

ME4252 Nanomaterials for Energy Engineering

Introduction to Semiconductors continued....

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Carrier Transport Phenomena

REFERENCES:

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2. The Physics of Solar Cells
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4. Web site: <http://pvedrom.pveducation.org/>

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Carrier Transport

- Transport is the process by which the free carriers *i.e.* electrons and holes, moves in a semiconductor
 - **Electron transport : electrons** (in the conduction band) move almost like free particles
 - **Hole transport is due to positively charged particles in the** valence band
- Such a motion of free carriers in a semiconductor leads to a current
- The two processes that cause free electrons and holes to move in a semiconductor are drift and diffusion
- Drift and diffusion currents make up the total current density in the semiconductor

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Carrier Transport: Mechanisms

drift and diffusion:

Drift – *the movement of holes and electrons due to an electric field*

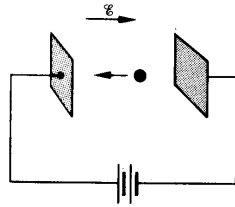
Diffusion – *the movement of holes and electrons due to variations in concentrations*

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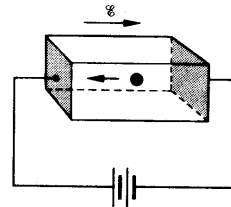
Carrier Drift

In vacuum



$$F = (-q)E = m_0 a$$

In semiconductor



$$F = (-q)E = m_n^* a$$

where
 m_n^* is the electron effective mass

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Carrier Drift

In an electric field, \mathbf{E} , an electron or a hole accelerates:

$$a = \frac{-q \mathbf{E}}{m_n^*} \quad \text{electrons}$$

$$a = \frac{q \mathbf{E}}{m_p^*} \quad \text{holes}$$

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Carrier Drift

Assume that an electric field, \mathbf{E} is applied to a semiconductor. This field acts on holes and electrons

The electric field creates a force due to which electrons will accelerate in a direction opposite to \mathbf{E}

The carriers will not accelerate indefinitely because of scattering from various sources such as impurity atoms, phonon scattering etc.

Averaged over time, carriers will tend to have a certain averaged velocity called drift velocity V_d

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Drift Velocity

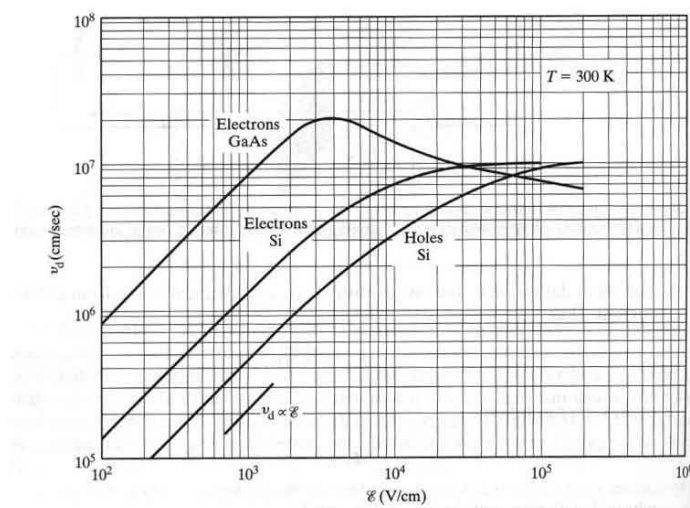


Fig. Carrier drift velocity versus electric field in high purity Si and GaAs

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Drift Currents - Electrons

For small to moderate values of E , the drift velocity is directly proportional to E

The drift velocity of electrons is

$$V_{de} = -\mu_e E$$

where μ_e is mobility of the electrons, constant of proportionality

μ has the dimension of **Velocity/Electric field** $\frac{cm^2}{volt - sec}$

The minus sign (-) in the above indicates that the electrons move in the opposite direction of the applied electric field.

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Drift Current Density - Electrons

Current = charge per unit time, $(coul/sec)$

Current density = current flowing through a specific area = amps/unit area = $coul/sec cm^2$

$$J_n|_{drift} = -qnV_{de} = (-qn)(-\mu_e E) = qn\mu_e E$$

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Drift Current Density - Electrons

q = the charge on an electron = $1.602 \times 10^{-19} \text{ coul.}$

n = concentration of electrons = $\# / \text{cm}^3$

qn = charge/ cm^3

$$J = qnV_d = \frac{\text{coul. cm}}{\text{cm}^3 \text{ sec}} = \frac{\text{coul.}}{\text{sec.cm}^2} = \frac{\text{amp}}{\text{cm}^2}$$

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Drift Current Density- Holes

Holes – The Electric field creates a force due to which the holes will accelerate in the same direction of the electric field E

V_{dp} , is the drift velocity of holes

J_p , is the current density due to holes

The holes acquire a drift velocity of

$$V_{dp} = \mu_p E$$

Where μ_p is the mobility of holes with units of $\text{cm}^2 / \text{volt} - \text{sec}$

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Drift Current Density - holes

$$J_p|_{drift} = qpV_{dh} = qp\mu_p E$$

q = the charge on a hole = 1.602×10^{-19} coul.

p = concentration of holes = $\#/cm^3$

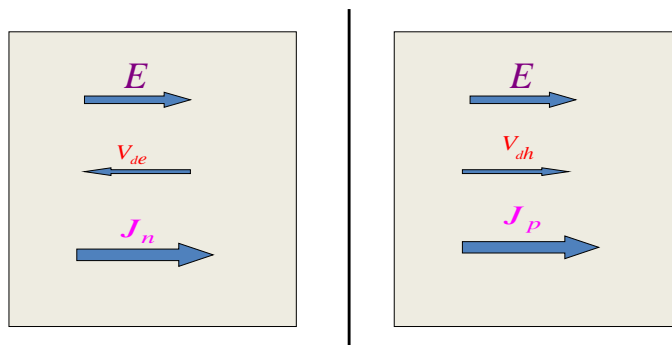
qp = charge/cm³.

$$J_p = qp v_d = \frac{\text{coul. cm}}{\text{cm}^3 \text{ sec}} = \frac{\text{coul.}}{\text{sec.cm}^2} = \frac{\text{amp}}{\text{cm}^2}$$

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Drift Current



➡ Drift current due to holes and electrons is in the same direction

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Total Drift Current

Since the hole current and the electron current are in the same direction, the currents add up

The total drift current is

$$J_{drift} = J_n|_{drift} + J_p|_{drift} = qn\mu_n E + qp\mu_p E$$

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Carrier Scattering

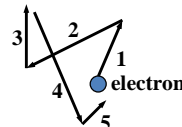
Mobile electrons and atoms in the Si lattice are always in random thermal motion

- Electrons make frequent collisions with the vibrating atoms
 - “lattice scattering” or “phonon scattering”
 - increases with increasing temperature
- Average velocity of thermal motion for electrons: $\sim 10^7$ cm/s @ 300K

Other scattering mechanisms:

- deflection by ionized impurity atoms
- deflection due to Coulombic force between carriers
 - “carrier-carrier scattering”
 - only significant at high carrier concentrations

The net current in any direction is zero, if no electric field is applied.



