-1}$. Units for (1/q)(dJ/dx) work out to be: $(C^{-1})(C\ s^{-1}\ cm^{-2})(cm^{-1}) = cm^{-3}s^{-1}$.

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 J = 1 kg-m$^2$-s$^{-2}$,
and [$h$] = m$^2$kg s$^{-1}$)

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

Fermi function (state occupation probability)

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

# Boltzmann approximation

Fermi function (state occupation probability)

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

If $E_F$ is sufficiently far from either band edge, then *f*(*E*) can be approximated by:

$$f(E) \approx \exp\left(\frac{E_F - E}{k_B T}\right)$$

From the textbook's (3.27), then, we can integrate to arrive at *n*:

$$n = \int_{E_C}^{\infty} N_C(E) f(E, E_F, T) dE$$

Integrating/solving for *n* yields (3.31):

$$n = N_0 \exp((E_F - E_C)/k_B T)$$

Where $N_0$ is called the effective conduction band density of states and is given by

$$N_0 = 2\left(\frac{m_c^* k_B T}{2\pi\hbar^2}\right)^{3/2}$$

# Optical absorption: direct vs. indirect gap

From the textbook's Chap. 4, "Generation and Recombination"

(4.43): $$\alpha(E) \propto \int g_c(\boldsymbol{k}(E_i + E))g_v(\boldsymbol{k}(E_i))dE_i$$

Quantity in integral known as the joint density of states (JDOS). For the parabolic band approximation and a direct-gap semiconductor, it follows that:

(4.44) $$\alpha(E) = \alpha_0(E - E_g)^{\frac{1}{2}}$$

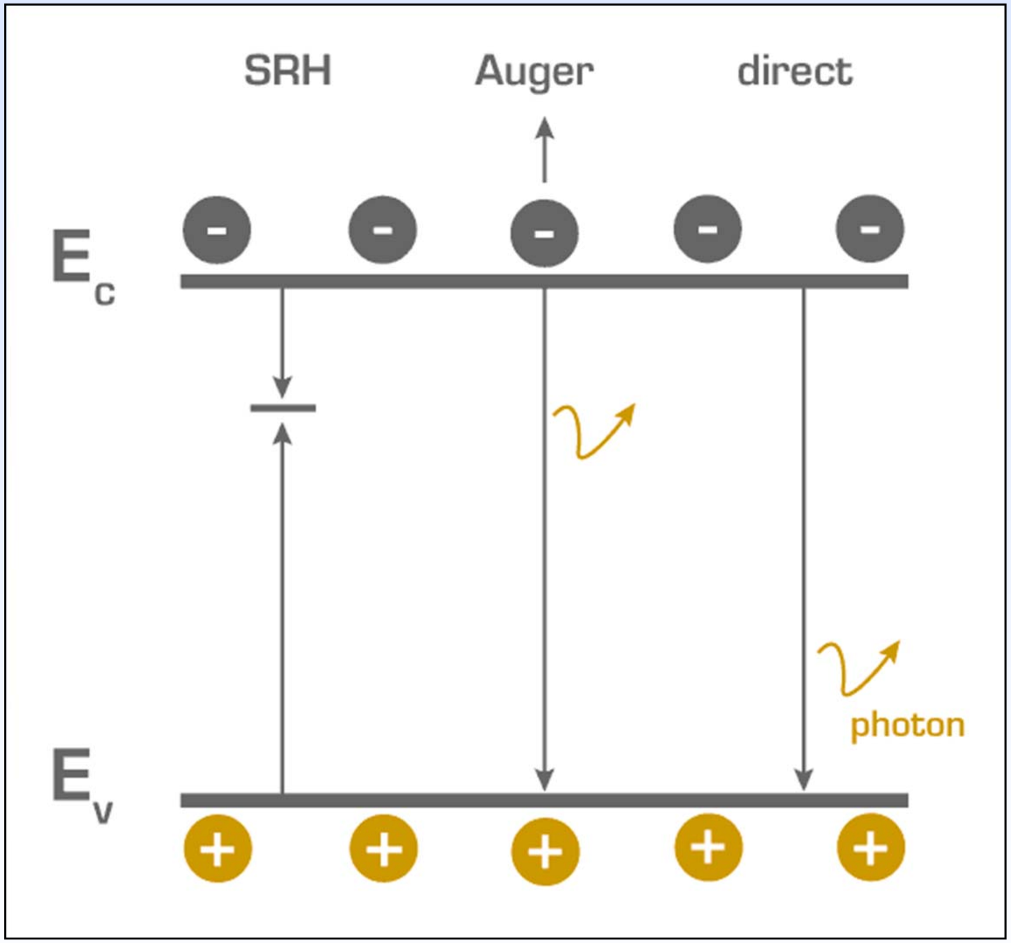
where $\alpha_0$ is a material-specific constant.

For an indirect gap semiconductor, one needs to account for the probability of finding a suitable phonon for the 3-particle (indirect) transition process.

(4.47) $$\alpha(E) \propto (E - E_g)^2$$

The textbook notes that the form for $\alpha$ shown in (4.44) is rarely seen in practice…

# Types of recombination (revisited)




$$\frac{1}{\tau_{bulk}} = \frac{1}{\tau_{SRH}} + \frac{1}{\tau_{Auger}} + \frac{1}{\tau_{rad}}$$

# Radiative (direct) and Auger recombination

$$U = Bnp$$

where U is the rate of recombination of e-h pairs due to radiative band-to-band recombination, *n,p* are the electron and hole concentrations, and *B* is a constant dependent on the material and the specific process.

