Chapter 2
From Radiated Energy to Electrical Energy: Physics of Photovoltaic Cells

2.1 Prologue: The Photoelectric Effect

The transformation of the radiated energy coming from the Sun into electrical energy implies the study of the interaction of electromagnetic waves with matter.

This mechanism can be understood starting from the photoelectric effect in which electrons are emitted from a material when it is exposed to electromagnetic radiation.

In particular, it was observed that (using visible light for alkali metals, near-ultraviolet for other metals, and extreme ultraviolet for non-metals) the energy of emitted electrons increased with the frequency and did not depend on the intensity of the radiation.

This effect was first observed by Heinrich Hertz in 1887 and for several years it was apparently in contrast with James Clerk Maxwell's wave theory of light; according to this theory, the electron energy would be proportional to the intensity of the radiation.

The following main experimental results, for given material, were observed:

1. the rate at which photoelectrons are ejected is directly proportional to the intensity of the incident light;
2. a threshold frequency, below which no photoelectrons are emitted, exists;
3. above the threshold frequency, if the intensity of light is increased, the number of emitted electrons is increased as well but their maximum energy does not vary; moreover very low intensity of incident light, with frequency greater that the threshold, is able to extract electrons;
4. above the threshold frequency, if the frequency of incident light is increased, the maximum energy of photoelectrons is also increased;

Albert Einstein theorized, in 1905, that light is composed of discrete quanta, now called photons, and that the energy of a quantum of light is given by the product of the frequency of the corresponding wave multiplied by a constant, later called Planck's constant.

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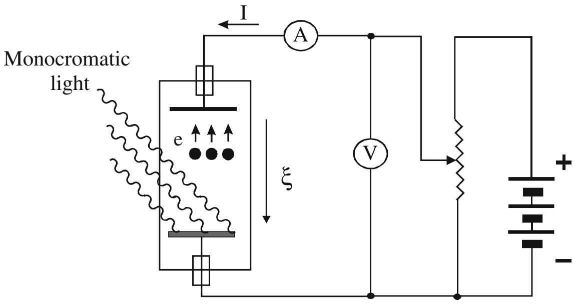
Fig. 2.1 Experimental setup for evaluation of the photoelectric effect



$$E = h\nu \tag{2.1}$$

where E is the energy of a single quantum of light, $h = 6.62 \times 10^{-34}$ J·s is the Planck's constant and ν is the frequency of the electromagnetic wave (incident photon). For this discovery, Einstein earned the Nobel Prize in Physics in 1921 and the quantum revolution in physics began.

If a photon has enough energy, it can give its energy to an electron and it is ejected.

The maximum kinetic energy $K_{\max}$ of an ejected electron is given by:

$$K_{\max} = h\nu - \varphi \tag{2.2}$$

where $\varphi = hf_0$ is the work function (sometimes denoted W), which is the minimum energy required to remove a delocalized electron from the surface of any given metal. It follows that the frequency ν of the incident photon must be greater than f_0 to extract electrons.

The experimental setup to verify the photoelectric effect is sketched in Fig. 2.1. The light beam hits the material that is situated inside a bulb. Two plates, subjected to a variable potential, generate an electric field (ξ) that is able to break the photoelectrons. The galvanometer measures the current generated by photoelectrons.

When the frequency of the incident beam is greater that the threshold frequency, by applying a potential such that $K_{\max} = eV$, the measured current is null.

It should be noted that it is convenient to measure energy in electronvolt [eV] instead of Joule (1 eV = $1.6 \cdot 10^{-19}$ J).

It is easy to calculate that the energy associated with a photon emitted by Sun having $\lambda = 0.5$ µm (see Fig. 1.5) is equal to:

$$E\big|_{\lambda=0.5\,\mu\text{m}} = h\nu = h\frac{c}{\lambda} = 6.62 \cdot 10^{-34}\frac{3 \cdot 10^8}{0.5 \cdot 10^{-6}} = 3.972 \cdot 10^{-19} J = 2.48\,\text{eV}$$

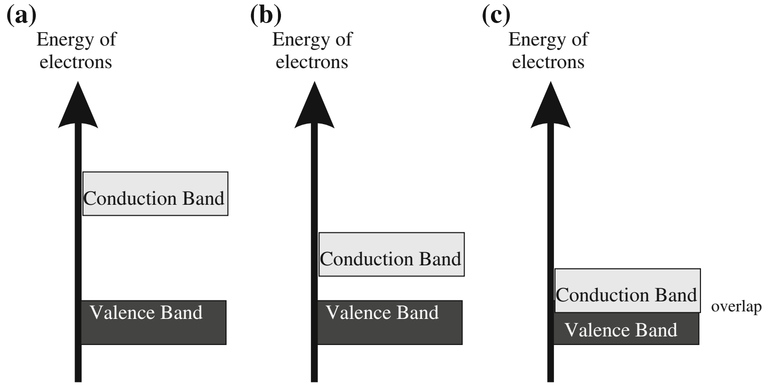


Fig. 2.2 Schematic representation of the band structure for: **a** insulator, **b** semiconductor, **c** conductor

2.2 Metals, Semiconductors, Insulators

In a single isolated atom, energy levels of electrons are discrete. For hydrogen atom, the Bohr's model gives:

$$E_H = \frac{-m_o q^4}{8\,\varepsilon_o^2 h^2}\,\frac{1}{n^2} \tag{2.3}$$

where m_o is the free electron mass and q its charge, ε_o^2 is the free space permittivity and n is a positive integer known as principal quantum number. The fundamental level corresponds to $n = 1$ and the related energy is $E_{H(n=1)} = -13.6\,\mathrm{eV}$.[1]

If N atoms interact (for example in a crystal), N outer levels have energy only slightly different and thermal energy allows electrons to pass from one level to another (the energy corresponding to $T = 300$ K is $kT \approx 0.026$ eV). Resulting energy levels are grouped in bands. Two main bands are recognizable: conduction band and valence band. These two bands are separated by a forbidden region that is characterized by an energy value E_g. This value makes the difference among insulators, conductors, and semiconductors.

In an insulator, the forbidden band has a wide energy (for example $E_g = 9$ eV for SiO_2) neither thermal energy nor an electric field is able to raise the energy of an electron to send it into the conduction band. Due to the absence of free electrons for conduction, the material behaves as an insulator.

On the contrary, in a conductor the conduction band is partially superimposed to the valence band. As a consequence, there are many electrons available for conduction and an electric field can give them sufficient energy to perform conduction.

In a semiconductor, the two bands are separated but the energy of the forbidden band is low ($E_g = 1.12$ eV for Si at T = 300 K) and it is easy to give energy to an

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[1] The negative value of this energy corresponds to a tied electron

electron to go into the conduction band. In this case, the hole in the valence band contributes to the conduction as well as the electron in the conduction band (Fig. 2.2).

The forbidden band amplitude varies with temperature, for Si the amplitude is:

$$E_g(T) = 1.17 - \frac{(4.73 \cdot 10^{-4})T^2}{T + 636} \tag{2.4}$$

The temperature coefficient is negative, it means that the forbidden band amplitude decreases with temperature.

2.3 Inside the Band Structure of a Semiconductor

The motion of electrons inside a crystal is influenced by the periodical crystalline structure of the semiconductor that determines a periodic potential field due to the atom's nucleus and the tightly bound core electrons.

The dynamic behavior is obtained by solving the Schrödinger equation.

$$\varDelta^2\psi + \frac{2m_0}{(h/2\pi)^2}[E - U(\vec{r})]\,\psi = 0 \tag{2.5}$$

where m_0 is the free electron mass, E is the energy of the electron, and $U(\vec{r})$ is the periodic potential inside the semiconductor. The solution of Schrödinger equation defines the band structure, the allowed energy, and the crystal momentum $p = \hbar k$ where k is the wave vector and $\hbar = h/2\pi$.

The relationship between energy and momentum near the minimum of the conduction band and near the maximum of the valence band is nearly parabolic; as a consequence, the effective mass is defined as the inverse of the second derivative of the energy respect to the momentum[2]:

$$m* \equiv \left[\frac{d^2E}{dp^2}\right]^{-1} \tag{2.6}$$

This definition allows a particle to be considered as a classical particle with an effective mass $m*$. The effective mass $m*$ depends on the band.

Near the top of the valence band this value is negative. These places are usually empty due to electrons thermally excited (as it will be explained in the next section) that are in the conduction band.

It is easier to consider these states as occupied by another kind of particles said *holes* that behaves as classical free particles with a positive effective mass m_p^*, while electrons are considered as classical free particles with effective mass m_n^*.

Figure 2.3 describes a simplified energy band diagram for a semiconductor at $T > 0$ in energy versus momentum diagram.

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[2] It should be borne in mind that $E = p^2/2m$

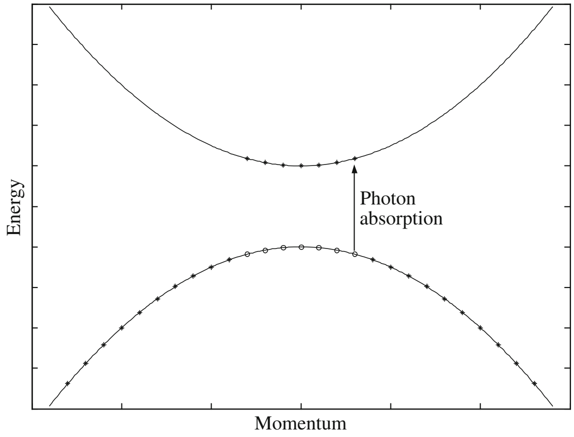

Fig. 2.3 Energy versus momentum representation of the energy band structure for a direct band-gap semiconductor

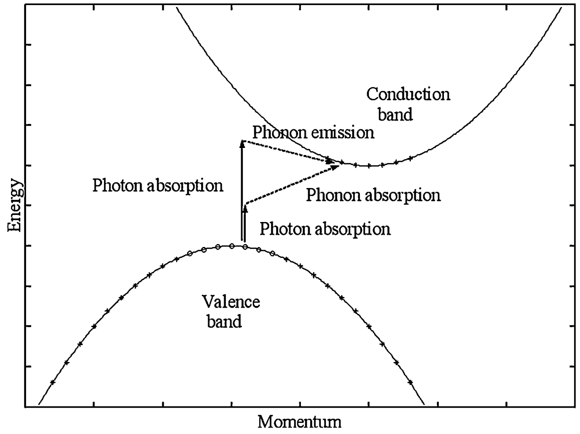

Fig. 2.4 Energy versus momentum representation of the energy band structure for indirect band-gap semiconductor

It should be noted that the minimum of the conduction band occurs for the same momentum values of the maximum of the valence band. As a consequence, an electron can do a transition maintaining constant the momentum. This kind of semiconductor is a *direct band-gap* semiconductor.