<http://www.youtube.com/watch?v=cDcprgWiQEY&feature=related>

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Mobility – relationship to scattering

Dominant scattering mechanisms in doped materials:

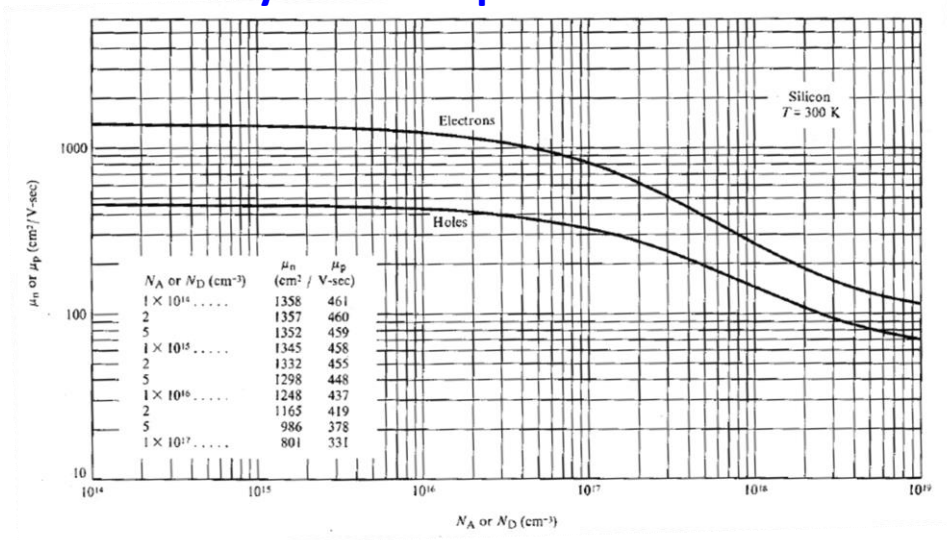
(i) lattice scattering – involving collisions of thermally agitated atoms/ions

(ii) ionized impurity (i.e. donor-site and/or acceptor-site) scattering.

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Mobility – with dopant concentration



Room temperature carrier mobility in Si as a function of dopant concentration

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Mobility with doping & temperature

For higher doping, the carrier mobilities systematically decrease with doping

In the lowest doped samples, carrier mobility monotonically decreases with increase in temperature

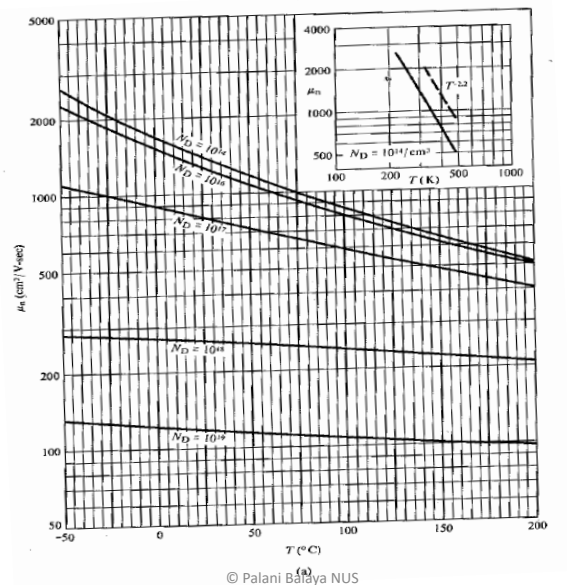
$$\mu_n \propto T^{-2.3 \pm 0.1}$$

$$\mu_p \propto T^{-2.2 \pm 0.1}$$

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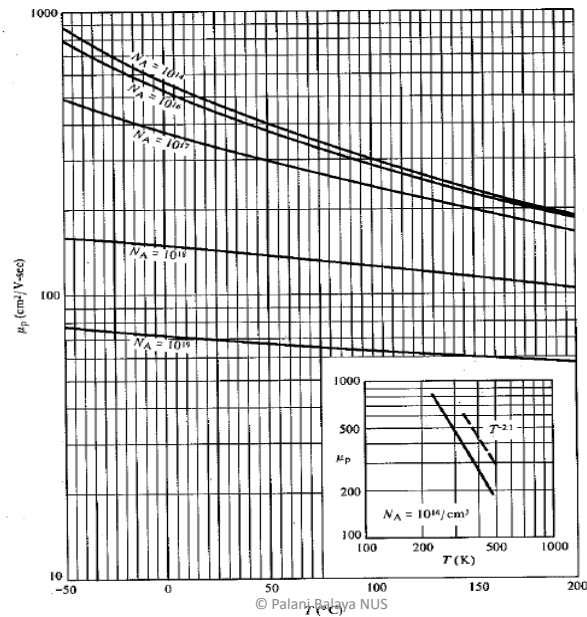
Temperature dependence of electron mobility in Si



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Temperature dependence of hole mobility in Si



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Conductivity

We can find the conductivity of a semiconductor:

$$\sigma = qn\mu_n + qp\mu_p$$

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Resistivity

$$\rho = \frac{1}{q(\mu_n n + \mu_p p)}$$

In a donor doped semiconductors:

