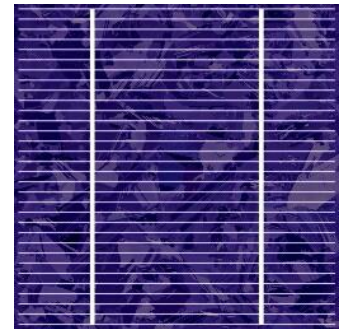


# Photovoltaic junctions



# Overview

- Theoretical background
- Main idea
- Driving forces
- Junctions
- Surfaces and interfaces
- The p-n homojunction

# Approach

- This lecture
  - Analysis of spatial energy band diagrams
  - Little mathematical formalism
  - Overview of function of main junctions
- Next lecture
  - Detailed derivation of the I-V characteristics of a semiconductor homojunction solar cell
    1. Ideal, infinite diode/"solar cell"
    2. Finite diode/solar cell with recombination

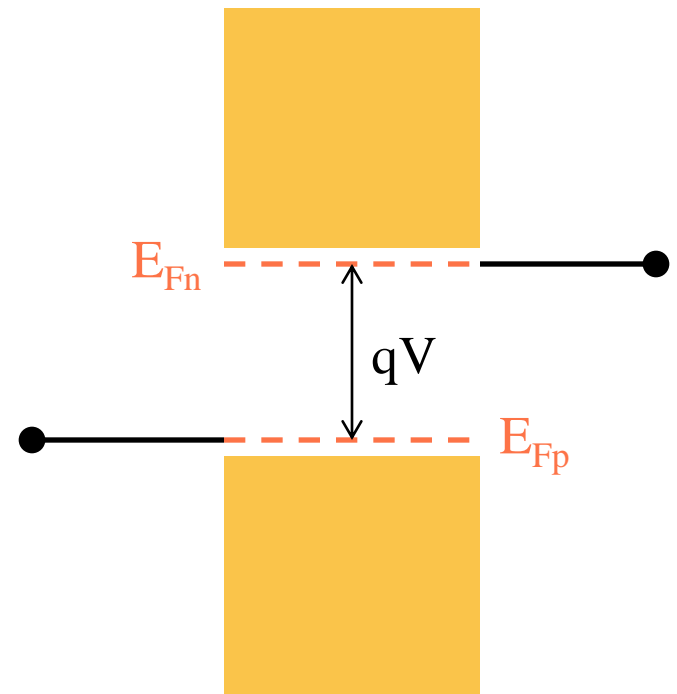
# Theoretical background

# Theoretical background

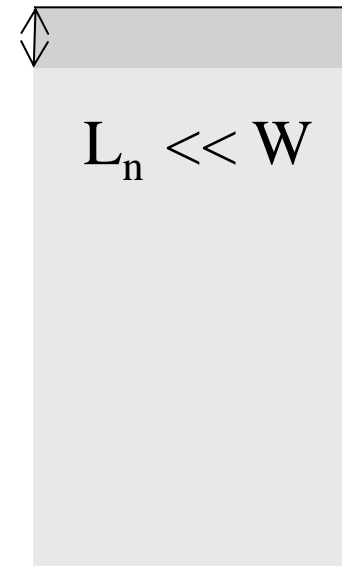
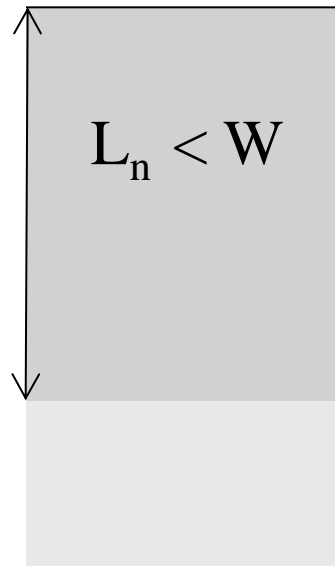
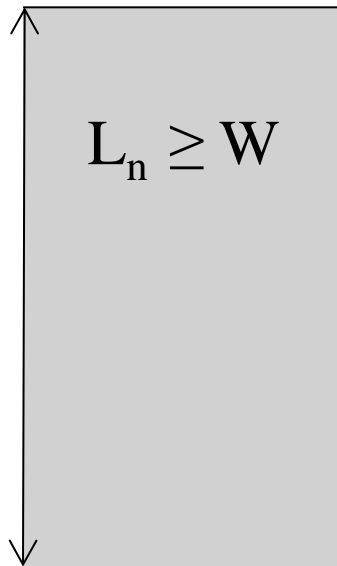
- Available voltage:  $qV = E_{Fn} - E_{Fp}$ 
  - Difference between quasi Fermi levels at points of contact
- A gradient in quasi Fermi levels required for net current

$$J_{TOT} = \mu_n n \nabla E_{Fn} + \mu_p p \nabla E_{Fp}$$

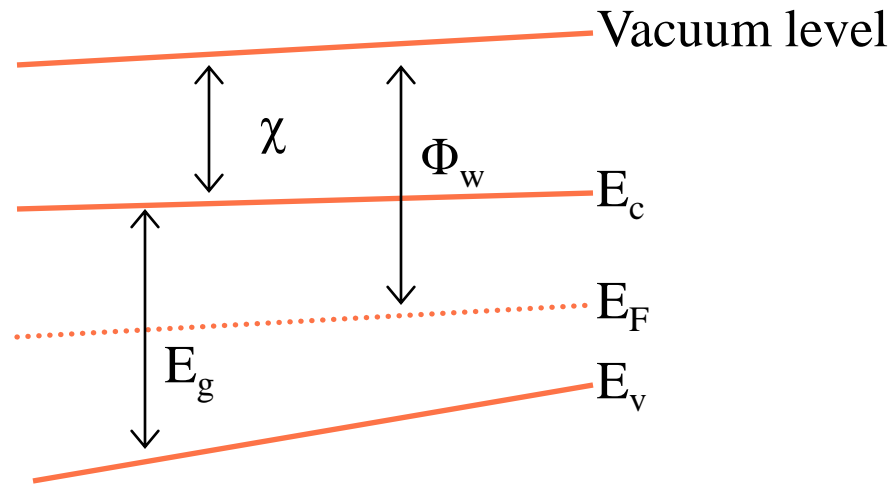
- A mechanism for charge separation can be provided in many ways



# Reminder: the importance of diffusion length



# Theoretical background



$\chi$  = electron affinity  
 $E_g$  = band gap energy  
 $E_F$  = Fermi level

$E_c$  = conduction band energy  
 $E_v$  = valence band energy  
 $\Phi_w$  = work function

# Transport

Total current density:

$$J_{\text{TOT}} = J_n + J_p$$

$$J_{\text{TOT}} = \mu_n n \nabla E_{Fn} + \mu_p p \nabla E_{Fp}$$

Electron current density:

$$J_n = \underbrace{+ q D_n \nabla \delta n}_{\text{DIFFUSION}} + \underbrace{\mu_n \delta n [qE - \nabla \chi - kT \nabla \ln(N_c)]}_{\text{DRIFT}}$$

Hole current density:

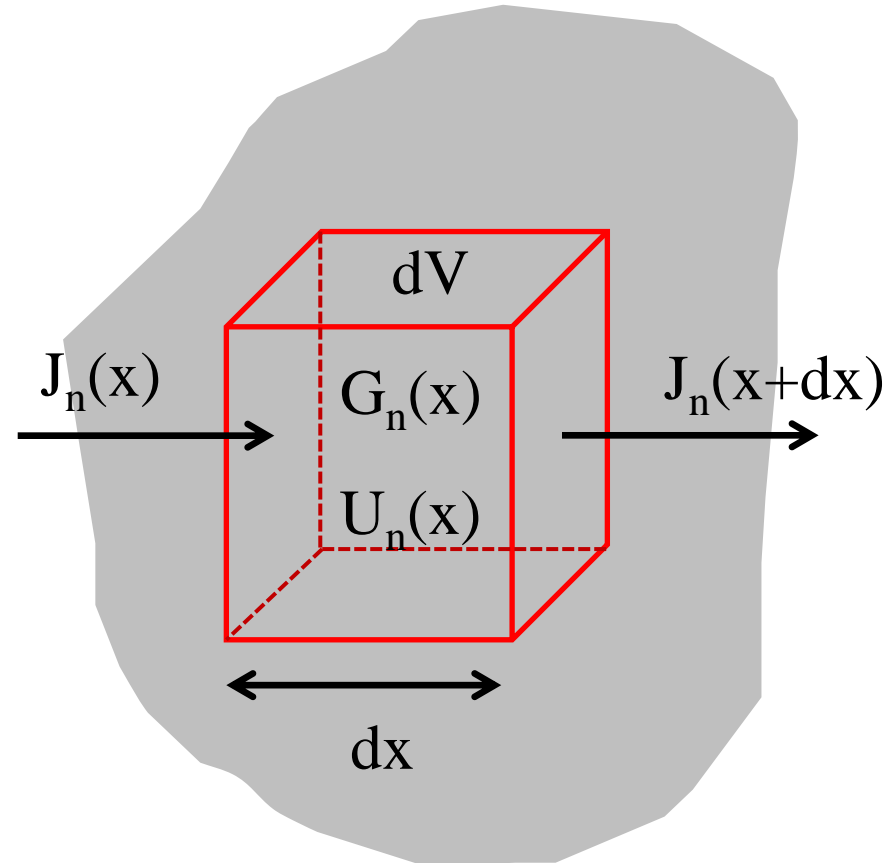
$$J_p = - q D_p \nabla \delta n + \mu_p \delta n [qE - \nabla \chi - \nabla E_g + kT \nabla \ln(N_c)]$$

- A net current density can be obtained in many ways!



