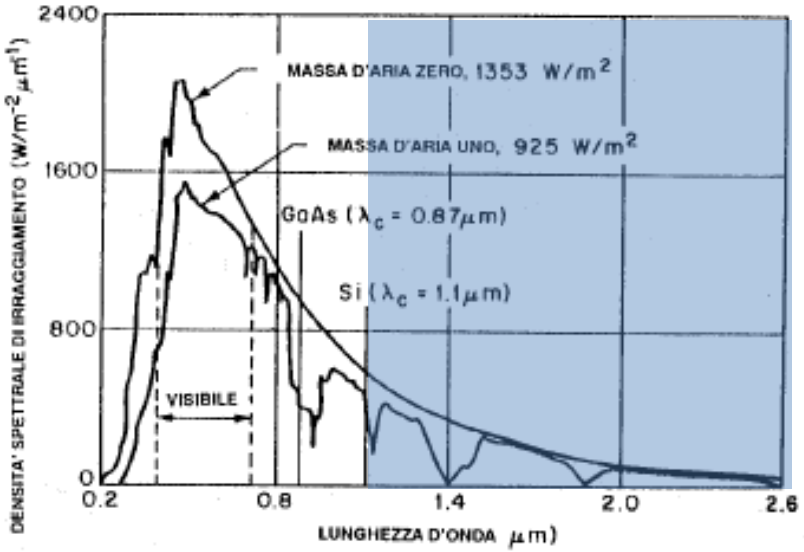
Solar Cells

The sun radiation intensity in the free space at the distance Hearth-Sun is defined as **Solar Constant 1353 W/m^2**

Our atmosphere influence such radiation, let's define the Air Mass, AM

This part of the spectrum has sufficient energy generate current

Radiation associated to this part of the spectrum does not have sufficient energy to excite silicon



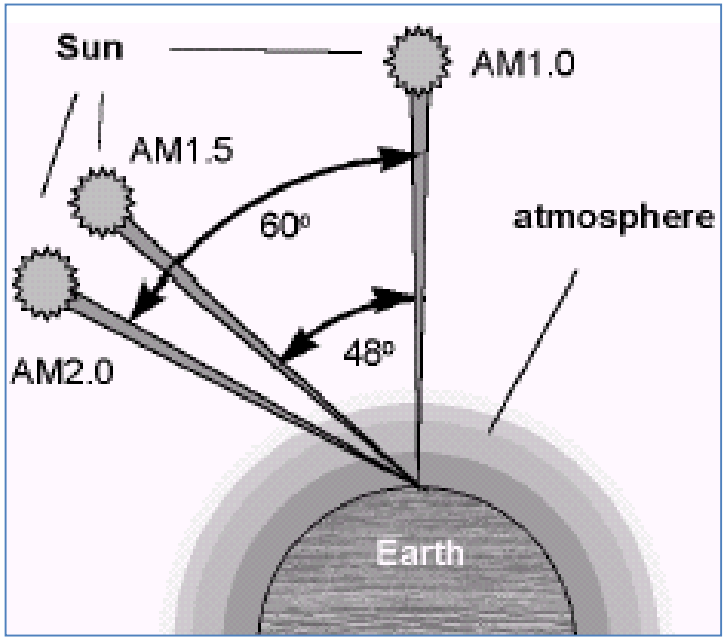
$E(eV)=1240/\lambda(nm)$

- AM0 in the free space

- AM1 on hearth when sun is at the zenith

- AM1,5 when the sun is 48° with respect to the zenith it is the value typically employed for defining the efficiency of solar cells.

- AM2 whe the sun is 60° with respect to the zenith



Solar cells

So far the most of them is fabricated employng Silicon
In the last years many different materials have been considered

Even if silicon is the most employed

- It is not ideal for photovoltaic conversion
- To achieve 90% assorbance → 1 μm GaAs (direct gap)
- 100 μm Si (indirect gap)

BUT:

Silicon technology was largely developed before photovoltaics concepts took place, changing technology is too costy

Materials

- **Crystalline silicon (c-Si), thin films**

Due to its thickness requires a mechanical support (5 - 50) μm

- Compatibility issues between support and active material
- Highest efficiency, but costy
- Not flexible

- **amorphous silicon(a-Si)**

- Do not absorb in the infrared
- Lower efficiency, but lower costs

Le 3 principali tecnologie sul mercato

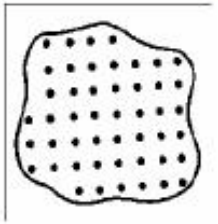
Tecnolgia **cristallina**

Silicio **monocristallino**	Single crystal Si	sc-Si (m-Si)	
Silicio **policristallino**	Multi crystal Si	mc-Si (p-Si)	

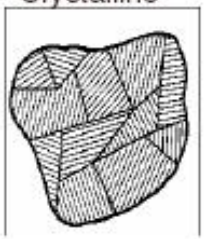
Tecnolgia **film sottile**

Silicio **amorfo**	Amorphous Si	a-Si	

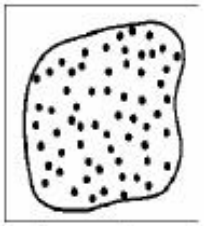
Silicio monocristallino	η = 13-17 %
Silicio policristallino	η = 12-14 %
Film sottili (silicio amorfo)	η = 6-10 %



Crystalline



Polycrystalline



Amorphous

Le 3 principali tecnologie Thin Film (a film sottile)

- a-Si silicio amorfo
- CIS diseleniuro di indio e di rame
- CdTe telluro di cadmio

Novel approaches to photovoltaics

- **dyes: Graetzel cells**

  photoelectrochemical process

  the dye is the responsible for light absorbance

- **Organic Materials**

  polymeric solar cells

  high absorbance coefficients, very thin and flexible devices

Solar cells working principle

When light shines on a semiconductor (band gap E_g) some of the photons are absorbed from the material (**energy $h\nu \geq E_g$**), an electron-hole pair is generated, the other photons (**energy $h\nu < Eg$**) freely pass through the material

Such **electron-hole pairs** are charge carriers bond together due to coulomb attraction

In order to obtain acurrent, such charges must be separated. This can be done by means of an electric field which can be applied or intrinsecally be present due to the device architecture

- **Metal-semiconductor interface (Schottky)**
- **Metal-Insulator-Semiconductor (MIS)**
- **p-n junction**

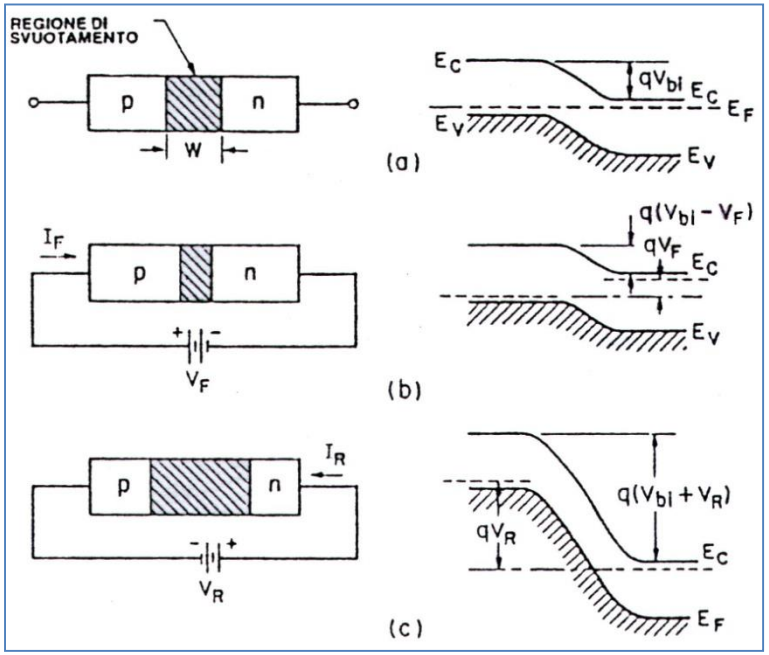
Solar cells working principle

P-N junction V_{bi} (built-in potential)

$$V_{bi} = \frac{KT}{q} \frac{ln(N_a N_d)}{{n_i}^2}$$

V=0

Equilibrium, no current flowing in the device



Forward bias

P side positively biased

Reverse bias

N side positively biased

If there is no light, the behavior is identical to what seen in the normal p-n junction