$$N_D \gg n_i; n \sim N_D \text{ and } p \approx \frac{n_i^2}{N_D} \ll n$$

$$\mu_n n + \mu_p p = \mu_n N_D \quad \text{n-type}$$

$$\mu_n n + \mu_p p = \mu_p N_A \quad \text{p-type}$$

$$\rho = \frac{1}{q\mu_n N_D}$$

n-type

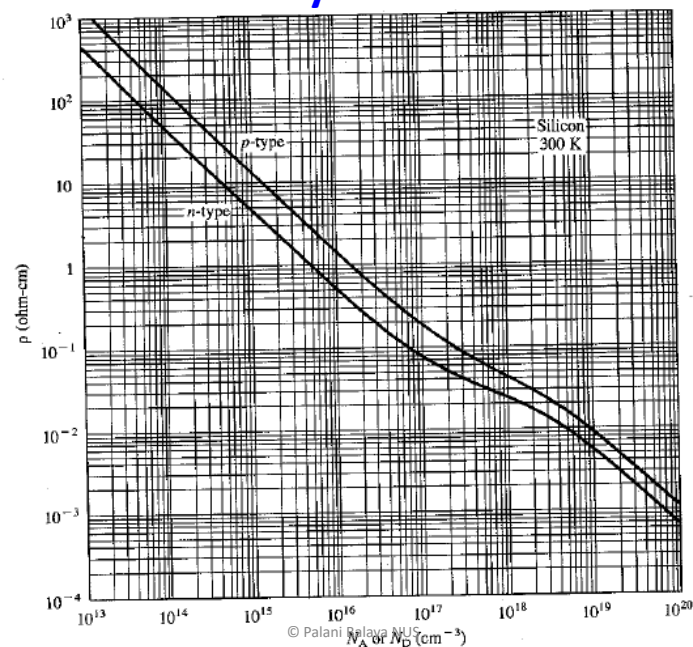
$$\rho = \frac{1}{q\mu_p N_A}$$

p-type

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Resistivity – Si at 300 K



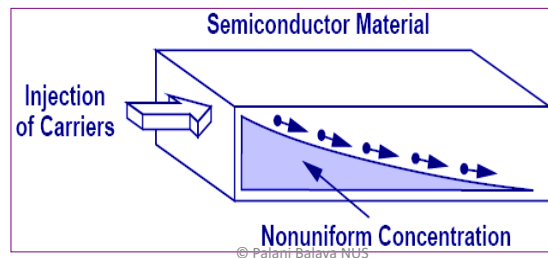
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Carrier Diffusion

Diffusion is transport process of the charge carriers driven by gradients of carriers

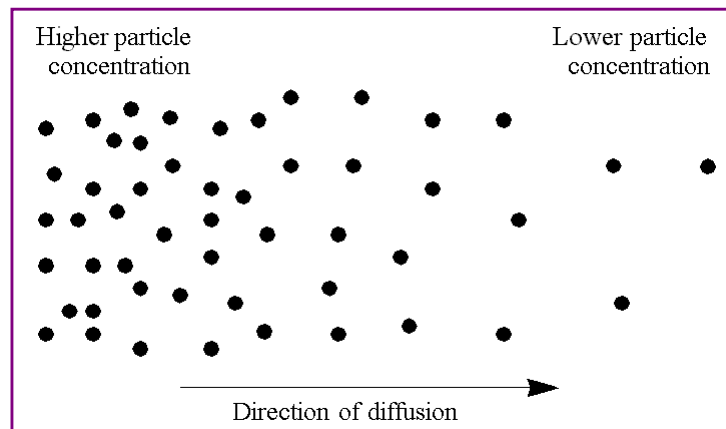
Due to thermally induced random motion, mobile carriers tend to move from a region of high concentration to a region of low concentration, producing a flux of carriers which gives rise to current. This current is called diffusion current

Diffusion does not need an external electric field



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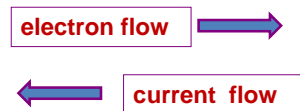
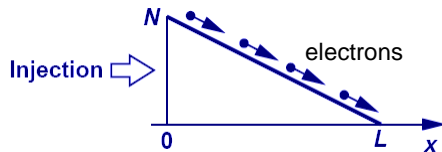
Carrier Diffusion



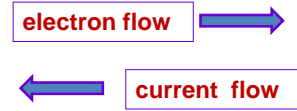
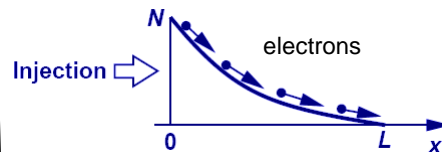
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Diffusion Examples

Linear concentration profile
→ constant diffusion current



Non-linear concentration profile
→ varying diffusion current



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Diffusion Current Density - Electrons

The diffusion current density due to diffusion is proportional to carrier concentration gradient

The proportionality constant is the **diffusion constant**

Units: **cm²/sec**

$$J_{n,diff} = (-q)D_n \left(-\frac{dn}{dx} \right)$$

(or)

$$J_{n,diff} = qD_n \frac{dn}{dx}$$

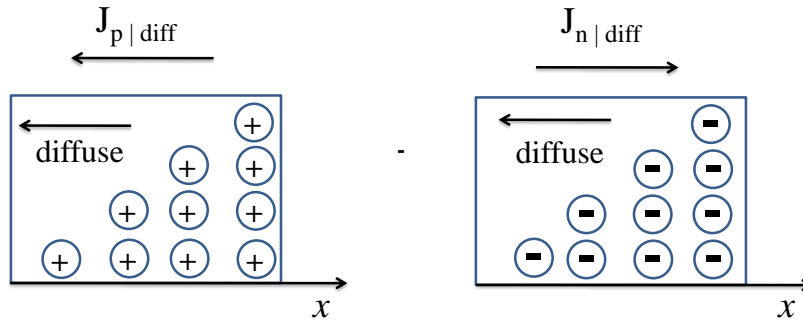
Negative sign for (dn/dx) is because the net motion of electrons due to diffusion is in the direction of decreasing electron concentration

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Diffusion Current

Visualization of electron and hole diffusion on a macroscopic scale



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Diffusion Current

Diffusion current within a semiconductor consists of hole and electron components

$$J_{p,diff} = -qD_p \frac{dp}{dx} \quad J_{n,diff} = qD_n \frac{dn}{dx}$$

$$J_{tot,diff} = q \left(D_n \frac{dn}{dx} - D_p \frac{dp}{dx} \right)$$

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Total Current: Steady State

$$J = J_n + J_p$$

$$J_n = J_{n,\text{drift}} + J_{n,\text{diff}} = qn\mu_n E + qD_n \frac{dn}{dx} \quad (a)$$

$$J_p = J_{p,\text{drift}} + J_{p,\text{diff}} = qp\mu_p E - qD_p \frac{dp}{dx} \quad (b)$$

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Einstein Relation

The characteristic constants for drift and diffusion are related:

$$\frac{D}{\mu} = \frac{kT}{q}$$

Note that $\frac{kT}{q} \cong 26\text{mV}$ at room temperature (300K)

This is often referred to as the “**thermal voltage**”

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Electron & Hole Currents: Quasi Fermi levels