Auger recombination is a 3-carrier (or 3-particle) process involving either two electrons and a hole, *or* one electron and two holes:

$$U_{Auger} = A_p\left(n^2 p - n_0^2 p_0\right)$$ for two-electron collisions

$$U_{Auger} = A_n\left(np^2 - n_0 p_0^2\right)$$ for two-hole collisions

# Junctions

**Reading assignment:**

Chapters 5 (Junctions) and 6 (Analysis of the p-n Junction) from *"The Physics of Solar Cells"*

**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



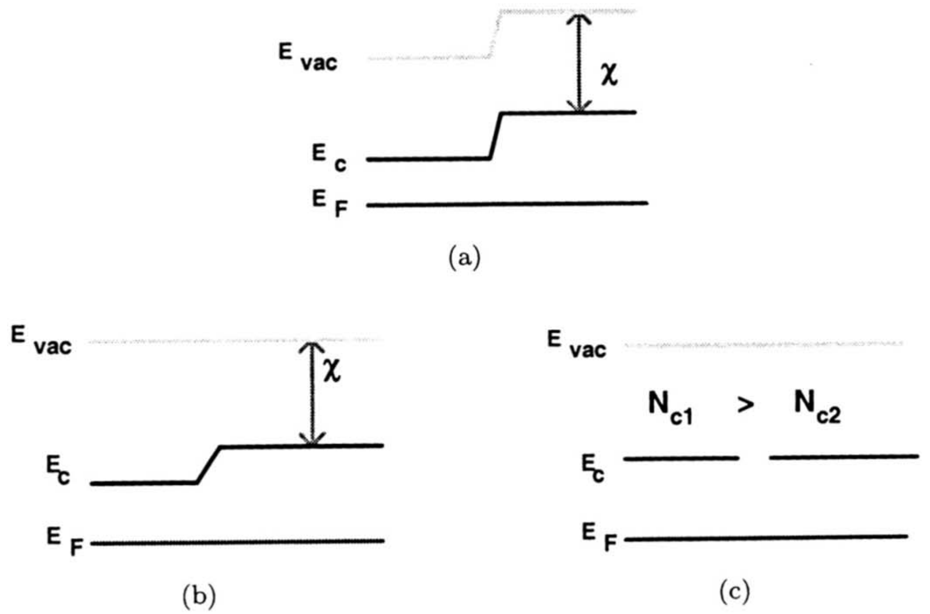



Fig. 5.2. Contributions to a built-in effective field for electrons. (See text for explanation.)

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

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

$$\Phi_m > \Phi_n$$

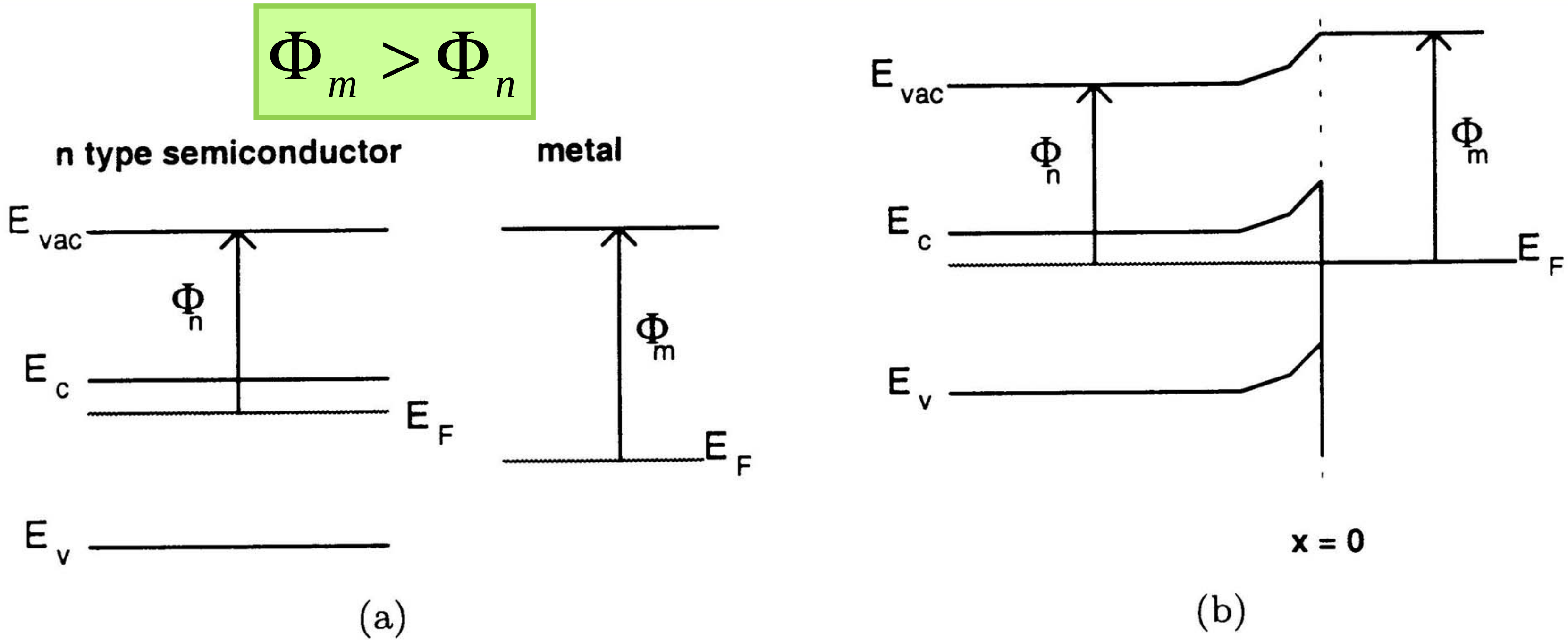



Fig. 5.4. (a) Band profiles of $n$-type semiconductor and metal in isolation. (b) Band profile of the semiconductor–metal junction in equilibrium.

- 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.)