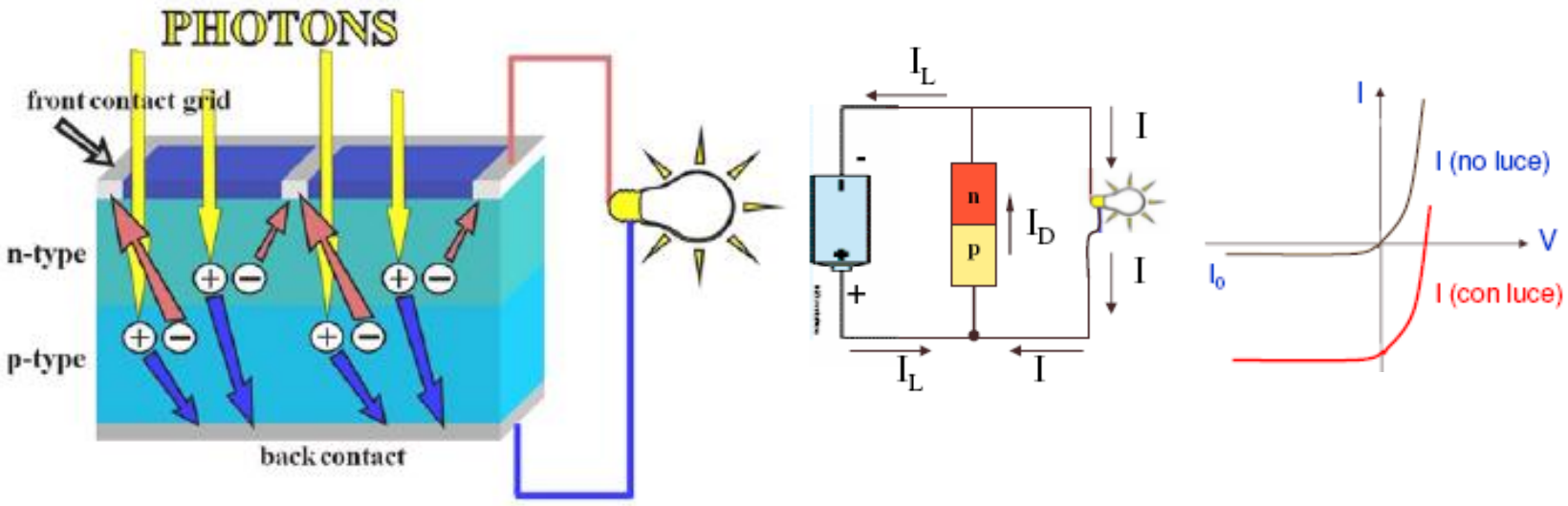
When light is shining on the device, we have two current contributions,

- **dark current density J_D**
- **photoinduced current density J_L**

Current supply, in parallel with the diode

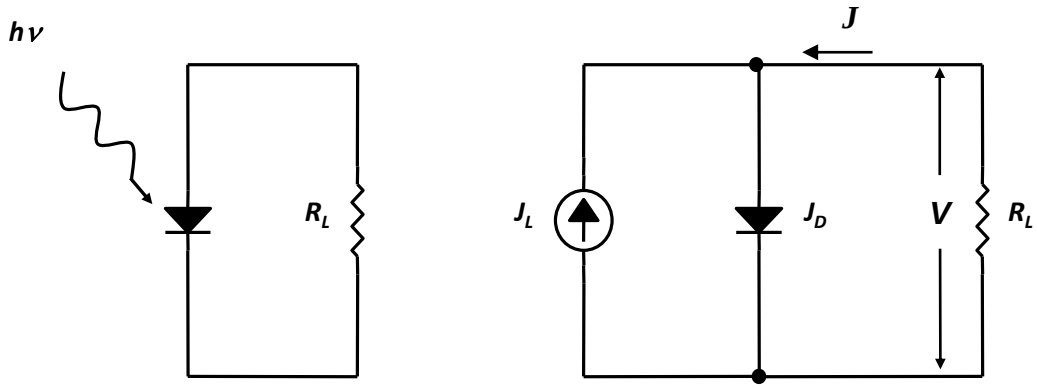
Solar cells working principle

By connecting the cell to an external load, the electrons generated in the n region or pushed by the field in the n region can reach the load, pass through it and eventually reach the p region of the cell



Photogenerated current is an inverse current that has to be subtracted from the diode current

Solar Cells: equivalent circuit



Total current density J is the difference between the dark current J_D and photogenerated current J_L:

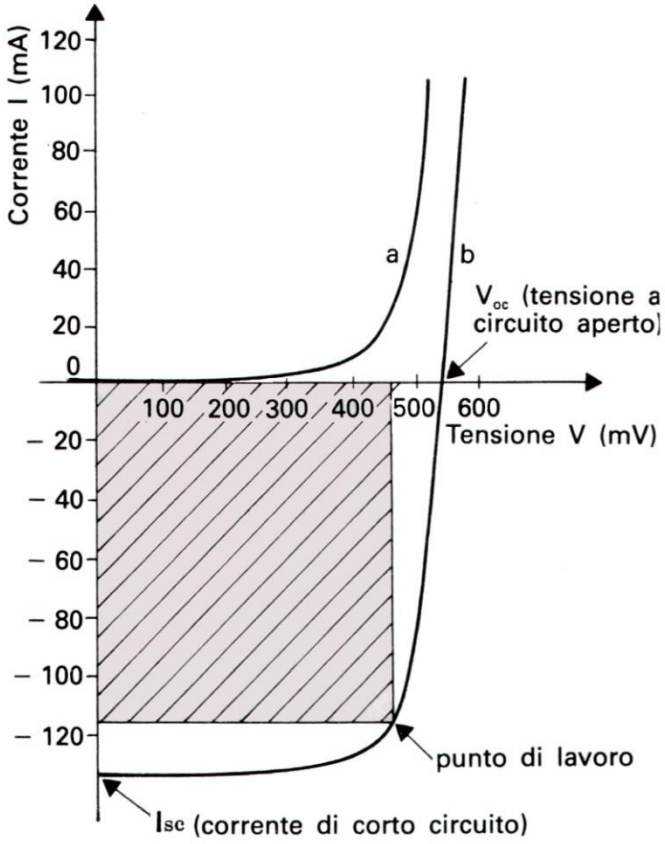
$$J = J_D - J_L$$

$$J_D = J_0\left[e^{qV/\eta KT} - 1\right]$$

$$J_L(\lambda) = Jn(\lambda) + Jp(\lambda) + Jdr(\lambda)$$

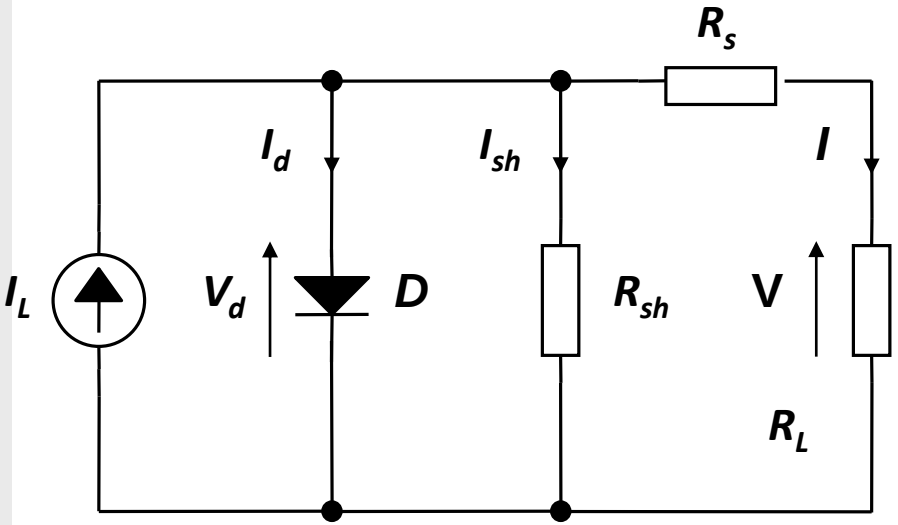
where Jn(λ) and Jp(λ) two contribution to the current in the two regions n and p whereas Jdr(λ) takes into account the charges generated in the depletion region

The curve under light (b) is in the IV quadrant, meaning that the device can give current to an external load



Non idealities: Rs e Rsh

Equivalent solar cell circuit



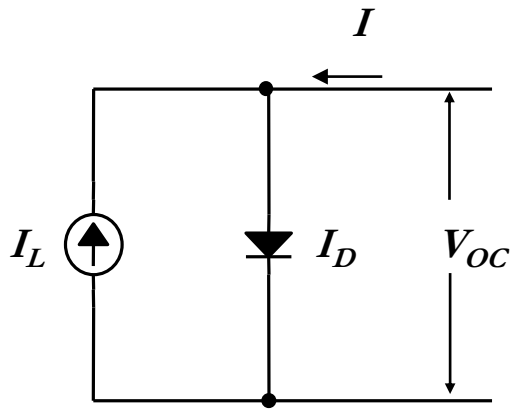
- Series resistance $\mathbf{R_s}$ **ohmic drops at the contacts**