The behavior of an *indirect band-gap* semiconductor and the energy band diagram is illustrated in Fig. 2.4.

The difference between these two kinds of semiconductors is important for the study of absorption and emission of light in a semiconductor.

2.4 Absorption of Light

As explained in Sect. 2.1, radiated energy interacts with the matter, including semiconductors, as photons, whose energy is $E = h\nu$, and momentum $p_\lambda = h/\lambda$.

The excitation of an electron from the valence band to the conduction band is called *fundamental absorption* and, as a consequence, a hole appears in the valence band.

Both the total energy and the momentum must be conserved; in particular, for direct band-gap semiconductors (GaAs, GaInP, CdTe, and CU(InGa)Se_2) a transition can occur remaining constant the momentum of the photon as shown in Fig. 2.3. The crystal momentum is equal to $p_\lambda = h/l$ where l is the lattice constant and it is bigger than the photon momentum. Being the wavelength of sunlight of the order of 10^{-4} cm and the lattice constant of 10^{-8} cm, it can be assumed that the conservation law can be applied only to the photon momentum.

The probability of an induced transition from a level E_1 into the valence band to a level E_2 into the conduction band for a photon with energy $E_2 - E_1 = h\nu$ is given by a coefficient α that depends on the difference between the photon energy and the forbidden band gap.

$$\alpha(h\nu) \approx \left(h\nu - E_g\right)^{1/2} \tag{2.7}$$

Some semiconductors allow only transitions with $p \neq 0$, in such cases:

$$\alpha(h\nu) \approx \frac{1}{h\nu}\left(h\nu - E_g\right)^{3/2} \tag{2.8}$$

In indirect band-gap semiconductor, like Si and Ge, the maximum of the valence band and the minimum of conduction band occur for different values of the momentum as sketched in Fig. 2.4. Conservation of the momentum implies in this case the emission or the absorption of a phonon.[3] In particular, if the photon energy is greater than the difference between the starting electron energy level in the valence band and the final level in conduction band, a phonon is emitted. On the contrary, if the photon energy is lower than the difference between the starting electron energy level in the valence band and the final level in conduction band, a phonon is absorbed.

The absorption coefficient is different depending on absorption ($\alpha_a(h\nu)$) or emission ($\alpha_e(h\nu)$) phenomenon.

$$\alpha_a(h\nu) \propto \frac{\left(h\nu - E_g + E_{ph}\right)^2}{e^{E_{ph}/kT} - 1} \tag{2.9}$$

$$\alpha_e(h\nu) \propto \frac{\left(h\nu - E_g - E_{ph}\right)^2}{1 - e^{E_{ph}/kT}} \tag{2.10}$$

where E_{ph} is the phonon energy. It should be noted that for indirect band-gap semiconductor, the absorption of a photon depends on the availability of energy states, and on the absorbed/emitted phonons as well. This makes the absorption

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[3] The phonon is considered as a particle representation of a lattice vibration in the semiconductor, it is a low energy particle with a relatively high momentum

coefficient for indirect transition smaller than the corresponding one for direct transition. As a result, light is able to penetrate more inside an indirect band-gap semiconductor.

2.5 Allowable States for Holes and Electrons

By the Schrödinger equation, it is possible to obtain the density of states both for electrons and holes. The influence of periodic potential is incorporated into the effective mass. The density of available states for unit volume and energy gives the energy levels allowable that could be occupied if the corresponding particle has sufficient energy.

In the conduction band $(E > E_C)$, the density of states is given by:

$$g_C(E) = \frac{m_n^* \sqrt{2m_n^*(E - E_C)}}{\pi^2 \hbar^3} \quad \left[\mathrm{cm}^{-3}\,\mathrm{eV}^{-1}\right] \tag{2.11}$$

And in the valence band $(E < E_V)$ the density of states is given by:

$$g_V(E) = \frac{m_p^* \sqrt{2m_p^*(E_V - E)}}{\pi^2 \hbar^3} \quad \left[\mathrm{cm}^{-3}\,\mathrm{eV}^{-1}\right] \tag{2.12}$$

where E_C and E_V are the energy of the conduction and valence band, respectively.

2.6 Energy Distribution for Holes and Electrons

Considering a semiconductor in thermal equilibrium, with no generation of carrier and insulated from the external, the probability that a state is occupied by an electron with energy E is given by the Fermi function.

$$f(E) = \frac{1}{1 + e^{(E - E_F)/kT}} \tag{2.13}$$

where E_F is the Fermi energy. This value depends on the material.

At $T = 0$, the Fermi function is a step function. All electrons have energy below or equal to E_F. When temperature rises there is a non-null probability that electrons could have energy above E_F. In Fig. 2.5 Fermi function is plotted for $T = 0$ K, $T = 300$ K, and $T = 3000$ K; Fermi level is set to 3 eV and the band gap is 1.1 eV as in the Silicon. It should be noted that at environmental temperature, the number of electrons with energy greater than the lower limit of conduction band is negligible.

In the conduction band, a state is occupied if there is an available state and if an electron has sufficient energy. As a consequence, to obtain the equilibrium electron

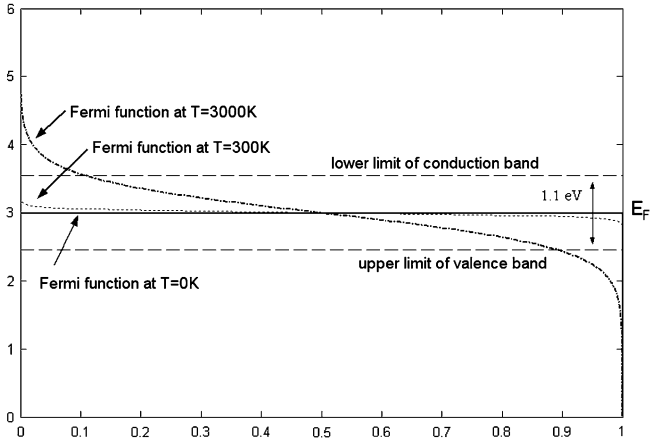


Fig. 2.5 Fermi level and state density

density, it is necessary to multiply the corresponding density of state (Eq. 2.11) for the probability that the electron has the corresponding energy (Eq. 2.13) and to integrate it from the minimum level to be occupied (E_C) to infinity.

$$n_0 = \int_{E_C}^{\infty} g_C(E) f(E) dE = 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2} e^{-(E_C - E_F)/kT} \tag{2.14}$$

where the following position can be done:

$$N_C = 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2} \tag{2.15}$$

N_C is the effective density of state in the conduction band. In the same way, the holes concentration at the equilibrium is given by:

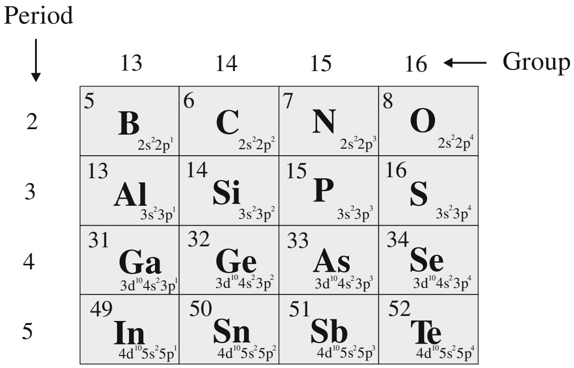
$$p_0 = \int_{-\infty}^{E_V} g_V(E)[1 - F(E)] dE = 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2} e^{(E_V - E_F)/kT} \tag{2.16}$$

and the following position can be done:

$$N_V = 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2} \tag{2.17}$$

Equations (2.14) and (2.16) are obtained under the hypothesis that E_F is sufficiently far from E_C and E_V (E_C—$E_F > 3kT$ and E_F—$E_V > 3kT$) in such a case, the semiconductor is said *nondegenerate* and the product of electrons and hole concentration does not depend on Fermi energy. In an undoped (intrinsic)

Fig. 2.6 Periodic table



Period ↓ / Group →	13	14	15	16
2	5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$
3	13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$
4	31 **Ga** $3d^{10}4s^23p^1$	32 **Ge** $3d^{10}4s^23p^2$	33 **As** $3d^{10}4s^23p^3$	34 **Se** $3d^{10}4s^23p^4$
5	49 **In** $4d^{10}5s^25p^1$	50 **Sn** $4d^{10}5s^25p^2$	51 **Sb** $4d^{10}5s^25p^3$	52 **Te** $4d^{10}5s^25p^4$

semiconductor, the electron and hole concentration is equal and this value is the intrinsic carrier concentration n_i.

$$n_i = \sqrt{n_0 p_0} = \sqrt{N_C N_V} e^{(E_V - E_C)/2kT} = \sqrt{N_C N_V} e^{-E_g/2kT} \tag{2.18}$$

This last equation represents the *law of mass action:* regardless of doping, the product of hole and electron densities is a material property that does not depend on temperature. It should be noted that the wider is the forbidden band the lower is the intrinsic carrier concentration.

