A. *OTHER JUNCTIONS*

B. *SEMICONDUCTOR HETEROJUNCTIONS -- MOLECULES AT INTERFACES*:

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

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SSARE, PVIC

Principles and Varieties of Solar Energy (PHYS 4400)

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.

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 <u>donors donate electrons</u>, leaving them <u>positively</u> charged)

N_A^- is the concentration of ionized acceptor atoms (recall that <u>acceptors accept electrons</u>, leaving them <u>negatively</u> charged)

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-m²-s⁻², and [h] = m²kg 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)

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

Junctions

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.

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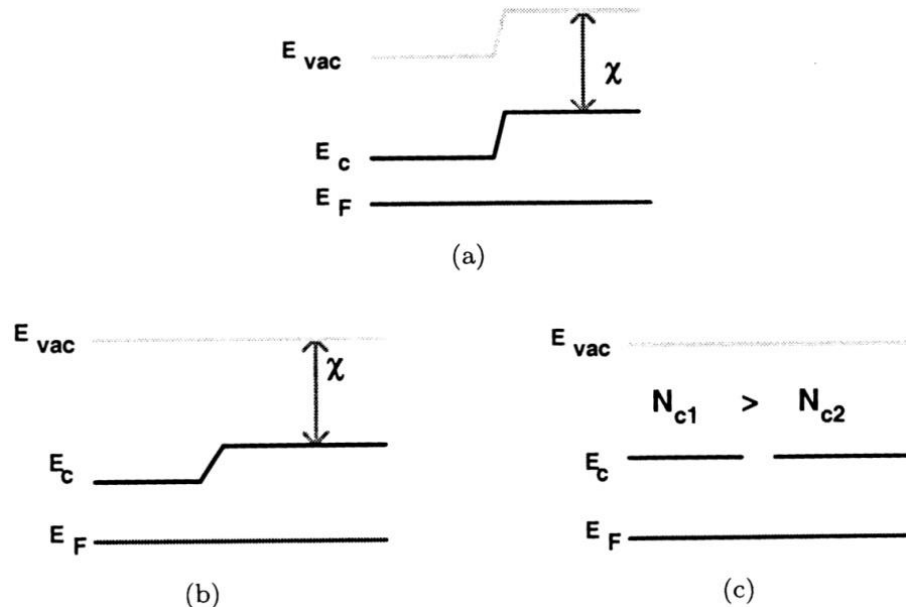

Fig. 5.2. Contributions to a built-in effective field for electrons. (See text for explanation.)