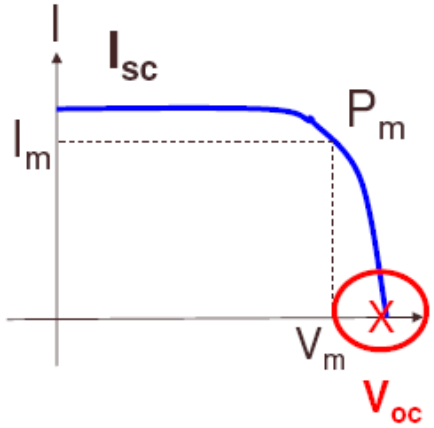
- Parallel resistance ***(shunt)*** $\mathbf{R_{sh}}$ short circuits or leakage current through the device due to defects

$$I = \frac{I_L - V/R_{sh}}{1 + R_s/R_{sh}} - \frac{I_0}{1 + R_s/R_{sh}}\left[e^{\frac{q(V+R_s I)}{\eta KT}} - 1 \right]$$

I_0 diode reverse current, η ideality factor, q electron charge I_L photogenerated current

Open circuit voltage: V_{OC}





V_{OC} **highest voltage generated by the cell when the current is zero (open circuit)**

$$V_{OC} = \frac{\eta KT}{q} ln\left(\frac{I_L}{I_0} + 1\right)$$ Dark, considering Rs=0 Rsh=∞

$$V_{OC} = \frac{\eta KT}{q} ln\left(\frac{I_L - V_{OC}/R_{sh}}{I_0} + 1\right)$$ Dark considering Rsh

Given a certain I_L V_{OC} increases as dark current decreases

Open circuit voltage: V_{OC}

In a real solar cell the generated charges can recombine, *radiative* or *not radiative* recombination

Radiative recombination ϕ_{PL}, is due to the decay of generated electrons from the conduction band (excited state) to the valence band (ground state), with a photon emission, having energy $h\nu=E_g$

Radiative recombination modifies the reverse current I_0 and, therefore, also I_D

$$I_D = \frac{I_{01}}{\phi_{PL}} \cdot \left(e^{\frac{qV}{\eta KT}} - 1 \right)$$

$$V_{OC} = \frac{\eta KT}{q} \ln\left(\frac{I_L - V_{OC} / R_{sh}}{I_{01} / \phi_{PL}} + 1 \right)$$

Short circuit current: I_{sc}

Current flowing in the device when the two electrodes are short circuited (V=0).

$$I_{sc} = \underbrace{\frac{I_L}{1+\frac{R_S}{R_{sh}}}}_{I_L\text{-}I_{sh}} - \underbrace{\frac{I_o/\phi_{PL}}{1+\frac{R_S}{R_{sh}}}\left(e^{\frac{IR_S}{\eta kT/q}}-1\right)}_{I_D}$$

Two contributions:

- Photogenerated current (excitons separated per second) minus the current in the shunt R_{sh} (I_{sh})
- Current flowing in the diode D (I_D)

$$I_{SC} = I_L - I_{sh} - I_D$$

Highest current that can be obtained by a solar cell

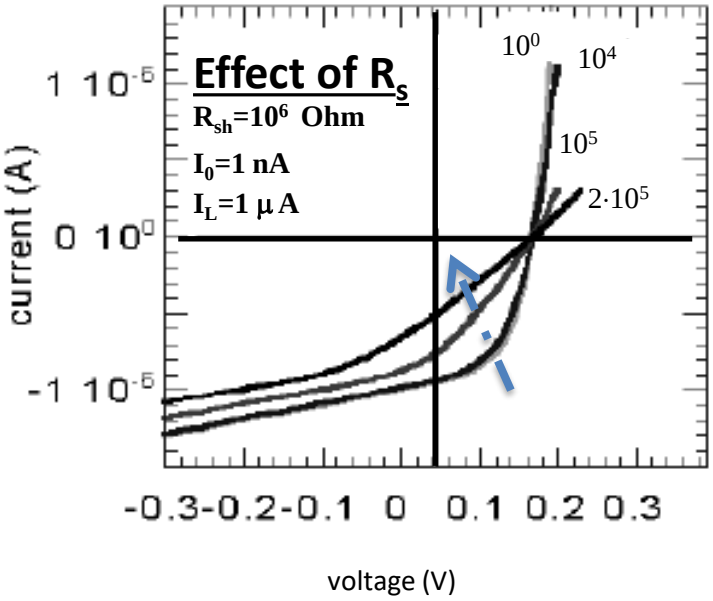
Short circuit current: I_{sc}

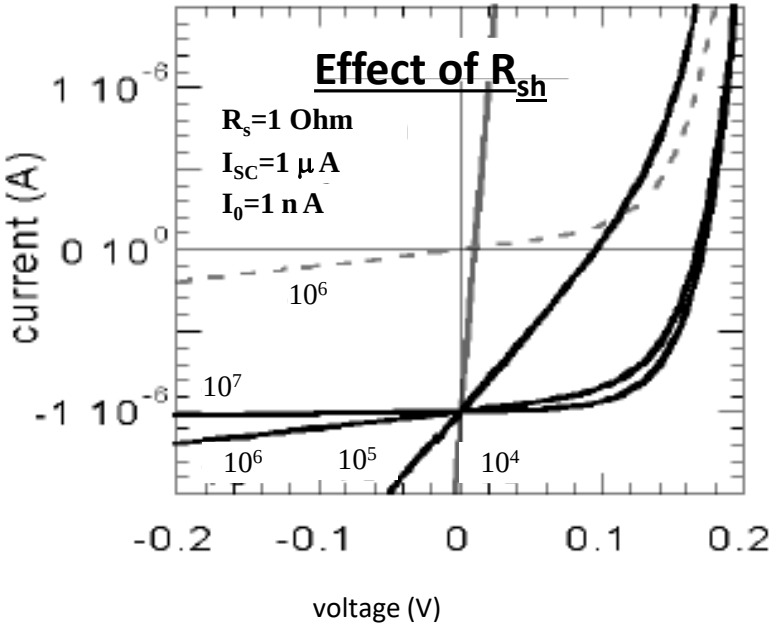
It depends on:

- **Area of the solar cell**
- **number of incoming photons (incoming power)**
- **incoming light spectrum**

  for the most of the measurements, as said before, we consider AM1.5
- **probability of absorbing light** *depends of the surface passivation and average life time of photogenerated charges*
- **solar cell optical properties (absorbance and reflectivity)**

R_S and R_{sh} effects on IV

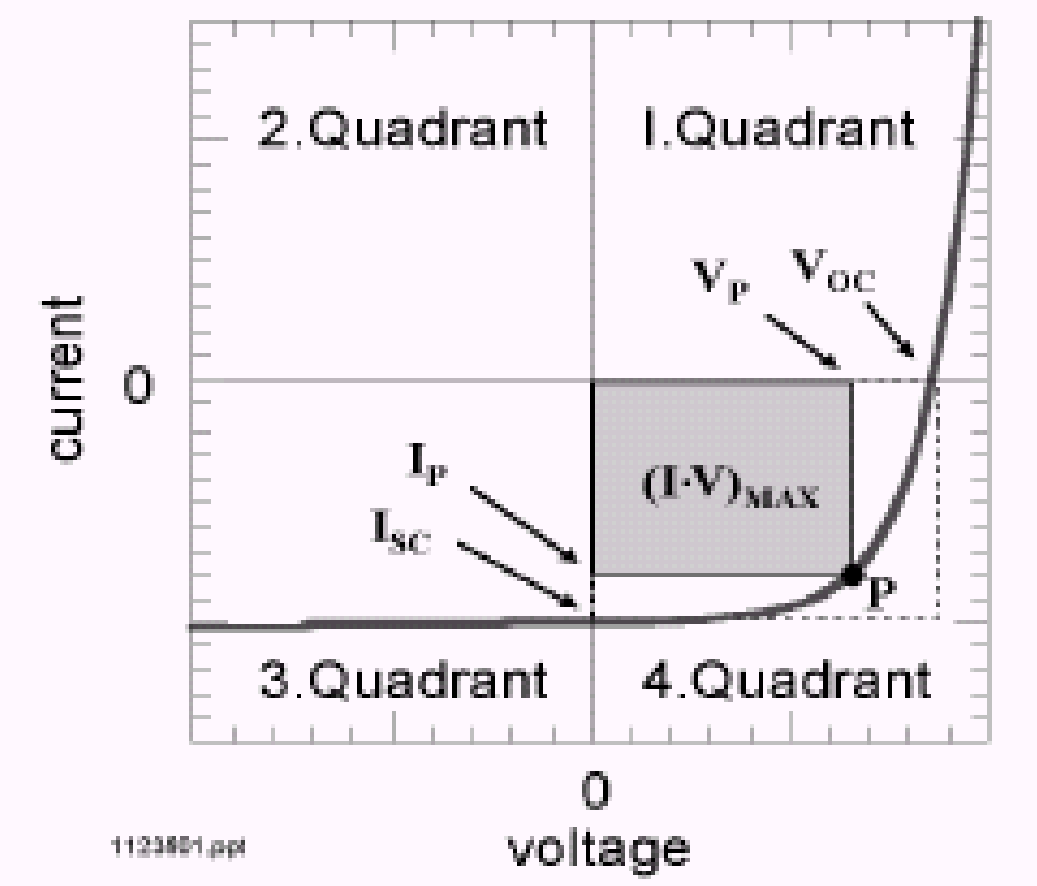




Which are the parameters taht we want to monitor in our solar cell?