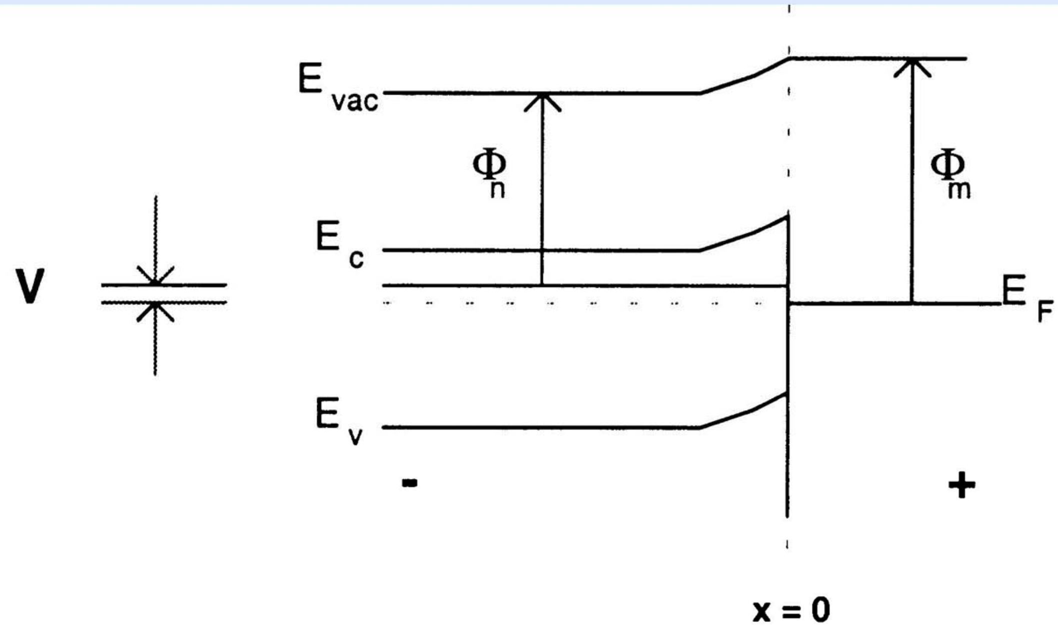



Fig. 5.5. Band profile of the semiconductor–metal junction under illumination at open circuit. The accumulation of photogenerated electrons in the $n$-type semiconductor raises the electron Fermi level and generates a photovoltage, $V$.

- 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.)



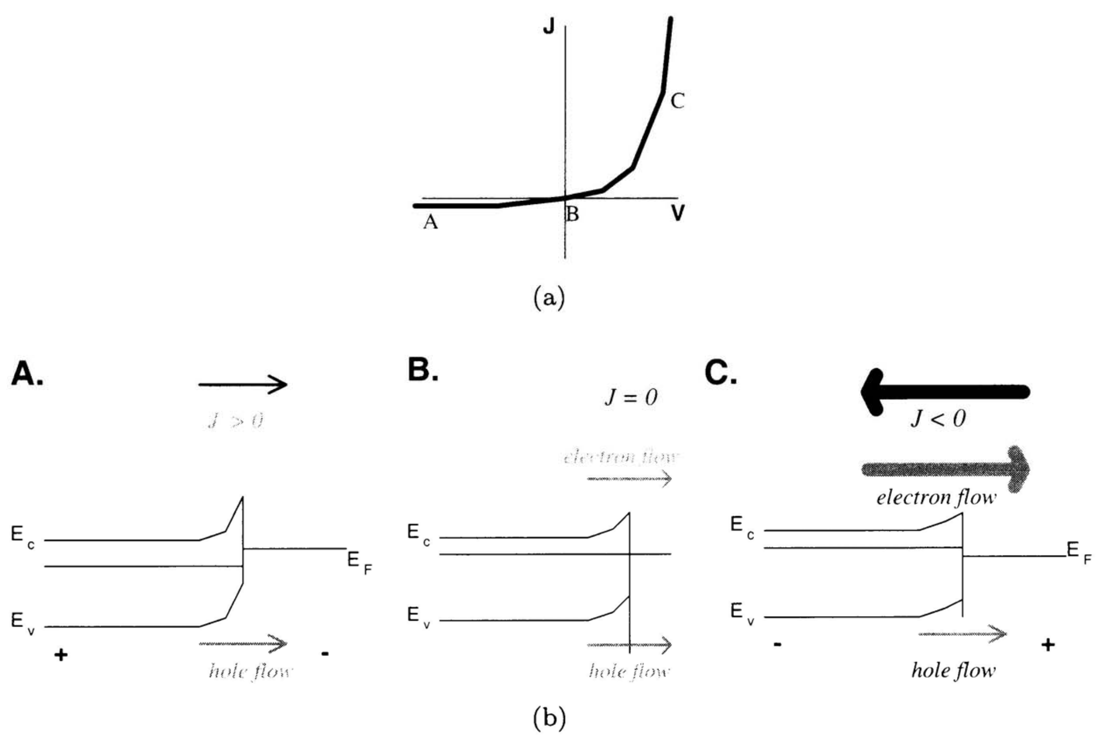



Fig. 5.6. (a) Schematic current–voltage characteristic of a Schottky barrier junction in the dark. A, B and C mark points on the curve where the device is at reverse bias, equilibrium and forward bias; (b) A: band profile of an $n$-type semiconductor–metal Schottky barrier at reverse bias. The only current 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.)