# Transport in semiconductors

- Solar cell device operation:
  1. The number of charge carriers must be conserved
  2. The electrostatic potential  $\phi(x)$  obeys Poisson's equation



$$\delta n / \delta t = 1/q \cdot \delta / \delta x (J_n(x)) + G_n(x) - U_n(x)$$

# Transport in steady state

$$\delta n / \delta t = 1/q \cdot \delta / \delta x (J_n(x)) + G_n(x) - U_n(x) = 0$$

$$\delta p / \delta t = 1/q \cdot \delta / \delta x (J_p(x)) + G_p(x) - U_p(x) = 0$$

$$(\delta / \delta x)^2 \varphi(x) = (q / \epsilon_0 \epsilon_s) (-Q_{\text{fixed}} + n - p)$$

# The transport problem

Electrons in the (neutral) p-region:

$$(\delta^2/\delta x^2)n + (qE/kT)(\delta/\delta x)n + G_n(x)/D_n - U_n(x)/D_n = 0$$

Holes in the (neutral) n-region:

$$(\delta^2/\delta x^2)p + (qE/kT)(\delta/\delta x)p + G_p(x)/D_p - U_p(x)/D_p = 0$$

$$L_n^2 = \tau_n D_n$$

Electrons in the (neutral) p-region:

$$(\delta^2/\delta x^2)n + (qE/kT)(\delta/\delta x)n + G_n(x)/D_n - (n - n_0)/L_n^2 = 0$$

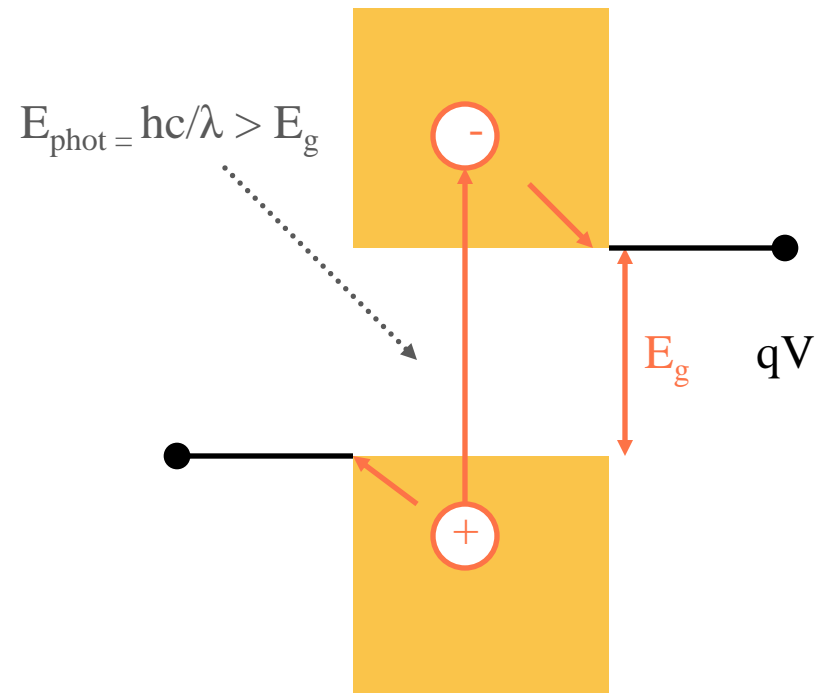
Holes in the (neutral) n-region:

$$(\delta^2/\delta x^2)p + (qE/kT)(\delta/\delta x)p + G_p(x)/D_p - (p - p_0)/L_p^2 = 0$$

Main idea

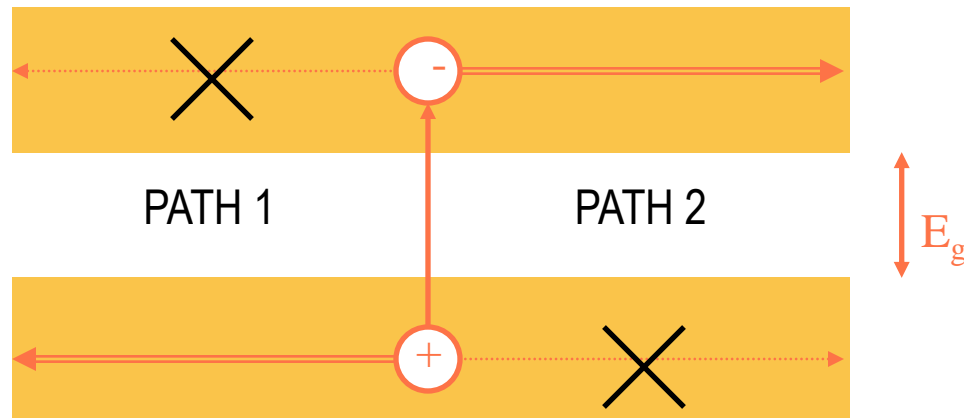
# Main idea

- The junction is responsible for supplying a driving force for the photocurrent in a solar cell
- It is worth recalling that we want to be able to collect excited  $h^+$  and  $e^-$  at separate contacts while maintaining as big a voltage difference as possible between the contacts



# Main idea

- Alternative picture: the light absorbing material is connected to the external circuit through two paths of different resistance
  - Path 1: low resistance for  $h^+$  , high resistance for  $e^-$
  - Path 2: low resistance for  $e^-$  , high resistance for  $h^+$



# Driving forces



# Diffusive current

$$J_{\text{diff}} = q D_n \nabla \delta n - q D_p \nabla \delta n$$

- Carrier concentration gradients result from gradients in carrier generation or carrier removal (recombination, extraction) rates
- A solar cell driven only by diffusivity can only yield net current under steady-state conditions if diffusivities are different
  - The so-called Dember effect
  - The Dember effect is usually not strong enough for useful exploitation in photovoltaics

# Electrostatic fields and band bending

- An electrostatic field will, due to Poisson's equation, lead to a redistribution of charge around the junction

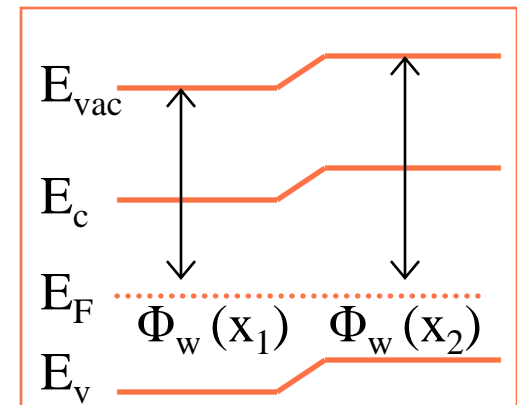
$$dE(x)/dx = q\rho(x)/\epsilon_s$$

- A redistribution of charge manifests itself in the relative positions of the bands and the Fermi level in a spatial band diagram
  - Band bending
- In the following, this will be illustrated for a range of junctions

# Work functions and electric fields

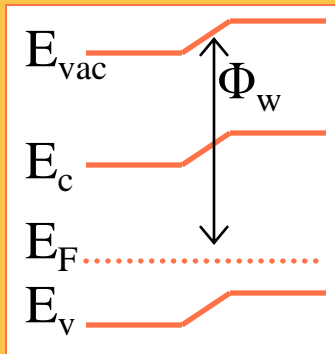
- The work function ( $\Phi_w$ ) of a material is the potential required to remove the least tightly bound electron from the material
  - $\Phi_w = E_{\text{vac}} - E_F$
  - In metals:  $\Phi_w = \chi$
  - Spatial variations in  $\Phi_w$  give spatial variations in  $E_{\text{vac}}$ , which correspond to an electrostatic field  $E$

$$q \int_{x_1}^{x_2} E \, dx = \Phi_w(x_1) - \Phi_w(x_2)$$



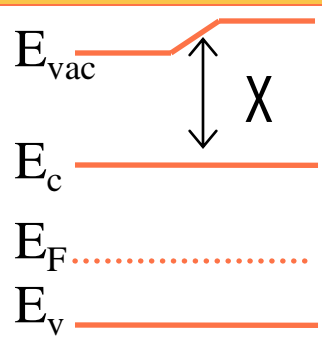
# Drift currents

$\Phi_w$



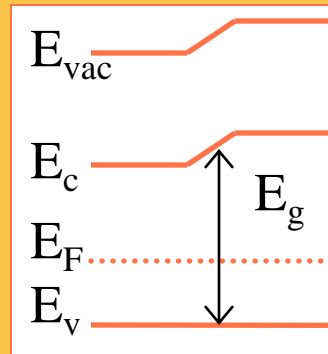
- Gives a built-in E
- Realization
  - Doping
  - Heterojunc.

$\chi$



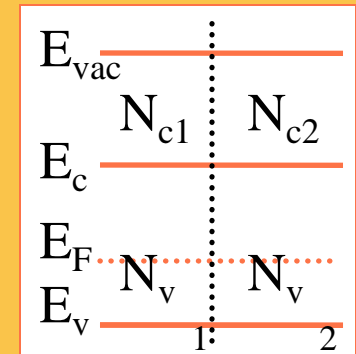
- Gives an effective E
- Realization
  - Heterojunc

$E_g$



- Gives an effective E
- Realization
  - Heterojunc

$N_{c,v}$



- Gives an effective E
- Realization
  - Heterojunc

# Junctions

# Junctions

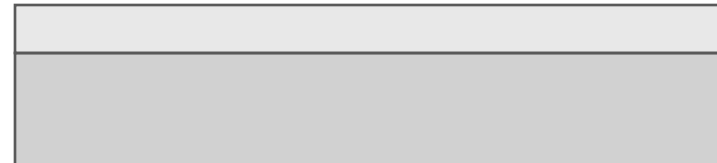
- Homojunctions

- Exploits work function gradients
- One material
- Made by doping



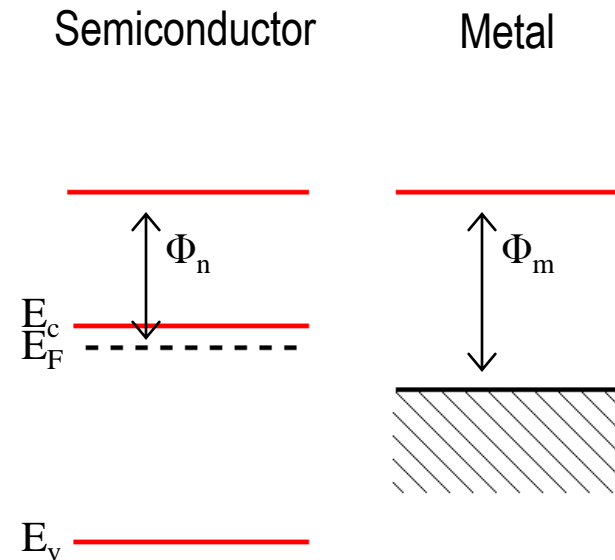
- Heterojunctions

- Can utilize any term in  $\nabla E_{Fp,n}$
- Two materials
  - Metal-semiconductor junctions
  - Semiconductor heterojunctions
  - Electrochemical junctions
  - Junctions in organic materials
  - (Surfaces and interfaces)
- Metallurgical interface



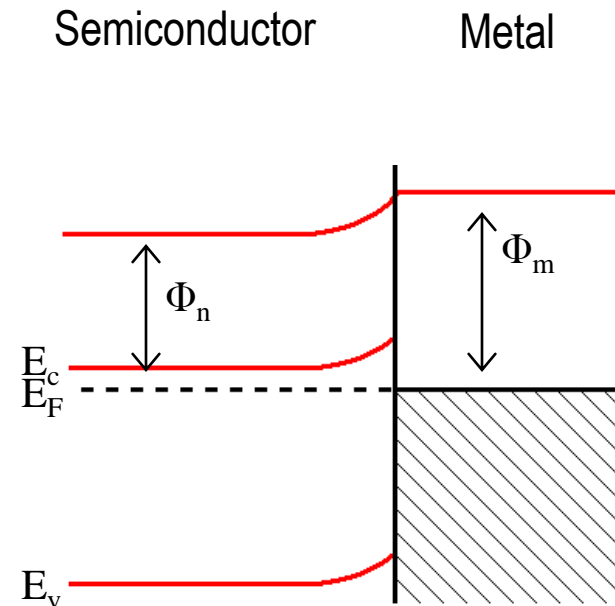
# The metal – semiconductor junction

- Spatial band diagram of junction depends on work function differences
- Example:
  - n-type semiconductor
  - $\Phi_n < \Phi_m$
- When brought in contact, Fermi levels must align in equilibrium!