- IV
- Conversion efficiency
- Fill Factor
- Spectral Response
- External Quantum Efficiency

IV characteristics

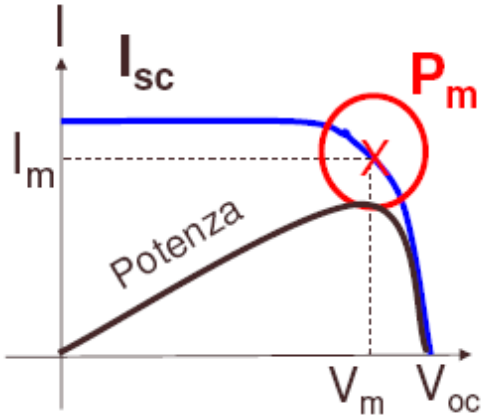


Conversion efficiency

η Is defined as:

$$\eta = P_{max} / P_{inc}$$

Where $P_{max} = I_m V_m$ maximum power given by the device P_{inc} incoming power, due to incoming radiation



The power give by the cell increases with voltage until the Pm point, aftewards decreases La potenza prodotta da una cella

Incoming power density depends also on the employed AM:

AM1.5 → 100 mW/cm^2

For silicon solar cells at 300K, recombination current can give rise to an efficiency reduction around 25%

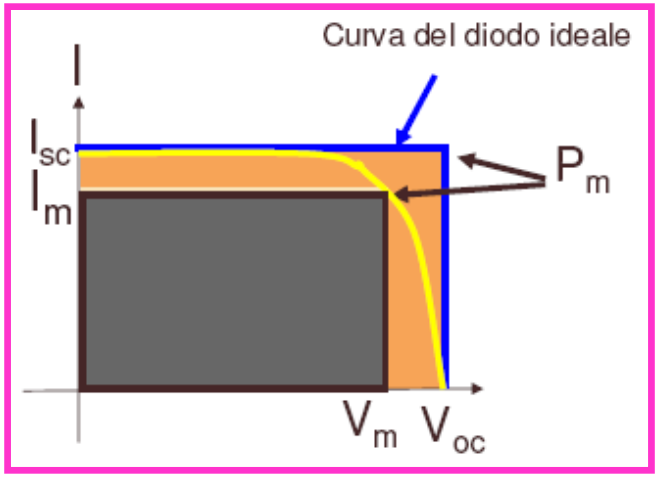
Fill Factor: FF

Ratio between the area given by the maximum power rectangle and the area of the rectangle given by V_{OC} and I_{SC}

$FF = I_m V_m / I_{SC} V_{OC}$

Conversion efficiency becomes:

$$\eta = I_{sc} V_{oc} FF / P_{inc}$$



The higher the FF the more the solar cell can be approximated to a constant current supply with the maximum given voltage. In other words, the higher is the produced power

Spectral response: SR

Conversione efficiency betwee incoming photons into current ***considering the dependance of*** Isc from incoming radiation (which varies with the wavelength)

$$SR(\lambda) = \frac{I_{SC}(\lambda)}{\phi(\lambda)}$$

where ϕ light intensity per Area (W/m^2), I_{SC} short circuit current

External Quantum Efficienvy: EQE

Percentage of incoming photons which are converted into electrons :

$$EQE = \frac{numero\ di\ elettroni\ nel\ circuito\ esterno}{numero\ di\ fotoni\ incidenti}$$

If the spectral response is known, EQE can be derived as follows, considering that Ep=hc/λ

$$EQE(\lambda) = SR(\lambda) \cdot \frac{hc}{q\lambda}$$

Organic Solar Cells (OSCs)

Organic Solar Cells (OSC)

The working principle is basically the same one
However there exist some differences in the photogeneration process and also charge carrier separation

Inorganic Solar Cells
The electron-hole pair in a photogenareìated exciton (Mott-Wannier exciton) is generally very small, in the range of **1 to 40 meV**

Organic Solar Cells
In this case the photogenerated escitons (Frenkel excitons) are bond together by a very stron interaction force, in the range of **100 meV÷300 meV** **(polymers or small molecules)**

Excitons in an OSC require a very **high electrical field** in order to get separated

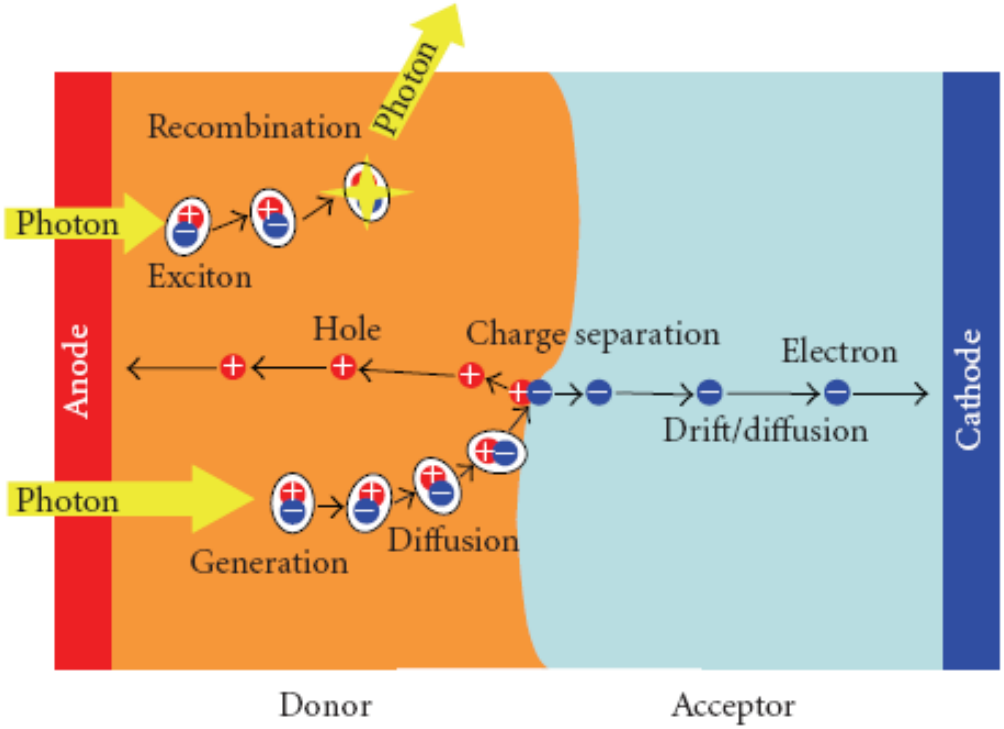
Such field can be localized in the **electrode/semiconductor** interface or in a **bulk heterojunction** between donor and acceptor materials

However, due to the very high concentration of trap sites, which is not the case in inorganic SCs, the **recombination** process is very active

Traps are energetic states within the band gap which allows adsorption and recombination at smalle energies compared to the material band gap.