Finally, the Fermi level for an intrinsic semiconductor can be evaluated by equating the electrons and hole concentration given by Eqs. (2.14) and (2.16), respectively.

$$E_{F_i} = \frac{E_C + E_V}{2} + \frac{kT}{2} \ln\left(\frac{N_V}{N_C}\right) \tag{2.19}$$

The Fermi level is very close to the middle of band gap.

The intrinsic carrier concentration for Silicon ($n_i \approx 10^{10}$ cm^{-3}) makes it an insulator, to exploit it as a semiconductor the introduction of specific impurities or dopants is necessary.

2.7 Doping

The conductivity of a semiconductor can be varied by introducing specific dopants. With reference to the part of periodic table sketched in Fig. 2.6, it can be noted that phosphorous has five valence electrons ($3s^23p^3$) whereas boron has three valence electrons ($3s^23p^1$).

If phosphorous atoms are introduced in a silicon crystal, one of its five valence electrons becomes available for conduction, the remaining four electrons are tied with covalence bonds of silicon lattice (see Fig. 2.7a). This kind of dopant is said *donor*. In the same way by introducing boron, its three valence electrons are tied

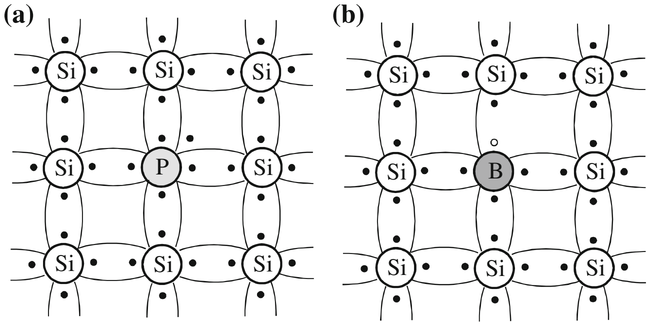


Fig. 2.7 **a** *n-type* doping with Phosphorous As, **b** *p-type* doping with Boron

with covalence bonds of silicon lattice and a hole remains (see Fig. 2.7b). This kind of dopant is said *acceptor*.

From the point-of-view of energy levels, the presence of donor introduces additional energy levels near the conduction band (within few *kT*), hence thermal energy can allow the added electron to move to the conduction band. In the same way, the presence of an acceptor introduces additional energy levels near the valence band.

In case of donor introduction, electrons are the primary source of conduction and the semiconductor is said *n-type*, on the contrary, if an acceptor is introduced, conduction is due to hole, and the semiconductor is said *p-type*.

The atoms of donors (N_D) or acceptors (N_A) are usually completely ionized, as a consequence for *n-type* semiconductor $n_0 \approx N_D$ and for *p-type* semiconductor $p_0 \approx N_A$. This hypothesis will be maintained in the following, throughout the chapter.

The presence of dopant changes the Fermi level compared to an intrinsic semiconductor, this value can be recalculated by using Eq. (2.19); for an *n-type* semiconductor:

$$E_{Fn} = E_{F_i} + kT \ln\left(\frac{N_D}{n_i}\right) \tag{2.20}$$

Compared to an intrinsic semiconductor the Fermi level is increased.

For a *p-type* semiconductor:

$$E_{Fp} = E_{F_i} - kT \ln\left(\frac{N_A}{n_i}\right) \tag{2.21}$$

and the Fermi level is lower compared to the intrinsic semiconductor.

The Eq. (2.18) holds even for doped semiconductors, for an *n-type*:

$$n_i^2 = n_0 \cdot p_0 = p_0 \cdot N_D \tag{2.22}$$

and the donors' concentration can be expressed versus the Fermi level for an intrinsic semiconductor:

$$n_0 = N_C e^{-(E_C - E_{Fn})/kT} = N_C e^{-(E_C - E_{Fi})/kT} e^{(E_{Fn} - E_{Fi})/kT} = n_i e^{(E_{Fn} - E_{Fi})/kT} \tag{2.23}$$

where the n_i is obtained by using Eqs.(2.18) and (2.19) with the position $N_C \approx N_{V.}$

For a *p-type*:

$$n_i^2 = n_0 \cdot p_0 = n_0 \cdot N_A \tag{2.24}$$

$$p_0 = n_i e^{-\left(E_{Fp} - E_{Fi}\right)/kT} \tag{2.25}$$

In an *n-type* semiconductor, electrons represent majority carriers and holes minority carriers. Usually, if necessary, their concentration symbol includes a pedex to indicate the semiconductor type. Hence, in an *n-type* semiconductor there are n_n majority carriers and p_n minority carriers. In a *p-type* semiconductor, there are p_p majority carriers and n_p minority carriers. If necessary, to specify the equilibrium conditions a further pedex "*o*" can be added.

When double doping with both donors and acceptors is performed, the type of the semiconductor is determined by the greatest impurity concentration.

Supposing the total ionization of both donors and acceptors, if $N_D > N_A$ an *n-type* results with $n_n \approx N_D - N_A$ electrons and p_n holes concentration, on the contrary if $N_A > N_D$ a *p-type* results with $p_p \approx N_A - N_D$ holes and n_p electrons concentration. As a matter of fact, considering, for example, the case of $N_D > N_A$, being the intrinsic semiconductor and both the dopants neutral after doping, the final positive charge (due to holes and ionized donors) must be equal to the negative charge (due to electrons and ionized donors):

$$n_n + N_A = p_n + N_D \tag{2.26}$$

using the action mass law written in the form $n_i^2 = n_n p_n$ it is possible to obtain:

$$\begin{cases} n_n = \frac{1}{2}\left[N_D - N_A + \sqrt{(N_D - N_A)^2 + 4n_i^2}\right] \\ p_n = \dfrac{n_i^2}{n_n} \end{cases} \tag{2.27}$$

usually the difference between donors and acceptors is greater than the intrinsic concentration, it means $|N_D - N_A| > n_i^2$.

2.8 Carrier Transport

Until now, the semiconductor has been considered in equilibrium status with n_o electron and p_0 holes concentration. In this condition, electrons move continuously inside the lattice in all directions but, if observed for sufficiently long time, its displacement is null. The mean distance between two collisions is known as the

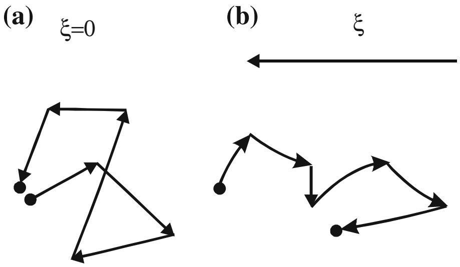


Fig. 2.8 **a** Random thermal motion, **b** thermal motion under electric field

free mean path (L_c) and the corresponding time interval between two collisions as the *mean free time* (τ_c). This situation is schematically sketched in Fig. 2.8a.

By using the effective mass m_n^*, the electrons' kinetic energy can be expressed by assigning $kT/2$ for each degree of freedom.

$$\frac{1}{2}m_n^* v_{th}^2 = \frac{3}{2}kT \tag{2.28}$$

where v_{th} is the mean free speed, at environment temperature ($T = 300$ K) it is equal to 10^7 cm/s both for Si and GaAs. Considering a typical value of 10^{-5} cm for the free mean path it follows $\tau_c = L_c/v_{th} = 10^{-12}$ s $= 1$ ps.

If an electric field is applied to the semiconductor, a carriers' displacement occurs. The motion is schematically sketched in Fig. 2.8b: the electron (hole) is continuously scattered but there is a non-null mean displacement.

The motion of electrons and holes can be changed by applying an electric field or by varying locally their concentration. In the former case the process is called *drift*, in the latter *diffusion*.

2.8.1 Drift Current

With regard to drift current, if an electric field is applied to a uniformly doped semiconductor, the energy of the bands does not remain constant but it is raised in the direction of the field. Electrons are moved to the opposite direction of the field toward lower energy of conduction band and holes toward higher energy of the valence band. The motion is schematically sketched in Fig. 2.9: the electron (hole) is continuously scattered but there is a non-null mean displacement.

Electrons have a drift velocity in the opposite direction of the electric field.

$$\vec{v}_{\text{drift\_}n} = -\mu_n\vec{\xi} = \mu_n\nabla\phi \tag{2.29}$$

where ϕ is the electrostatic potential and μ_n is the electrons mobility coefficient. As a consequence a drift current occurs; its density is equal to the product of drift velocity for the density of electrons (or holes) and for the unit charge.

$$\vec{J}_{\text{drift\_}n} = -qn\vec{v}_{\text{drift\_}n} = qn\mu_n\vec{\xi} = -qn\mu_n\nabla\phi \tag{2.30}$$

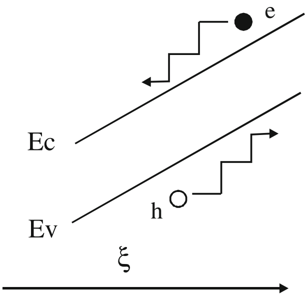


Fig. 2.9 Energy levels and electrons (holes) motion in presence of an electric field

For a semiconductor whose length (corresponding to the x direction) is bigger than the other two dimensions and the electric field is in the x direction. A one-dimensional (1D) representation can be used, as depicted in Fig. 2.10; Eq. (2.30) becomes:

$$J_{\mathrm{drift\_}n} = -qnv_{\mathrm{drift\_}n} = -qn\mu_n\xi = -qn\mu_n\frac{\partial\phi}{\partial x} \tag{2.31}$$

where $\nabla\phi$ reduces to the potential derivative along x.