Quasi Fermi levels are by definition related to the non-equilibrium carrier concentration in the same way E_i is related to the equilibrium carrier concentration

E_{Fn} \Rightarrow quasi Fermi level for electrons

E_{Fp} \Rightarrow quasi Fermi level for holes

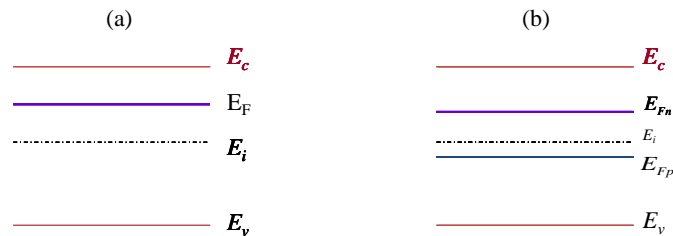


Fig. Energy band diagram: (a) equilibrium conditions (b) non equilibrium conditions

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Electron & Hole Currents: Quasi Fermi levels

$$n = n_i e^{(E_{Fn} - E_i)/kT} \quad \text{or} \quad E_{Fn} = E_i + kT \ln(n/n_i) \quad (c)$$

$$p = n_i e^{(E_i - E_{Fp})/kT} \quad \text{or} \quad E_{Fp} = E_i - kT \ln(p/n_i) \quad (d)$$

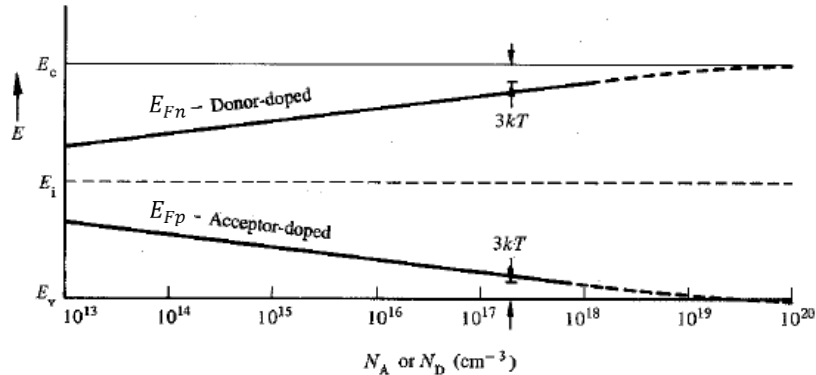
In general E_{Fn} and E_{Fp} will be two distinct values that will tend to move back to E_i as the semiconductor goes back to equilibrium

n_i is the intrinsic concentration $\sim 10^{10} / \text{cm}^3$

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Determination of E_F (doped semiconductor)



Fermi level systematically moves upward in energy from E_i with increasing donor doping, and systematically downward in energy from E_i with increasing acceptor doping

Fig. above refers to exact positioning of E_F in Si at room temperature as a function of doping concentration ($kT = 0.0259$ eV and $n_i = 10^{10}/\text{cm}^3$).

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Charge Separation: Types of Junctions

REFERENCES:

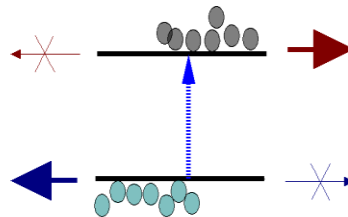
The Physics of Solar Cells
Jenny Nelson; ISBN 1 86094 349 7

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Charge Separation

- Charge separation is a key step in photovoltaic energy conversion
- Charge separation requires some kind of driving force, which should be built in the device
- The driving force is an electric field which effectively separates the charge carriers and drives them in opposite directions
- In solar cells a junction between two electronically different materials provides necessary driving force

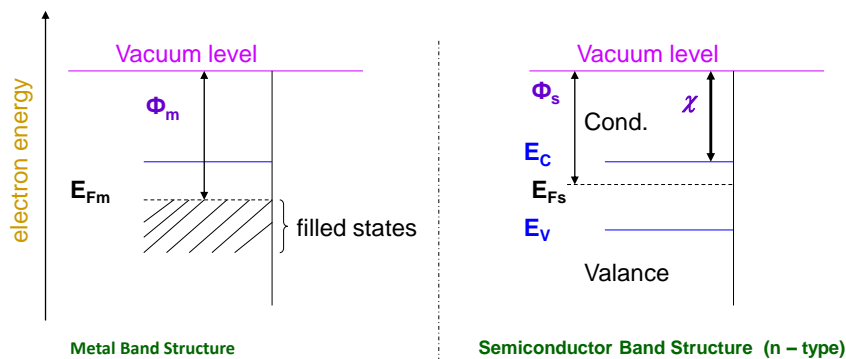


Schematic of charge separation mechanism in a PV device

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Ideal Band Diagrams



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Work Function

Work function (Φ): Work function of a material is the energy required to remove the least tightly bound electron from the Fermi level to vacuum level

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

Electron affinity (χ): Electron affinity is the energy to remove electron from C.B

$$\chi = E_{\text{vac}} - E_C$$

- Work function of a material is strongly dependent on the surface preparation
- Work function of metal is always equal to the electron affinity where as in semiconductor it depends on doping

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Charge Separation

- In crystalline semiconductors a junction between two electronically different materials provides an electrostatic force
- In photosynthesis – where charge separation is also a requisite- excited electrons are driven across the photosynthetic membrane by differences in free energy of molecular acceptors
- In both cases, force arises from a compositional gradient.

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Origin of Photovoltaic Action

- In a photovoltaic device, light produces a pair of charges which are then separated
- That charge separation then gives rise to a photocurrent (in short circuit) or a photo-voltage (in open circuit)
- Photovoltaic action arises from the driving force separating charges.