$$\Phi_m < \Phi_p$$

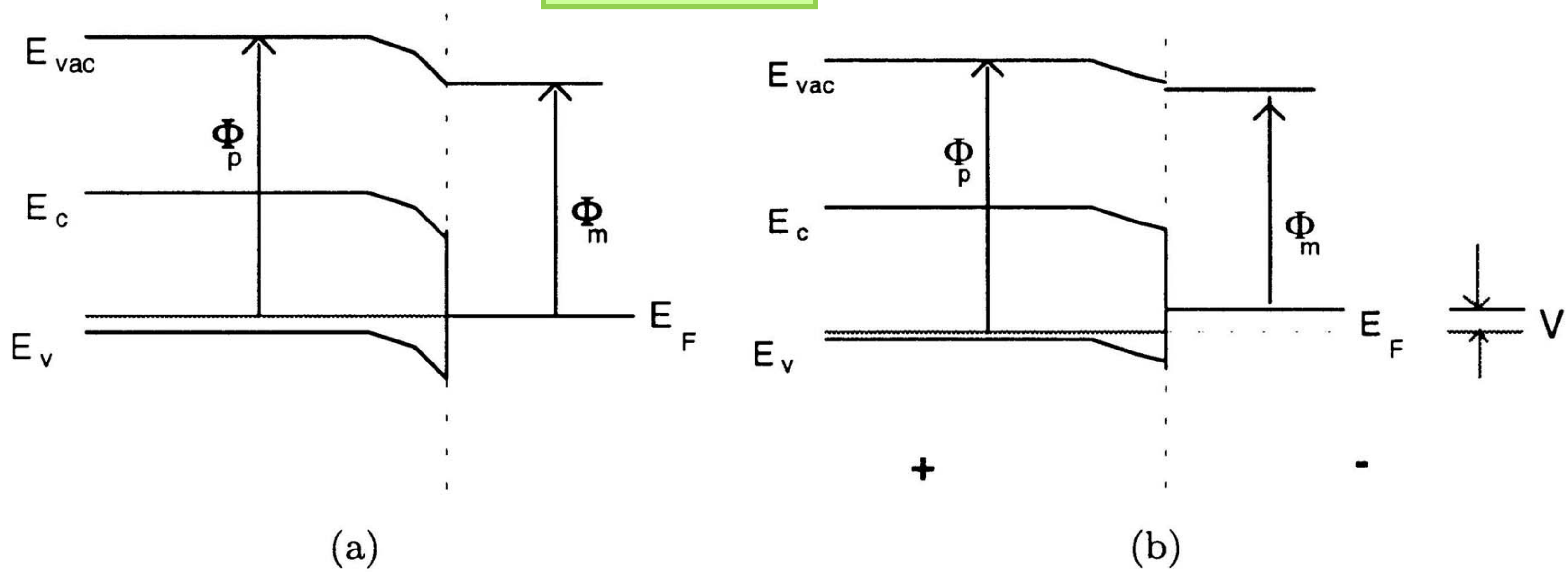



Fig. 5.7. Band profile of the *p*-type semiconductor–metal junction (a) at equilibrium and (b) under illumination at open circuit.