The drift velocity is proportional to the electric field ξ or to the derivative along x direction of the electrostatic potential φ.

$$v_{\mathrm{drift\_}n} = -\mu_n\xi = \frac{\partial\phi}{\partial x} \tag{2.32}$$

In the same way for holes:

$$\vec{J}_{\mathrm{drift\_}p} = qp\vec{v}_{\mathrm{drift\_}p} = qp\mu_p\vec{\xi} = qp\mu_p\nabla\varphi \tag{2.33}$$

$$\vec{v}_{\mathrm{drift\_}p} = \mu_p\vec{\xi} = \mu_p\nabla\phi \tag{2.34}$$

The coefficients that tie velocity to electric field can be evaluated by equating the impulse of the force ($-q\xi$) multiplied for time interval to the quantity of motion achieved in the same time. For electrons:

$$-q\xi\tau_n = m_n^* v_{\mathrm{drift\_}n} \tag{2.35}$$

$$\mu_n = \frac{q\tau_n}{m_n^*} \tag{2.36}$$

And for holes:

$$q\xi\tau_p = m_p^* v_{\mathrm{drift\_}p} \tag{2.37}$$

$$\mu_p = \frac{q\tau_p}{m_p^*} \tag{2.38}$$

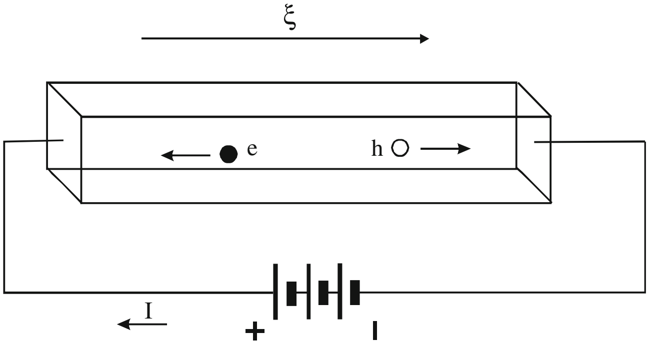


Fig. 2.10 Semiconductor with electric field applied: a drift current formed by holes and electron occurs

Mobility coefficient takes into account scattering mechanism for lattice interaction and ionized impurity

2.8.2 *Diffusion Current*

When concentration is not uniform, carriers tend to move from regions with high concentration to regions with low concentration. A diffusion current occurs and its density is given respectively for electrons and holes by:

$$\vec{J}_{\text{diff}\_n} = qD_n \nabla n \tag{2.39}$$

$$\vec{J}_{\text{diff}\_p} = -qD_p \nabla p \tag{2.40}$$

where D_n and D_p are the diffusivity coefficients for electrons and holes respectively, and q is the electron charge.

Considering a long semiconductor where the injection is performed on a lateral surface, the current occurs in x direction:

$$J_{\text{diff}\_n} = qD_n \frac{\partial n}{\partial x} \tag{2.41}$$

$$J_{\text{diff}\_p} = -qD_p \frac{\partial p}{\partial x} \tag{2.42}$$

The total current induced in a semiconductor is the sum of diffusion and drift currents for electrons and holes:

$$\vec{J}_n = \vec{J}_{\text{drift}\_n} + \vec{J}_{\text{diff}\_n} \tag{2.43}$$

$$\vec{J}_p = \vec{J}_{\text{drift}\_p} + \vec{J}_{\text{diff}\_p} \tag{2.44}$$

In thermal equilibrium, diffusion current and drift current must balance. Comparing these two terms, the *Einstein relationship* is obtained.

$$D_n = \left(\frac{kT}{q}\right)\mu_n \tag{2.45a}$$

$$D_p = \left(\frac{kT}{q}\right)\mu_p \tag{2.45b}$$

By using Eqs. (2.28), (2.36), and (2.38), the mean free path is obtained versus diffusivity and mean free time:

$$L_n = \sqrt{D_n \tau_n} \tag{2.46a}$$

$$L_p = \sqrt{D_p \tau_p} \tag{2.46b}$$

Finally, a further term due to dielectric displacement field should be added.

$$\vec{J}_{\text{disp}} = \frac{\partial \vec{D}}{\partial t} = \varepsilon \frac{\partial \vec{\xi}}{\partial t} \tag{2.47}$$

where ε is the electric permittivity of the semiconductor. However, it should be considered that in case of photovoltaic cell that is operated in DC, this term can be neglected.

For Silicon at $T = 300$ K and impurity concentration of 10^{16} cm^{-3}, electron mobility is about 1400 cm^2/Vs and consequently diffusivity is about 35 cm^2/s. Lower values are exhibited by holes for which mobility is about 490 cm^2/Vs and consequently diffusivity is about 10 cm^2/s. Another semiconductor as GaAs has values greater of about five times. Mobility and diffusivity decrease with impurity concentration.

2.8.3 Semiconductor Resistivity

Considering Eqs. (2.30) and (2.33), the total current density due to an electric field is given by:

$$J = J_n + J_p = \left(qn\mu_n + qp\mu_p\right)\xi \tag{2.48}$$

This equation defines the resistivity of the semiconductor as:

$$\rho = \frac{1}{\sigma} = \frac{1}{\left(qn\mu_n + qp\mu_p\right)} \tag{2.49}$$

2.9 Semiconductor Fundamental Equations

The semiconductor obeys to two fundamental laws: the Poisson's equation and the continuity equation.

The Poisson's equation comes from Gauss' law for electricity, it says that in a control volume the divergence of electric displacement field $\vec{D}$ is equal to the free charge density ρ_s. For a linear, isotropic, and homogeneous medium $\vec{D} = \varepsilon\vec{E}$.

The continuity equation is a local conservation law. It affirms that a quantity (no matter what: particles, charges or people) in a given volume can change in the time only for a flux variation of the quantity through the surface that contains the volume.

2.9.1 The Poisson's Equation

The general form for a semiconductor was proposed by Van Roosbroeck in 1950:

$$\nabla \cdot \varepsilon\vec{\xi} = \rho_s \tag{2.50}$$

where ρ_s is the spatial charge density. For a semiconductor, ρ_s can be expressed as the contribution of positive charge (holes density plus the ionized donors) and the negative charge (electron density and ionized acceptors).

$$\nabla \cdot \varepsilon\vec{\xi} = q(p + N_D - n - N_A) \tag{2.51}$$

This last equation can be particularized along x direction:

$$\varepsilon\frac{d\xi}{dx} = q(p + N_D - n - N_A) \tag{2.52}$$

2.9.2 Continuity Equation

The continuity equation can be written both for electrons and holes. The general form for electrons is:

$$\nabla \cdot \vec{J}_n = q\left(R_n - G_n + \frac{\partial n}{\partial t}\right) \tag{2.53}$$

The first member is the divergence of electron current density. It represents the flux of electrons through an arbitrary volume.

The second member is the variation of the electrons' number during the time. It is composed of a first term that gives the velocity of the recombination R_n. The

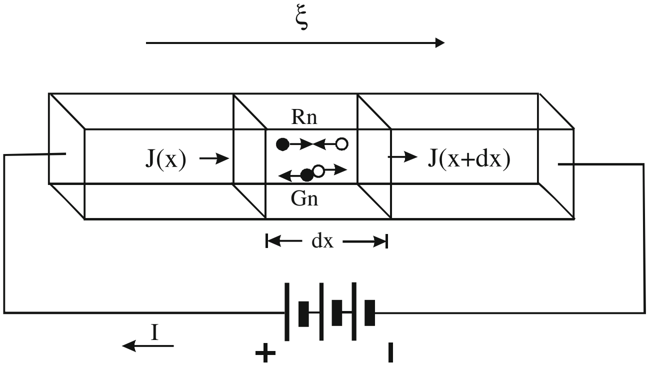


Fig. 2.11 Semiconductor with electric field applied: application of the continuity equation to a volume with length *dx*

recombination process occurs when an electron falls from conduction band to valence band and a couple electron–hole disappears.

Several recombination mechanisms are possible: by defects in the forbidden band, radiative recombination, and a further term called Auger recombination.

The first type of recombination occurs when an electron or a hole makes a transition to a parasitic energy level inside the forbidden band and phonons are emitted. In radiative recombination, a transition from conduction band to valence band origins a photon emission.

In Auger recombination, an electron and a hole recombine in a band-to-band transition, but in this case the resulting energy is given off to another electron or hole, in this last case three particles are involved.

The second term of Eq. (2.53), G_n, gives the velocity of generation, this occurs for light absorption or carrier injection.

The third term is the time variation of electron density.

In 1D representation, as depicted in Fig. 2.11, the continuity equation for electrons is:

$$\frac{\partial J_n}{\partial x} = q\left(R_n - G_n + \frac{\partial n}{\partial t}\right) \tag{2.54}$$

For holes:

$$\nabla \cdot \vec{J}_p = q\left(G_p - R_p - \frac{\partial p}{\partial t}\right) \tag{2.55}$$

$$\frac{\partial J_p}{\partial x} = q\left(G_p - R_p + \frac{\partial p}{\partial t}\right) \tag{2.56}$$

2.10 Minority Carrier Diffusion Equations

A 1D representation of the semiconductor is considered in the following.

For steady state conditions, Eq. (2.54) can be used neglecting the time derivative. Moreover, current density derivative considering Eqs. (2.30) and (2.39) is given by:

$$\frac{d}{dx}J_n = q(R_n - G_n) = \frac{d}{dx}\left(-qn\mu_n\xi + qD_n\frac{\partial n}{\partial x}\right) \tag{2.57}$$

and for holes

$$\frac{d}{dx}J_p = q\left(R_p - G_p\right) = \frac{d}{dx}\left(-qn\mu_p\xi + qD_p\frac{\partial p}{\partial x}\right) \tag{2.58}$$

For small electric field, the contribution of electric field space derivative can be neglected. It corresponds to neglect the drift current compared to diffusion current.

