

Chapter 2

Theoretical Aspects of Materials Physics

2.1 Bands Energies Formation in Solids Crystalline Materials

The properties of solids materials, especially the electrons dynamics are determined by the characteristics of the crystalline lattice.

In an isolated atom the electrons orbit around the nucleus and occupied discrete energy levels. The two levels with the highest energy can be labelled E_1 and E_2 . The electrons on highest energy levels can be easily delocalized from the neighbourhood of the nucleus and move. When two identical atoms are brought closer together, the quantized energy levels hybridize and split into two different levels because of the reciprocal interaction of the two atoms. More generally, when N atoms are moved closer, until they reach the equilibrium at inter-atomic distance d , the energy levels split into N levels. If N is very large as is the case in a crystal, these N levels are very close to each other so that they eventually form a continuous energy band (see Fig. 2.1). Hence the energy levels E_1 and E_2 split and form two continuous bands called as: conduction band (CB) and the valence band (VB) separated by a forbidden band, which is not accessible for electrons, called the «gap». The lowest energy level of the conduction band is denoted E_C and the highest energy level of the valence band is called E_V so that we have the relationship $E_g = E_C - E_V$. The electrons can move in the crystal if their energy is equal or higher to E_C , that means, when there are located (from energetic point of view) in the conduction band. For a semiconductor material at $T = 0$ K all electrons are situated in the valence band. At temperature $T \neq 0$ K the electrons can pass from the valence band into the conduction band by thermal activation. The place remained unoccupied in the valence band is call a “hole”. The more the temperature increases the more the electrical conductivity of semiconductors increases. The charge carriers (electrons and holes) can flow through the semiconductor material (at $T \neq 0$ K) when electric, magnetic or temperature gradients are applied.

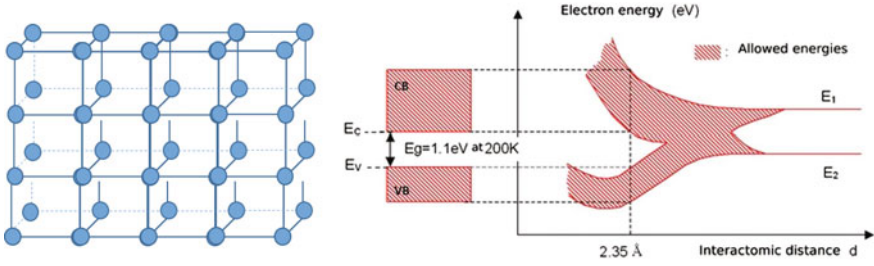


Fig. 2.1 The formation of the band energies in a crystalline material as a function of the inter-atomic distance

The understanding of charge transport in low dimensional systems (thin films, quantum wires, quantum dots or organic materials) is a key point in the development of future devices.

Due to the fact that in thin films one of the dimensions is much reduced comparing to the other two, often the physical properties and consequently the charge carriers transport are different from the bulk material. Different models were proposed to describe the transport phenomena in thin films.

For monocrystalline films, in the limits of semi-classical mechanics (assuming that the thickness of films is greater than the mean free path of carriers) the most known are the models of Fuchs [1], Sonheimer [2] and Schrieffer [3].

For polycrystalline films, also remaining in the limits of semi-classical mechanics, the most known model to calculate the transport coefficients (electrical conductivity, Seebeck coefficient, Hall coefficient, etc.) is the model of Petritz [4]. More sophisticated theories taking into account the energy band bending at the surface and the inhomogeneity of carrier concentration in the volume and at the surface were developed by Anderson [5].

The transport phenomena in thin films can be understood easier by particularizing Boltzmann's equation for the bulk materials in the case in which, one of the dimensions is much reduced compared to the other two.

2.2 Charge Carriers Transport in Bulk Semiconductors

The calculus of transport coefficients in bulk materials (electrical conductivity, Seebeck coefficient, Hall coefficient, etc.) is generally given in literature for particular cases. Here we preferred to present a general calculus method, starting from the considerations of Kireev [6], by considering the most general case of a material in the presence of an electric field ($E \neq 0$), a magnetic field ($B \neq 0$) and temperature gradient ($\nabla T \neq 0$). After establishing the expression of non-equilibrium function in the most general case, this one could be simplified, depending on the

analysed situation by combining one, two or the three parameters (E , B , ∇T) and different transport coefficients for different type of effects can be calculated:

- Electrical conductivity ($E \neq 0$, $B = 0$, $\nabla T = 0$)
- Galvanomagnetics effects ($E \neq 0$, $B \neq 0$, $\nabla T = 0$)
- Thermoelectrics effects ($E \neq 0$, $B = 0$, $\nabla T \neq 0$)
- Thermomagnetics effects ($E = 0$, $B \neq 0$, $\nabla T \neq 0$).

In the absence of external actions, the carriers charge (electrons and holes) are in thermodynamically equilibrium and their behaviour is described by Fermi-Dirac equilibrium distribution functions, f_{F-D} . These distribution functions are usually noted with f_0 and they depend only on temperature and charge carriers energy.

$$\text{For electrons: } f_{on} = \frac{1}{e^{\frac{E-E_F}{kT}} + 1} \text{ while for holes } f_{op} = 1 - f_{on} = \frac{1}{e^{\frac{E-E_F}{kT}} + 1} \quad (2.1)$$

If an external perturbation is applied to the solid, such as: an electric field, a magnetic field, or temperature gradient, etc. the system (in our situation the bulk or the thin film) will no longer be in an equilibrium state.

The charge carriers movement get a directional character and their distribution will be given by non-equilibrium distribution functions.

In the following we will present the calculation method for the non-equilibrium distribution function for electrons and f_n and f_{on} will be simply denoted by f and f_0 , respectively. The calculus for holes non-equilibrium distribution function is similar.

The charge carrier's non-equilibrium distribution function is the Boltzmann distribution function $f(\mathbf{r}, \mathbf{k}, t)$ and the variation in time of this function is given with enough precision by Boltzmann's kinetic equation [6–11]. The function $f(\mathbf{r}, \mathbf{k}, t)$ depend on the electron position \mathbf{r} , the wavevector \mathbf{k} and the time t .

The electron in crystal differs from a free electron because it is submitted to different interactions with other electrons and ions in the crystal. To resume the influence of these electrostatic interactions the mass of electron in vacuum is replaced by the effective mass m_e^* .

Hence the momentum of the electron is expresses by:

$$\vec{p} = \hbar \vec{k} = m_e^* \vec{v} \quad (2.2)$$

where

$$\vec{v} = \frac{1}{\hbar} \nabla_{\vec{k}} E \quad (2.3)$$

is the velocity of electron in the crystal and E —the energy.

We consider an n-type semiconductor crystalline solid with isoenergetic spherical surfaces in the presence of an electric field, a magnetic field and of a

temperature gradient. The Boltzmann's kinetic equation for the stationary case, in the relaxation time approximation, is given by [6]:

$$\vec{v}\nabla_{\vec{r}}f + \frac{\vec{F}}{\hbar}\nabla_{\vec{k}}f = -\frac{f-f_0}{\tau} \quad (2.4)$$

where F is the force acting on charges, τ is the relaxation time, $\tau = \tau(E)$, f the non-equilibrium function in the presence of external fields for the electrons and f_0 the equilibrium distribution function (in the absence of external fields), which is replaced with the Boltzmann distribution for non-degenerate semiconductors and the Fermi-Dirac distribution function for degenerate semiconductors.