- 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

$\Phi_m < \Phi_n$

$\Phi_m > \Phi_p$



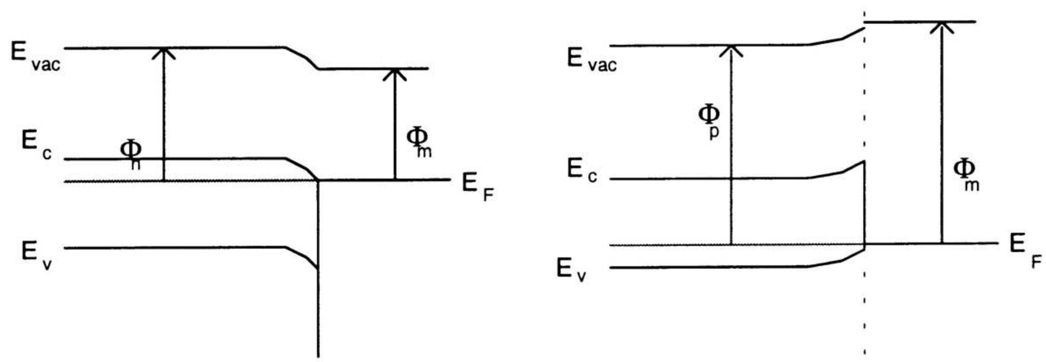


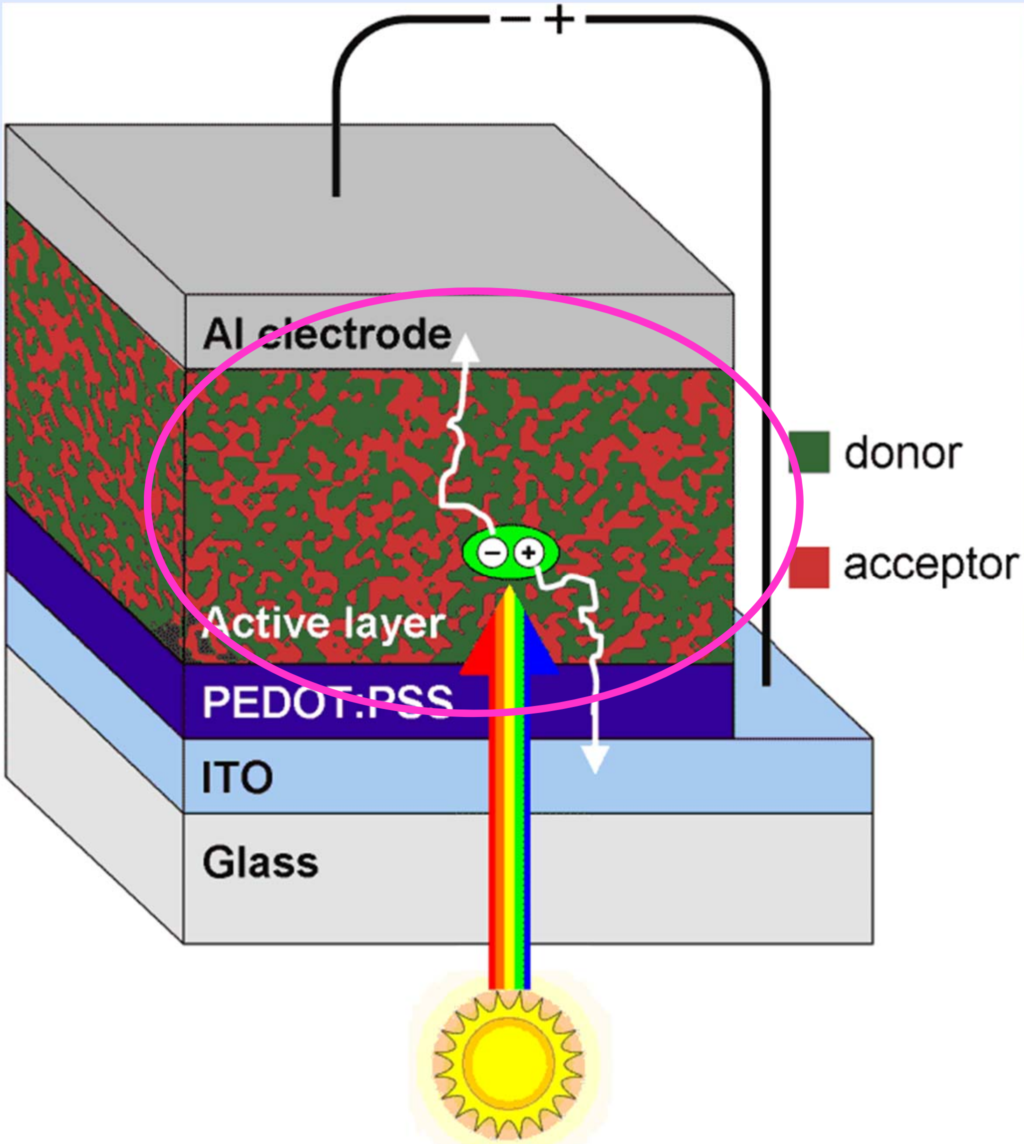

Fig. 5.8. Ohmic metal–semiconductor contacts for (a) an $n$-type semiconductor and (b) a $p$-type semiconductor. In each case the difference in work functions is supplied by the build up of majority carriers in an accumulation layer near the interface. An accumulation layer is generally narrow compared 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

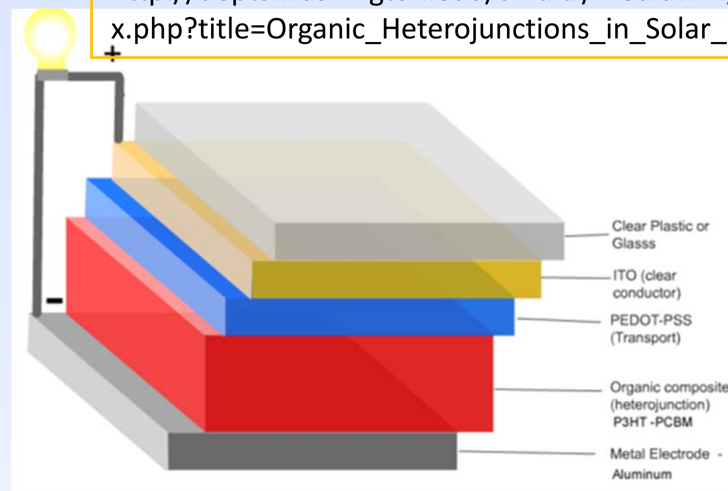
- Note that at Ohmic contact provides a low resistance pathway for majority carrier from the semiconductor to the metal