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
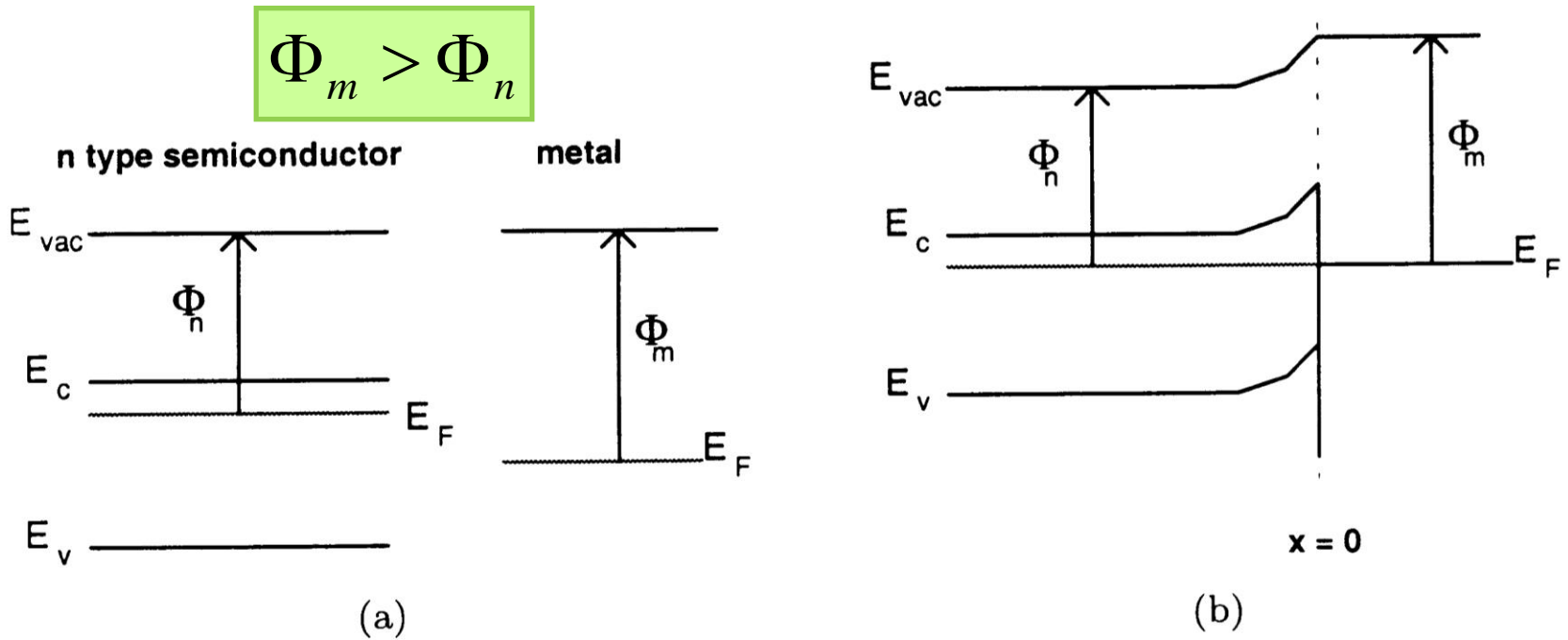
$$\Phi_m > \Phi_n$$

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);
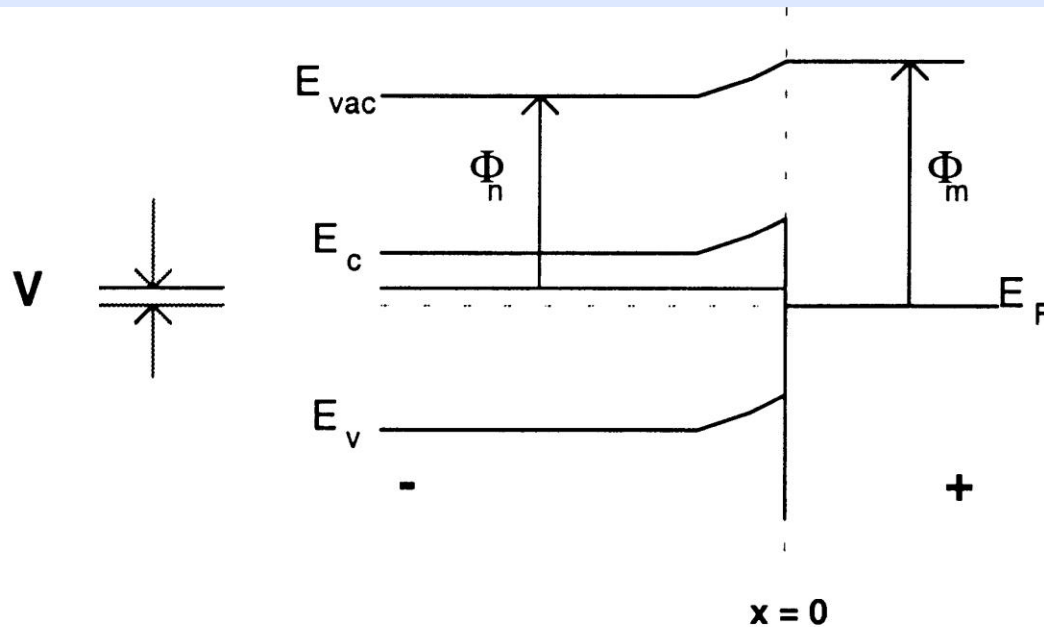- Result is a lower resistance pathway for holes than for electrons

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

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(a)