In the approximation of first order it is considered that f is close to f_0 and in the two first terms of the Eq. (2.4) we can replace f by f_0 , and then calculate the non-equilibrium distribution function f :

$$f = f_0 + f_1 + f_2 + f_3 + \dots, \quad (2.5)$$

Hence, in the approximation of first order:

$$f = f_0 + f_1 \quad (2.6)$$

with f_1 :

$$f_1 = -\frac{\partial f_0}{\partial E}\vec{\chi}(E) \cdot \vec{k}, \quad (2.7)$$

Here, $\vec{\chi}(E)$ being an unknown vector function, which depends on energy. By calculating $\vec{\chi}(E)$ we can determine f_0 and then the non-equilibrium distribution function: f .

The force F acting on charges subjected at electrical and magnetic fields (the most complex situation) will be expressed by:

$$\vec{F} = -e(\vec{E} + \vec{v} \times \vec{B}) \quad (2.8)$$

The equilibrium distribution function of electrons for degenerate semiconductors is given by Fermi-Dirac distribution function:

$$f_0 = \frac{1}{e^{\frac{E-E_F}{kT}} + 1} \quad (2.9)$$

and for non-degenerate semiconductors, by Boltzmann distribution function:

$$f_o = e^{-\left(\frac{E-E_F}{kT}\right)} \quad (2.10)$$

Taking into account the relations from (2.5) to (2.8), the relation (2.4) becomes:

$$\vec{v}\nabla_{\vec{r}}f_0 - \frac{e}{\hbar}\vec{E}\nabla_{\vec{k}}f_0 - \frac{e}{\hbar}(\vec{v} \times \vec{B})\nabla_{\vec{k}}f = -\frac{f_1}{\tau_n} \quad (2.11)$$

and more

$$\vec{v}\nabla_{\vec{r}}f_0 - \frac{e}{\hbar}\vec{E}\nabla_{\vec{k}}f_0 - \frac{e}{\hbar}(\vec{v} \times \vec{B})\nabla_{\vec{k}}f = \frac{1}{\tau_n}\frac{\partial f_0}{\partial E}\vec{\chi}(\mathbf{E}) \cdot \vec{k} \quad (2.12)$$

We consider the case of non-degenerate semiconductors and we replace f_0 with Boltzmann distribution function (2.10).

Calculating each term on the left member of the Eq. (2.12) in the hypothesis that the semiconductors are monocrystalline, with spherical isoenergetic surfaces, we obtain:

$$\vec{v}\nabla_{\vec{r}}f_0 = \vec{v}\frac{\partial f_0}{\partial E}\left[\frac{E_F - E}{T}\nabla_{\vec{r}}T - \nabla_{\vec{r}}E_F\right] = \frac{\hbar\vec{k}}{m_n^*}\frac{\partial f_0}{\partial E}\left[\frac{E_F - E}{T}\nabla_{\vec{r}}T - \nabla_{\vec{r}}E_F\right] \quad (2.13)$$

$$-\frac{e}{\hbar}\vec{E}\nabla_{\vec{k}}f_0 = -\frac{e}{\hbar}\vec{E}\frac{\partial f_0}{\partial E}\frac{\hbar^2\vec{k}}{m_n^*}, \quad (2.14)$$

m_n^* being the effective mass of the electron, in the crystal,

$$-\frac{e}{\hbar}(\vec{v} \times \vec{B})\nabla_{\vec{k}}f = -\frac{e}{\hbar}(\vec{v} \times \vec{B})\nabla_{\vec{k}}(f_0 + f_1) = -\frac{e}{\hbar}(\vec{v} \times \vec{B})\nabla_{\vec{k}}f_0 - \frac{e}{\hbar}(\vec{v} \times \vec{B})\nabla_{\vec{k}}f_1 \quad (2.15)$$

It is easy to show that $\nabla_{\vec{k}}f_0 = 0$ and the relation (2.15) becomes:

$$-\frac{e}{\hbar}(\vec{v} \times \vec{B})\nabla_{\vec{k}}f = -\frac{e}{\hbar}(\vec{v} \times \vec{B})\nabla_{\vec{k}}f_1 \quad (2.16)$$

Considering the expression (2.7) for f_1 we deduce:

$$\nabla_{\vec{k}}f_1 = -\frac{\partial f_0}{\partial E}\vec{\chi}(\mathbf{E}) \text{ and finally } -\frac{e}{\hbar}(\vec{v} \times \vec{B})\nabla_{\vec{k}}f = \frac{e}{\hbar}(\vec{v} \times \vec{B})\frac{\partial f_0}{\partial E} \cdot \vec{\chi}(\mathbf{E}) \quad (2.17)$$

Now introducing (2.13), (2.14) and (2.17) into (2.12) we obtain:

$$\begin{aligned} \frac{\hbar\vec{k}}{m_n^*}\left(\frac{\partial f_0}{\partial E}\right)\left[\frac{E_F - E}{T}\nabla_{\vec{r}}T - \nabla_{\vec{r}}E_F\right] - \frac{e}{\hbar}\vec{E}\left(\frac{\partial f_0}{\partial E}\right)\frac{\hbar^2\vec{k}}{m_n^*} + \frac{e}{\hbar}(\vec{v} \times \vec{B})\left(\frac{\partial f_0}{\partial E}\right) \cdot \vec{\chi}(\mathbf{E}) \\ = \frac{1}{\tau_n}\left(\frac{\partial f_0}{\partial E}\right)\vec{\chi}(\mathbf{E}) \cdot \vec{k} \end{aligned} \quad (2.18)$$

and after simplification:

$$\frac{\hbar \vec{k}}{m_n^*} \left[\frac{E_F - E}{T} \nabla_{\vec{r}} T - \nabla_{\vec{r}} E_F \right] - \frac{e \hbar k}{m_n^*} \vec{E} + \frac{e}{\hbar} (\vec{v} \times \vec{B}) \cdot \vec{\chi}(E) = \frac{1}{\tau_n} \vec{\chi}(E) \cdot \vec{k} \quad (2.19)$$

Here

$$(\vec{v} \times \vec{B}) \cdot \vec{\chi}(E) = \vec{v} \cdot (\vec{B} \times \vec{\chi}(E)) = \frac{\hbar k}{m_n^*} (\vec{B} \times \vec{\chi}(E)) \quad (2.20)$$

So rel. (2.19) becomes:

$$\frac{\hbar}{m_n^*} \left[\frac{E_F - E}{T} \nabla_{\vec{r}} T - \nabla_{\vec{r}} E_F \right] - \frac{e \hbar}{m_n^*} \vec{E} + \frac{e}{m_n^*} (\vec{B} \times \vec{\chi}(E)) = \frac{1}{\tau_n} \vec{\chi}(E) \quad (2.21)$$

and we obtain the vector equation:

$$\vec{\chi}(E) = \frac{\tau_n \hbar}{m_n^*} \left\{ \frac{E_F - E}{T} \nabla_{\vec{r}} T - \nabla_{\vec{r}} E_F - e \vec{E} + \frac{e}{\hbar} (\vec{B} \times \vec{\chi}(E)) \right\} \quad (2.22)$$

The equation is of type: $\vec{\chi} = \vec{a} + \vec{b} \times \vec{\chi}$ and the solution is:

$$\vec{\chi} = \frac{\vec{a} + (\vec{b} \times \vec{a}) + \vec{b}(\vec{b} \cdot \vec{a})}{1 + b^2} \quad (2.23)$$

This means that we can find the final solution $\vec{\chi}(E)$ and determine the non-equilibrium function:

$$f = f_0 - \frac{\partial f_0}{\partial E} \vec{\chi}(E) \cdot \vec{k} \quad (2.24)$$

The problem could be reduced now at different particular cases in order to calculate different needed transport coefficients.