# The metal – semiconductor junction

- A result of the aligning of Fermi levels is that the vacuum level changes by  $(\Phi_m - \Phi_n)$ 
  - Band bending arises
  - An electrostatic field is established close to the junction
- We assume that no bending occurs within the metal
  - Perfectly conducting metal



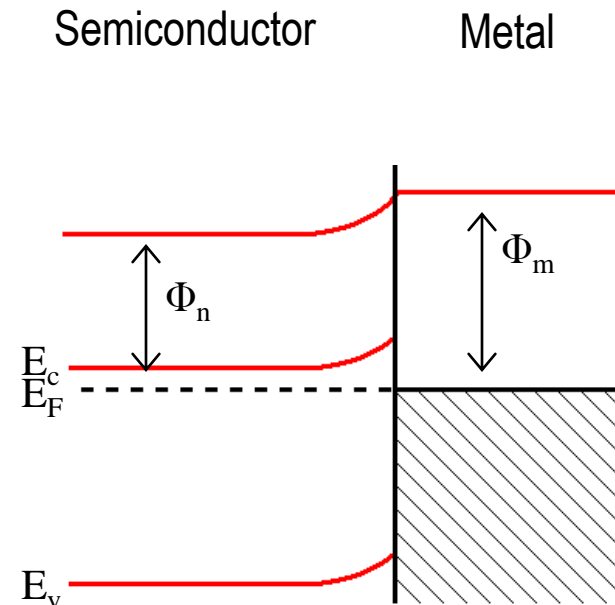


# The metal – semiconductor junction

- Far from the junction,  $n$  and  $p$  will have equilibrium values in the semiconductor
  - $n \sim N_d$
  - $p \sim n_i^2/N_d$
- What happens close to the junction?
  - Electrons flow from the n-type semiconductor into the metal until new equilibrium state is reached

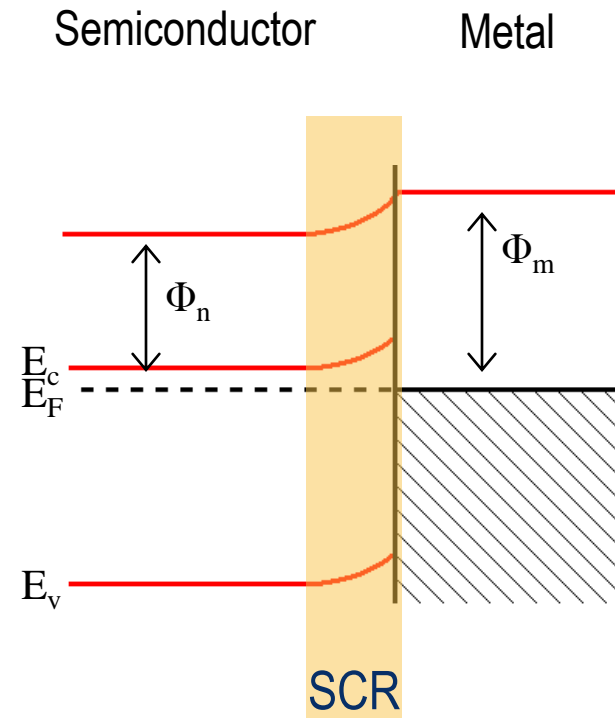
$$n = N_c e^{-(E_c - E_F)/kT}$$

- The material becomes less n-type as we approach the junction



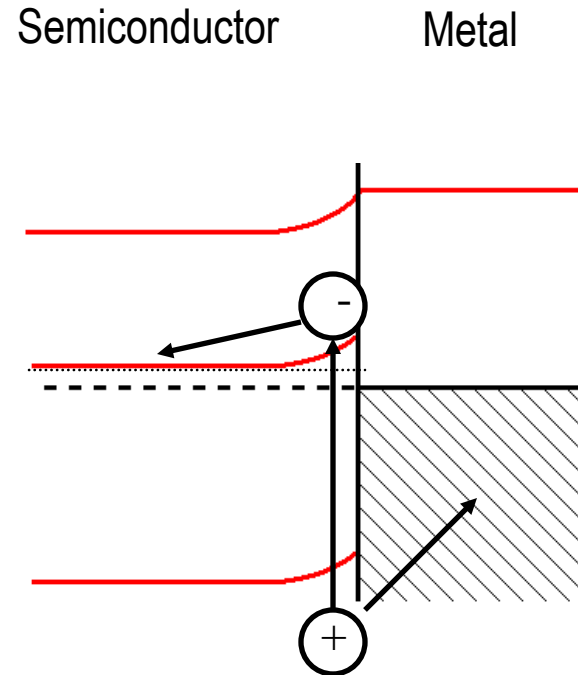
# The metal – semiconductor junction

- Close to the junction, we get many fewer mobile electrons but only a few more mobile holes
- We can assume that the region is more or less depleted of charge carriers
- A so-called space charge region (SCR) is formed
  - Depleted of carriers
  - Also called depletion region



# The illuminated junction

- The SCR separates photogenerated electrons and holes
  - Electrons will accumulate in semiconductor
  - Holes will accumulate in metal

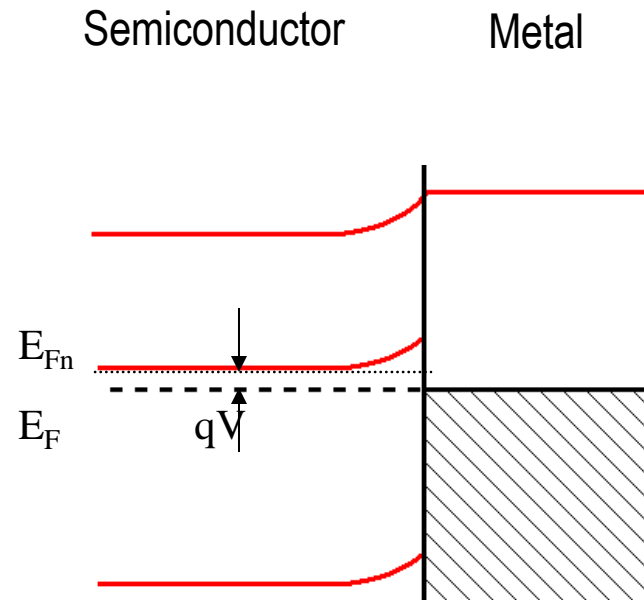


# The illuminated junction

- The semiconductor becomes negatively charged
  - Quasi Fermi level for electrons under illumination higher than Fermi level of semiconductor
  - The potential difference is often called the **photovoltage** (V)

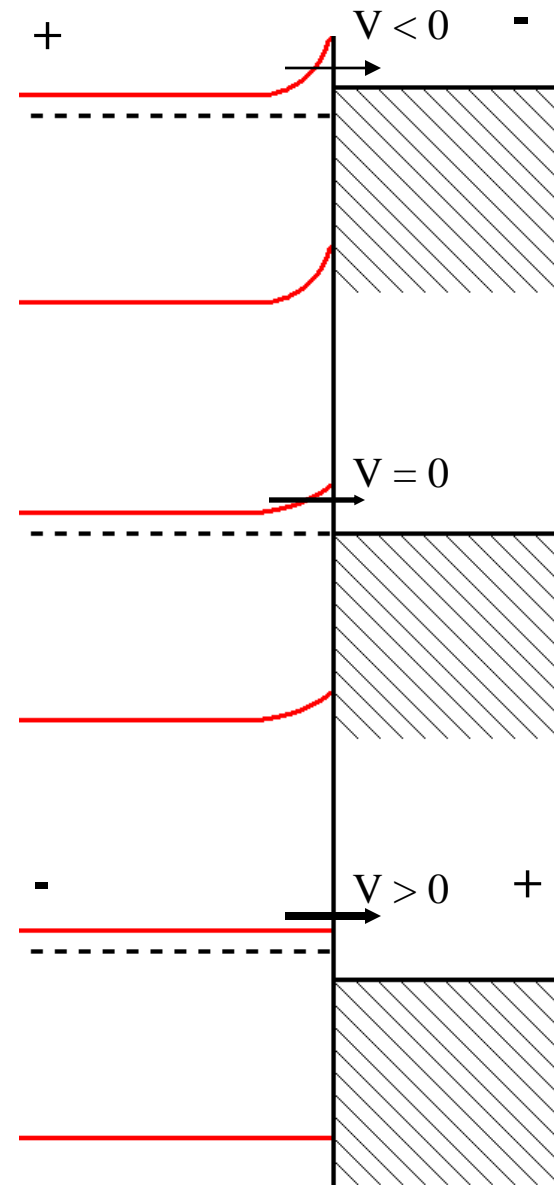
$$qV = E_{Fn} - E_F$$

- The ability to sustain a difference in quasi Fermi levels under illumination is the key requirement to photovoltaic energy conversion!