Converzion steps and loss mechanisms

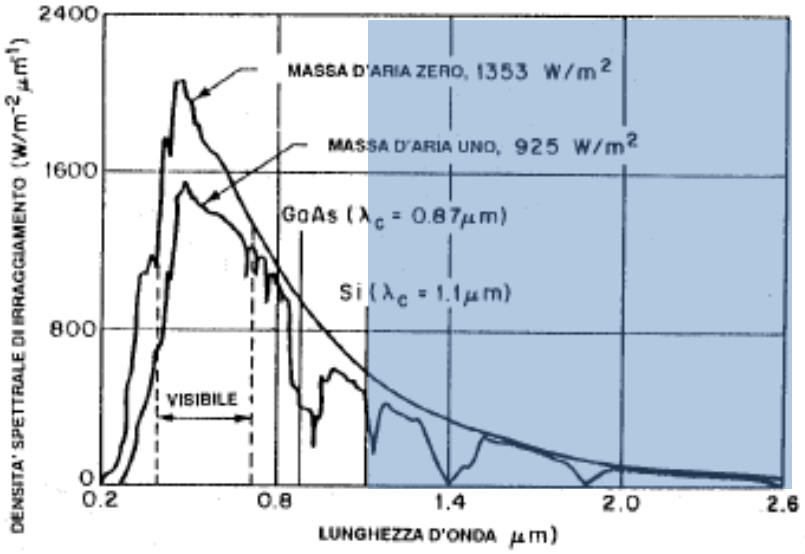
- Photon absorption
- Exciton diffusion
- Charge separation
- Charge transport
- Charge collection



$$\eta_{EQE}=\eta_A \cdot \eta_{ED} \cdot \eta_{CS} \cdot \eta_{CT} \cdot \eta_{CEx}$$

Photon absorption

In order to absorb the **77%** of the incoming solar radiation a semiconductor should have a **band gap in the range of 1.1 eV** (1100 nm) however the most of organic semiconductors have a band gap around **2.0 eV** (600 nm) therefore, the absorption is only around 30%



Exciton diffusion

The typical **diffusion length in a polymer or small molecule are very small** in the range 10-100nm

Imagine to have a dissociation center at a certain position, the photogenerated excitons shoud travel into the material in order to reach such point.
If the distance is much higher than the diffusion length, recombination process is highly probable, therefore **no charge collection** can be obtained

Materials thickness → in order to avoid charge recombination
Multilayer → for the phtogenarated carriers recombination must be energetically unfavourable

Charge separation

Holes and electrons in the exction must be separated → free charge carriers

The device should have some sort of disomogeneities required to produce a high field to allow charge separation

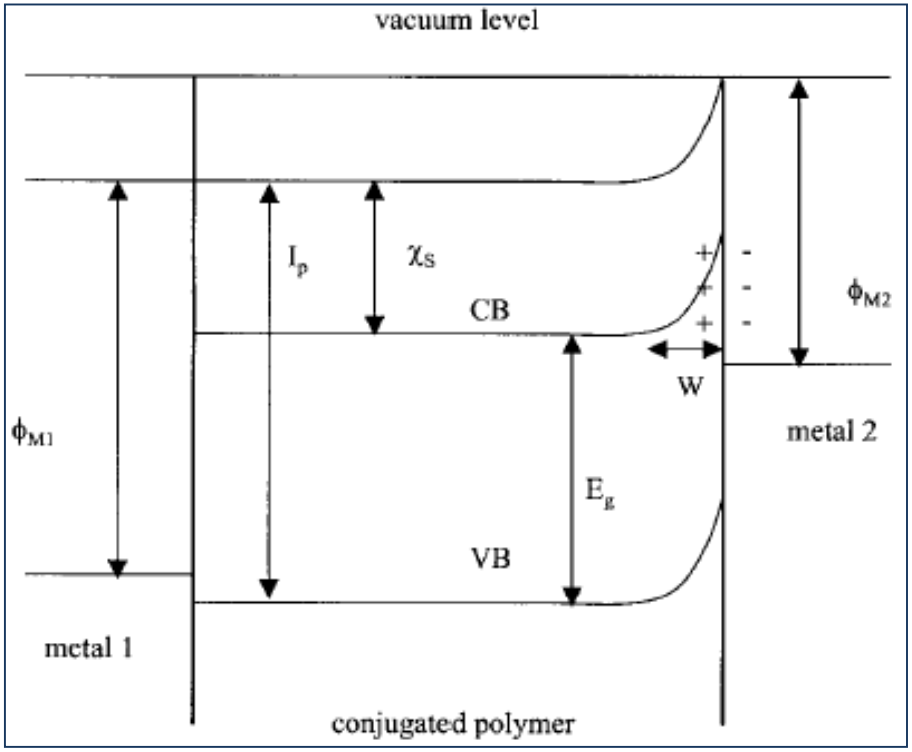
1) Metal/semiconductor interface
2) Organic Heterojunction

Charge separation happens at the very interface between donor and acceptor
Such interfacial area must be maximised!

Two ways to obtain a high electrical field:

Metal/semiconductor interface.

WF must be chosen in order to form a rectifying junction or Schottky diode



Mott Schottky

n tyoe:

rectifying

$q\phi_M > q\phi_{SC}$

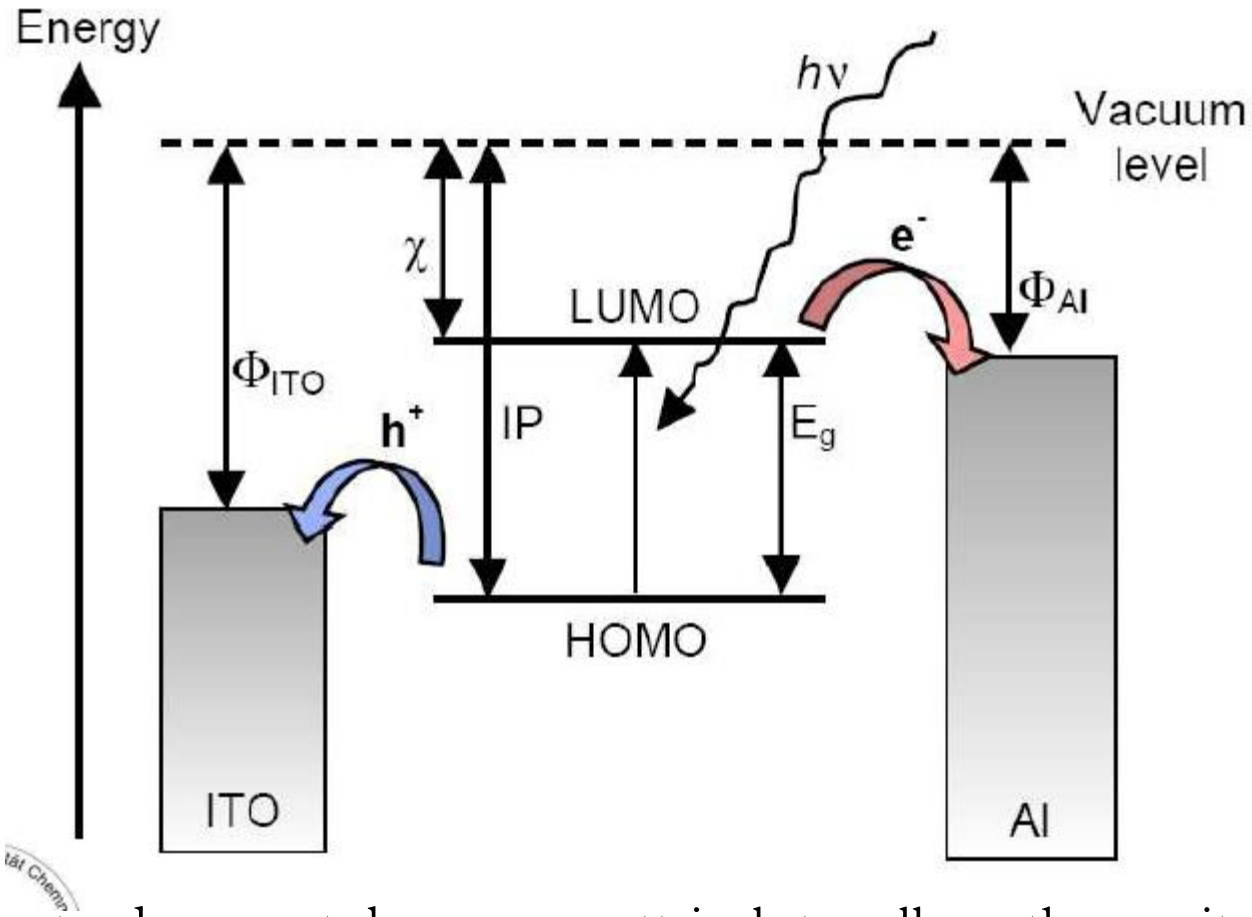
ϕ_{SC} *semiconductor WF*

Ohmic contact

$q\phi_M < q\phi_{SC}$

In the case of a p type semiconductor the conditions are the opposite $q\phi_M < q\phi_{SC}$, rectification, for $q\phi_M > q\phi_{SC}$ ohmic