The Electrical Conductivity in the Relaxation Time Approximation for Bulk Materials

Considering now that we apply only an electric field $\vec{E} = \vec{E}(\mathbf{E}_x, 0, 0)$, the temperature gradient and the magnetic field being zero, the expression of $\vec{\chi}(E)$ becomes:

$$\vec{\chi}(E) = -e \frac{\tau_n \hbar}{m_n^*} \vec{E} \quad (2.25)$$

The electron current density is given by:

$$\vec{j}_n = -\frac{e}{4\pi^3} \int_{V(k)} \vec{v}_n f(\vec{k}) d\tau_k \quad (2.26)$$

where $d\tau_k = dk_x dk_y dk_z$ is the elementary volume in the space \mathbf{k} .

As we chose $\vec{E} = \vec{E}(\mathbf{E}_x, 0, 0)$, we have only the component of the vector \vec{j}_n in the direction x :

$$\begin{aligned} j_{nx} &= -\frac{e}{4\pi^3} \int_{V(k)} v_{nx} \left(f_0 - \frac{\partial f_0}{\partial E} \vec{\chi}(\mathbf{E}) \cdot \vec{k} \right) d\tau_k \\ &= -\frac{e}{4\pi^3} \int_{V(k)} v_{nx} \left(f_0 + \frac{\partial f_0}{\partial E} e \frac{\tau_n \hbar}{m_n^*} \vec{E} \cdot \vec{k} \right) d\tau_k \end{aligned} \quad (2.27)$$

Taking into account that f_0 is an even function, v_{nx} an odd function and $V(k)$ implies an integration between symmetric limits (Brillouin zone) the first term in the expression (2.27) is zero and j_{nx} could be expressed as:

$$j_{nx} = -\frac{e}{4\pi^3} \int_{V(k)} v_{nx} \left(\frac{\partial f_0}{\partial E} e \frac{\tau_n \hbar}{m_n^*} \vec{E}_x \cdot k_x \right) d\tau_k \quad (2.28)$$

By changing the variable k to E (the energy) we have:

$$k = \left(\frac{2m_n^*}{\hbar^2} \right)^{1/2} E^{1/2} \quad \text{and} \quad d\tau_k = 4\pi \frac{m_n^*}{\hbar^2} \left(\frac{2m_n^*}{\hbar^2} \right)^{1/2} E^{1/2} dE \quad (2.29)$$

By calculus and taking into account that:

$$I(a) = \int_0^\infty x^n e^{-ax^n} = \frac{1}{n} \frac{\Gamma\left(\frac{n+1}{n}\right)}{a^{\frac{n+1}{n}}} \quad \text{and} \quad \Gamma(n+1) = n\Gamma(n), \quad \Gamma(1) = 1, \quad \Gamma(1/2) = \sqrt{\pi} \quad (2.30)$$

we can express j_{nx} as:

$$j_{nx} = en\mu_n E_x, \quad \text{with} \quad \mu_n = \frac{e \langle \tau \rangle}{m_n^*} \quad \text{and} \quad \langle \tau \rangle = \frac{\int_0^\infty \tau_n(E) \left(-\frac{\partial f_0}{\partial E} \right) E^3 dE}{\int_0^\infty \left(-\frac{\partial f_0}{\partial E} \right) E^3 dE} \quad (2.31)$$

Here n is the charge carriers concentration (electrons), μ_n —electrons mobility, $\langle \tau \rangle$ the mean relaxation time.

To calculate the mean values $\langle \tau \rangle$ or $\langle \tau^2 \rangle$ precisely, it is necessary to express the relaxation time τ as function of energy $\tau = \tau(E)$. This function depends on the nature of scattering mechanism dominating in the studied sample.

Accepting that, this dependence is given by:

$$\tau_n = \tau_0 E^{-p} \quad (2.32)$$

where, τ_0 is a parameter depending on material nature and sometimes on temperature, and the exponent p characterizes the scattering mechanism nature ($p = -3/2$ scattering on ionized impurities, $p = 1/2$ scattering on longitudinal acoustics phonons [6]).

Taking into account the relations (2.31), (2.32), and the distribution function we can express the mean relaxation time as:

$$\langle \tau \rangle = \frac{\int_0^\infty \tau_0 E^p \left(-\frac{f_0}{KT}\right) E^{\frac{3}{2}} dE}{\int_0^\infty \left(-\frac{f_0}{KT}\right) E^{\frac{3}{2}} dE} = \frac{\int_0^\infty \tau_0 E^p \left(e^{-\frac{E}{KT}} e^{\frac{E_F}{KT}}\right) E^{\frac{3}{2}} dE}{\int_0^\infty \left(e^{-\frac{E}{KT}} e^{\frac{E_F}{KT}}\right) E^{\frac{3}{2}} dE} = \tau_0 \frac{\Gamma(5/2 - p) \left(\frac{1}{KT}\right)^{5/2}}{\left(\frac{1}{KT}\right)^{5/2-p} \Gamma(5/2)} \quad (2.33)$$

and finally

$$\langle \tau \rangle = \tau_0 (KT)^{-p} \frac{\Gamma(5/2 - p)}{\Gamma(5/2)} \quad (2.34)$$

Hence, the electrons mobility for non-degenerate semiconductors can be expressed as:

$$\mu = \frac{e \langle \tau \rangle}{m_n^*} = \frac{e}{m_n^*} \frac{\int_0^\infty \tau_n(E) \left(-\frac{\partial f_0}{\partial E}\right) E^{\frac{3}{2}} dE}{\int_0^\infty \left(-\frac{\partial f_0}{\partial E}\right) E^{\frac{3}{2}} dE} = \frac{e}{m_n^*} \tau_0 (KT)^{-p} \frac{\Gamma(5/2 - p)}{\Gamma(5/2)} \quad (2.35)$$

According to (2.29), the **electrical conductivity for n-type non-degenerate semiconductors** is expressed by the well know formula:

$$\sigma = en\mu \quad (2.36)$$

The different charge transport mechanisms are comprised into the expression of the mobility which depends on the different type of scattering processes.

In a similar mode one could calculate other coefficients, e.g., Hall coefficient, Seebeck coefficient, etc.