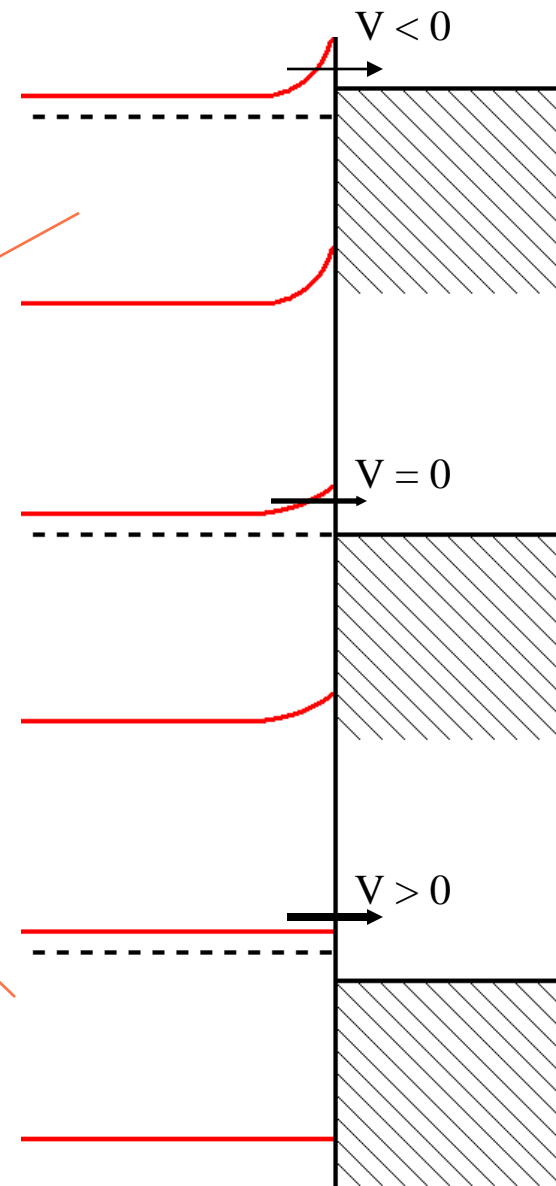
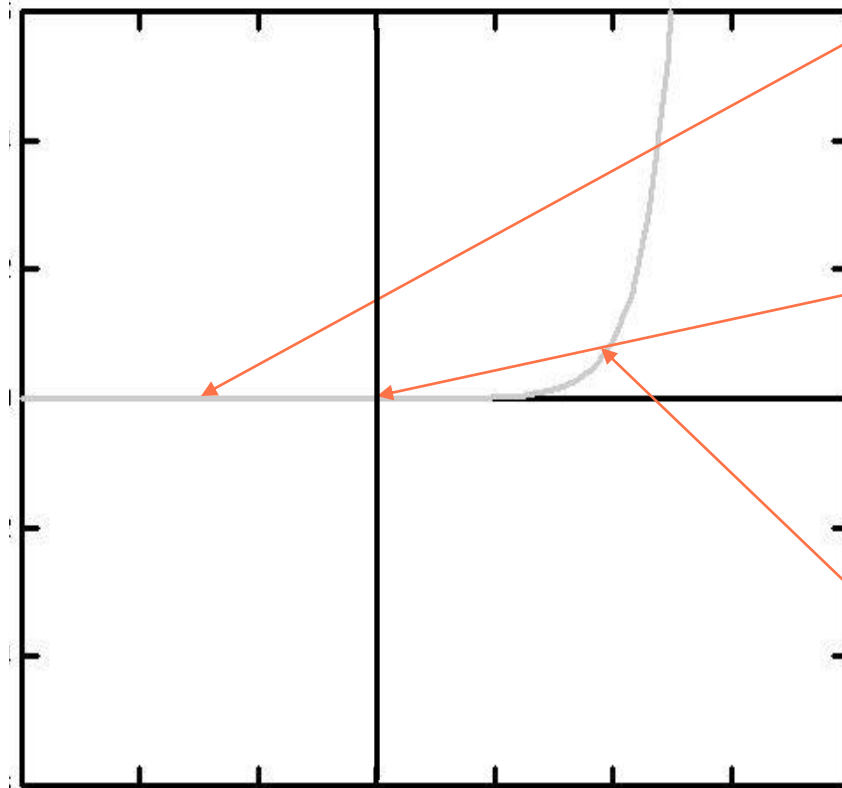


# I-V curve

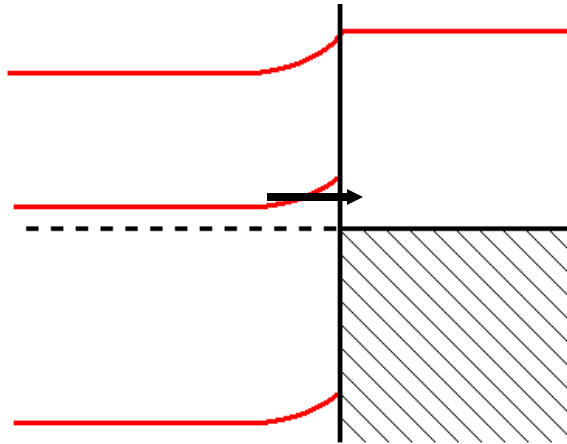
- The current in an n-type semiconductor is almost purely electron current
  - **Majority carrier device**
- The current density is regulated by the voltage
  - Reverse bias ( $V < 0$ ): barrier increased
  - Forward bias ( $V > 0$ ): barrier lowered
- Rectifying junction
  - Junction resistance strongly dependent on applied voltage
  - Often called a Schottky barrier junction
- Analogous for a p-type semiconductor



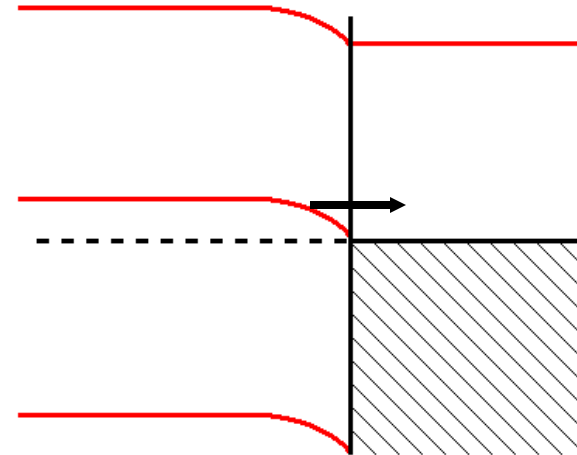
# I-V curve



# Schottky diodes and Ohmic contacts



- Example: n-type semiconductor
  - $\Phi_m > \Phi_n$
  - Barrier to electron flow
  - Rectifying contact



- Example: n-type semiconductor
  - $\Phi_m < \Phi_n$
  - No barrier to electron flow
  - Ohmic contact

# The Schottky diode as a solar cell

- The very first solar cells were Schottky junction devices
- There are several limitations to the usefulness of this type of junctions in solar cells
  - Limited obtainable photovoltage
    - $qV < E_g/2$
    - Inversion gives accumulation of charge carriers at the junction
  - Limited SCR width (W)
  - Interface states will be generated
  - A limited choice of materials

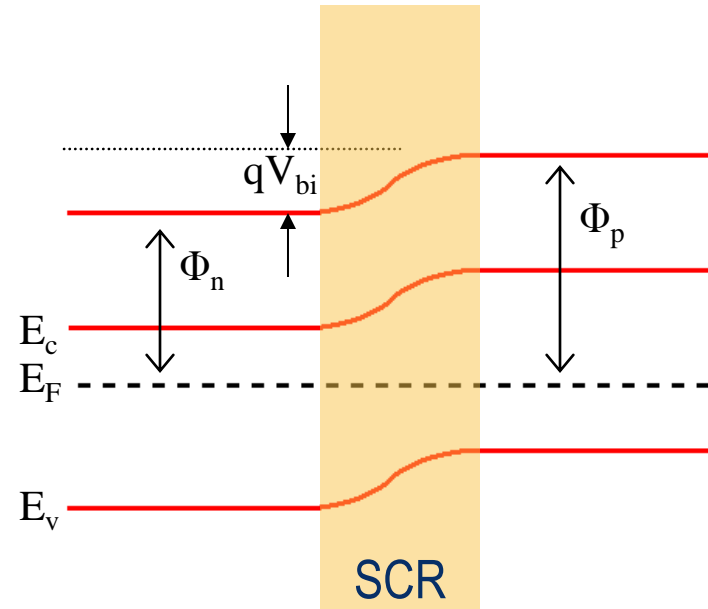


# The p-n homojunction

- The most common junction for use in solar cells by far
- By combining n- and p-type semiconductors, a built-in voltage ( $V_{bi}$ ) and a corresponding  $E$  is obtained
  - In equilibrium:

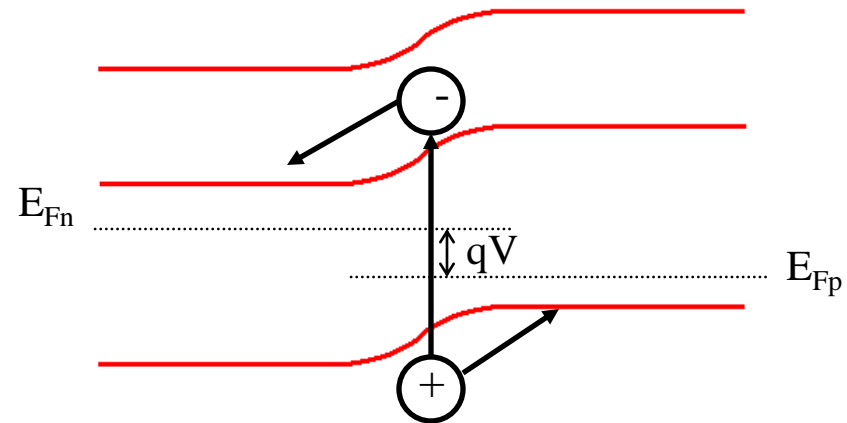
$$qV_{bi} = \Phi_p - \Phi_n$$

- Note, this spatial band diagram corresponds to a short-circuit condition!