Charge separation



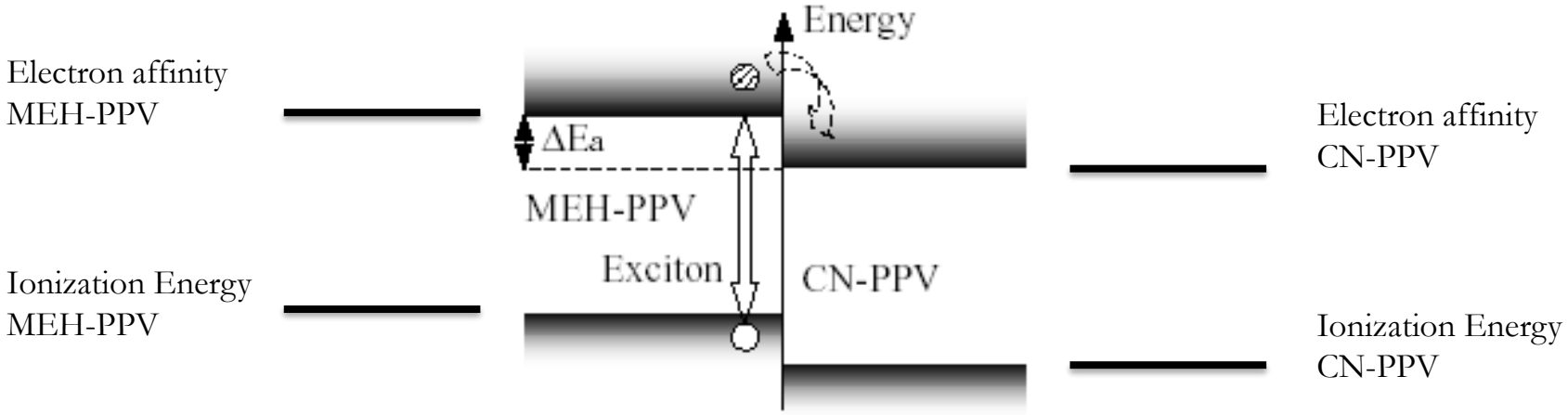
The electrodes must be asymmettrical to allow the exciton to get separated

In this case holes see a hige barrier with Al, whereas electrons do not and voiceversa with ITO

Electron extraction from Al, holes extraction from ITO

Charge separation

The same behavior can be obtained by using an heterojunction , the two materials should have a sufficiently high difference in their electron affinity and ionization potential (AE) (IP). The lower IP material can act as p-type material, electron donor, and the higher AE as n-type, electron acceptor.



If ΔEa is sufficiently high for the electrons is energetically favourable to jump into the higher EA material, in this case CN-PPV, on the contrary, holes see an energetic barrier, therefore they will stay in the MEH-PPV.
The dissociated electron in the CN-PPV sees an energetic barrier towards the MEH-PPV → it cannot come back!!! NO RECOMBINATION
MEH-PPV electron donor, CN-PPV electron acceptor

Charge Transport

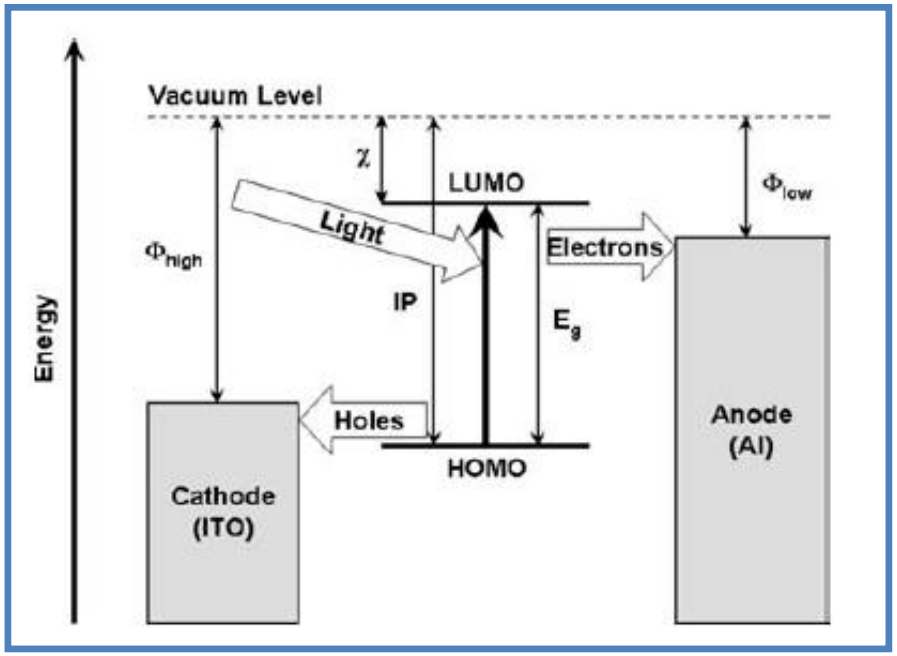
Charge carriers, after dissociation, have to reach the electrodes, hopefully before recombination happens, so that they are available to supply current to a certain load

1) N.B. charge trasport is always dominated by the presence of trap sites due to impurities or defects
2) L_D small in organic semiconductors!

Charge transport mechanism → hopping
Charge transport is perpendicular to the device surface, vertical!

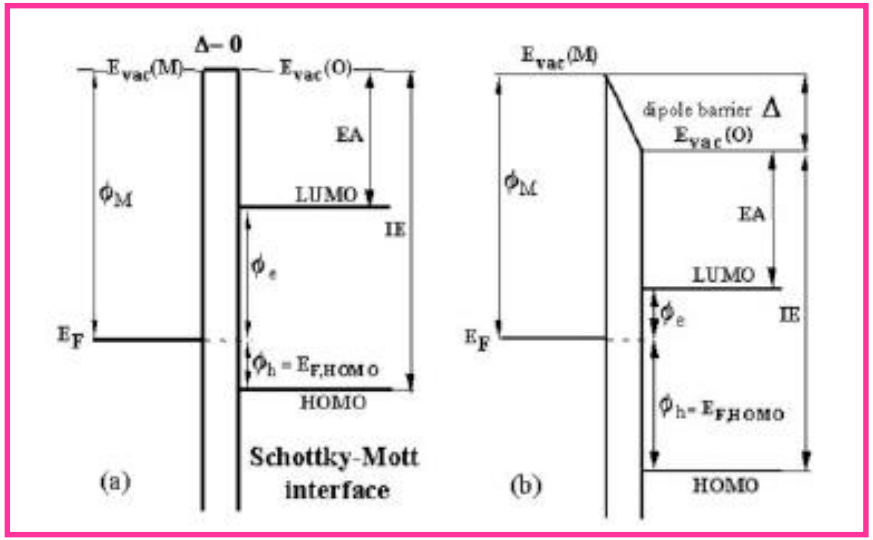
Moprhology must be optimized in order to get the higher mobility in the vertical direction
Structure msu be optimized in order to maximize charge separation and transport

Charge extraction



Organic/semiconductor interface!

We already discussed about this interface



Structures for OSCs

Single layer cell

The OSC is made by employing a single organic semiconductor layer

Holes are generally collected through a high WF, trasnparent material, typically Pedot or ITO (Cathode) whereas electrons are collected by means of a low WF material Alluminum or Calcium (Anode)

In this case we need a Schottky diode as the only way to separate charges is to have a rectifying interface

L_D small in organic

In order to have a good absorption we need thicknesses in the range of 100nm

High recombination rate

Structure for OSCs

Double layer cell

In this case the active layer is made by the deposition of two different films, typically one with low IE and one with a higher IE

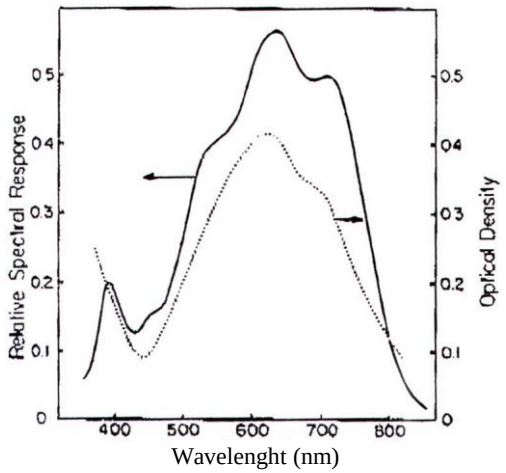
- The enrgetic difference between IE and EA must be sufficiently high to allow charge separation and avid recombination
- The two materials must have a complementary absorption spectrum, in order to maximise the photogeneration of excitons

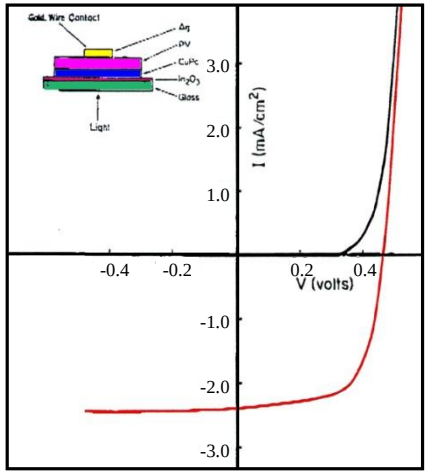
It can be done in two ways

- Thermal deposition of two small molecules films
- Deposition of two layers of solution processable materials (orthogonal solvent!!)