Hall Coefficient in the Relaxation Time Approximation

The calculus of Hall coefficient, for electrons in a n-type non degenerate semiconductor conducts to [6, 7]:

$$R_n = -\frac{r}{ne} \quad (2.37)$$

For a p type non-degenerate semiconductor, the Hall coefficient of holes is:

$$R_p = \frac{r}{pe} \quad (2.38)$$

and for mixed conduction:

$$R_m = \frac{r}{|e|} \frac{p - b^2 n}{(p + nb)^2}, \quad \text{where } b = \frac{\mu_e}{\mu_h} \quad (2.39)$$

r is called Hall factor and for low magnetic fields it could be expressed by:

$$r = \frac{\langle \tau^2 \rangle}{\langle \tau \rangle^2} \quad (2.40)$$

In the hypothesis $\tau = \tau_0 E^{-p}$ using the formulae of average value we deduce:

$$r = \frac{\Gamma(\frac{5}{2} - 2p) \cdot \Gamma(\frac{5}{2})}{[\Gamma(\frac{5}{2} - p)]^2} \quad (2.41)$$

Seebeck Coefficient in the Relaxation Time Approximation

The calculus for Seebeck coefficient conducts to [6, 7]:

$$\alpha(T) = -\frac{1}{eT} \left[\frac{\langle \tau E \rangle}{\langle \tau \rangle} - E_F \right] \quad (2.42)$$

and in the assumption $\tau = \tau_0 E^{-p}$

$$\begin{aligned} \langle \tau E \rangle &= \frac{\int_0^\infty \tau_0 E^{-p} E \left(-\frac{f_0}{kT}\right) E^{\frac{3}{2}} dE}{\int_0^\infty \left(-\frac{f_0}{kT}\right) E^{\frac{3}{2}} dE} = \frac{\int_0^\infty \tau_0 E^{1-p} \left(e^{-\frac{E}{kT}} e^{\frac{E_F}{kT}}\right) E^{\frac{3}{2}} dE}{\int_0^\infty \left(e^{-\frac{E}{kT}} e^{\frac{E_F}{kT}}\right) E^{\frac{3}{2}} dE} \\ &= \tau_0 (kT)^{1-p} \frac{\Gamma(7/2 - p)}{\Gamma(5/2)} \end{aligned} \quad (2.43)$$

and taking into account the expression of $\langle \tau \rangle$ from (2.34) results as:

$$\alpha(T) = -\frac{1}{eT} \left[\frac{\tau_0 (KT)^{1-p} \frac{\Gamma(7/2-p)}{\Gamma(5/2)}}{\tau_0 (KT)^{-p} \frac{\Gamma(5/2-p)}{\Gamma(5/2)}} - E_F \right] = -\frac{1}{eT} \left[KT \left(\frac{5}{2} - p \right) - E_F \right] \quad (2.44)$$

2.3 Transport Coefficients in Thin Films. Semi-classical Theory

In addition to the carriers scattering mechanisms presented in the bulk single crystals materials, in thin films, due to the large diminution of one of the three dimensions and due to the fact that films are usually polycrystalline, we should consider also the scattering on the surfaces and the scattering at the limits of grain boundaries.

For thin films the scattering mechanisms inside the crystallites corresponds to the scattering mechanisms in monocrystalline bulk materials, and that's why are designed as “bulk scattering mechanisms”.

A direct consequence to the fact that the thickness is much reduced and becomes comparable to the mean free path is that the non-equilibrium distribution function and obviously the transport coefficients will depend on the films thickness. We call this “**dimensional effect**”.

The dimensional effect for the electrical conductivity could be explained equally on the basis of Boltzmann transport equation, the difference comparing to bulk analysis consists in the dependence of non-equilibrium distribution function on the position variable.

Thin Films Electrical Conductivity

Considering the geometry of the thin films in the coordinates (x, y, z) as is presented in Fig. 2.2 the kinetic equation of Boltzmann for homogenous and monocrystalline thin films in the absence of magnetic fields is given by [7, 12]:

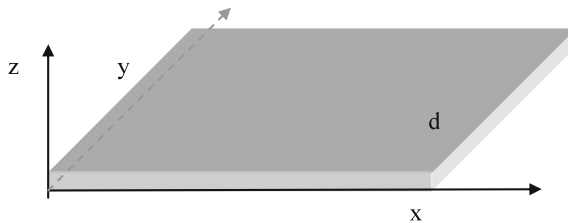


Fig. 2.2 We consider that the thin film has infinite surface with the inferior surface in the plane $z = 0$ and the superior surface in the plane $z = d$. The electric field $E(E, 0, 0)$ is oriented along the surfaces planes

$$v_z \frac{\partial f(\vec{k}, z)}{\partial z} - \frac{e}{\hbar} \vec{E} \frac{\partial f(\vec{k}, z)}{\partial k_x} = -\frac{f - f_0}{\tau_n} \quad (2.45)$$

The distribution function on the spatial coordinates will depend only on z variable and could be expressed by:

$$f = f_0 E + f_1(\mathbf{v}, z) \quad (2.46)$$

The electrical conductivity is obtained in a similar way as in the case of bulk material, with the difference that in this situation due to the dependence of current density j_x on the position variable z , the current density will be expressed as an average of j_x values along the direction z [7, 12, 13]:

$$j_n = \frac{1}{d} \int_0^d j_x(z) dz = \frac{1}{d} \int_0^d \left(-\frac{e}{4\pi^3} \int v_x f_1(\vec{v}, z) d\tau_k \right) dz = \sigma_n E \quad (2.47)$$

σ_n , represents the electrical conductivity of the thin film considered as semiconductor of n type.

The scattering mechanisms on the surface were characterized by a parameter p call scattering factor, having the values 1 or 0 for the limit situations: (a) elastic scattering; (b) inelastic scattering.

The electrical conductivity σ in thin films is determined by calculus in connection with the value corresponding to bulk material σ_0 , for different situations, such as degenerate and non-degenerated semiconductors, thick and thin films.

For degenerated semiconductors [7, 12]:

$$\sigma = \frac{\gamma}{\phi(\gamma)} \sigma_0 \quad (2.48)$$

$\phi(\gamma)$ being a function depending on film thickness and the free mean path of charge carriers:

$$\frac{1}{\phi(\gamma)} = \frac{1}{\gamma} - \frac{3(1-p)}{2\gamma^2} \int_1^\infty \left(\frac{1}{a^3} - \frac{1}{a^5} \right) \left\{ \frac{1 - e^{-\gamma a}}{1 - p e^{-\gamma a}} \right\} da \quad (2.49)$$

$a = 1/\cos\theta$ is the integration variable, θ the angle between the direction of velocity vector and Oz axis, $\gamma = d/l$, is the ratio between the thickness of the film d , and the free mean path, l .

This relation could be simplified for some limit cases: very thin films ($\gamma \ll 1$), very thick films ($\gamma \gg 1$), and for pure diffuse scattering ($p = 0$) or pure elastic scattering ($p = 1$) [1-3, 13].

$$\frac{\sigma}{\sigma_0} = \frac{3}{4} \frac{1+p}{1-p} \gamma \ln \frac{1}{\gamma}, \quad \gamma \ll 1, \quad (2.50)$$

$$\frac{\sigma}{\sigma_0} = 1 - \frac{3}{8\gamma} (1-p), \quad \gamma \gg 1. \quad (2.51)$$

For Non-degenerated Semiconductors [12]

$$\frac{\sigma}{\sigma_0} = 1 - (1-p)(2/\gamma) + (1-2p)(2/\gamma)\Gamma_1(2/\gamma) + (2p/\gamma)\Gamma_1(1/\gamma) \quad (2.52)$$

with $\Gamma_1(1/\gamma)$ and $\Gamma_1(2/\gamma)$ given by:

$$\Gamma_1(c/\gamma) = \int_0^\infty \exp\left[-\varepsilon - (\gamma/c)(\pi\varepsilon)^{-1/2}\right] d\varepsilon, \quad c = 1 \text{ and } c = 2 \text{ respectively.} \quad (2.53)$$

The presented formulas correspond to the Fuchs-Sondheimer and Schrieffer theories [1–3] for n-type semiconducting thin films, in the hypothesis of spherical isoenergetic surfaces and flat bands (the concentration of carrier charge is the same at the surface as in the bulk). The case of ellipsoidal isoenergetic surfaces was studied by Ham and Mattis [14].