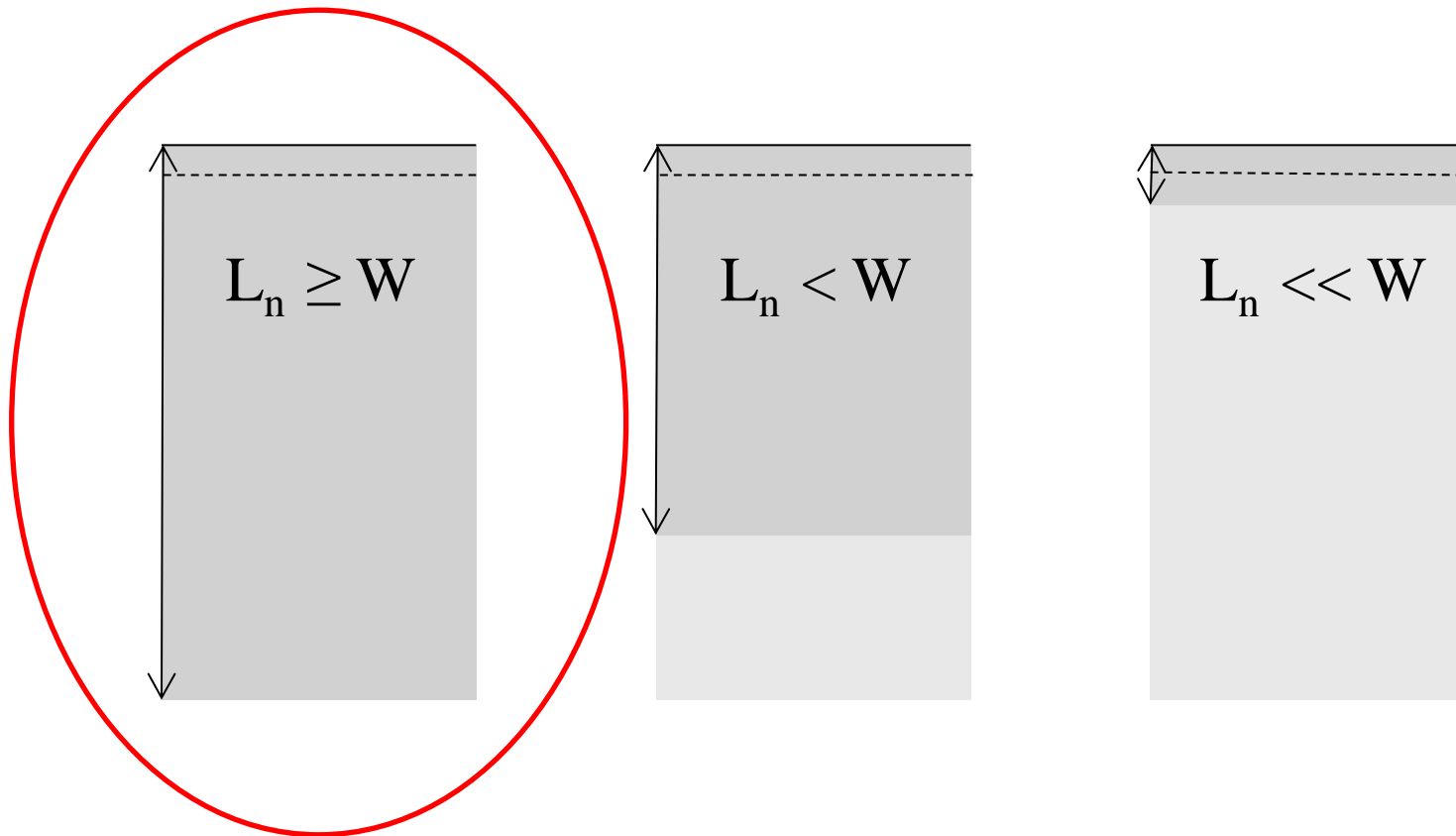


# The p-n homojunction

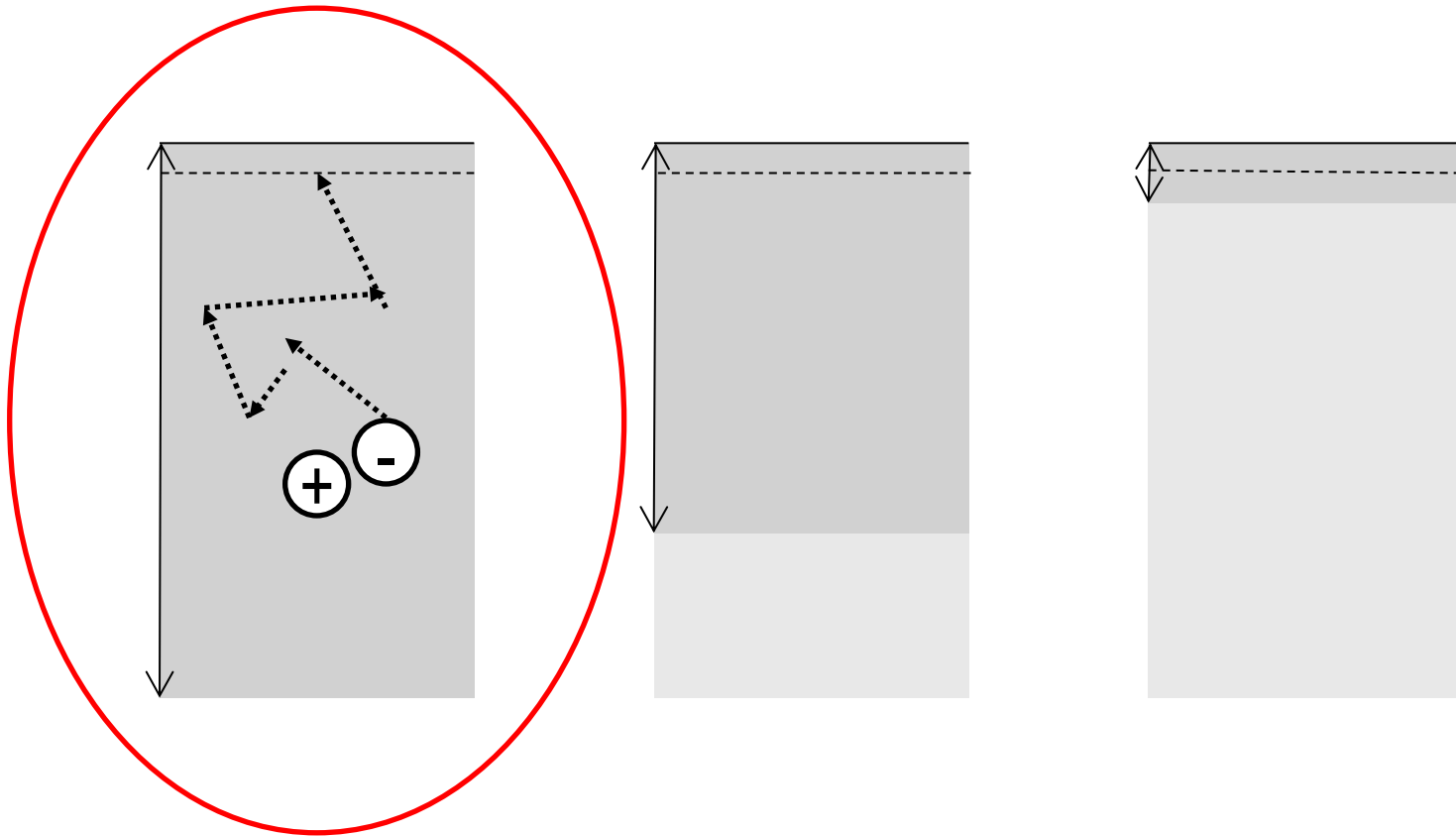
- Advantages
  - Large photovoltage obtainable
    - $qV \sim E_g$
  - No metallurgical junction
  - Relatively easy to manufacture
- Much more on this junction in subsequent lectures
- Real world
  - Limited physical extent
  - Rarely «abrupt»



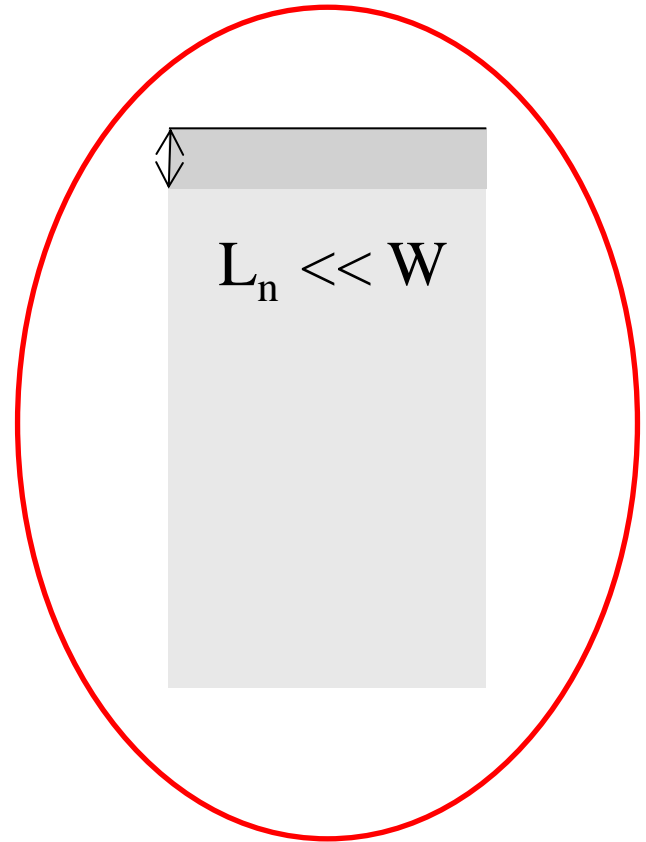
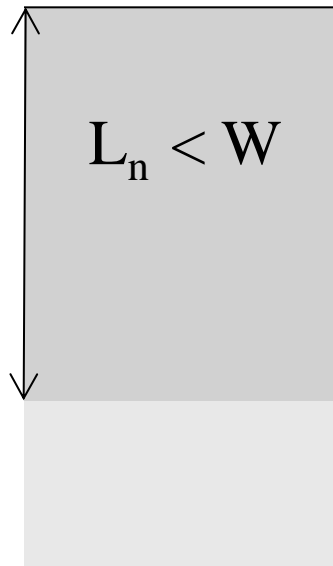
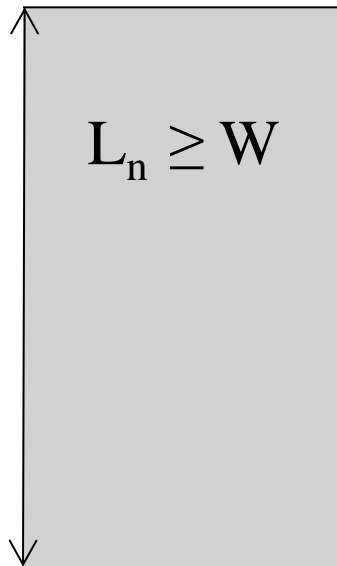
# Good solar cell