A.   **B.**   **C.**

$J = 0$ $J < 0$

$J > 0$ electron flow   electron flow

E_c ——————— E_c ——————— E_c ———————

                    E_F E_F

E_v —————— E_v —————— E_v ——————

  +   +

hole flow   hole flow   hole flow

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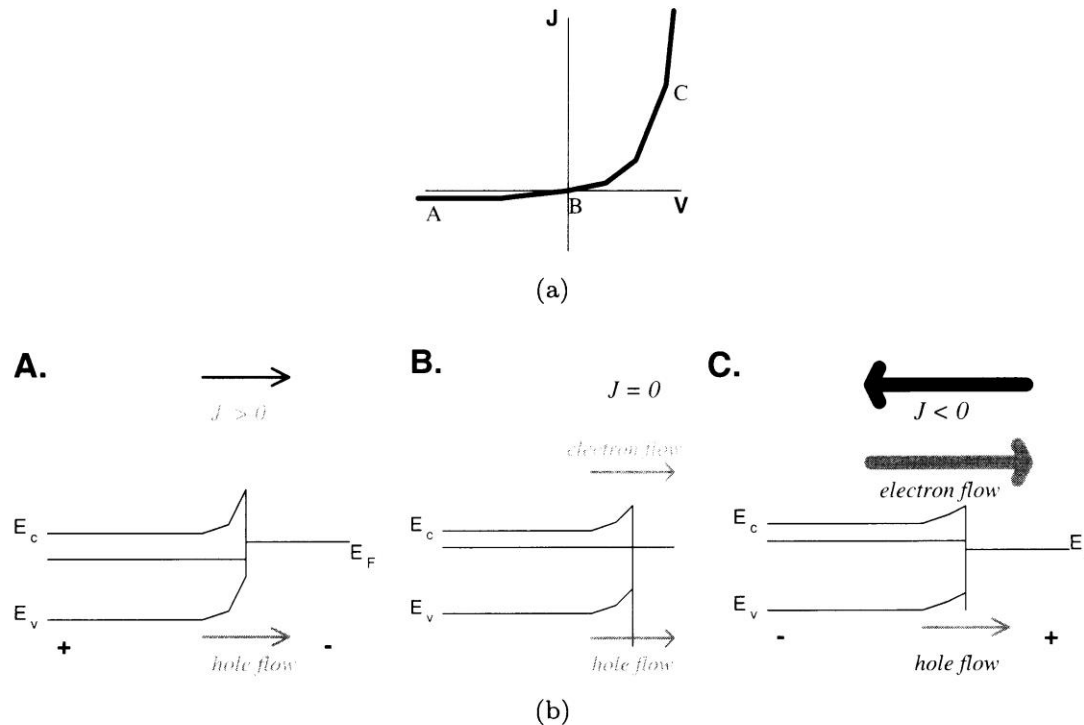