As, in general, the concentration on the surface of films is different from that in the volume due to the existence of donors or acceptors states at the semiconductor surface, different authors elaborated later, more sophisticated theories [5, 15, 16], taking into account the energy band bending at the surface (Anderson model).

Another scattering mechanism, specific to thin films is the scattering on grain boundaries. This problem is rather complicated due to the fact that it is difficult to control and reproduce films having exactly the same polycrystalline morphology.

To explain the electrical and optical properties of polycrystalline films various models were proposed (Volger [17], Petritz [4], Seto [18], Berger and Mankarious [19]).

Most of analysis and simulating techniques are based on the consideration that the boundaries between crystallites presented a spatial charge, which corresponds in terms of energy bands to a band bending and existence of potentials barriers.

One of the most employed models is the model of Petritz [4] in which it is considered that the polycrystalline semiconductor films are constituted by homogenous separated (structural and electrical) domains with very low electrical resistivities ρ_1 (corresponding to the crystalline grains) and very high resistivities ρ_2 , (corresponding to the boundary grains), connected in series.

The thickness of high resistivity domains is neglected, as compared with the thickness of low resistivity domains. For a big number of grains, the characteristic parameters are described by mean values.

Petriz deduced the electrical conductivity of a polycrystalline film as following [4]:

$$\sigma_b = e\mu_1 n \exp(-q\phi_b/KT) \quad (2.54)$$

with μ_1 the mobility inside the crystalline grains, n the concentration of charge carriers and ϕ_b the barrier height.

Since $\rho_2 \gg \rho_1$ Petriz consider that the exponential factor is not due to the concentration changes but to carriers mobility changes.

So that all charge carriers participate to the conduction but with a reduced mobility due to the presence of barriers:

$$\mu_g = \mu_1 \exp(-q\phi_b/KT) \quad (2.55)$$

The barrier height at the grain boundaries is determined by the concentration of charge carrier in grains and grain boundaries.

$$q\phi_b = KT \ln(n_1/n_2) \quad (2.56)$$

where n_1 and n_2 are the concentrations in the grain and grain boundary, respectively.

Berger and then Mankarious [18] extended Petriz model. Mankarious and co-workers made the observation that the electrical conductivity in a polycrystalline thin film could be expressed in a more general way as:

$$\sigma_g \sim \exp(-E_a/KT) \quad (2.57)$$

here E_a is the thermal activation energy.

For degenerated semiconductors, the effect of potential barriers at the grain boundaries is not very significant [19], furthermore it should be mentioned that for strong degeneration, the grain boundaries scattering does not depend on temperature and it is not possible to distinguish it from the scattering on the ionized impurities.

Besides, if the mean free path of carriers is 4–5 times smaller than the size of crystallites, the boundaries inter-crystallite scattering mechanisms can be considered negligible.

Hall Coefficient in Thin Films

The calculus of the other kinetics coefficients is even more complicated. From Sondheimer model [2] the Hall coefficient R , is given by:

$$R_{film} = R_{bulk} \frac{4}{3} \frac{1-p}{1+p} \frac{1}{\gamma \left(\ln \frac{1}{\gamma} \right)^2} \quad (2.58)$$

p being the scattering factor, and $\gamma = d/l$, the ratio between the thickness of the film d , and the free mean path, l and $\gamma \ll 1$.

Seebeck Coefficient in Thin Films

The relations for Seebeck coefficient in thin films, considered as monocrystalline are expressed as [2]:

$$\alpha_{film} = \alpha_{bulk} \left(1 - \frac{\gamma \phi'(\gamma)}{\phi'(\gamma)} \frac{U}{1+U} \right); \quad (2.59)$$

with

$$\phi'(\gamma) = \frac{d\phi(\gamma)}{d\gamma}; U = -\frac{E_F}{\gamma} \frac{\partial \gamma}{\partial E}; \phi(\gamma) = \begin{cases} 1 - \frac{3(1-p)}{8\gamma}, & \gamma \gg 1 \\ \frac{3}{4} \frac{1+p}{1-p} \gamma \ln \frac{1}{\gamma}, & \gamma \ll 1 \end{cases} \quad (2.60)$$

p being the scattering factor, and $\gamma = d/l$, the ratio between the thickness of the film— d , and the free mean path— l , E_F is the Fermi energy.

These mechanisms explain the behaviour of charge carriers when crosses the solid semiconductor material under the action of different fields.

2.4 Quantum Effects in Charge Transport. Quantum Well, Quantum Wires, Quantum Dots

The development of molecular beam epitaxy since the late 1960s, made possible to grow ultrathin layers (≈ 20 Å) of different materials with atomically sharp interfaces. On such small length scales the semi-classical distribution function is no longer a valid concept, due to the uncertainty relation between \mathbf{r} and \mathbf{k} .

To analyse and design devices on a sub 100 nm scale it will be necessary to go beyond the Boltzmann equation and develop simulation techniques based on quantum kinetic equations. The development of an appropriate kinetic equation is an active topic of theoretical research [20]. The last twenty years have seen the emergence of new research areas, such as: nanostructure physics and nano-electronics.

Quantum effects in electron transport can broadly be divided into two categories: those involving devices whose transverse dimensions are either much longer or either much shorter than the phase coherence length.

For the devices belonging to the first category, the sub-band energies are nearly continuous and one can describe electron transport in terms of plane waves. For those belonging to the second category it is more appropriate to view transport in terms of discrete waveguide modes [20].

We define as quantum well a zone in which the electrons are situated in a one-dimensional potential well. We suppose that the thickness “ a ” of the layer

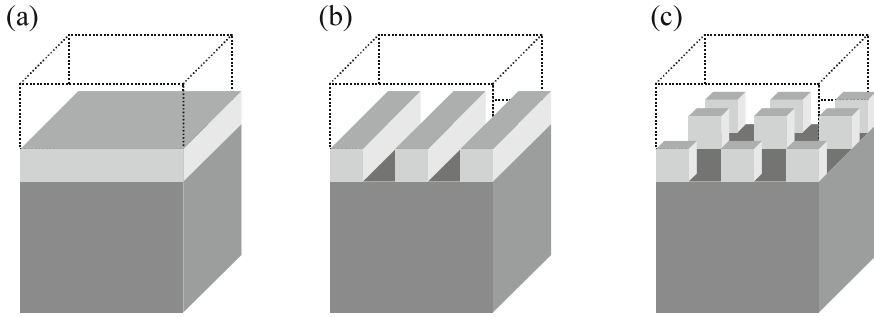


Fig. 2.3 Quantum well, quantum wires, quantum dots

which represent the quantum well is large enough ($a > 20 \text{ \AA}$), as the layer keeps the characteristic of macroscopic crystal and small enough ($a < 400 \text{ \AA}$) to suppose that the electron crosses the wall without suffering collisions ($a < \text{the mean free path}$). Hence the electrons are confined (2D electronic gas) in this zone, which is a uni-dimensional potential well.

In a quantum well structure, the electrons confinement occurs perpendicular to the interface (Fig. 2.3a).

The structures in which the electrons are confined along two directions (bi-dimensional potential well) and along the three spatial directions (tri-dimensional potential well) were called quantum wires (Fig. 2.3b) and respectively quantum dots (Fig. 2.3c). In these structures we consider that we have a 1D and respectively 0D electronic gas.

The simplest way to create a quantum well is by designing hetero-structures or MOS-type structures (Fig. 2.4).