# Good solar cell

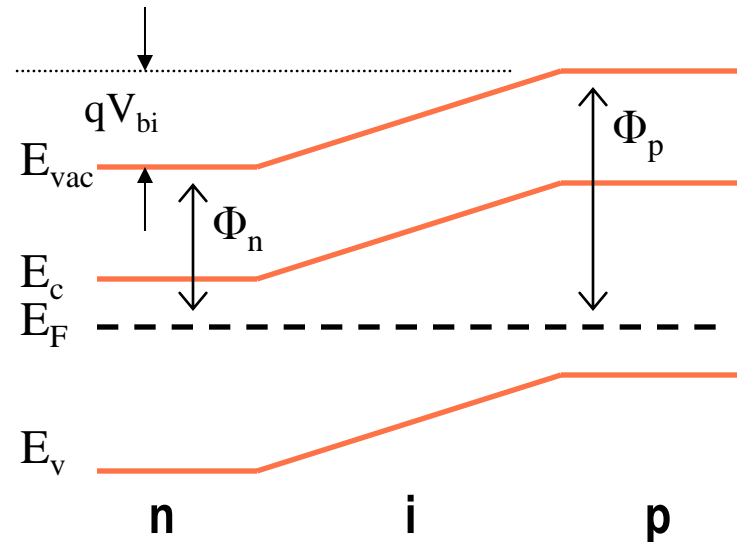


# What to do if diffusion length is *really* short?



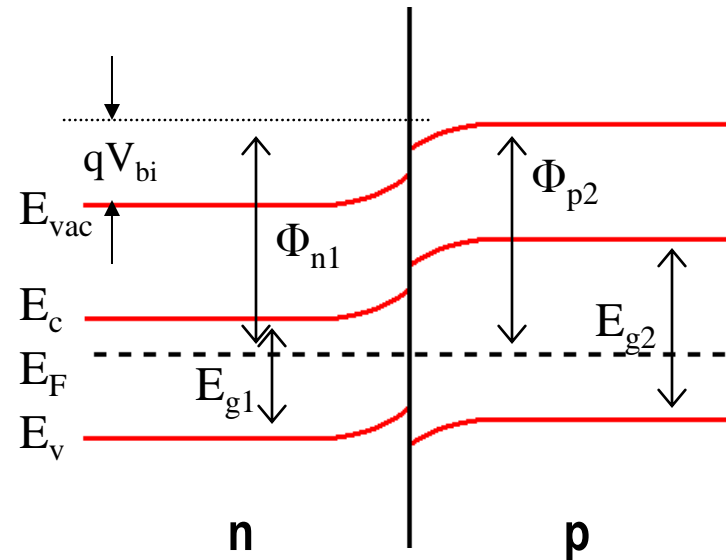
# The p-i-n junction

- A junction frequently used in materials with low lifetimes
  - Carriers generated in n and p-regions unlikely to contribute to current
  - Lifetime in i-region higher than in n and p-regions
- Advantages
  - Same obtainable  $V_{bi}$  as for a p-n homojunction
  - E is extended over a large distance, stimulating drift current
- Disadvantages
  - i-region highly resistive
  - High recombination in i-region where n and p are similar
  - Charged static defects will affect the useful thickness of the i-region



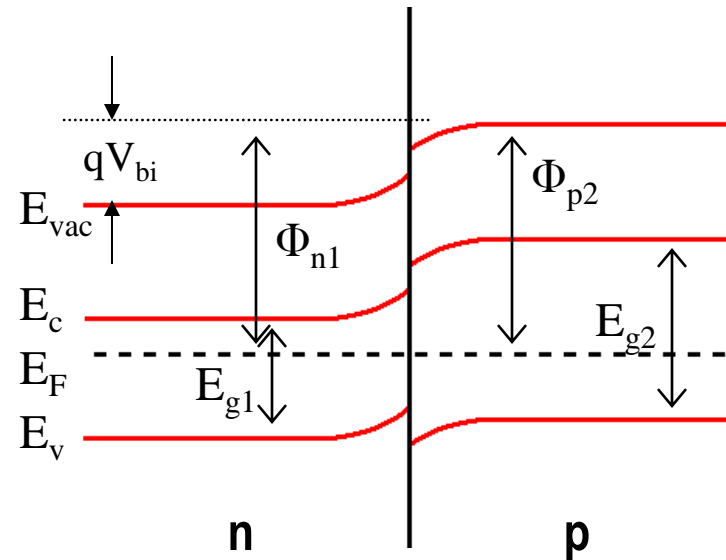
# The p-n heterojunction

- A p-n junction made using materials systems with different material properties (e.g.  $E_g$ ) in combination with doping
- Motivation
  - Can increase photocurrent compared with homojunctions
  - Certain materials can only be doped in with one polarity
  - Surface passivation
- Band offsets determined by  $\Phi$ ,  $\chi$  and  $E_F$



# The p-n heterojunction

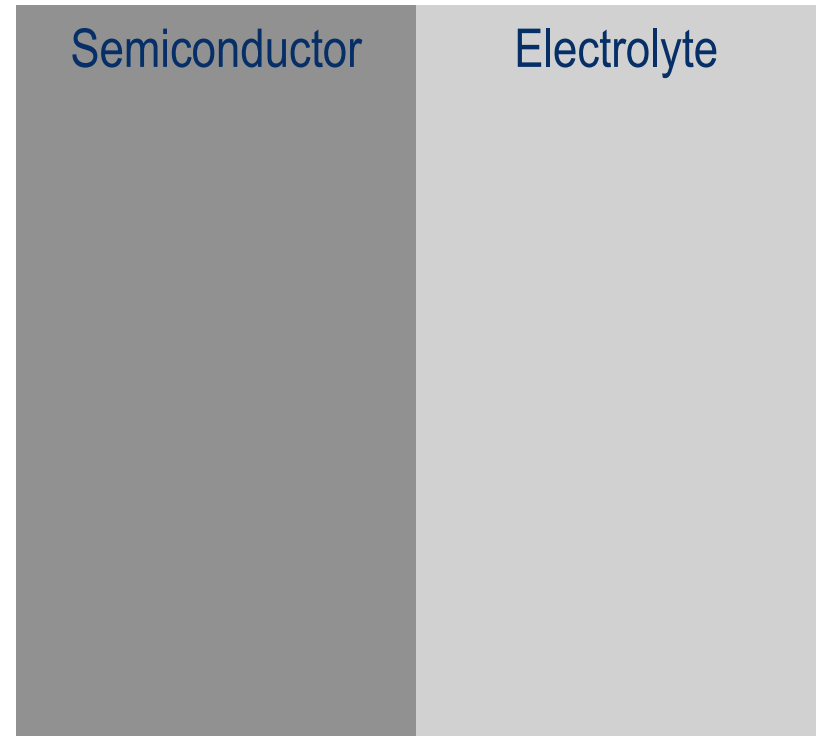
- Examples
  - The HIT cell from Sanyo
    - a-Si:H on sc-Si
  - CIS/CIGS
    - Uses n-type CdS as the emitter material on p-type CIS/CIGS





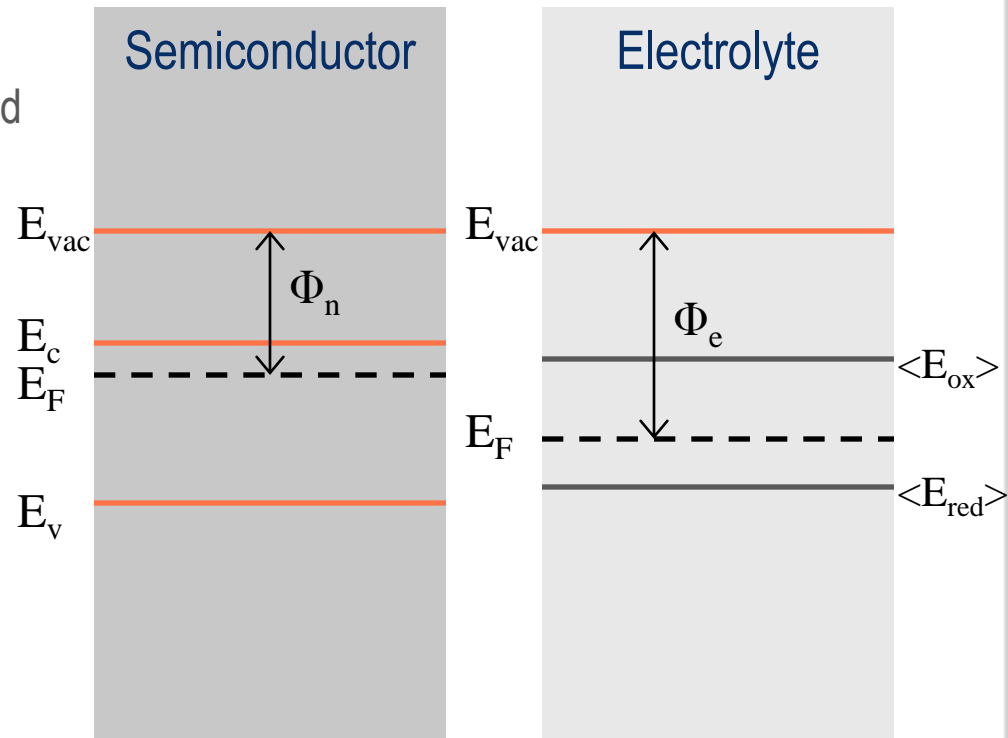
# The electrochemical junction

- A junction between an electrolyte and a semiconductor
- Advantages
  - Possibly very cost effective
  - Possibly easy to fabricate
- Disadvantages and challenges
  - Low efficiencies
    - ~ 10% in laboratory cells
  - Stability



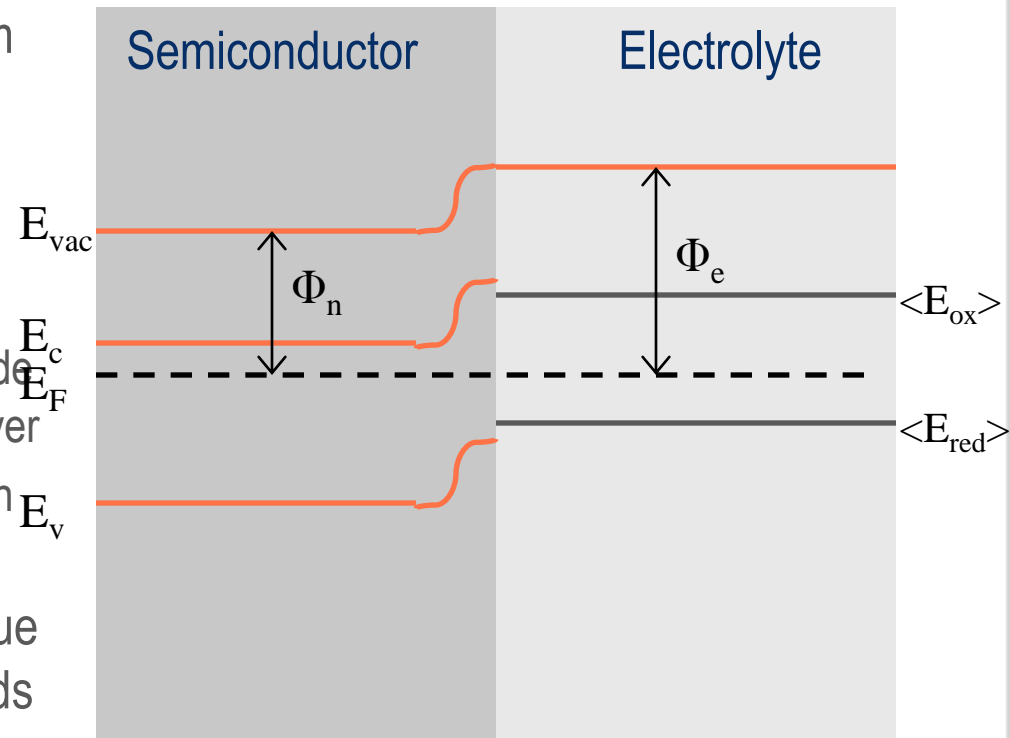
# The electrochemical junction

- How does it work?
  - The electrolyte contains so-called redox-couples
    - Ionic species with different possible oxidation states
    - Oxidation states give energy levels
  - The energy levels in the electrolyte are average values