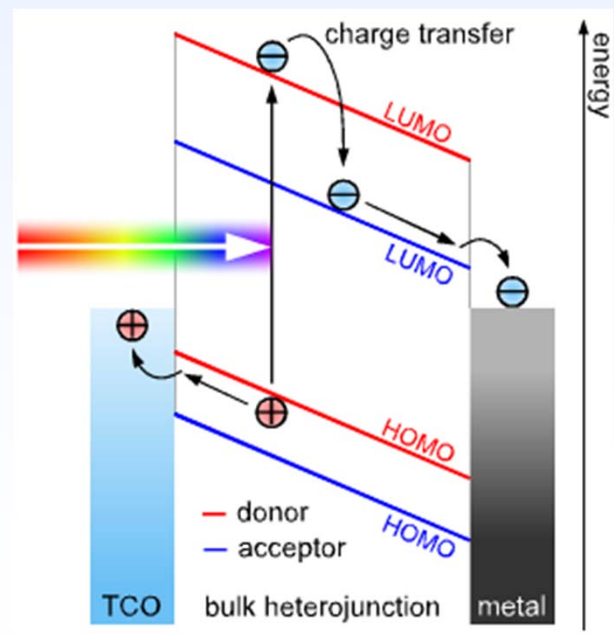
# Organic PV: Bulk heterojunction



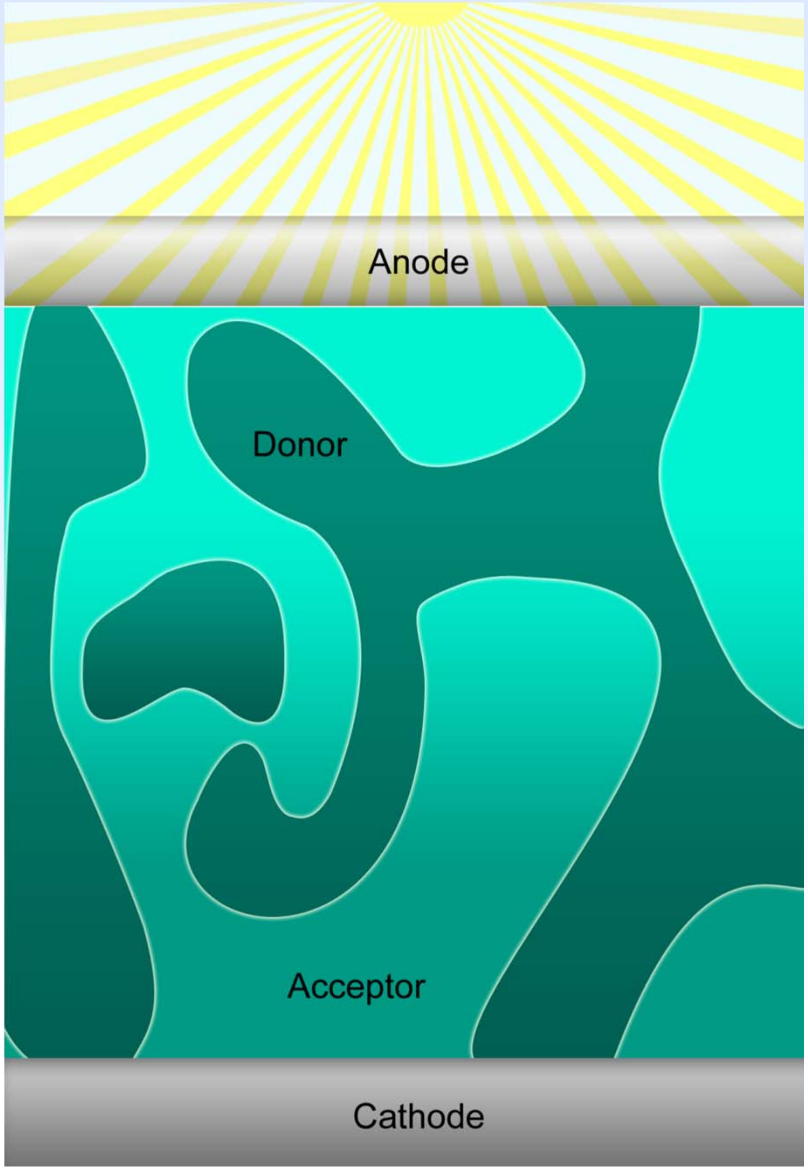

http://www-ssrl.slac.stanford.edu/sites/default/files/science-highlights/images/2011/January/Verploegen--fig1_0.png