Fig. 5.6. (a) Schematic current–voltage characteristic of a Schottky barrier junction in the dark. A, B and C mark points on the curve where the device is at reverse bias, equilibrium and forward bias; (b) A: band profile of an *n*-type semiconductor–metal Schottky barrier at reverse bias. The only current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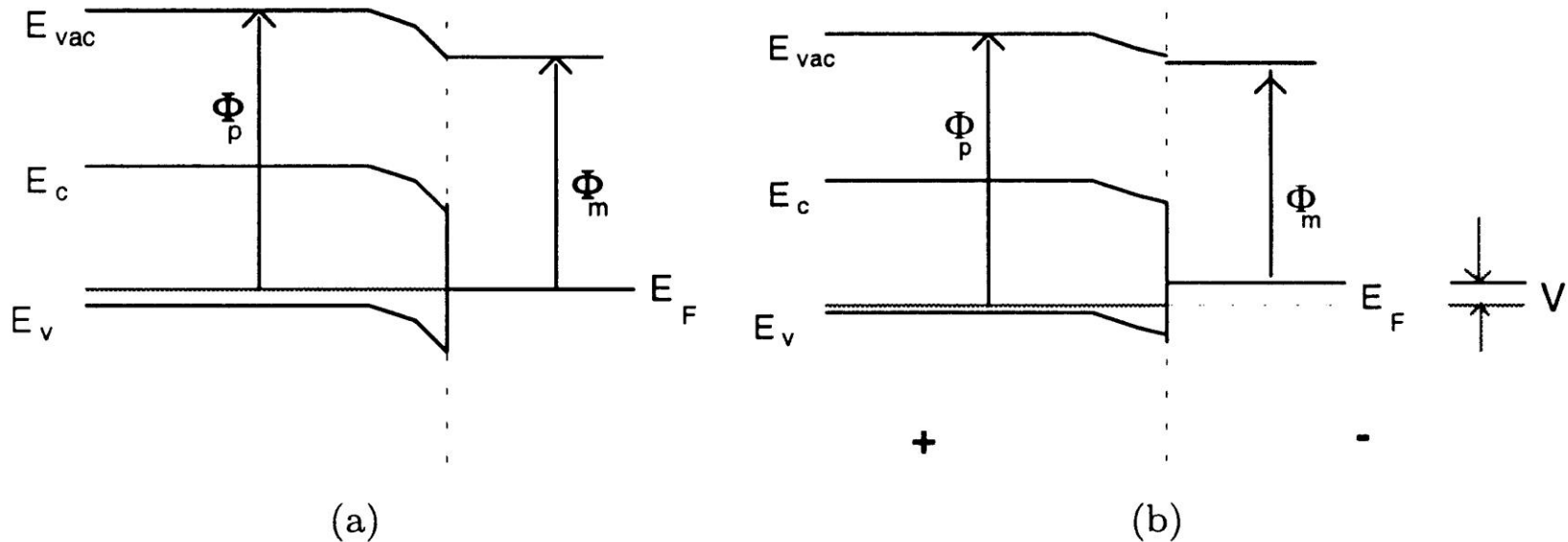
$$\Phi_m < \Phi_p$$