# The electrochemical junction

- At contact, electrons will flow from n-type semiconductor into electrolyte until equilibrium is reached
  - The Fermi energies match
  - The charge on the electrolyte side is balanced within a very thin layer
  - Most band bending occurs within the semiconductor
- The current in the electrolyte is due to a flux of species from or towards the junction



# Junctions in organic materials

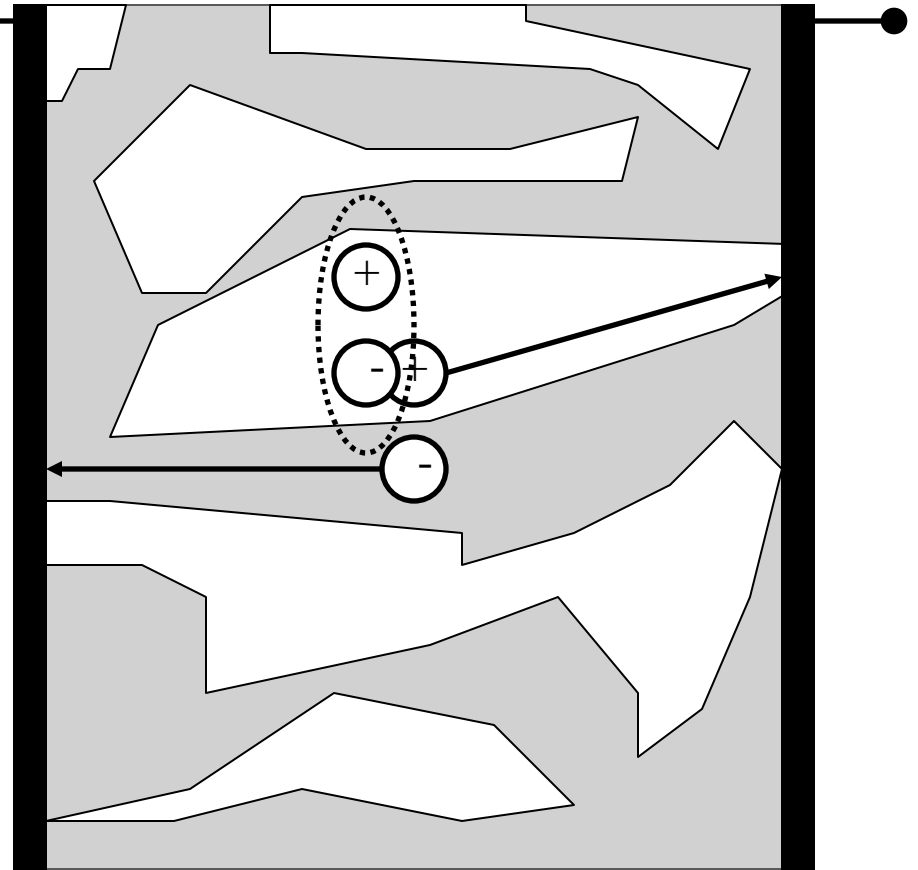
- Organic (molecular) materials hold much promise for cost-effective solar cells
- In general, photons generate excitons within molecular materials
- From a photovoltaic view-point, we can divide organic materials into two types:
  1. Materials wherein intermolecular forces dominate
    - Excitons can be split easily into mobile  $e^-$  and  $h^+$
    - Cells can be made in a similar fashion to the inorganic junctions we have reviewed
    - Material types: crystalline organic solids
  2. Materials wherein intramolecular forces dominate
    - Excitons are not easily split by  $E$ , and are mobile carriers
    - Excitons can be split into mobile  $e^-$  and  $h^+$  at certain interfaces
    - Material types: amorphous organic solids or polymers

# Junctions in organic materials

- The challenge of making solar cells from materials wherein intramolecular forces dominate
  - Recombination is a big problem
    - $L \sim 10 \text{ nm}$
  - Absorption is generally weak
    - $1/\alpha \sim 100 - 1000 \text{ nm}$
  - A planar interface will give a solar cell with poor performance
  - Solution: distribute the interface by making a porous material

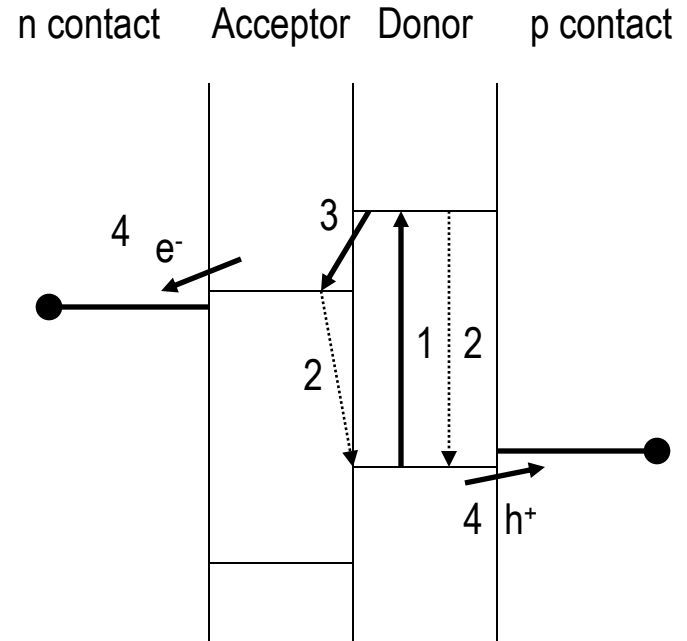
# Junctions in organic materials

- Principle of operation (schematic)
  1. An exciton is generated somewhere in the material
  2. The exciton is separated into mobile  $e^-$  and  $h^+$  at an interface
  3. The mobile  $e^-$  and  $h^+$  are transported through selective electron and hole conductors towards the external contacts
- A similar technique is also used in dye sensitized cells
  - Porous semiconductor



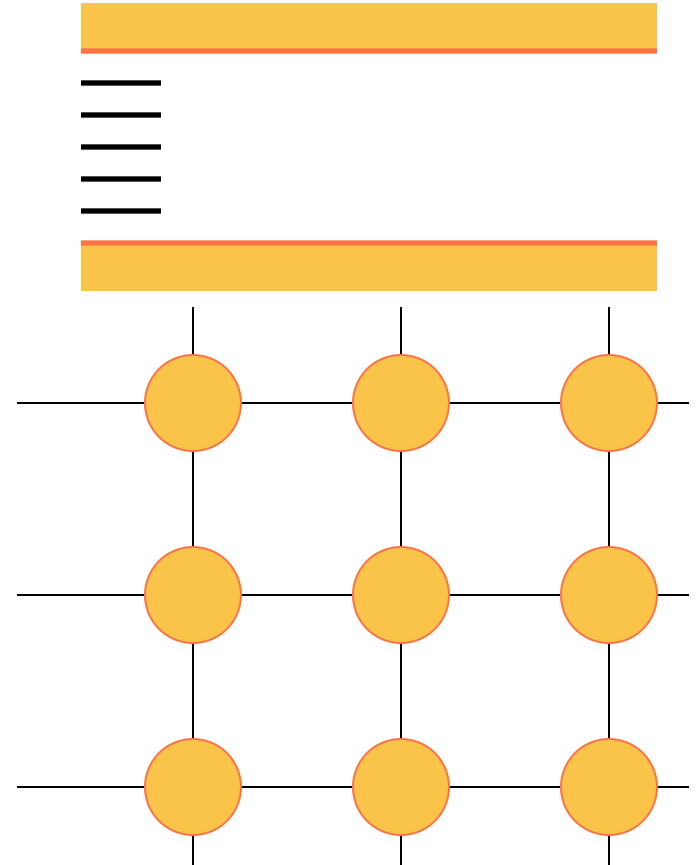
# Junctions in organic materials

- Principle of operation (band diagram)
  1. Photon absorption
  2. Recombination
    - Unwanted loss mechanisms
  3. Exciton separation
  4. Carrier extraction



# Surfaces and interfaces

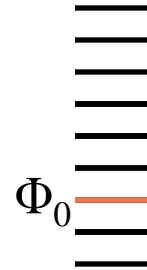
- Surfaces and interfaces are likely to contain defects
  - Intrinsic defects: defects due to an interrupted crystal structure
  - Extrinsic defects: e.g. Impurities adsorbed at the interface
- These defects often introduce states in the band gap
- These defects are localized at the interface and can trap charge
  - Will influence potential distribution across interface
  - Will affect band bending across interface





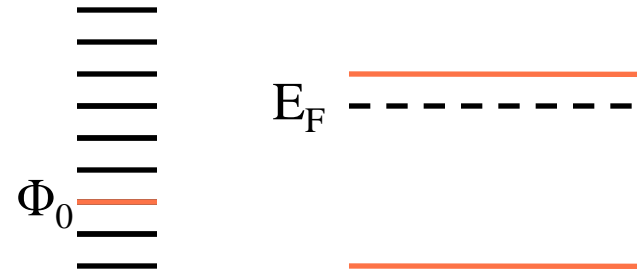
# Surfaces and interfaces

- States near  $E_v$  tend to trap  $e^-$ 
  - Acceptor states
- States near  $E_c$  tend to trap  $h^+$ 
  - Donor states
- Whether a state acts as a donor or acceptor state depends on the occupancy of the states and the  $E_F$  of the semiconductor
- It is useful to define a **neutrality level**,  $\Phi_0$ , the level up to which the states are filled for a neutrally charged interface