Under low level injection, the recombination rate for electrons can be written as the difference between the minority carriers in that position and their equilibrium value divided by the minority carrier lifetime.

$$R_n = \frac{p_n - p_{n0}}{\tau_p} = \frac{\Delta p_n}{\tau_p} \tag{2.59}$$

It should be noted that electron recombination depends on the corresponding minority carriers. As a matter of fact, the recombination can occur when a minority carrier is available. For an *n-type* material, from Eq. (2.58) the corresponding minority carrier diffusion equation is obtained:

$$D_p\frac{d^2}{dx^2}\Delta p_n - \frac{\Delta p_n}{\tau_p} = -G(x) \tag{2.60}$$

For a *p-type* material the corresponding minority carrier diffusion equation is:

$$D_n\frac{d^2}{dx^2}\Delta n_p - \frac{\Delta n_p}{\tau_n} = -G(x) \tag{2.61}$$

When an n-doped semiconductor is lighted on a lateral surface, a carrier injection is performed, the minority carrier concentration is given by Eq. (2.57) imposing $G(x) = 0$ with boundary conditions:

$$\begin{cases} p_n(x=0) = p_n(0) \\ p_n(x \Rightarrow \infty) = p_{n0} \end{cases} \tag{2.62}$$

At the surface, the injection causes a constant value of minority carriers' concentration $p_n(0)$, on the contrary, for x sufficiently far from the injection surface, the concentration returns to the equilibrium value p_{n0}.

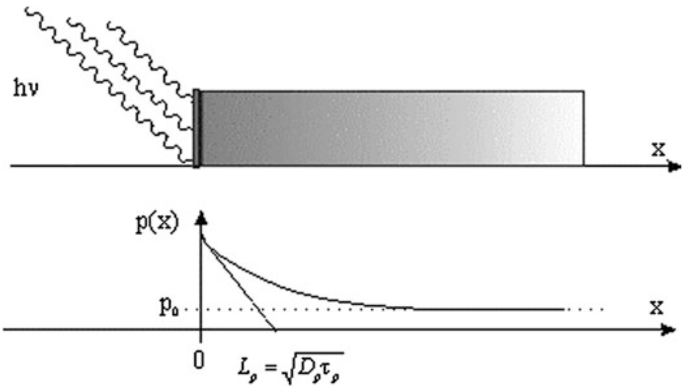


Fig. 2.12 Representation of a semiconductor bar with an incident light on the lateral surface that causes charge injection: the charge concentration relaxes with spatial constant L_p, for x sufficiently far from the injection zone the equilibrium concentration is restored

The solution is:

$$p_n(x) = p_{n0} + [p_n(0) - p_{n0}]e^{-x/L_p} \tag{2.63}$$

The minority carriers' concentration relaxes with exponential law. The relaxation space constant is given by Eqs. (2.46a, b).

The resultant diffusion current can be obtained by Eq. (2.41).

It should be noted that, if the semiconductor length is about L_p, a different boundary condition must be imposed on the corresponding surface where the minority concentration carriers are different from equilibrium value.

Figure 2.12 shows a typical situation in which the incident light on the lateral surface causes charge injection, their concentration relaxes with spatial constant L_p, if the distance is sufficiently far from the injection zone, the equilibrium concentration is restored and the charge concentration equals the equilibrium value p_O.

2.11 P–N Junction

A p–n junction can be conceptually conceived as a two doped semiconductor of *n-type* and *p-type* that have a surface in common. When both semiconductors are separated, they are electrically neutral. As soon as they get in touch, majority carriers of *n-type* semiconductors (the electrons) begin to diffuse into the *p-type* semiconductor and vice versa. As a result, near the surface of separation between the two semiconductors, in *n-type* semiconductor, holes coming from *p-type* semiconductor tend to combine with electrons and the positive charge of the corresponding ionized donors is not more compensated by majority carriers. Inside the *n-type* region, near the junction, where there are no more majority

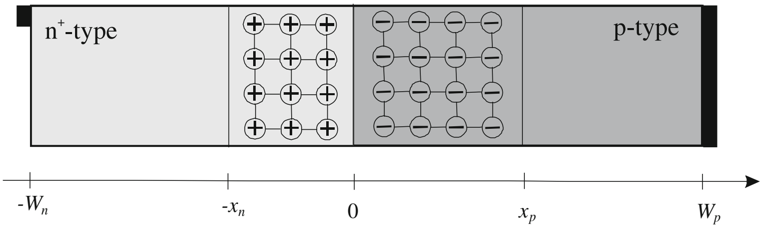


Fig. 2.13 Schematic representation of a p–n junction

charges, a depletion is observed and the corresponding zone remains with fixed positive charges.

In the same way, in *p-type* side, electrons coming from *n-type* semiconductor tend to combine with holes and the negative charge of the ionized acceptors is not more compensated by majority carriers. Inside the *p-type* region, near the junction, where there are no more majority charges, a depletion is observed and the corresponding zone remains with fixed negative charges.

As the fixed charges are uncovered, an electric field is produced and the diffusion process is slowed down. A p–n junction is drawn in Fig. 2.13 in 1D representation; the origin ($x = 0$) is the junction surface, x_p and W_p are the depletion boundary at the end of *p-type* region, while $-x_n$ and $-W_n$ are the depletion boundary at the end of *n-type* region. It should be noted that, if a semiconductor is more doped than the other (usually indicated with apex +), the greater quantity of free carrier diffused in the other semiconductor cause a more extended depletion.

It is assumed a uniformed and nondegenerated doping and that dopants are fully ionized.

The whole zone in which there are fixed uncompensated charge is called *depletion region* or *space charge region*. The remaining zones can be considered as neutral (often called *quasineutral*). The electric field due to the fixed charges origins an electrostatic potential difference called *built-in voltage*.

The Poisson's Eq. (2.50) can be rewritten as:

$$\frac{d\xi}{dx} = -\nabla^2\phi = \frac{q}{\varepsilon}(p_0 + N_D - n_0 - N_A) \tag{2.64}$$

where ϕ is the electrostatic potential, p_O and n_o are the hole and electron equilibrium concentration, N_D is the concentration of ionized donors (positive fixed charges), and N_A is the concentration of ionized acceptors (negative fixed charges).

Equation (2.64) can be particularized for each zone. In quasineutral zone, the net charge is null and it follows $\nabla^2\phi = 0$, inside the positive charged depletion region $\nabla^2\phi = -qN_D/\varepsilon$ and inside the negative charged depletion region $\nabla^2\phi = qN_A/\varepsilon$.

The built-in voltage is the potential difference between points $x = -x_n$ and $x = x_p$.

$$V_{bi} = \phi(-x_n) - \phi(x_p) \tag{2.65}$$

Assuming that $\phi(x_p) = 0$ The process of the potential along x is:

$$\phi = \begin{cases} V_{bi} & for \quad x \leq -x_n \\ V_{bi} - \frac{qN_D}{2\varepsilon}(x + x_n)^2 & for \quad -x_n < x < 0 \\ \frac{qN_A}{2\varepsilon}(x - x_p)^2 & for \quad 0 \leq x < x_p \\ 0 & for \quad x \geq x_p \end{cases} \tag{2.66}$$

Imposing that the second and the third relationship in Eq. (2.66) give the same values of ϕ for $x = 0$ and the continuity of the electric field in the same point, that gives:

$$x_n N_D = x_p N_A \tag{2.67}$$

the length of depletion zone is obtained versus built-in voltage.

$$W_D = x_n + x_p = \sqrt{\frac{2\varepsilon}{q}\left(\frac{N_A + N_D}{N_A N_D}\right) V_{bi}} \tag{2.68}$$

Equation (2.68) says that the length of depletion zone depends on the built-in voltage. For diode operation, this value can be lessened by applying a positive voltage on p-side (forward bias) or widened by a positive voltage on n-side (reverse bias).

In particular, in case of forward bias, the built-in voltage V_{bi} is lessened by a quantity equal to the applied voltage and the corresponding electric field changes the equilibrium conditions allowing holes belonging to p zone to pass through the junction and reaching the n zone and electrons belonging to n zone to pass through the junction and reaching the p zone, as well.

The depletion zone length can be calculated by Eq. (2.68) using the new value of (V_{bi}−V) where V is the applied voltage.

For low level charge injection, a diffusion current due to minority charges as described by Eq. (2.63) for holes in n zone occurs. The corresponding current is calculated by (2.42)

$$J_{diff\_p} = qD_p \frac{\partial p}{\partial x} = q\frac{D_p}{L_p}[p_n(0) - p_{n0}]e^{-x/L_p} \tag{2.69}$$

Now, taking into account that the total current remains the same along x because inside the quasineutral region there is no appreciable generation–recombination rate, it is easy to evaluate Eq. (2.69) for $x = 0$.

$$J_{diff\_p}(0) = q\frac{D_p}{L_p}[p_n(0) - p_{n0}] = q\frac{D_p}{L_p}\Delta p_n \tag{2.70}$$

It should be noted that, because current is constant along x direction, decreasing the minoritary carriers current, a complementary current due to majority carriers occurs along x. For $x \gg L_p$ the current is due only to majority carriers.