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

$$\Phi_m < \Phi_n$$

$$\Phi_m > \Phi_p$$

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E$_{vac}$

E$_c$ Φ_n

E$_F$

Φ_m

E$_v$

(a)

E$_{vac}$

Φ_p

E$_c$

Φ_m

E$_F$

E$_v$

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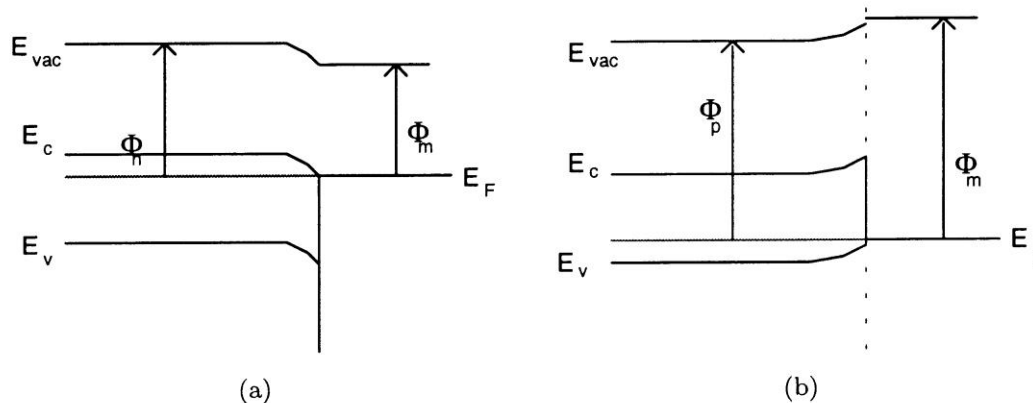
Fig. 5.8. Ohmic metal–semiconductor contacts for (a) an *n*-type semiconductor and (b) a *p*-type semiconductor. In each case the difference in work functions is supplied by the build up of majority carriers in an accumulation layer near the interface. An accumulation layer is generally narrow compared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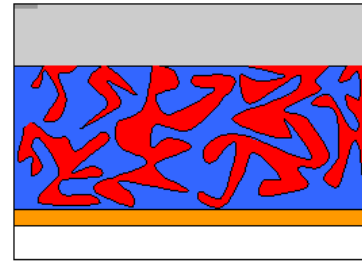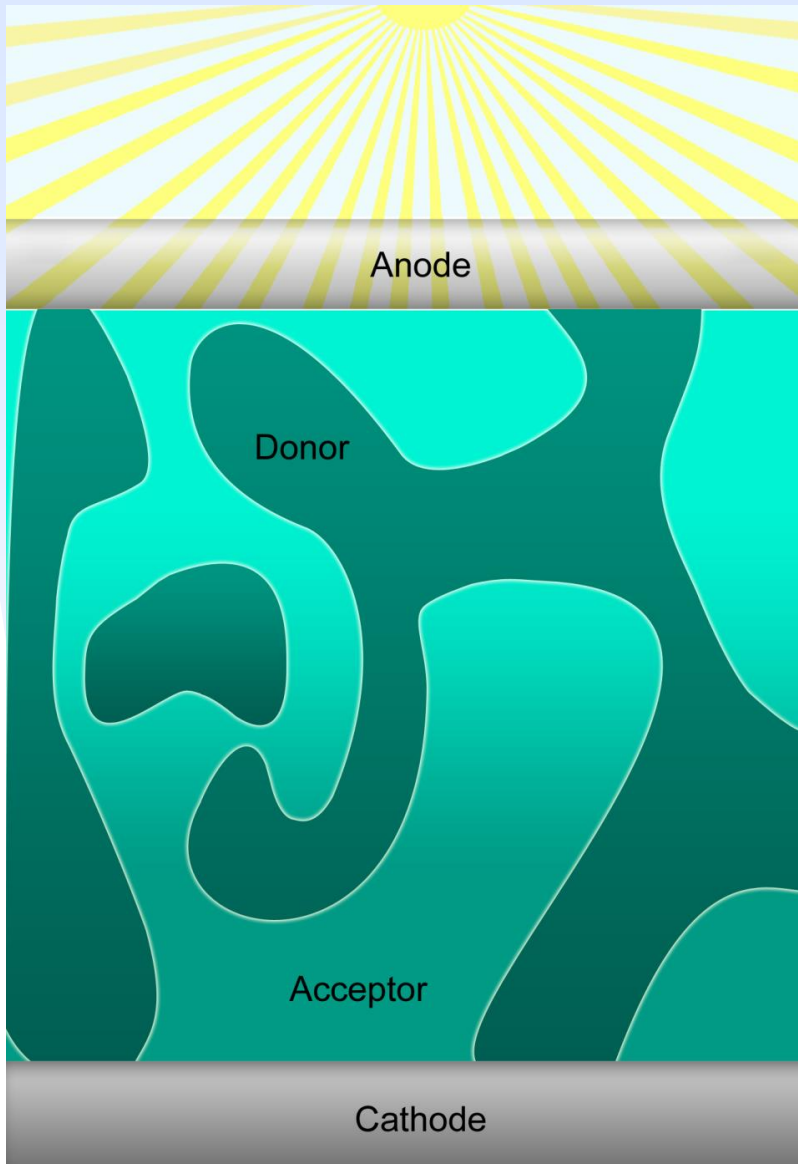
Organic PV: Bulk heterojunction

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Organic PV: simplified BH structure