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Types of Junctions

- An electrostatic field can be established at the junction between any two regions of different work functions, due to gradient in vacuum level
- Types of junction:
 1. **Hetero junction**: a semiconductor and a metal or two semiconductors of different work functions
 2. **Homo junction**: two layers of same semiconductor with different levels of doping
- In solar cells, the most widely used technique for establishing the charge separating field is by employing homo-junctions

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Metal – Semiconductor Junction

- Metal – Semiconductor junctions are the simple photovoltaic junctions
- A charge separating field is established due to the difference in work functions of metal and semiconductor
- Two types:
 1. Schottky barrier
 2. Ohmic contact

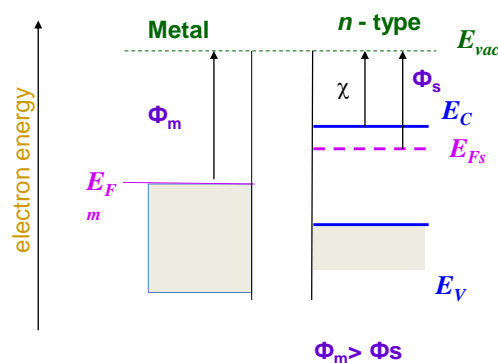
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Schottky Barrier

Schottky barrier is formed between a metal and a n - or p - semiconductor when are brought into contact, such that

$$\Phi_m > \Phi_s$$

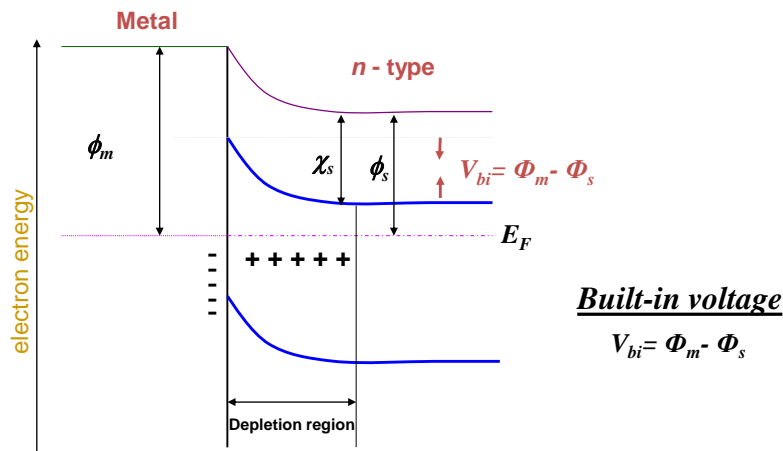


Energy band diagram of the metal and the semiconductor in isolation

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Schottky Barrier (in dark)



Energy band diagram of a metal-semiconductor contact in thermal equilibrium, in the dark

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Schottky Barrier (in dark)

- When the two materials are isolated from each other, the Fermi levels are independent (Fig)
- After the metal and semiconductor have been brought into contact, electrons start to flow from the semiconductor “down” into the metal until the Fermi energies of both solids are equal (equilibrium condition) (Fig)
- Upon the electrons leaving the semiconductor, a layer of fixed positive charge behind and a negative surface charge layer on the metal appear
- This creates depletion region in semiconductor and hence a built-in electric field (or potential barrier) which prevents further flows of electrons

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Schottky Barrier (in dark)

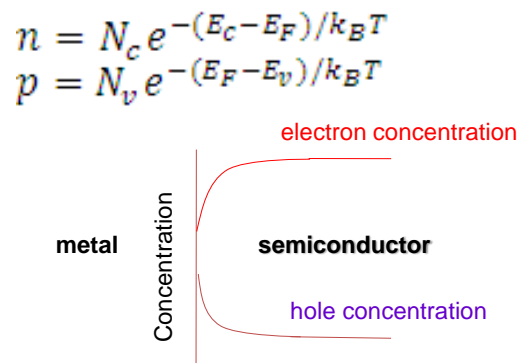
- Since the electron affinity and band gap are invariant in the semiconductor, hence E_{vac} changes by a certain amount, so the conduction and valence band energies must vary, by the same amount. This is referred to as *band bending*
- Band bending energy, is qV_{bi} is equal to the gradient in the vacuum level (or difference in work functions)
- The greater the difference in work functions, larger the bending and the higher is V_{bi}

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Schottky Barrier

Concentration profile



By joining metal and semiconductor we set up an electric field in a layer close to interface

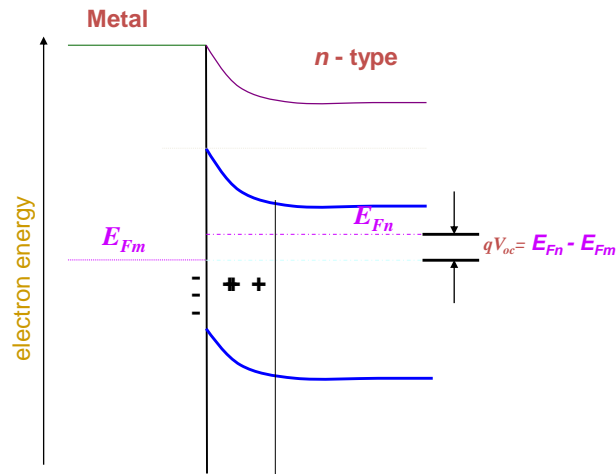
Electric field will drive electrons and holes in opposite direction – separation

Contacts presents a lower resistance path for holes than electrons – from semiconductor to metals – this type of junction is an example for Schottky barrier

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Schottky Barrier (upon illumination)



Band profiles of the semiconductor and metal junction under illumination at open circuit

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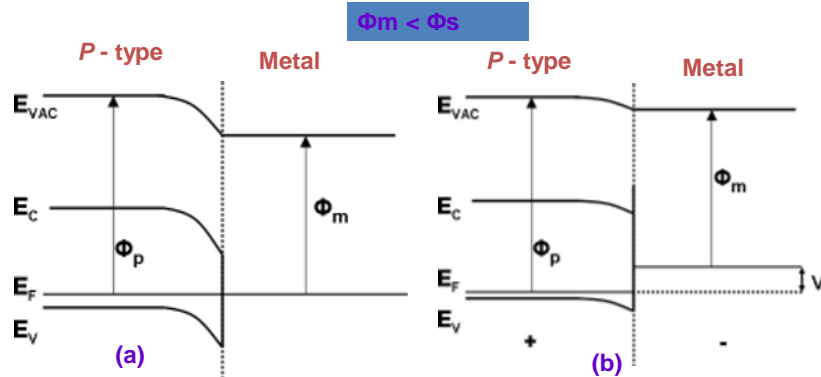
Schottky Barrier (upon illumination)

- When the semiconductor is illuminated with photons of energy greater than band gap, the built-in electric field will cause EHP's generated in the semiconductor to be separated so that the electrons accumulate in the semiconductor and holes in the metal.
- As a result the electron quasi Fermi level in semiconductor from the junction moves up and becomes higher than it was in dark, and higher than the Fermi level in metal E_{Fm} (Fig.) and generates a voltage called photo voltage.
- Magnitude of photo voltage is equal to the difference in the Fermi levels of semiconductor and metal.
- **This ability to sustain a difference in quasi Fermi levels under illumination – key requirement in PV energy conversion**

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Schottky Barrier (upon illumination)



Band profiles for the p-type semiconductor-metal junction

(a) at equilibrium and (b) under illumination at open circuit

Aligning Fermi levels at equilibrium requires a positive charge on metal side and a negative charge at semiconductor side (due to diffusion of holes to metal) forming the junction. The depletion region and hence the potential barrier will retard the hole diffusion. Upon equilibrium no further hole moves.