Next step consists on evaluating the term inside square brackets. Considering the Eq. (2.58), its second member contains two terms with a high value. As a matter of fact, there is a big value of the electric field and a great variation of the concentration carriers. Being the first member small, as it represents a low level injection the following approximated relationship can be used:

$$qp\mu_p\vec{\xi} = qD_p\frac{dp}{dx} \tag{2.71}$$

By using Einstein relationship (2.45a) and assuming $V_T = kT/q$, Eq. (2.71) becomes:

$$\xi = \frac{V_T}{p}\frac{dp}{dx} = -\frac{dV}{dx} \tag{2.72}$$

As for the holes concentration, it should be observed that, inside the p zone it assumes the value corresponding to the thermal equilibrium p_{p0}, at the edge of the n zone, near the depletion zone it is equal to $p_n(0)$. Rewriting Eq. (2.72) and integrating over the depletion zone:

$$\int_{p_{p0}}^{p_n(0)} \frac{dp}{p} = -\frac{1}{V_T}\int_{0}^{V_{bi}-V} dV \tag{2.73}$$

it follows that:

$$p_n(0) = p_{p0}e^{-(V_{bi}-V)/V_T} \tag{2.74}$$

Finally, the relationship between p_{p0} and p_{n0} can be found by integrating Eq. (2.72) under no bias condition (it means $V = 0$) obtaining:

$$p_{n0} = p_{p0}e^{-(V_{bi})/V_T} \tag{2.75}$$

from which

$$p_n(0) - p_{n0} = p_{n0}\left[e^{V/V_t} - 1\right] \tag{2.76}$$

and the Eq. (2.70) becomes:

$$J_{diff\_p}(0) = q\frac{D_p p_{n0}}{L_p}\left[e^{V/V_t} - 1\right] \tag{2.77}$$

Finally, the junction current is determined by adding the contribution of electrons and multiplying for the section area A.

$$I = I_s(e^{V/V_t} - 1) \tag{2.78}$$

where

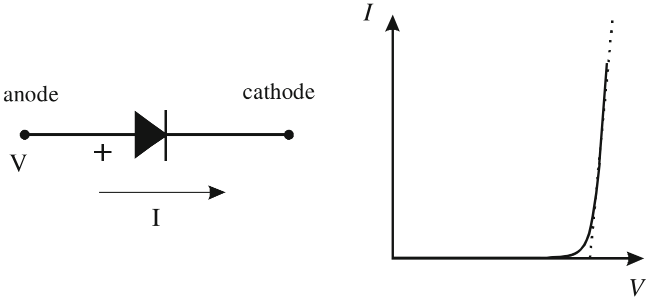


Fig. 2.14 Electric symbol and voltage versus current diode characteristic

$$I_s = Aq\left(\frac{D_p p_{n0}}{L_p} + \frac{D_n n_{p0}}{L_n}\right) \tag{2.79}$$

Equation (2.78) is known as the Shockley diode equation.

When the forward bias voltage approaches V_{bi} the depletion zone tends to vanish and the current is limited by the semiconductor and ohmic contact, as well. In this case, the voltage versus current characteristic is approximated by straight line.

When a reverse bias is applied, it means that a positive voltage is applied to the n zone contact, and Eq. (2.78) can be still utilized. As a matter of fact, the exponential term is negligible and a reverse saturation current given by Eq. (2.79) is obtained. In this case, the obtained small current is given only by carriers generated inside the junction and it does not depend on the applied reverse bias.

Figure 2.14 shows the voltage versus current characteristic of a diode.

From what explained above, it is clear that a diode allows the current to pass from p zone to n zone when it is forward biased. The ohmic contact belonging to the p zone is called *anode* while the ohmic contact belonging to the n zone is called *cathode*.

2.12 P–N Junction Capacitance

In Sect. 2.11, it has been explained that current near the junction is due to minority carrier injection. When the bias voltage changes, the corresponding charge concentration varies as well, but similarly to a capacitor, this concentration requires a finite time interval to reach a new equilibrium.

The equivalent capacitance can be calculated by considering the minority carrier diffusion in Eq. (2.63) in which injection is due to junction direct voltage polarization for which electrons are injected in p region. If the p region is more doped than the n region, it can be assumed that current is given only by holes injected into the n region.

The whole charge variation compared to equilibrium condition can be calculated as:

$$Q = A\int_0^\infty q[p_n(x) - p_{n0}]dx = A\int_0^\infty q[p_n(0) - p_{n0}]e^{-x/L_p}dx = \\ = Aq[p_n(0) - p_{n0}]L_p = AqL_p\Delta p_n \tag{2.80}$$

where A is the junction cross-sectional area. By comparing Eqs. (2.80) with (2.70) and using Eq. (2.46b), it follows that:

$$J_{\text{diff\_}p} = \frac{Q}{\tau_p} \tag{2.81}$$

It means that the current is proportional to the excess of minority charges.

For direct polarization the capacitance of the junction is called *diffusion capacitance*, for inverse junction polarization the capacitance is called *transition capacitance* and it has lower value than the diffusion capacitance; moreover under PV cells operation the inverse polarization of the junction does not occur, on the contrary, diffusion capacitance evaluation gives information about dynamic behavior.

By using Eq. (2.81), under static condition:

$$C_D = \frac{dQ}{dV} = \tau_p\frac{dI}{dV} = \tau_p g \tag{2.82}$$

where g is the differential conductance of the junction; it can be obtained on the basis of Eq. (2.78) neglecting the terms corresponding to the inverse saturation current.

$$g = \frac{dI}{dV} = \frac{d}{dV}\left[I_s\left(e^{V/V_T} - 1\right)\right] = \frac{I_s}{V_T}e^{V/V_t} = \frac{I}{V_T} \tag{2.83}$$

then:

$$C_D = \tau_p\frac{I}{V_T} \tag{2.84}$$

The diffusion capacity is proportional to the current. If both holes and electrons contribute to the current, the diffusion capacity is the sum of two terms due to electrons and holes respectively. Finally, comparing Eqs. (2.82) and (2.84), it can be seen that the time constant of the RC equivalent circuit is equal to the minority charges lifetime:

$$\frac{C_D}{g} = \tau_p \tag{2.85}$$

If applied voltage varies with time, the dynamic diffusion capacity is defined on the basis of charge variation in time interval *dt* as:

$$i = \frac{dQ'}{dt} = \frac{dQ'}{dv} \cdot \frac{dv}{dt} = C'_D \frac{dv}{dt} \tag{2.86}$$

During the time interval *dt*, only the charge near the junction varies, as a matter of fact, carrier diffusion requires more time to reach a new equilibrium condition. For this reason, the charge variation is lower compared to static condition and a lower value of diffusion capacity is expected. In any case, the dynamic value of diffusion capacitance depends on the applied voltage waveform; an expression of this voltage can be obtained for a sinusoidal case with amplitude V_m and pulsation ω superimposed to a fixed bias V_1.

$$v(t) = V_1 + V_m e^{j\omega t} \tag{2.87}$$

if V_m is a small signal, nonlinear effect of I–V curve can be neglected and the resulting current has the form

$$i(t) = I_1 + gV_m e^{j\omega t} + j\omega C'_D V_m e^{j\omega t} \tag{2.88}$$

The excess minority carrier concentration contains, in addition to the term due to static polarization, a further time dependent term:

$$\Delta p_n(x,t) = \Delta p_n(x) e^{j\omega t} \tag{2.89}$$

By utilizing Eqs. (2.57) and (2.58) where there is no charge generation and neglecting the electric field derivative, the differential equation for the excess minority charges is obtained:

$$D_p \frac{d^2}{dx^2} \Delta p_n - \frac{\Delta p_n}{\tau_p} - \frac{d(\Delta p_n)}{dt} = 0 \tag{2.90}$$

By substituting Eq. (2.89) in Eq. (2.90) and taking into account that from Eq. (2.46a) $L_p = \sqrt{D_p \tau_p}$:

$$\frac{d^2}{dx^2} \Delta p_n = \frac{1 + j\omega\tau_p}{L_p^2} \Delta p_n \tag{2.91}$$

that gives:

$$\Delta p_n = k e^{-\frac{(1 + j\omega\tau_p)\frac{1}{2} x}{L_p}} e^{j\omega t} \tag{2.92}$$

the resulting excess minority carriers' concentration is given by the time constant term defined by Eq. (2.63) plus the time varying term defined by Eq. (2.92).

$$\Delta p_n = p_{no}\left(e^{\frac{V_1}{V_T}} - 1\right)e^{-x/L_p} + ke^{-\dfrac{(1+j\omega\tau_p)^{\frac{1}{2}}x}{L_p}}e^{j\omega t} \tag{2.93}$$

where k is a constant that can be found by equating the junction law Eq. (2.76) considering that the junction voltage is defined by Eq. (2.87)

$$\Delta p_n = p_{no}\left(e^{\dfrac{V_1 + V_m e^{j\omega t}}{V_T}} - 1\right)e^{-x/L_p} \tag{2.94}$$

with the resulting excess minority carriers' concentration expression Eq. (2.93) both evaluated for $x = 0$.

Since, for $y \ll 1$, $e^y \approx 1 + y$ assuming $(V_m/V_T)e^{j\omega t} = y$, the following expression of k is obtained:

$$k = p_{n0}\frac{V_m}{V_T}e^{\frac{V_1}{V_T}} \tag{2.95}$$

Finally, the junction current is obtained by using Eq. (2.42) for $x = 0$.

$$J_{diff\_p} = -qD_p\left.\frac{\partial p}{\partial x}\right|_{x=0}$$

$$I_p(0) = \frac{AqD_p p_{n0}}{L_p}\left(e^{\frac{V_1}{V_T}} - 1\right) + \frac{AqD_p p_{n0}V_m e^{V_1/V_T}}{V_T}\cdot\frac{\sqrt{(1+j\omega\tau_p)}}{L_p}e^{j\omega t} \tag{2.96}$$

It should be noted that the first term of the second member of Eq. (2.96) corresponds to the static current of the p–n junction, I_1.