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

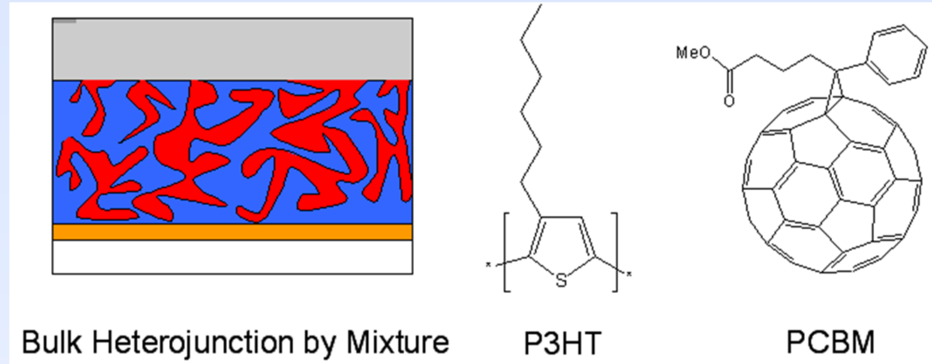


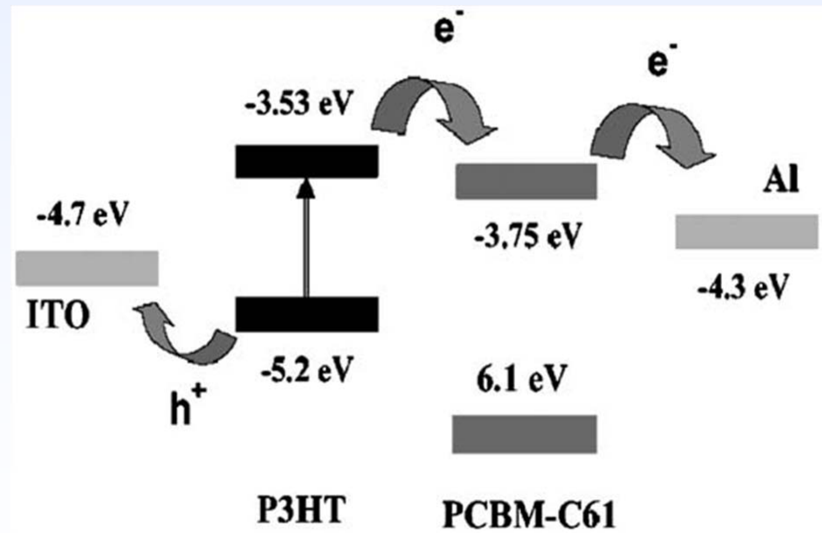
# Organic PV: simplified BH structure




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

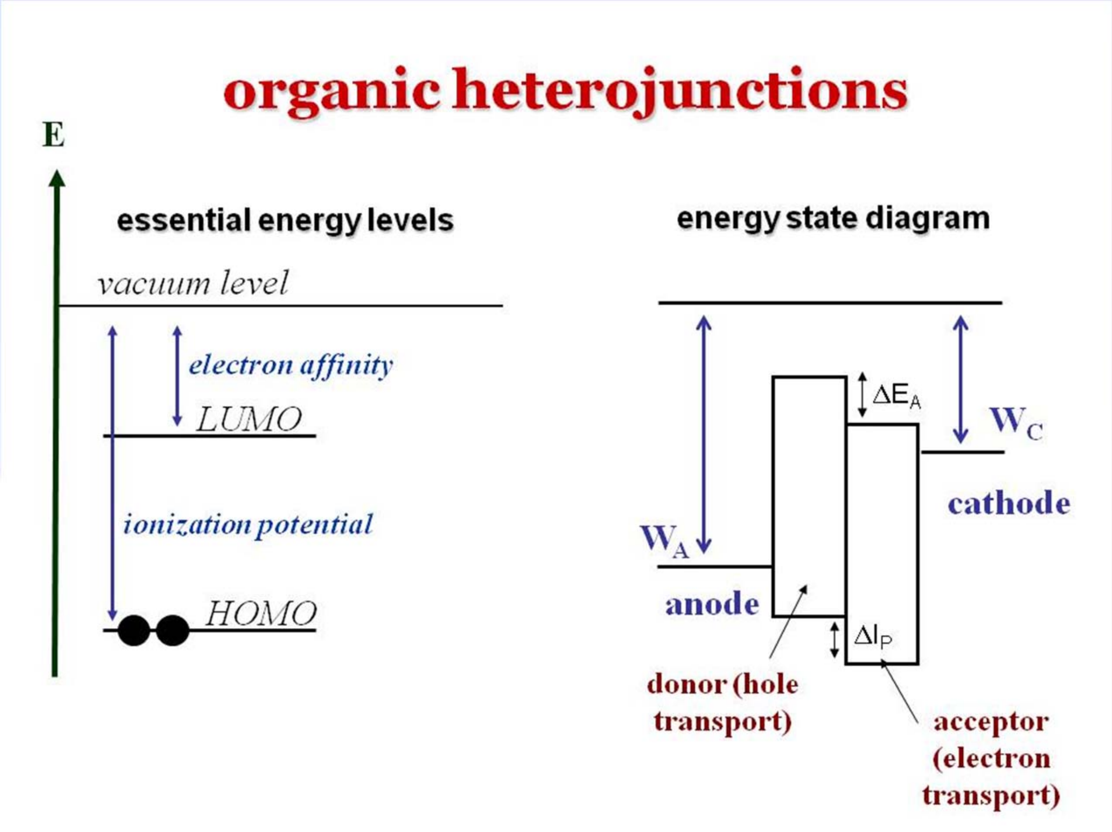



http://www.light.t.u-tokyo.ac.jp/english/photovoltaic/Introduction.html




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

# Organic PV: interface energetics

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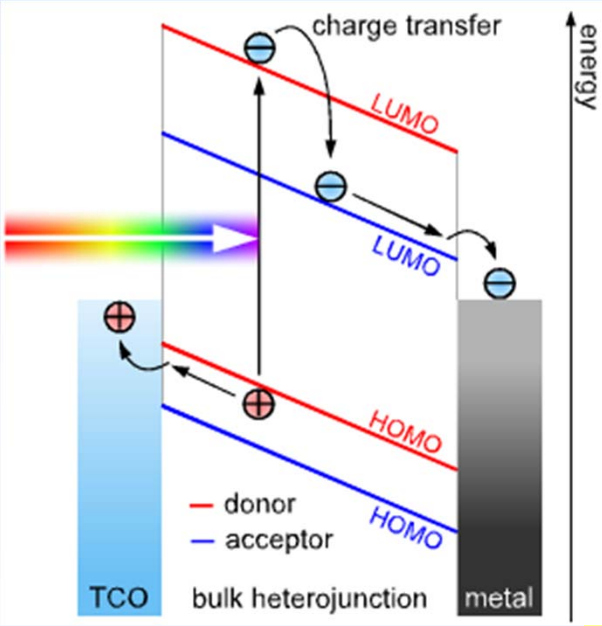
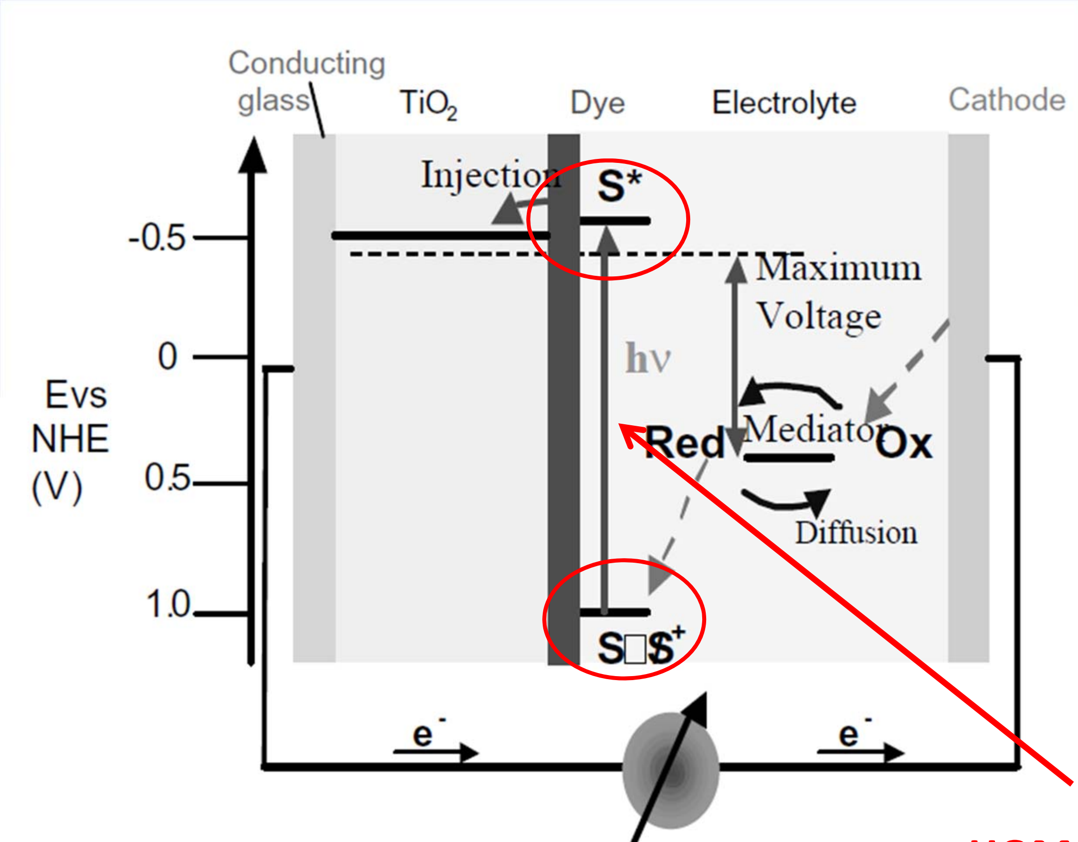
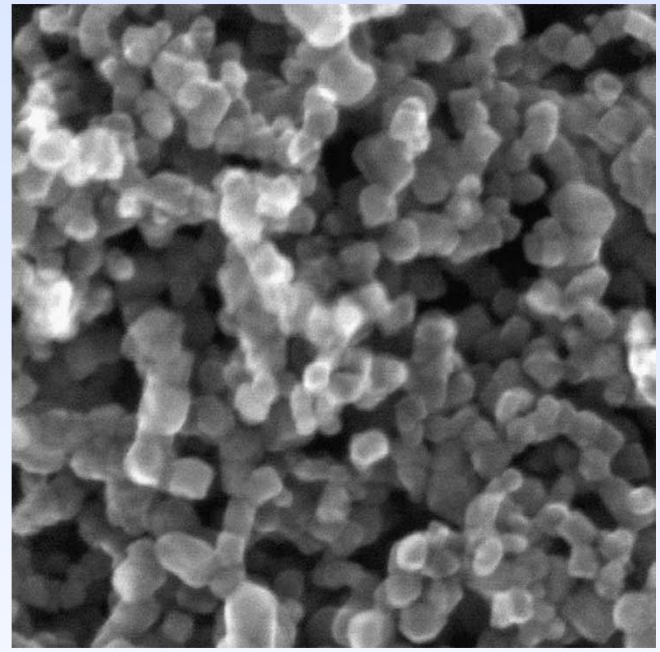