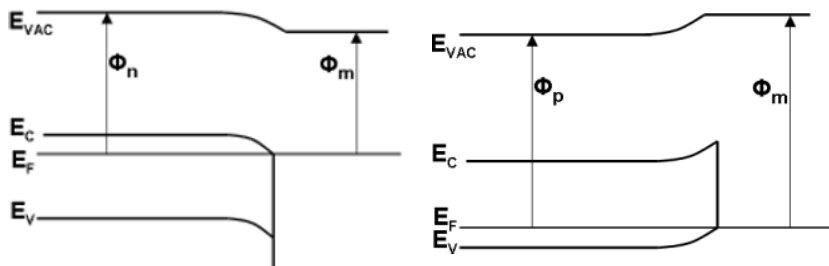
Upon illumination, electron-hole pairs are formed, the charges are separated by potential barrier thus accumulating holes on semiconductor and electrons on metals. This lowers the Fermi level on semiconductor side thus generating an OCV.

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Ohmic Contacts

- The opposite case to the Schottky barrier is *Ohmic contact*, where for the *n*-type semiconductor-metal junction, $\Phi_m < \Phi_n$, and for the *p*-type semiconductor-metal junction, $\Phi_m > \Phi_p$



Band profiles for ohmic metal-semiconductor contacts for (a) an n-type semiconductor and (b) a p-type semiconductor

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Ohmic Contacts

- When n -type semiconductor-metal are brought into contact the semiconductors bands bends in such a way that they encourage transport of majority carriers across the junction and inhibits only flow of minority carriers.
- Majority carriers accumulate near the interface to establish the necessary potential difference, and the junction is rich with carriers. This means it can pass current easily in either direction, and so have a low contact resistance for majority carriers usually an *Ohmic* contact.
- The difference in work function between the two layers causes build-up of majority carriers near the interface
- Under illumination, the charges separated at the junction pass across the junction relatively easily so that the resultant photovoltage is negligible – mechanism which gives rise to photovoltage in a barrier junction – selective removal of minority carriers is absent.

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p-n Junction

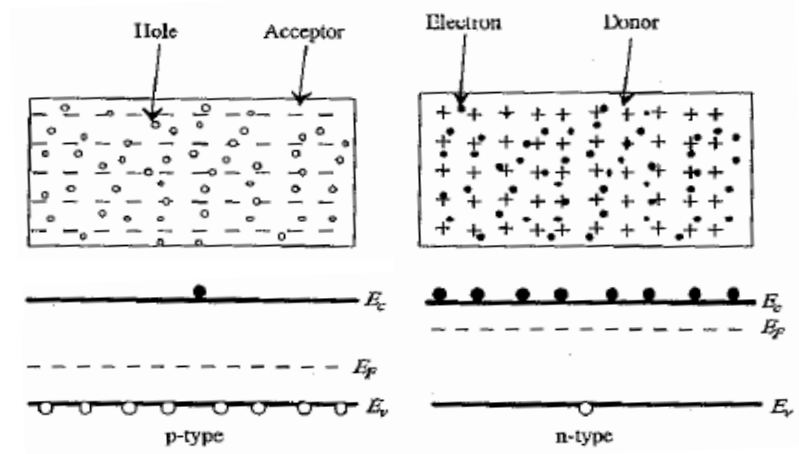
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The Physics of Solar Cells
Jenny Nelson; ISBN 1 86094 349 7

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Formation of a p-n junction



Energy band pictures and majority carriers of n- and p-type semiconductors

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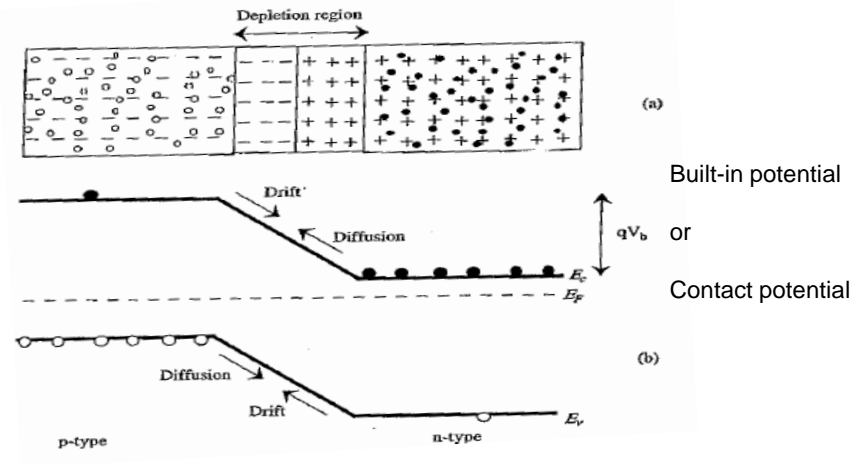
Formation of a p-n junction

- *p-n* junction is established when a layer of p-type semiconductor and a layer of n-type material are brought together
- When a p-n junction is formed, the majority carriers diffuse across the junction leaving behind a layer of fixed charge, due to the ionized impurity atoms, on either side
- This space charge sets up an electrostatic field which opposes further diffusion of carriers across the junction (Fig.2a)
- When diffusion of majority carriers across the junction is balanced by the drift of minority carriers back across the junction in the built-in field, equilibrium is established
- At this point, the Fermi levels of the p-type and n-type semiconductors are equal (Fig.2b)

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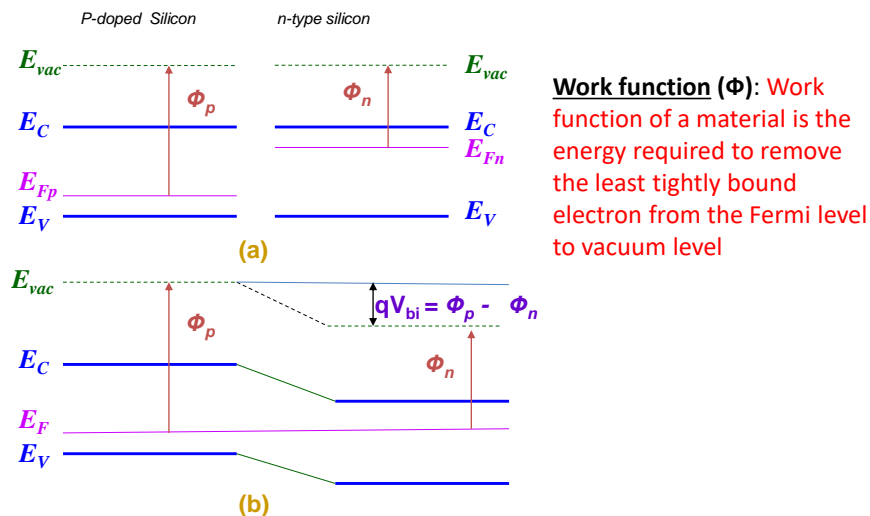
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Formation of a p-n junction