For low frequencies, corresponding to $\omega\tau_p \ll 1$, the approximation $\sqrt{1+j\omega\tau_p} \approx 1 + j\omega\tau_p/2$ is valid, then Eq. (2.96) gives:

$$I_p(0) = I_1 + \frac{AqD_p p_{n0}V_m e^{V_1/V_T}}{V_T L_p}\left(1 + \frac{j\omega\tau_p}{2}\right)e^{j\omega t} \tag{2.97}$$

$$\begin{cases} g = g_0 = \frac{AqD_p p_{n0}e^{V_1/V_T}}{V_T L_p} \\ C_D = \frac{g\tau_p}{2} \end{cases} \tag{2.98}$$

It should be noted that the conductance is the same one of static value g_0 but capacitance is divided by two. They both depend on the static polarization voltage by exponential term.

For high frequencies corresponding to $\omega\tau_p \gg 1$

$$\sqrt{(1+j\omega\tau_p)} = \sqrt{(j\omega\tau_p)} = \sqrt{(\omega\tau_p)}e^{j\frac{\pi}{4}} = \sqrt{\left(\frac{\omega\tau_p}{2}\right)}(1+j)$$

and Eq. (2.96) gives:

$$\begin{cases} g = g_0\sqrt{\left(\frac{\omega\tau_p}{2}\right)} \\ C_D = g_0\sqrt{\left(\frac{\tau_p}{2\omega}\right)} \end{cases} \tag{2.99}$$

In this last case, both diffusion capacitance and conductance depend on frequency.

2.13 The PV Cell

The photovoltaic (PV) cell is basically a p–n junction with a central depletion region and two lateral quasineutral zone. At the end of each zone an electrical contact is placed. The more heavily doped zone is called the *emitter* zone and the other is the *base* zone. This last region is also called the *absorber region* because the great part of incident light is absorbed here. Differently from a diode, the PV cell is designed so to allow holes–electrons couples to be generated inside the junction due to incident light.

The aim of this section is to define the law that ties voltage and current of a PV cell including the dependence on incident light.

In a word, the total current due to both electrons and holes has to be found.

$$I = A[J_p(x) + J_n(x)] \tag{2.100}$$

where A is the semiconductor's surface. To this aim, the electrons continuity equation (2.54) in steady state condition can be integrated over the depletion region obtaining:

$$\int_{-x_N}^{x_P} \frac{\partial J_n}{\partial x} dx = J_n(x_P) - J_n(-x_N) = q \int_{-x_N}^{x_P} [R_n(x) - G_n(x)]\, dx \tag{2.101}$$

Now, evaluating Eq. (2.100) for $x = -x_N$ and using Eq. (2.101) to deduce $J_n(-x_N)$, the following equation is obtained:

$$I = A\left[J_p(-x_N) + J_n(x_P) + q\int_{-x_N}^{x_P} G_n(x)dx - q\int_{-x_N}^{x_P} R_n(x)dx\right] \tag{2.102}$$

This last equation contains four terms. The first one is the hole density current evaluated at the end of depletion zone in n-type region, the second is the electron density current evaluated at the end of depletion zone in p-type region. These two terms are referred to minority carriers. The third term is the optical generation rate and the last term represents the recombination rate in the space charge region.

2.13.1 Minority Carriers Current Density

The minority carrier diffusion equations in the quasineutral n-type and p-type regions have to be solved with suitable boundary conditions. In particular, for n-type semiconductor Eq. (2.60) with boundary condition at $x = -W_N$ and $x = -x_{N;}$ and for *p-type* semiconductor Eq. (2.61) with boundary condition at $x = W_P$ and $x = x_P$.

It has been explained in Sect. 2.8 that doping changes Fermi energy level. Thus, the law of mass action can be written as:

$$n_i^2 = pn\,e^{-(E_{Fn}-E_{Fp})/kT} = pne^{-(\Delta E_{Fnp})/kT} \tag{2.103}$$

where ΔE_{Fnp} is the difference between Fermi level due to n doping and Fermi level due to p doping.

Assuming that the majority carriers maintain a constant concentration in their respective quasineutral zones, for n-type it means that Fermi energy level is constant for $-W_n \leq x \leq -x_n$ and for p-type that Fermi energy level is constant for $x_p \leq x \leq W_p$, therefore it can be assumed everywhere inside the semiconductor:

$$\Delta E_{Fnp} = E_{Fn}(-W_n) - E_{Fp}(-W_p) = E_{Fn}(x) - E_{Fp}(x) = qV \tag{2.104}$$

Now, being in n-type semiconductor quasineutral region $n = N_D$, the first boundary condition is obtained:

$$p_n(-x_n) = \frac{n_i^2}{N_D} e^{qV/kT} \tag{2.105}$$

And, being in p-type semiconductor quasineutral region $p = N_A$, it follows that:

$$n_p(x_p) = \frac{n_i^2}{N_A} e^{qV/kT} \tag{2.106}$$

It should be noted the presence of the factor $e^{qV/kT}$ in Eqs. (2.105) and (2.106), that will be present in the final expression of the current generated by the PV cell.

The last two boundary conditions are obtained considering that the front contact at the n-type zone is built by a metallic grid with an effective front surface $S_{F,eff}$, and the effective recombination is given by:

$$\frac{d}{dx}\Delta p = \frac{S_{F,eff}}{D_p}\Delta p(-W_n) \tag{2.107}$$

This situation is different from an ideal ohmic contact in which $\Delta p = 0$.

For the *p-type* semiconductor the back contact is quite an ohmic contact, however, if a thin more heavily doped region near this contact is introduced to increase the number of collected minority carriers, a condition similar to Eq. (2.107) can be imposed introducing the effective back surface S_{BSF}:

$$\frac{d}{dx}\Delta n = \frac{S_{BSF}}{D_n}\Delta p(W_p) \tag{2.108}$$

2.13.2 Optical Generation Rate

As explained before, only photons with wavelength $\lambda \leq hc/E_g$ can contribute to generate holes–electrons couples. The generation rate depends on a grid shadowing factor s, on the reflectance $r(\lambda)$, on the absorption coefficient $\alpha(\lambda)$ and on incident photon flux $f(\lambda)$ according to the Eq. (2.109).

$$\int_{-x_N}^{x_P} G_n(x)dx = (1-s)\int_{\lambda} [1-r(\lambda)]f(\lambda)\left(e^{-\alpha(W_N-x_N)} - e^{-\alpha(W_N-x_P)}\right)d\lambda \tag{2.109}$$

2.13.3 Recombination Rate

This term depends on the length of the depletion zone and on intrinsic carrier concentration, it is inversely proportional to the effective lifetime in the depletion region τ_D. Moreover, a further term is present in which the exponential contains the voltage multiplied for $(q/2kT)$ it is equal to about 19.23 J/C for $T = 300$ K.

$$\int_{-x_N}^{x_P} R_n(x)dx = \frac{W_D n_i}{\tau_D}\left(e^{(qV/2kT)} - 1\right) \tag{2.110}$$

2.13.4 Current Versus Voltage Law of Photovoltaic Cell

By solving minority carrier diffusion equation with boundary conditions and considering the generation and recombination, the current versus voltage law of photovoltaic cell is obtained after non-trivial calculations, not included here.

$$I = I_{ph} - I_{s1}\left(e^{qV/kT} - 1\right) - I_{s2}\left(e^{qV/2kT} - 1\right) \tag{2.111}$$

The first term is the short circuit current and collects the contributes of the two quasineutral zones and of the depletion zone.

The second term contains the dark saturation current due to the recombination in the quasineutral region I_{s1}. It should be observed that in Eq. (2.111) this

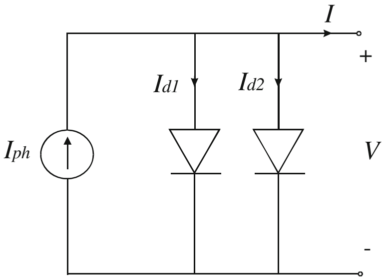


Fig. 2.15 Physical circuit model of a PV cell

phenomenon is considered ideal. When the non-ideality of the diffusion is taken into account, an ideality factor should be introduced in the exponential, as will be discussed in Chap. 3.

Finally, the last term contains the dark saturation current due to the recombination in the space charge region I_{s2}. This last term is bias dependent because it is proportional to the length of the depletion zone.

2.14 Physical Model of a PV Cell

Equation (2.111) reproduces the physical phenomena of a PV cell. It can be regarded as a Kirchhoff's current law (KCL) written for a node in an electrical circuit for which the sum of currents flowing into that node is equal to the sum of currents flowing out of that node. On the basis of this law, an equivalent circuit can be deduced. It represents a physical circuit model of a PV cell. This circuit is drawn in Fig. 2.15.

It should be noted that the output current is the sum of a current given by a generator that depends on solar irradiance minus the current that flows through the two diodes. The first current corresponds to I_{ph} in Eq. (2.111), the second current corresponds to $I_{s1}(e^{qV/kT}-1)=I_{d1}$ and the third current corresponds to$I_{s2}(e^{qV/2kT}-1)=I_{d2}$.

As a matter of fact, the second and the third term of Eq. (2.111) can be considered as Shockley diode equations. Finally, the output voltage is obtained by the diodes direct bias due to the current generator.

During operating conditions, when solar radiation occurs, the generator current flows through the diodes and a voltage appears at the terminals. If no load is applied this voltage is an "open circuit" voltage, i.e., the voltage of a directly polarized p–n junction and it is the maximum value achievable by a PV cell. If a load is connected, a part of the current of the generator flows into the load, voltage decreases and electric power is supplied to the load. The conversion process is completed.

Starting from solar radiation, electric energy has been obtained.

It should be noted that if the load is raised (it corresponds to a lower resistance) current rises too and voltage decreases; the supplied power reaches a maximum and then decreases until the short circuit condition.