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

Bulk Heterojunction by Mixture   P3HT   PCBM

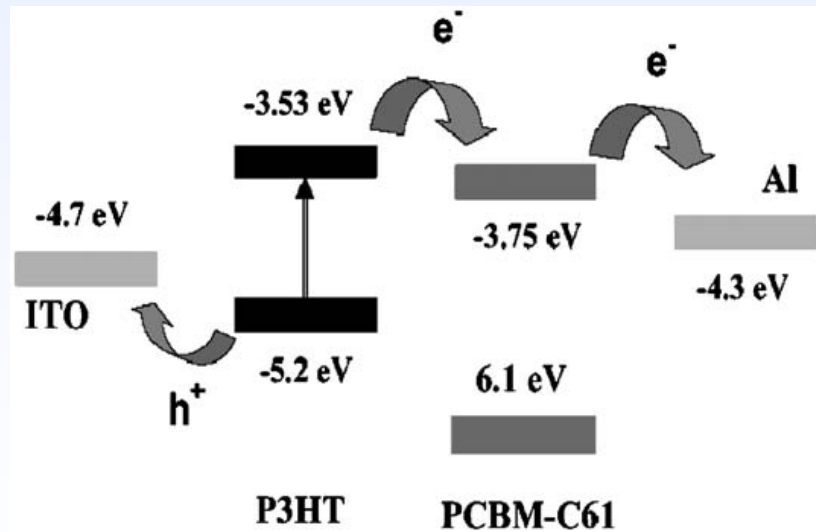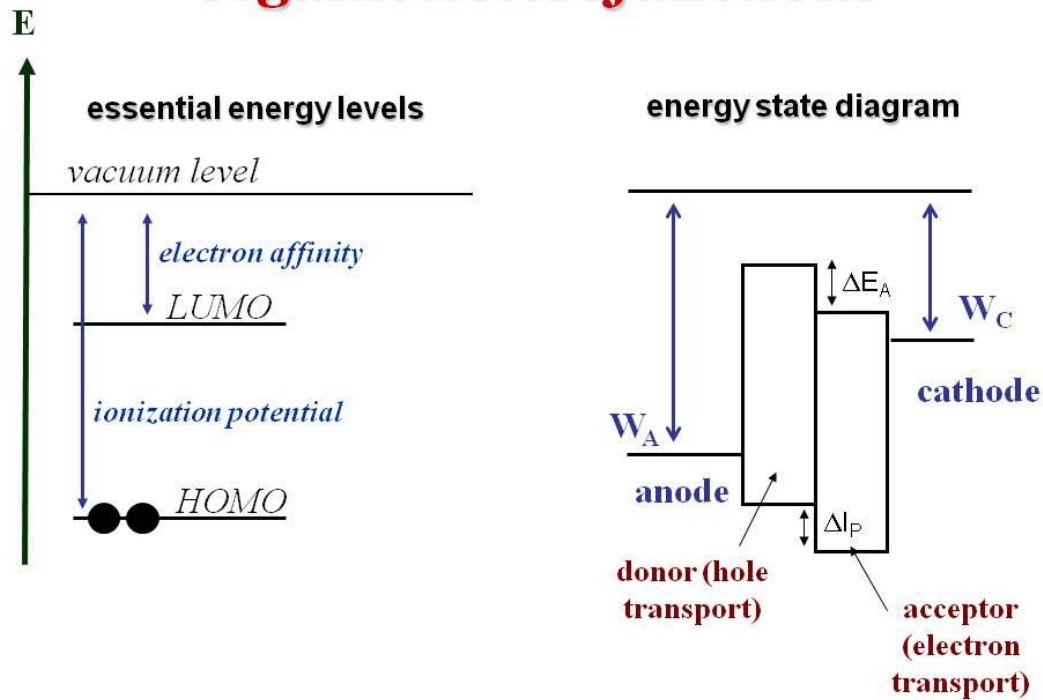http://www.light.t.u-tokyo.ac.jp/english/photovoltaic/Introduction.html
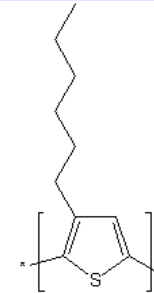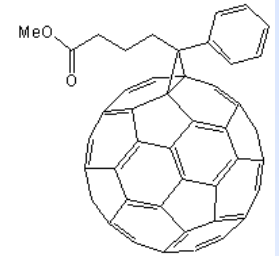
M. Al-Ibrahima et al., Solar Energy Materials & Solar Cells 85 (2005) 13–20

organic heterojunctions

essential energy levels

energy state diagram

E

vacuum level

electron affinity

LUMO

ionization potential

HOMO

ΔE_A

W_C

cathode

W_A

anode

ΔI_P

donor (hole transport)

acceptor (electron transport)