Structures per OSCs: Double Layer

This approach is preferrable because it minimized recombination issues, once the exciton is separated is very difficult for charges to come back in the previous material





Spettro di assorbimento di un film bi-layer CuPc/PV e risposta spettrale di una cella ITO/CuPc (250 Å)/PV (450 Å)/Ag;

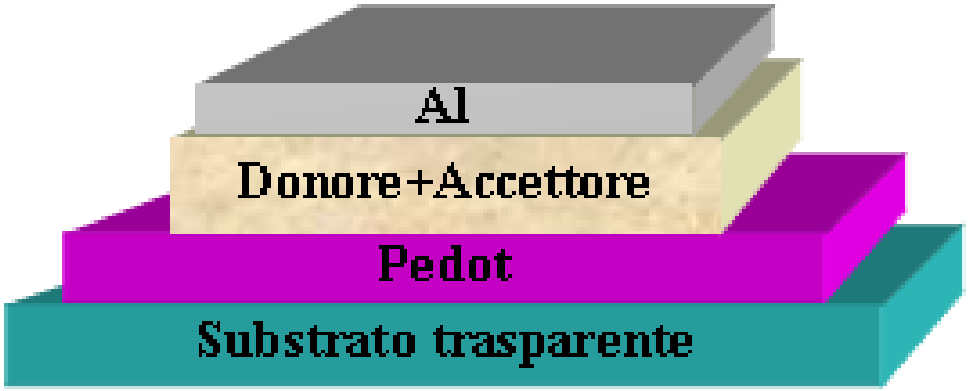
Caratteristica I-V della stessa cella con area uguale a 0,1 cm^2. La curva alla luce (in rosso) è stata ottenuta in condizioni di AM2 (75 mW/cm^2). Il Fill Factor è di 0,65 mentre il rendimento è pari a 0,95%

Structures per OSCs

Bulk heterojunctions

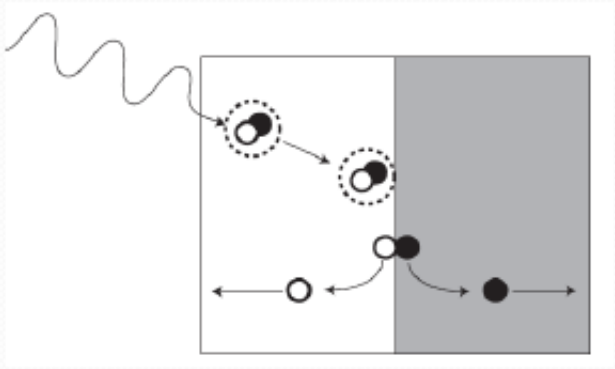
In this case the active layer is one, but it is composed by two materials with differen Ies and Eas. Such mixed layer can be obtained in two ways

- Coevaporation of the two molecules
- Blend of two solution processable molecules (same solvent)

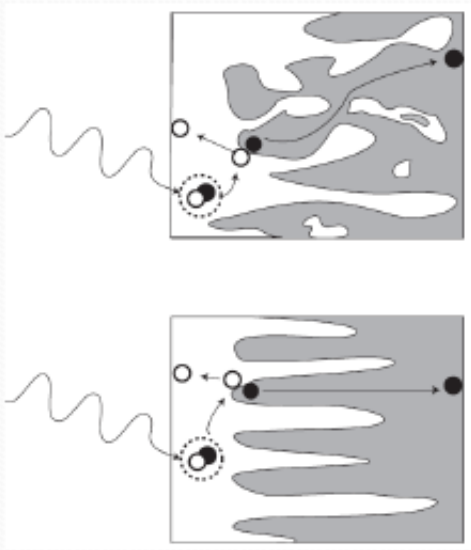


Structures for OSCs: bulk heterojunctions

- Limited exciton diffusion length
  - "Bulk heterojunction" concept



F. Yang, et. al. *Nature Materials* 4 (2005)



Maximise the interface

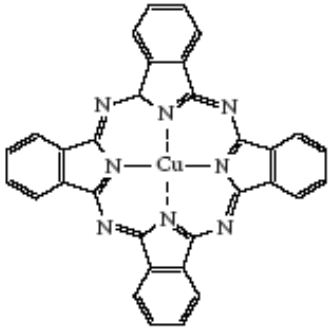
Phase separation of the two materials

increases junction area

Good domains interconnection

Maximize charge transport

Polymers or small molecules?

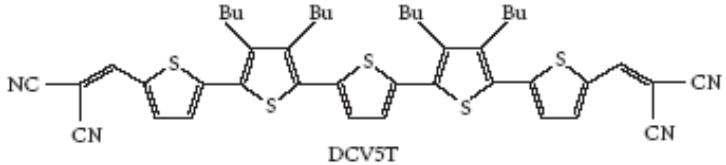


CuPc

(a)

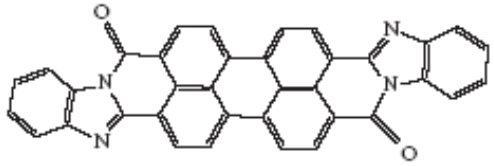
C60

(b)



DCV5T

(c)

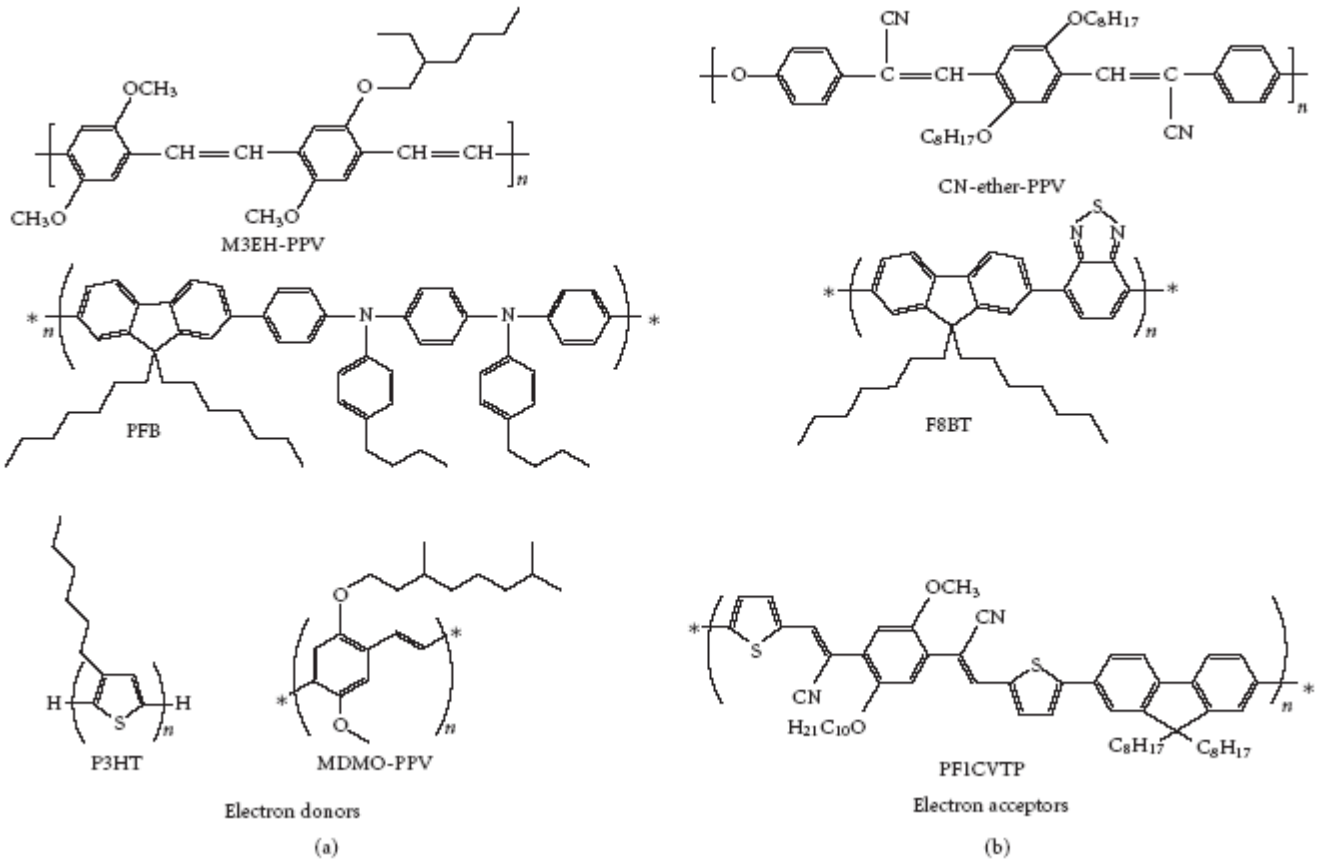


PTCBI

(d)

Esempio delle **small molecules** più utilizzate per la realizzazione di OSCs sia single che double layer

Polymers or small molecules?