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p-n junction (in dark)



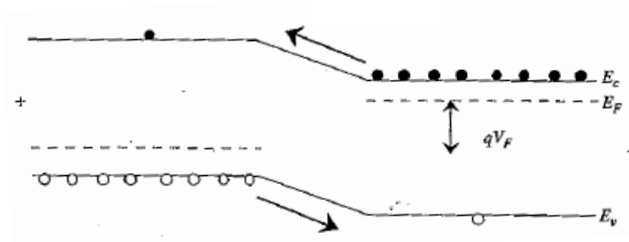
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p-n junction (in dark)

- The *p-n* junction is the ideal model of a solar cell.
- A *p-n* junction is created by doping different regions of the same semiconductor with different elements, so that we have *p*- and *n*-type doping
- An electric field is established because of the difference in a work function of *n*- and *p*-type material
- Majority carrier electrons in *n*-type diffuse to *p*-type leaving behind positively charged donors
- Similarly, holes diffusing from the *p*-type, leaves negatively charged acceptors
- Thus, depletion region (free of mobile charge carriers) develops on either side of the junction with fixed +ve ions on *n*-side and fixed -ve ions on *p*-side. These residual charges prevent further diffusion.
- The potential difference develops across the junction which acts as barrier to the flow of charge carriers across the junction

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Ideal Current-Voltage Characteristics under dark



Energy band diagram under forward bias

- When a bias voltage, V_F with the positive terminal to the *p*-side and the negative terminal to the *n*-side is applied, the applied voltage reduces the electrostatic potential across the depletion region as shown in Fig. This is called the forward bias
- In this case the drift current is reduced and the diffusion of electrons and holes increases from the *n*-side to the *p*-side and from the *p*-side to the *n*-side, respectively

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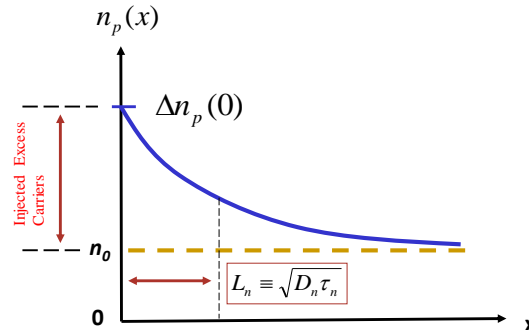
Minority carrier diffusion length

$$\Delta n_p(x) = \Delta n_{p0} e^{-x/L_n} \quad x = L_n$$

The injected excess electron concentration dies out exponentially in x due to recombination

$$\Delta n_p(x) = \Delta n_{p0} / e$$

Therefore, diffusion length L_n can be defined as distance at which the excess electron concentration is reduced to $1/e$ (which is 0.36) of its value at the point of injection



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Forward Bias: Total Current

The total current density is the sum of the two (diffusion current density in n-side due to minority carrier and diffusion current density in p-side due to minority carrier), as follows:

$$J = J_n + J_p = \left(\frac{qD_p p_{n0}}{L_p} + \frac{qD_n n_{p0}}{L_n} \right) (e^{qV_F/k_B T} - 1) = J_0 (e^{qV_F/k_B T} - 1)$$

J_0 is called the saturation current density and is expressed as

$$J_0 = \frac{qD_p p_{n0}}{L_p} + \frac{qD_n n_{p0}}{L_n} = \frac{qD_p n_i^2}{L_p N_D} + \frac{qD_n n_i^2}{L_n N_A}$$

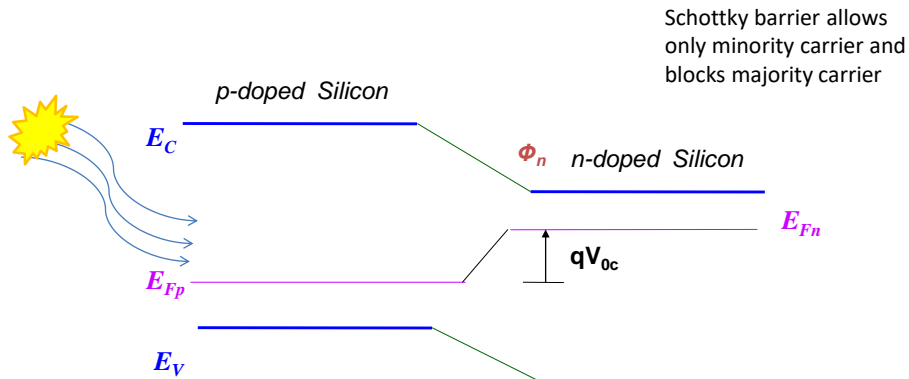
$$n * p = n_i^2$$

$$n \sim N_D \text{ and } p \sim N_A$$

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p-n junction (ILLUMINATION)



Band profile of Illuminated *p-n* homojunction cell

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p-n junction (ILLUMINATION)

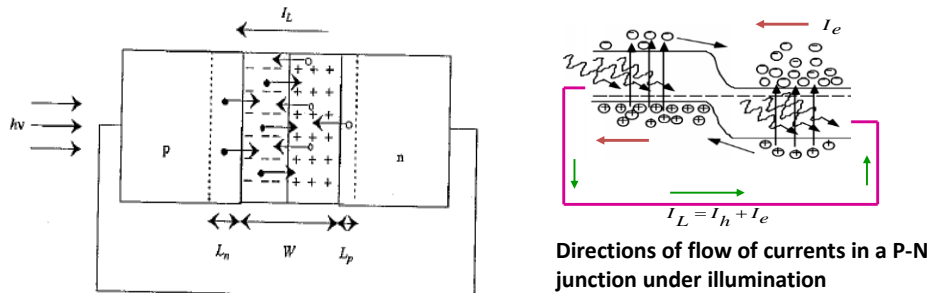
- When the *p-n* junction is illuminated, absorption of photons of energy greater than the bandgap energy of the semiconductor creates excess minority carriers throughout the illuminated region of the cell and diffuse towards the junction, where they are swept across it by strong junction field
- Also, minority carriers generated thermally within a diffusion length of each side of the junction diffuse to the depletion region and swept to the other side by electric field
- This flux of minority carriers give rise to the photogenerated currents and photovoltage