charge transfer

energy

LUMO

LUMO

HOMO

HOMO

— donor
— acceptor

TCO

bulk heterojunction

metal

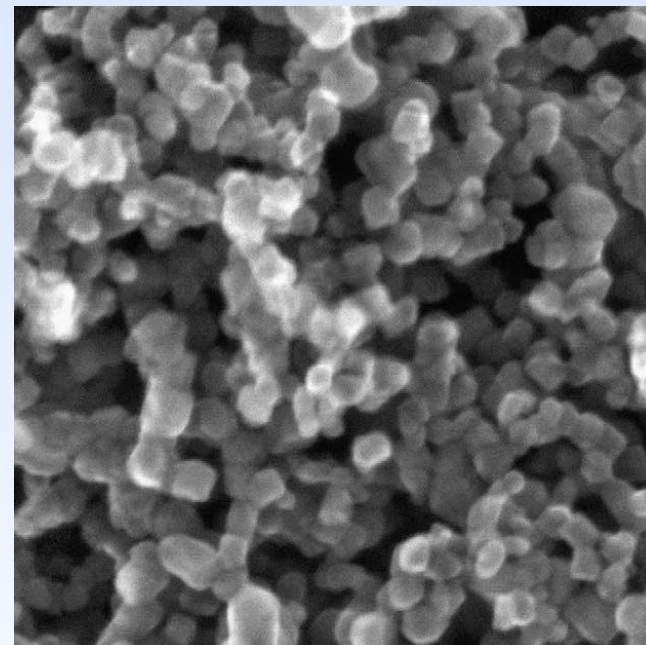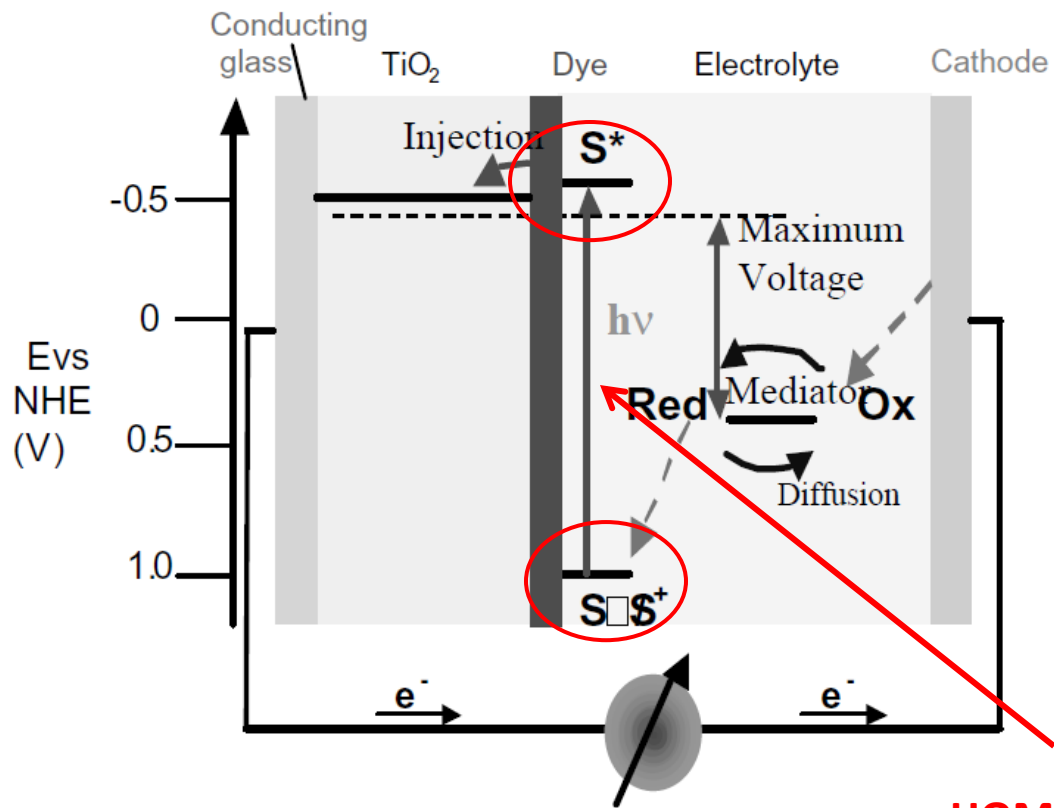http://www.physik.uni-wuerzburg.de/EP6/research-oe.html