Esempio polimeri organici coniugati più utilizzati per la realizzazione di OSCs sia single che double layer

Polymers or small molecules?

Table 1: Best in class solar cells: small molecule-based solar cells.

Donor	Acceptor	η	V_{oc}	FF	IPCE	Reference
CuPc	C60	5.7%	1.0 V	59%	NA	Xue et al. [4]
CuPc	C60	5.0%	0.6 V	60%	64%	Xue et al. [6]
MeO-TPD, ZnPc (stacked)	C60	3.8%	1.0 V	47%	NA	Drechsel et al. [51]
CuPc	C60	3.5%	0.5 V	46%	NA	Uchida et al. [46]
DCV5T	C60	3.4%	1.0 V	49%	52%	Schulze et al. [49]
CuPc	PTCBI	2.7%	0.5 V	58%	NA	Yang et al. [44, 45]
SubPc	C60	2.1%	1.0 V	57%	NA	Mutolo et al. [47]
MeO-TPD, ZnPc	C60	2.1%	0.5 V	37%	NA	Drechsel et al. [51]
TDCV-TPA	C60	1.9%	1.2 V	28%	NA	Cravino et al. [50]
Pentacene on PET	C60	1.6%	0.3 V	48%	30%	Pandey and Nunzi [52]
SnPc	C60	1.0%	0.4 V	50%	21%	Rand et al. [48]

Table 3: Best in class solar cells: polymer-polymer (bilayer) solar cells.

Donor	Acceptor	η	V_{oc}	FF	IPCE	Reference
PPV	BBL	1.5%	1.1 V	50%	62%	Alam and Jenekhe [96]
MDMO-PPV:PF1CVTP	PF1CVTP	1.4%	1.4 V	34%	52%	Koetse et al. [95]
M3EH-PPV	CN-Ether-PPV	1.3%	1.3 V	31%	29%	Kietzke et al. [97]
MEH-PPV	BBL	1.1%	0.9 V	47%	52%	Alam and Jenekhe [96]
M3EH-PPV	CN-PPV-PPE	0.6%	1.5 V	23%	23%	Kietzke et al. [97]

Polymers or small molecules?

Table 2: Best in class solar cells: polymer-polymer (blend) solar cells.

Donor	Acceptor	η	V_{oc}	FF	IPCE	Reference
M3EH-PPV	CN-Ether-PPV	1.7%	1.4 V	35%	31%	Kietzke et al. [92]
MDMO-PPV	PF1CVTP	1.5%	1.4 V	37%	42%	Koetse et al. [95]
M3EH-PPV	CN-Ether-PPV	1.0%	1.0 V	25%	24%	Breeze et al. [12]

Table 3: Best in class solar cells: polymer-polymer (bilayer) solar cells.

Donor	Acceptor	η	V_{oc}	FF	IPCE	Reference
PPV	BBL	1.5%	1.1 V	50%	62%	Alam and Jenekhe [96]
MDMO-PPV:PF1CVTP	PF1CVTP	1.4%	1.4 V	34%	52%	Koetse et al. [95]
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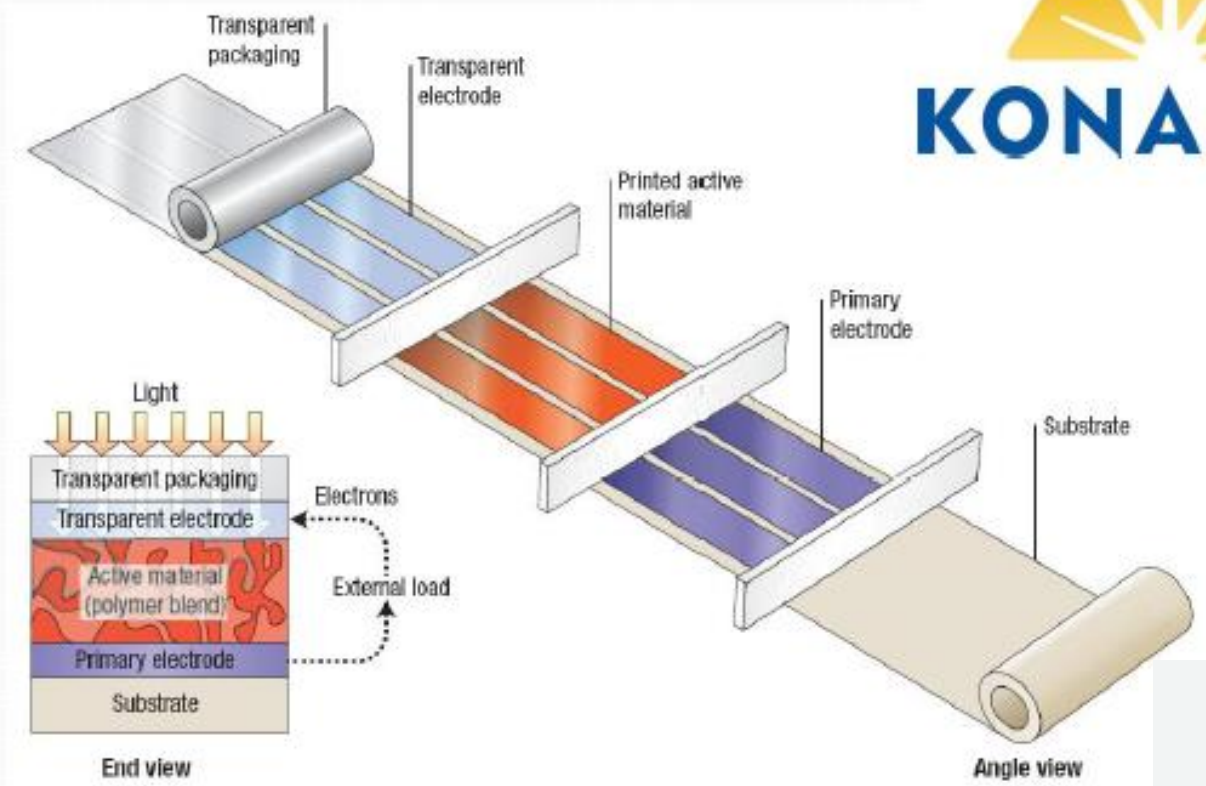
MEH-PPV	BBL	1.1%	0.9 V	47%	52%	Alam and Jenekhe [96]
M3EH-PPV	CN-PPV-PPE	0.6%	1.5 V	23%	23%	Kietzke et al. [97]

Table 4: Best in class solar cells: blends of polymers and fullerene derivatives.

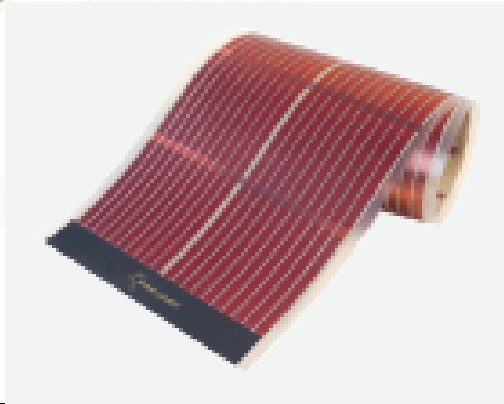
Donor	Acceptor	η	V_{oc}	FF	IPCE	Reference
P3HT	PCBM	5.0%	0.6 V	68%	NA	Ma et al. [114]
P3HT	PCBM	4.9%	0.6 V	54%	NA	Reyes-Reyes et al. [5]
P3HT	PCBM	4.4%	0.9 V	67%	63%	Li et al. [115]
MDMO-PPV	$PC_{71}BM$	3.0%	0.8 V	51%	66%	Wienk et al. [17]
MDMO-PPV on PET	PCBM	3.0%	0.8 V	49%	NA	Al-Ibrahim et al. [116]

Commercialization

KONARKA®



R. Gaudiana, C.J. Brabec. *Nature Photonics* 2 (2008)



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The Challenge: Reinvent the traditional transit shelter to take advantage of solar power.

The Solution: Create a next-generation transit shelter that is both environmentally innovative and aesthetically pleasing.

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