http://www.physik.uni-wuerzburg.de/EP6/research-oe.html

# Dye-sensitized $TiO_2$ solar cell



~25 nm nano-porous $TiO_2$ electrode

**HOMO-LUMO transition**

"**Reaction**": $S + h\nu \rightarrow S^* \Longleftrightarrow S^+ + e^-$

M. Grätzel / Journal of Photochemistry and Photobiology C: Photochemistry Reviews 4 (2003) 145–153

# Dye-sensitized $TiO_2$ solar cell

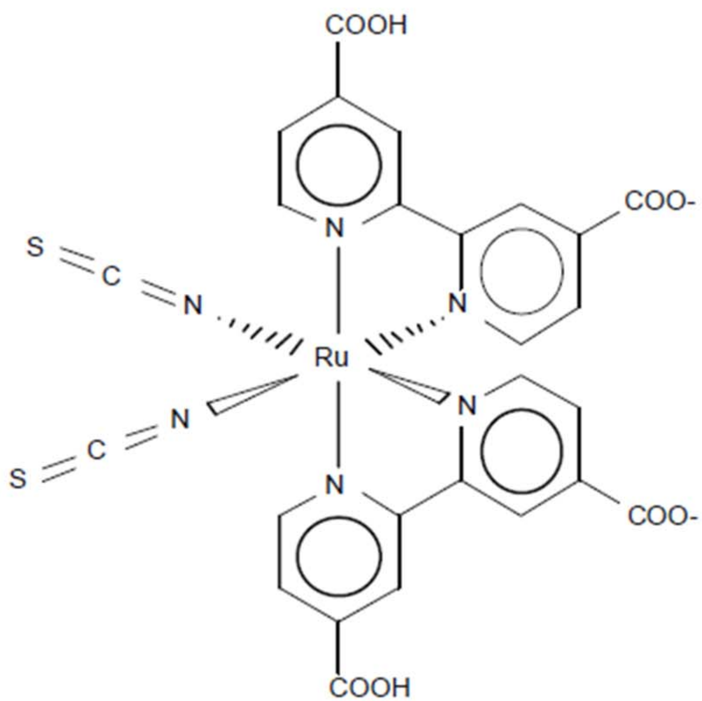
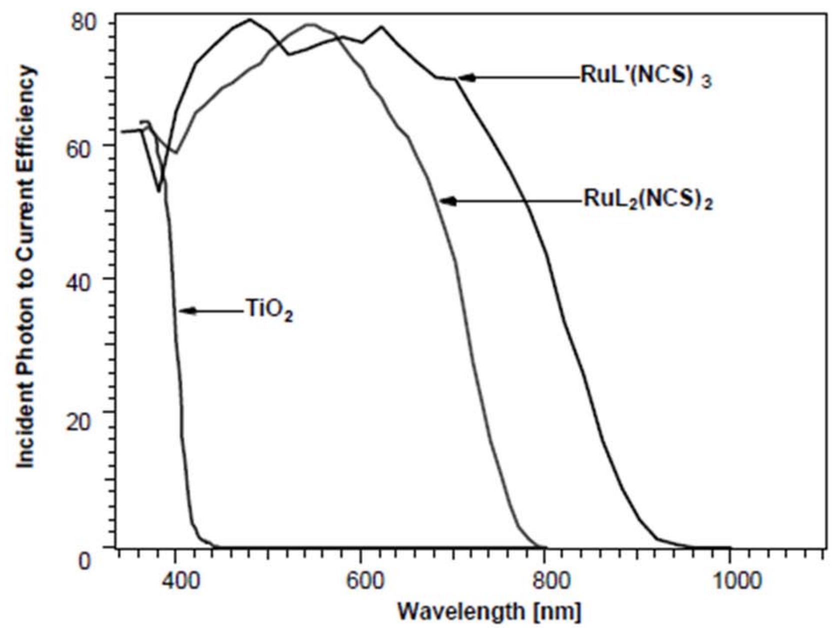



Fig. 4. Chemical structure of the N3 ruthenium complex used as a charge transfer sensitizer in dye-sensitized solar cells.




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 $TiO_2$ films is also shown for comparison. Detailed experimental

Binding of dye (monolayer) to $TiO_2$ through carboxylate groups; photon absorption results in metal-to-ligand charge transfer (MLCT) and rapid injection (<20 fs) of the $e^-$ into the $TiO_2$ CB.

M. Grätzel / Journal of Photochemistry and Photobiology C: Photochemistry Reviews 4 (2003) 145–153

# Projects (preliminary information)

Teams will be assigned after spring break

Analysis of the LCOE for PV technologies, from a materials science perspective

1. Thin film silicon
2. CIGS
3. CdTe
4. c-Si
5. Multi-junction III-V
6. OPV

# Analysis of the LCOE for PV technologies, from a materials science perspective

***Issues to be considered:***

- Starting materials: e.g. cost, availability, toxicity, recycling requirements

- Options within each material system: e.g. device structures, light trapping, substrate technologies, transparent conductors, deposition methods, energy inputs

- Technology challenges: e.g. stability, uniformity, laser processing, efficiency, production scaling/yield

- Prioritized future research directions to reduce LCOE: e.g. critical steps in process where costs are high or specific hurdles need to be overcome for cost competitiveness.

# Projects (preliminary information): expected output

***PowerPoint presentation:***

- 25 minutes, equally shared among team members
- Three teams of 3, one team of 4 (team of 4 gets 30 minutes)
- Completely referenced, with appropriate figures
- Original content/work (new ideas and ways of presenting data and results)
- Team-graded
- Presentations the week of April 24