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

Dye-sensitized TiO$_2$ solar cell

~25 nm nano-porous TiO$_2$ electrode

HOMO-LUMO transition

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

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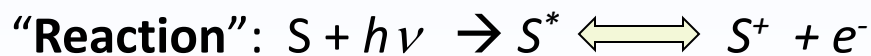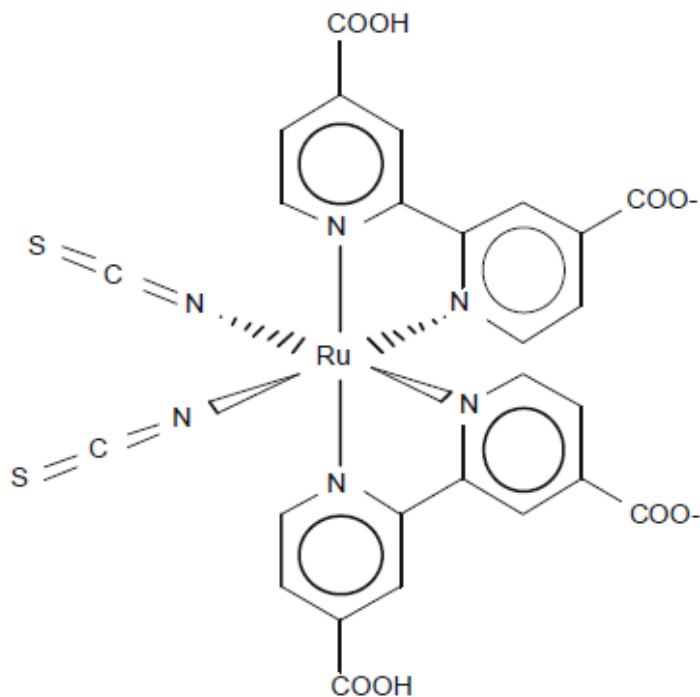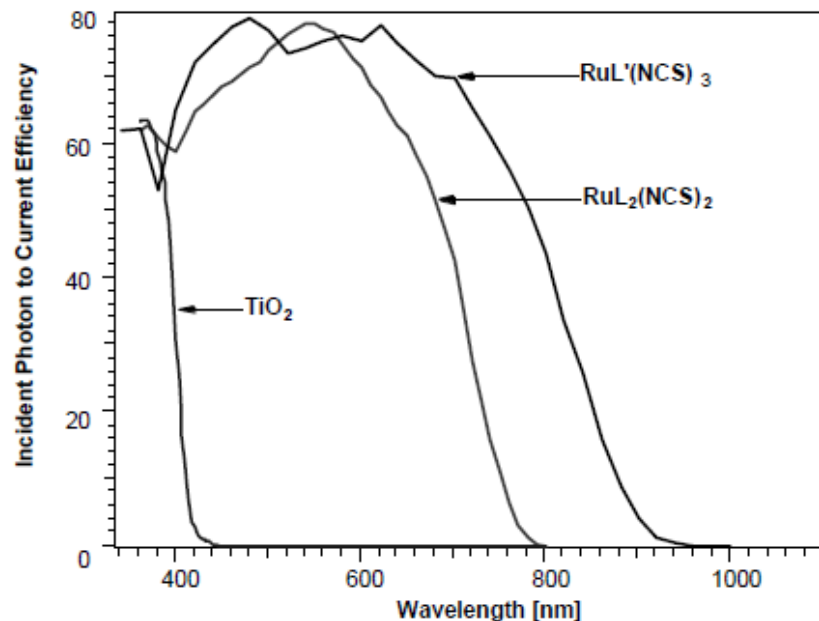
Dye-sensitized TiO₂ solar cell

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.

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