After putting in contact the metal and the semiconductor through an oxide interface, an electron transfer occurs since the two Fermi levels become equal. This conducts to a bending of semiconductor energy bands, and consequently to a potential barrier.

From Fig. 2.4c. one can remark that such a structure in terms of quantum mechanics could be approximated with a triangular one-dimensional quantum well.

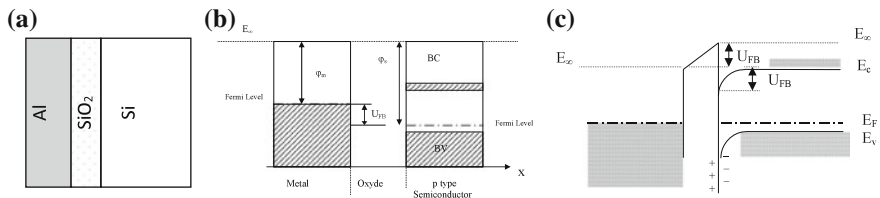


Fig. 2.4 **a** MOS structure **b** Energy band diagram of metal and semiconductor before contact **c** Energy band diagram of metal and semiconductor after contact

The wave function and the energy associated to the electrons could be determined using the Schrödinger equation [21], in the one-dimensional case.

$$\left[-\frac{\hbar^2}{2m^*} \frac{d^2}{dx^2} + V(x) \right] \varphi(x) = E\varphi(x) \quad (2.61)$$

$V(x)$ is the electric potential function, which describes the barrier height as a function of the coordinate x .

The equation of Schrödinger for uni-dimensional problems is generally quite easy to solve, much more complicated being the equation of Schrödinger in three dimensions (the case of quantum dots):

$$\left[-\frac{\hbar^2}{2m^*} \Delta + V(\vec{r}) \right] \varphi(\vec{r}) = E\varphi(\vec{r}) \quad (2.62)$$

By creating multilayer structures of very thin films we obtain complex devices with multiple quantum wells called superlattices.

2.5 Linear Conjugated Systems. Organic Semiconductors. Charge Transport in Organic Materials

A conjugated system is defined as a system presenting a simple-double carbon chemical bonding alternance.

We can distinguish two categories of linear conjugated systems: small molecules and polymers. Some examples of such conjugated system are given in Fig. 2.5.

Despite the saturated polymers which are insulators and less interesting from the point of view of electronics materials, in conjugated polymers, the chemical bonding leads to one unpaired electron (the π electron per carbon atom) in a delocalized state, with the results that such polymers can exhibit semiconductor or even metallic properties.

The electronic structure in conducting polymers is determined by the chain symmetry and the electronic delocalization provides a “highway” (as Heeger calls it) for charge mobility along the backbone of the polymer chain [22].

To understand in a simple way the electronic band structure formation in organic semiconductors, we can start from the example of polyacetylene $(-\text{CH})_n$ Fig. 2.6.

At molecular level the π electrons could be ejected from the Highest Occupied Molecular Orbital (HOMO) level (π) or captured on the Lowest Unoccupied Molecular Orbital (LUMO) level (π^*). With the increase of molecular length, by analogy with inorganic crystals, the energetic levels split and the degeneration increases with the number of atoms, conducting to continuous energetic bands for an infinite chain (Fig. 2.7).

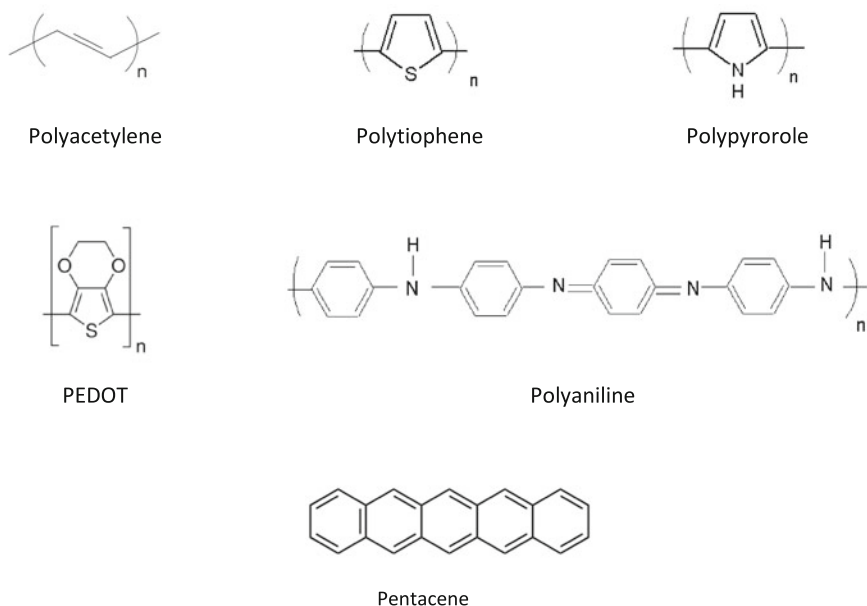


Fig. 2.5 Examples of a few conjugated polymers, note the bond-alternated structure

Fig. 2.6 Polyacetylene chain

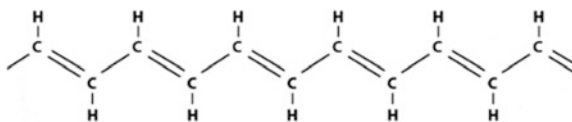
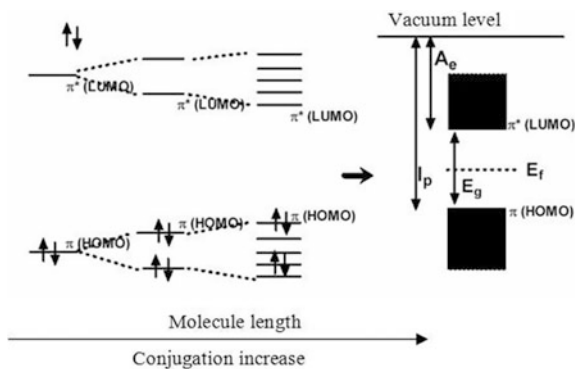


Fig. 2.7 Energy diagram evolution for molecular orbitals with the increase of conjugation, I_p is the ionization energy, A_e the electron affinity and E_g the gap of the material



Even if the terms HOMO and LUMO characterize an isolated molecule, they were extended to the solid phase and are the equivalents of the maximum of Valence Band (VB) and minimum of Conduction Band (CB) in the physics of semiconductor materials.

By the relative positions of HOMO and LUMO of materials putted in contact it is possible to define them as Donor or Acceptor, but this is not an intrinsic characteristic of the material.

The band gap is the difference between these two positions in the energetic diagram and since there are no partially filled bands, conjugated polymers are typically semiconductors. Because E_g depends upon the molecular structure of the repeat unit, this gave rise to the idea that the energy gap could be controlled by design at molecular level.

In the assumption of electron gas model, the problem of π electron travelling along the molecular chain, is equivalent, from quantum point of view, to the motion of an electron in a periodic potential (Fig. 2.8).

Hence the Schrödinger equation in the one-dimensional case for the motion of electron in a periodic potential can be solved. This potential can be approximated with a rectangular potential, as shown in Fig. 2.9.