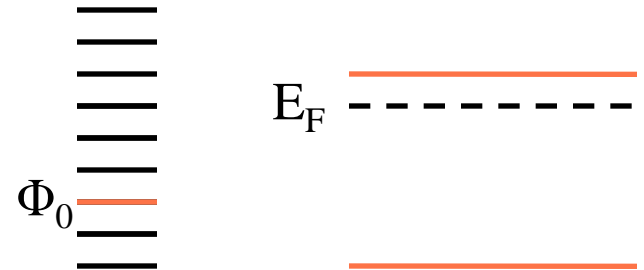
# Surfaces and interfaces

- When a semiconductor and a surface are brought together,  $\Phi_0$  is in general at a different energy than  $E_F$ 
  - Charge must be exchanged to bring the semiconductor and the interface into equilibrium
  - Band bending will occur



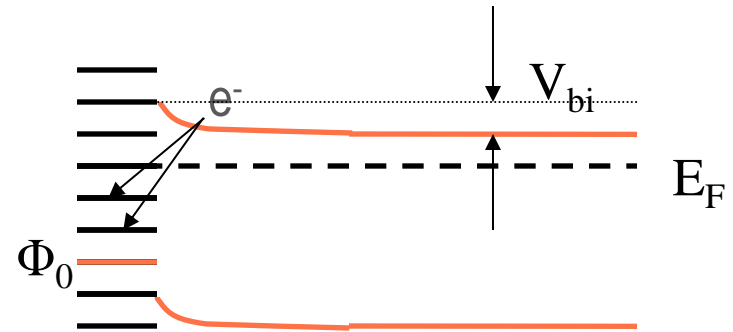
# Surfaces and interfaces

- $\Phi_0 < E_F$  : surface exhibits acceptor-like behaviour
  - Surface traps  $e^-$
- $\Phi_0 > E_F$  : surface exhibits donor-like behaviour
  - Surface traps  $h^+$
- Example: surface of an n-type semiconductor for which  $\Phi_0 < E_F$



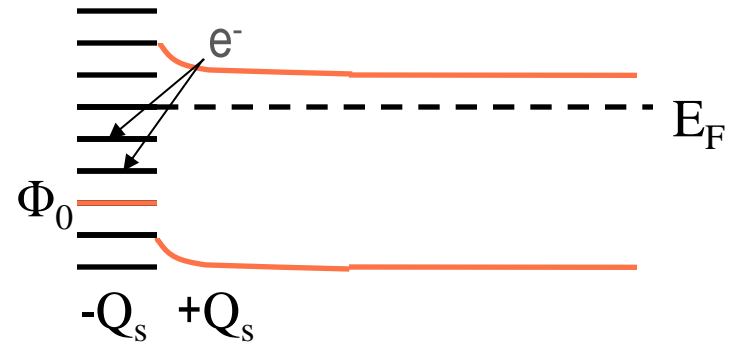
# Surfaces and interfaces

- Upon contact,  $e^-$  flow from the semiconductor onto the surface until equilibrium occurs
  - $e^-$  flow from the semiconductor, leaving a depletion zone with positively charged ions
  - Flow continues until the resulting potential barrier  $V_{bi}$  is large enough to hinder further flow



# Surfaces and interfaces

- The charge at the surface,  $-Q_s$ , becomes negative and must be compensated by a positive charge  $+Q_s$  inside the semiconductor



# The effect of interfaces on junctions

- At a junction, interface states may trap charge and influence the potential distribution
- Interface states do **not** affect the overall potential difference across the junction
  - This is determined by the difference in work functions

# The effect of interfaces on p-n junctions

- Interface states can alter the way the potential is distributed between the two sides of the junction
- Extreme cases
  1. High density of interface states:
    - $E_F$  at interface pinned at  $\Phi_0$
    - Two sides of junction screened from each other
  2. If  $\Phi_0$  is low enough for an acceptor-like surface, or high enough for a donor-like surface, the entire potential difference can be dropped on only one side of the junction

# The effect of interfaces on Schottky junctions

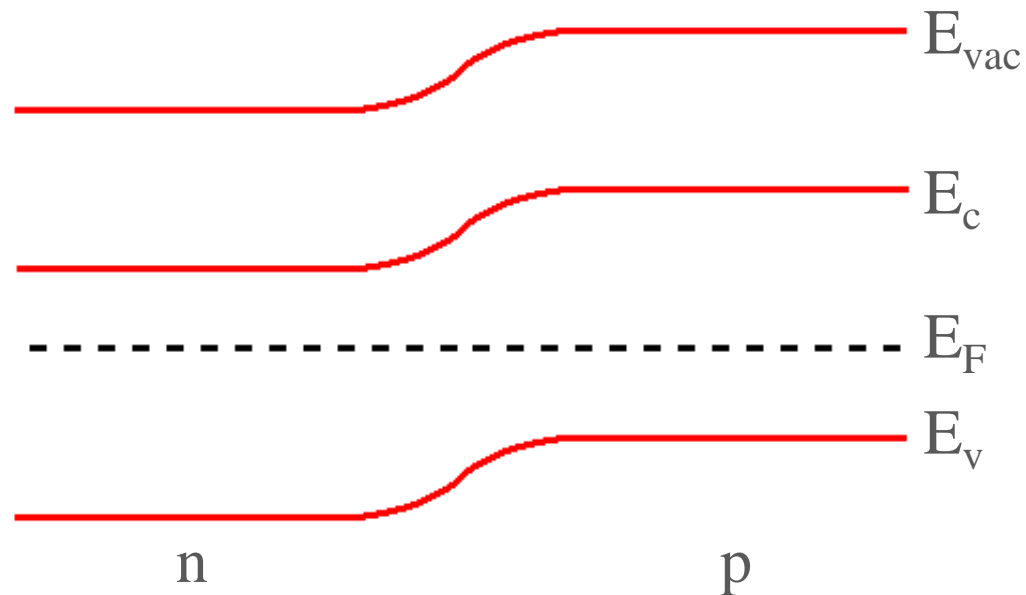
- Interface states immediately at a perfect Schottky junction will not modify the potential distribution
- In real cells, a thin insulator layer (oxide) can be present between the metal and the semiconductor
  - This layer can store charge
  - “MOS structure”
- This fixed charge will contribute to the change of work functions across the interface



# The p-n homojunction

- Next follows a detailed derivation of the I-V characteristics of a p-n homojunction

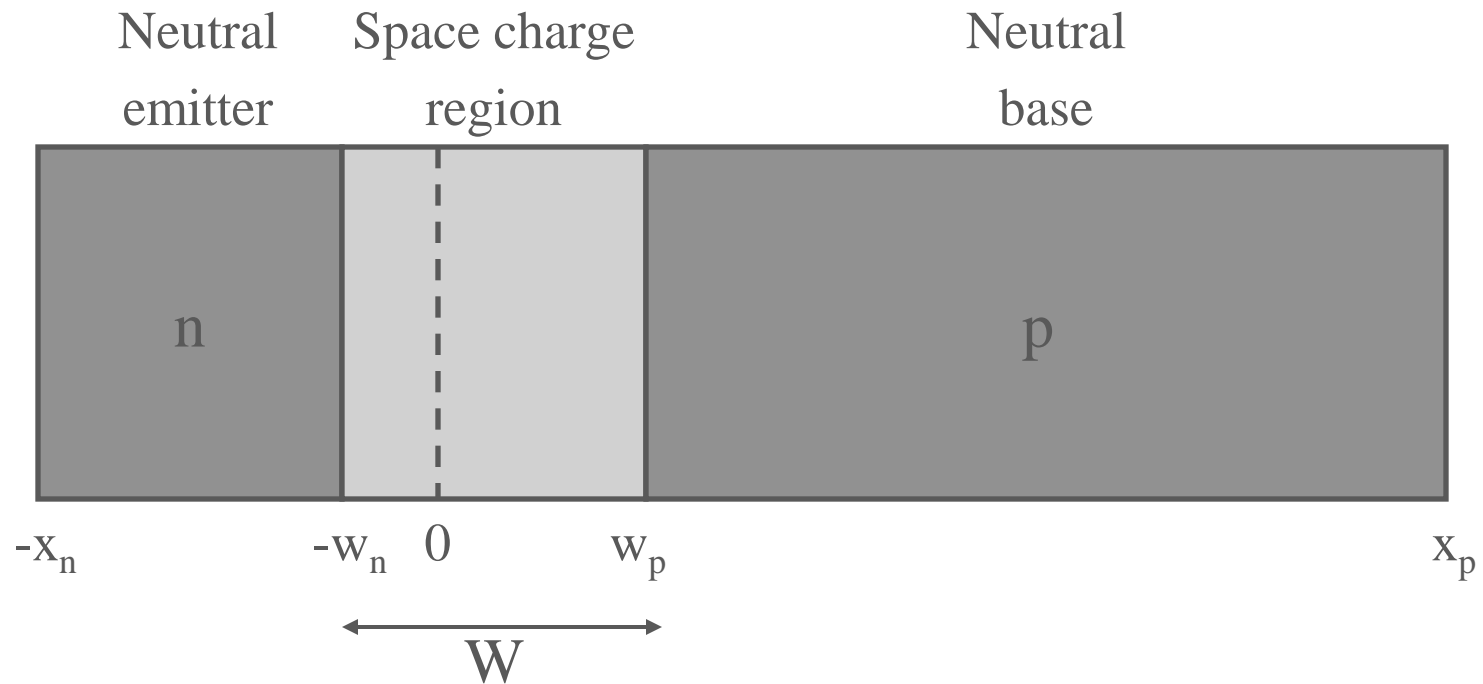
# The p-n homojunction



# The p-n homojunction

- The approach will be as follows
  1. Divide solar cell into three parts: two neutral parts and a space charge region (SCR) over which all change in potential and electric fields occur
    - Electrostatics
  2. Calculate SCR width and the electric field and potential across the SCR
    - Electrostatics
  3. Calculate Calculate carrier and current densities in neutral regions
    - Spatially varying minority carrier densities and diffusion currents
  4. Calculate carrier and current densities in SCR
    - Generation and recombination
  5. Calculate I-V characteristics of an ideal and infinite solar cell
    - Nice and readily interpretable solution
  6. Calculate I-V characteristics of a finite solar cell
    - Add surface recombination and get a **messy** solution
  7. Discuss the various factor that affect the I-V characteristics

# The p-n homojunction



# The p-n homojunction

$$(\delta/\delta x)^2 \varphi(x) = (q/\epsilon_0 \epsilon_s)(-Q_{\text{fixed}} + n - p)$$

$$(\delta^2/\delta x^2)n + (qE/kT)(\delta/\delta x)n + G_n(x)/D_n - (n - n_0)/L_n^2 = 0$$

$$(\delta^2/\delta x^2)p + (qE/kT)(\delta/\delta x)p + G_p(x)/D_p - (p - p_0)/L_p^2 = 0$$