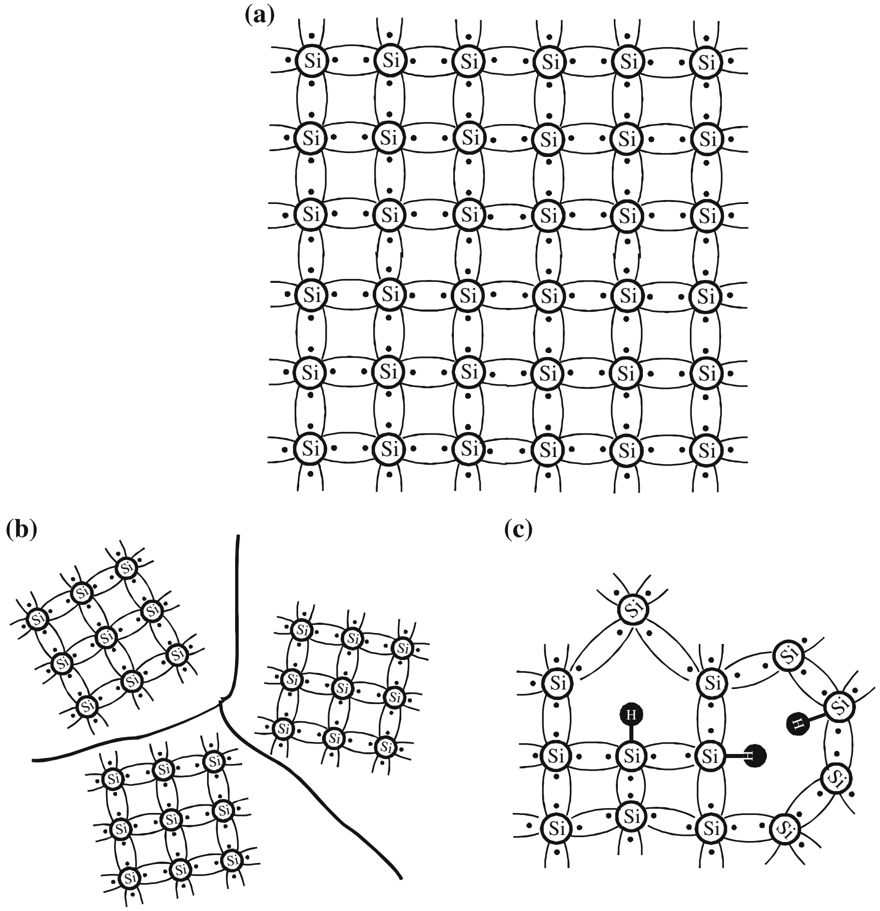


Fig. 2.16 Structure of crystalline (**a**), multicrystalline (**b**), and amorphous silicon (**c**)

When no solar radiation is present, the generated current is null and consequently the voltage at terminals. However, this does not correspond to a short circuit behavior, on the contrary, the PV cell does not allow negative current flow imposed by external circuits.

2.15 Semiconductor Types

Silicon can be arranged in different forms to obtain a photovoltaic cell depending on crystal structure. Following the classification on the basis of planar grain size, microcrystalline, polycrystalline, and multicrystalline can be distinguished. In particular, microcrystalline material exhibits a grain smaller than 1 μm, polycrystalline smaller than 1 mm, and multicrystalline smaller than 10 cm.

A schematic representation of structure of crystalline, multicrystalline, and amorphous silicon is drawn in Fig. 2.16.

2.15.1 Crystalline Silicon

Crystalline silicon is considered as an ideal structure where the pattern is regular throughout the whole surface. All theory explained above is developed with reference to this structure. The main advantage consists of highest ratio solar irradiance—produced electric power. With Monocrystalline silicon, power conversion efficiency ranging from 20 to 24 % is expected, with GaAs, power conversion efficiency ranging from 20 to 29 % is expected.

Crystalline silicon, on the other hand, is expensive owing to manufacturing process. For this reason, several alternative cheaper silicon structures have been developed.

2.15.2 Multicrystalline

Multicrystalline and polycrystalline silicon can be produced by a less sophisticated technique compared with crystalline. However, in this case, the presence of grain boundaries must be taken into account. In particular, cell performance is reduced because at the boundaries the carriers flow is blocked, the level structure is altered, and the current that would flow across p–n junction is shunted away.

Some remedies have been devised as, for example, the use of grains of few millimeters to cover the entire distance from the back to the front of the cell with minimum number of grains. With Polycrystalline silicon, a power conversion efficiency ranging from 13 to 18 % is expected.

2.15.3 Amorphous

Amorphous silicon presents a less regular structure with unsatisfied bonds. These “dangling” bonds are passivated by hydrogen by allowing doping (otherwise impossible) and raising the band gap form 1.1 eV of crystalline silicon to 1.7 eV; in this way, photons of higher energy can be absorbed and the required thickness of the material is lower. As a consequence, amorphous silicon can be used as a “thin film” form deposited on glass or other substrates for low cost applications.

The band structure of amorphous materials is similar to the crystalline material over short distance and a mobility gap, in which conduction occur, can be defined. However, there are a great number of localized energy states within mobility gap, corresponding to band tails and gangling bonds that make different the amorphous behavior compared to crystalline silicon.

2.15.4 Thin Film

The so called thin-film technologies, where thin-film cells are deposited on foreign substrate, are indicated for a transition from other technologies for module manufacturing.

It is possible, by increasing the ratio to hydrogen silane in the gas from which amorphous silicon is deposited, to obtain a microcrystalline material in which columns of crystallites are separated by amorphous region.

Actually, established thin-film technologies use amorphous silicon and nanocrystalline Si film (a-Si), cadmium telluride (CdTe), and copper indium/gallium diselenide (CIGs), they have efficiency of 8–13 % for a-Si, of 10–17 % for CdTe, and for 10–19 % for CIGs. Moreover, a reduced cost is expected. As a matter of fact, in a crystalline Si module about 40 % of cost is due to wafer or solar cell ribbon manufacturing.

2.15.5 Polymer Solar Cell

In addition to the previously cited inorganic material as Silicon (Si), Gallium Arsenide (GaAs), Cadmium Telluride (CdTe), and Cadmium-Indium-Selenide (CIS), endeavors to reduce costs due to solar grade silicon and fabrication processes have led to the exploitation of organic thin-film materials.

In particular, conjugated polymers and molecules are easy to be produced, they have mechanical flexibility as plastics, and can exhibit electronic properties similar to conductors and semiconductors. Moreover, recent progresses in soft lithography techniques as inkjet printing and microcontact printing have increased the interest toward the fabrication of integrated devices over both rigid and flexible substrates having a large area.

However, properties of organic and inorganic semiconductors are significantly different. In an organic semiconductor, as explained above, the absorption of a photon generates a hole–electron couple and they are transported for their high mobility and internal electric field.

On the contrary, in organic semiconductor dissociation into free charges carriers does not occur at room temperature. As a consequence, two different materials are necessary and charges are created as an effect of the transfer of photoinduced electrons from one to the other material.

In particular, after the absorption of solar irradiance, for which a matching between solar spectrum and absorption spectrum is desirable, a donor material (D) is required to give the excited electron to the acceptor material (A). As a result, a radical cation of the donor (D^+) and a radical anion of the acceptor (A^-) occur.

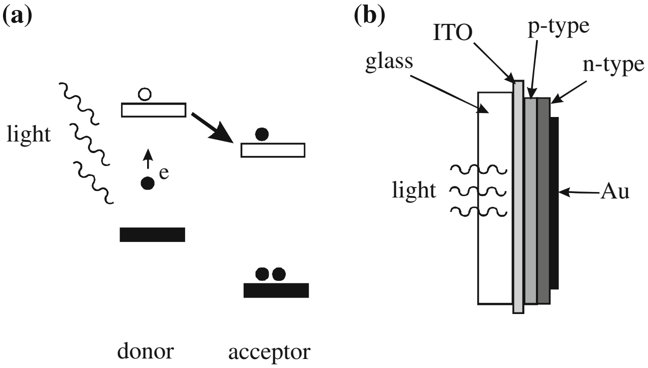


Fig. 2.17 Electron transfer from donor to acceptor material (**a**), section of an organic cell (**b**)

In addition, competitive processes as fluorescence and non-radiative decay must be inhibited and the transfer of photogenerated charges must be aided. For these reasons, the transferred electron should be slowed down as much as possible.

These last considerations are schematized in Fig. 2.17 (a). Here, an electron is excited by light absorption to the highest occupied molecular orbital (HOMO) in the donor material and then it is transferred to the lowest unoccupied molecular orbital (LUMO) in the acceptor material. Now, an extra electron is present in acceptor material and a hole appears in the donor material. Figure 2.17 (b) sketches the photovoltaic cell. Light passes through a glass and a transparent electrode (ITO); the electrodes are dissimilar but both are metallic to collect charges and to transfer them to external circuits.

Among organic cells the most successful appear to be: Dye-sensitized cells, Double layer cells, and Bulk heterojunction cells.

Dye-sensitized cells use an organic dye adsorbed at the surface of an inorganic wide band-gap semiconductor for absorption of light and injection of photoelectrons into the conduction band of the semiconductor.

Double layer cells consist on a sandwich of a single layer of organic dye between two dissimilar electrodes.

Finally, in bulk heterojunction cells, *p*- and *n*-type materials are mixed together, but, because of the intrinsic tendency of polymer materials to remain separate at nanometer dimension, junctions throughout the material are created.

2.16 Conclusions

The energy under the form of an electromagnetic wave is transformed in the electrons motion inside a semiconductor. Different semiconductor types allows a p–n junction to be obtained and used as a photovoltaic cell from which electric power, in terms of generated voltage and current at its terminal, is obtained.

Analyzing the electrons behavior inside a semiconductor, the fundamental equations of the PV cell and a physical circuit model, using a current generator and two diodes, is obtained.

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