The equation to solve is:

$$\begin{cases} \left[-\frac{\hbar^2}{2m^*} \frac{d^2}{dx^2} + V(x) \right] \varphi(x) = E\varphi(x) \\ \text{with } V(x) = \begin{cases} 0, & x \in (0, a) \\ V_0, & x \in (a, a+b) \end{cases} \end{cases} \quad (2.63)$$

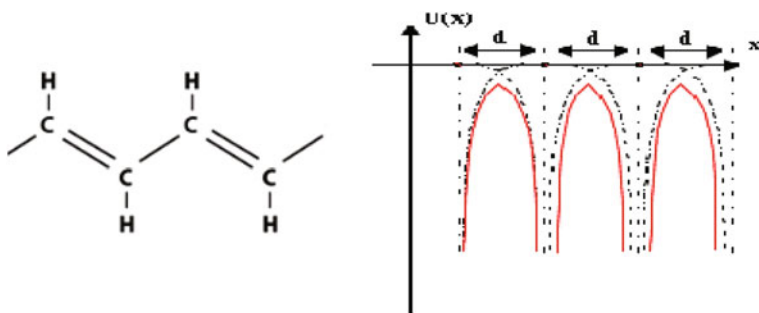


Fig. 2.8 Approximate potential curve $V(x)$ created by the atoms of polymer chain

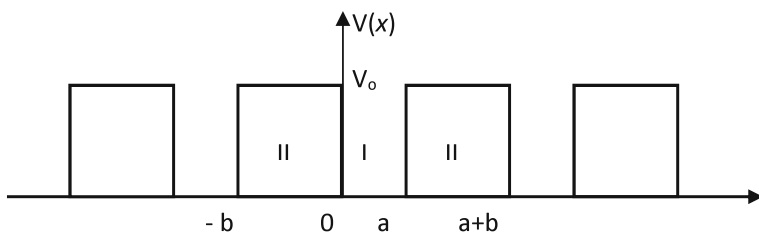


Fig. 2.9 Simplified periodic potential (as in crystals)

From solid state physics, we remember that this situation corresponds exactly to the Kroning-Penny model, which lead by calculus to the explanation of energy structure bands formation in crystals.

In this simplest way, on the basis of quantum mechanics and condensed matter physics, the formation of bands energy in organic semiconductors, can be explained. However, the discovery of nonlinear excitations (solitons, polarons and bi-polarons) indicated that the physics of organic materials is much more complex and entirely new concepts were developed in the last twenty years.

A soliton type excitation (or radical) results from the separation of the chain into two domains which differ by the simple-double bonding alternance. In the presence of an acceptor or donor electrons, the soliton (neutral defect) is positive or negative charged and becomes a positive or negative mobile polaron (charge defect) responsible of the conduction along the chain [22].

The studies on polyacetylene contributed to the development of important models concerning the non-linear excitations such as: soliton, polaron, bipolaron. The first model was the SSH model (Su, Schrieffer, Heeger). This model is built, assuming the alternance single-double bonding along the polymer chain, by considering that the two configurationally equivalent chains of polyacetylene (Fig. 2.10) are weak-coupled (quasi one-dimensional character). The formation of soliton excitations is studied along an infinite chain and in the one-electron approximation. The band structure is calculated by expressing the total Hamiltonian of the system.

The electrical conduction and charge transport in organic semiconductors need the creation of free charge carriers. A conjugated system could become conductive by doping.

The electrical conductivity results from the existence of charge carriers (through doping) and from the ability of those charge carriers to move along the π bonded "highway". Thus doped conjugated systems (polymers) are good conductors for two reasons [22]:

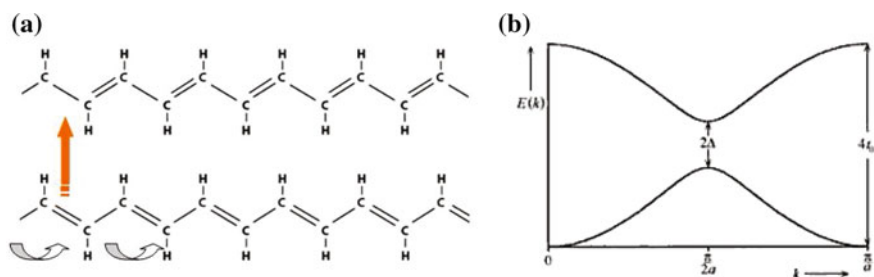


Fig. 2.10 a The two configurationally equivalent structures, from energetic point of view in polyacetylene b Band structure for a dimerised polyacetylene chain calculated from the SSH Hamiltonian

- (i) Doping introduce carriers into the electronic structure. Since every repeat unit is a potential redox site, conjugated systems can be doped n-type (reduced, creation of a negative charge) or p-type (oxidized, creation of a positive charge) to a relatively high density of charge carriers.
- (ii) The attraction of an electron in one repeat unit to the nuclei in the neighbouring units, leads to the carrier delocalization along the polymer chain and to the increase of charge carrier mobility which is extended into three dimensions through inter-chain electron transfer. However, disorder limits the carrier mobility.

Mobile charged defects in lightly doped one-dimensional chains and disorder-induced charge localization in heavily doped systems have attracted much attention. The knowledge of the electrical conduction process in organic solids is of great importance because it conducts to the explanation of organic electronics and optoelectronic devices operation. On the other hand, the understanding of the complex physical processes in conduction mechanisms, leads to the understanding of charge and energy transfer in biological systems.

A common problem in charge transport in organic materials is a lack of detailed knowledge of the organisation of the material. Today we know, both theoretically and experimentally, that for disordered electronic systems, even in the weak disorder limit, the Boltzmann transport equation for metals could not be applied. Instead new concepts which treated the disorder from the beginning were introduced.

A unified theory of the electrical conduction in conducting polymers and organic materials in general, doesn't exist yet.

Transport models for three-dimensional amorphous semiconductors have been used often to describe the charge delocalization phenomena in conducting polymers despite fundamentals differences. Covalent bonding along polymers chains and weak bonding between them result in a quasi-one dimensional morphology which has an important role in the charge delocalization of these systems. A central issue is whether the metallic states are predominately one dimensional (1D) or three dimensional (3D). For example the 1D random dimer model has been proposed to explain charge delocalization [23]. On the other hand, both theoretical and experimental studies emphasized the importance of inter-chain interaction. Another controversy is whether charge transport is due to variable range hopping (VRH) with emphasis on inter-chain hopping in disordered regions or charge energy-limited tunnelling based on granular metallic model. More details on the different charge transport mechanism proposed for describing organic solids behaviour are given in [22, 24, 25].

All these controversial issues originate from the complex morphology associated with organic materials.

2.6 Photon—Electron Interactions

- Plasmons. Absorption of light in a metallic material with a dielectric interface. Surface plasmon polaritons.
- Absorption of light in semiconductor materials.
- Absorption of light in a semiconductor material with a metallic interface.
- Absorption of light in organic semiconductors
- **Plasmons. Absorption of light in a metallic material with a dielectric interface. Surface plasmon polaritons.**

The energy of photons is given by: $E_{ph} = h \cdot \nu$, where $h = 6.62606957 \times 10^{-34}$ J·s is the Planck constant and ν is the photon frequency. Photons (electromagnetic radiation) can interact with the matter and transfer their energy in different ways.

If the frequency of the electromagnetic radiation corresponds to the microwave domain (300 MHz–300 GHz) the interaction with the matter conducts to molecular rotations and torsion, if the radiation frequency is in the infrared domain (3–300 THz) it conducts to molecular vibrations. For frequencies in the visible and ultraviolet domain (300 THz–3 PHz) the interaction of photons with atoms conduct to an increase of the electrons energies, hence the photon energy is transferred to an electron, and the electron moves to a higher energy level. For higher energies of photons, corresponding to X ray domain, (300 PHz–30 EHz) the electrons can even be extracted from the atoms (photoionization and Compton scattering).