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Ideal Current-Voltage Characteristics under Illumination

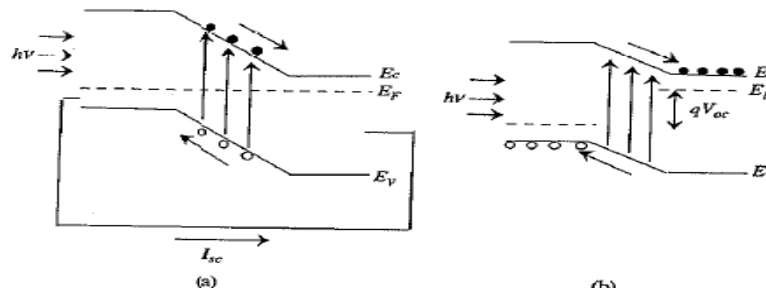
- When the p-n junction is illuminated by sunlight, electron-hole pair is generated by the photons that have energy greater than the band gap
- Because of the electric field in the depletion due to the ionized dopant atoms, drift of electrons toward n-side and that of holes toward p-side occur in the depletion region. This charge separation results in the current flow from n- to p- side when an external wire is short-circuited (Fig.)



Schematic illustration of carrier flow in illuminated p-n junction in case of short-circuited

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Energy band diagrams of illuminated p-n junction in (a) the short-circuited and (b) open-circuited

- The electron-hole pairs generated within a distance of diffusion length forming edge of the depletion region contribute to the photocurrent because of the diffusion of excess carriers up to the space charge region.
- When the p- and n- sides are short-circuited, the current is called the short-circuit current (I_{sc}) (Fig.) and equals to the photogenerated current I_L if the series resistance is zero.
- When the p- and the n-side are isolated, electrons move toward n-side and holes toward p-side, resulting in the generation of potential, the voltage developed is called the open-circuit voltage, V_{oc}

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Photo Current

Under uniform illumination,

Let g_{op} , be the generation rate (EHP/cm³-s)

The number of electrons created per second within a diffusion length of the transition region on the "p side" = $AL_n g_{op}$

The number of holes created per second within a diffusion length of the transition region on the "n side" = $AL_p g_{op}$

The number of carriers generated within depletion region, $W = AWg_{op}$

The resulting current due to collection of these

optically generated carriers by the junction, $I_L = qAg_{op}(L_p + L_n + W)$

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Total Current

Assuming that the area of the solar cell is unity, the current-voltage characteristic of the illuminated p-n junction is given by

$$I = q \left(\frac{D_p p_{n0}}{L_p} + \frac{D_n n_{p0}}{L_n} \right) (e^{qV/k_B T} - 1) - qg_{op}(L_p + L_n + W)$$

$$\text{or } I = I_0 (e^{qV/k_B T} - 1) - I_L$$

$$\text{or } I = I_0 (e^{qV/k_B T} - 1) - I_{sc}$$

Total current density:

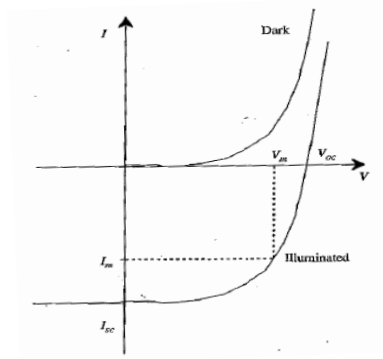
$$J = J_0 (e^{qV/k_B T} - 1) - J_{sc}$$

$$I(V) = I_0 [\exp(qV/kT) - 1] - I_L$$

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I – V Curve

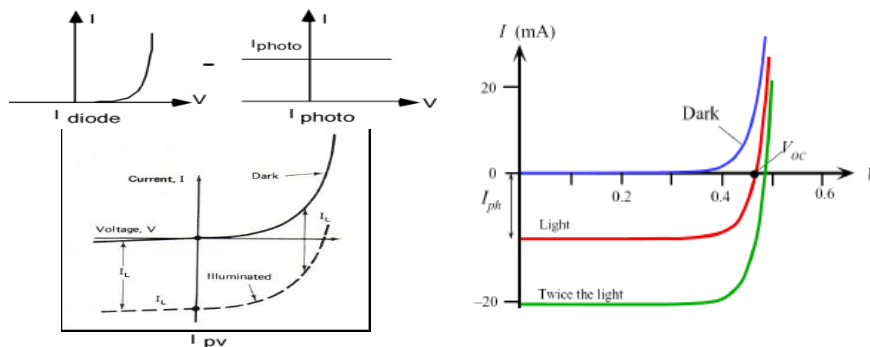


I – V characteristics of p-n junction under illumination and darkness

Thus, the I – V curve is lowered by an amount proportional to the generation rate

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(a) I-V curve of illuminated P-N junction (b) Effect of an intensity of light

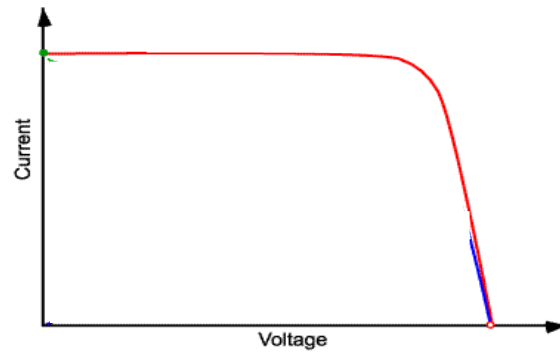
- Without illumination, a solar cell has same electrical characteristics as a large diode
- When the cell is illuminated, the I-V curve shifts down into the fourth quadrant where more power can be extracted from cell. Greater the intensity of light, greater is the amount of shift.
- Thus, the I-V curve of a solar cell is the superposition of the I-V curve of the solar cell diode in the dark with the light-generated current
- Since the cell is generating power the convention is to invert the axis

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I-V Curve of an Ideal Solar cell

The equation for the I-V curve in the first quadrant:

$$I = I_L - I_0 \left[\exp\left(\frac{qV}{kT}\right) - 1 \right]$$



I-V curve of a solar cells

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