A crystalline solid can be imagined as a “plasma” of electrons and ions in which the electrons can move (oscillate) in a collective organized way with respect to the fixed positive ions.

The plasma oscillations of the free electron gas density can be quantized and a particle can be associated to these waves.

The particle associated to the free electron density oscillations with respect to the fixed positive ions in a metal or semiconductor is called plasmon.

Surface plasmons (SPs) are those plasmons that are confined in surfaces for example at the interface between a metal and a dielectric, such as a metal sheet in air. SPs have lower energy than bulk (or volume) plasmons which quantise the longitudinal electron oscillations about positive ion cores within the bulk of an electron gas (or plasma).

In a bulk material (metal or semiconductor) the plasma oscillations cannot be produced by usual thermal excitations, that is why at normal temperatures plasmons are in their fundamental state and do not participate at the most electronic processes and their contribution can be neglected.

The plasmons can be excited by passing the electrons with high energies through thin metallic films or by interactions with light in the visible range of the electromagnetic spectrum.

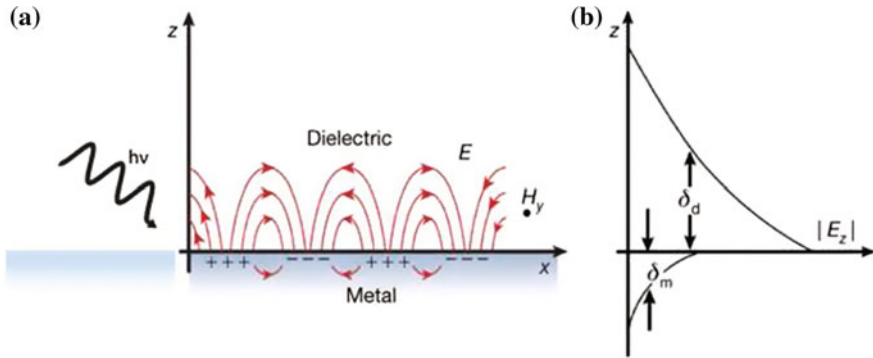


Fig. 2.11 Absorption of light in a metallic material with a dielectric interface. **a** Schematic representation of a SPP as a collective excitation propagating along a metal—dielectric interface. **b** The perpendicular electromagnetic field intensity E_z decays exponentially with the distance away from the interface with a characteristic length δ_d in the dielectric and δ_m in the metal. Adapted with permission from Benson [26], © 2011 Macmillan Publishers Limited, part of Springer Nature

Figure 2.11a gives the schematic representation of an electron density wave propagating along a metal—dielectric interface. The dependence of the electromagnetic field intensity on the distance away from the interface is shown in Fig. 2.11b.

These waves can be excited very efficiently with light in the visible range. The interaction (coupling) of a surface plasmon with a photon give rise to a new particle called “Surface Plasmon Polariton” (SSP).

• Absorption of light in semiconductor materials.

- Intrinsic Absorption (fundamental). Optical Transition between Bands.
- Factors Determining the Shift of Fundamental Absorption Edge.
- Extrinsic Absorption.
- Free Carriers Absorption.

For the absorption of electromagnetic radiation in semiconductors, generally, two mechanisms are responsible. The first one, referring to the excitation of electrons from Valence Band (VB) to Conduction Band (CB), or in an electron-hole bounded state (exciton), is defined as an inter-band absorption process and it is treated in quantum physics manner. The second one consisting in the acceleration of free carriers by the oscillating electrical field, is referred to as absorption on free carriers and could be discussed in the limits of classical electrodynamics [27–31]. In the domain of low wavelength the strong absorption is determined by the Band to Band (B-B) transitions and in the domain of large wavelengths the low transmission is determined by the high reflection due to free carriers [32]. Analysing the transmission spectra in the domain of fundamental absorption one can get information concerning the optical band gap and the study of reflection and transmission

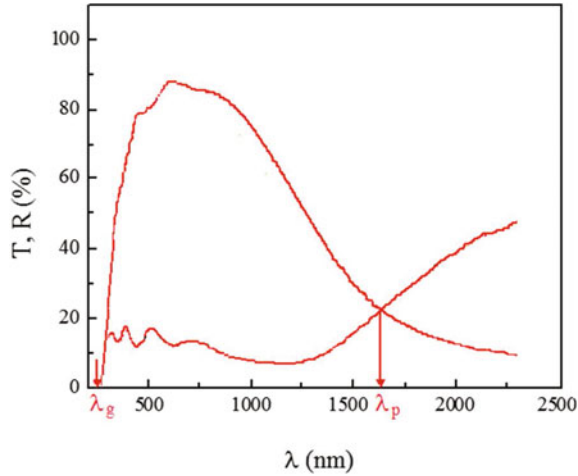


Fig. 2.12 Semiconductor optical window

spectra in the IR range may conduct to an important series of information such as: the superior limits of the optical window, the value of plasma frequency, etc.

The transparency domain of a semiconductor (“the optical window”) is comprised between the edge of fundamental absorption corresponding to the λ_g (gap) wavelength and λ_p the wavelength of conduction electron plasma oscillations (Fig. 2.12).

• **Intrinsic Absorption (fundamental). Optical Transition between Bands.**

In an intrinsic semiconductor, photons with energies below the gap cannot excite an electron-hole pair and their energy is lost (Fig. 2.13a). If the energy of photon is equal or higher that the bandgap energy E_g , the photon absorption determines a transition of the electron from valence band to conduction band (intrinsic transition). In the case in which the photons energy exceeds the gap, the excess of energy is lost in a rapid thermalization process.

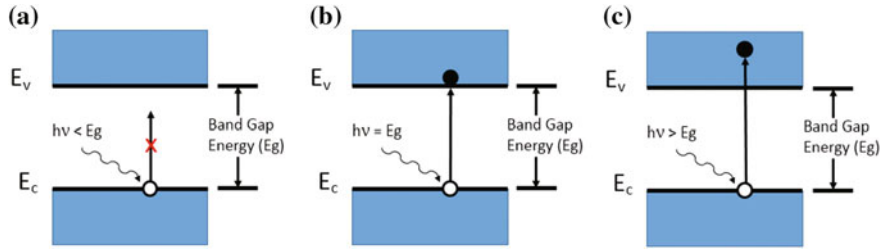


Fig. 2.13 Energy-band diagrams showing the light-absorption mechanism in a bulk semiconductor

The transitions from conduction band to valence band can be direct or indirect ones. In a direct intrinsic transition the wave vector k of charge carriers remains unchanged after the transition between bands. The indirect transitions occur when the minimum of conduction band and the maximum of valence band are not aligned and the transitions of charge carriers occur with the change of k vector value. Both direct and indirect transitions could be allowed or forbidden. The calculus of transition probabilities is strictly of quantum nature.

The minimal energy (hc/λ_g) of absorbed photons which conducts to intrinsic transitions is called fundamental absorption edge (optical band gap). From the spectral dependence of absorption coefficient near the edge of fundamental absorption one can obtain information concerning the nature of transitions involved in the absorption process.

- **Factors Determining the Shift of Fundamental Absorption Edge.**

In a n-type degenerate semiconductor (high doped semiconductor), the electrons occupying the inferior positions into the conduction band block the transitions B-B (Band to Band) and lead to a shift of the fundamental absorption edge to higher energies. The phenomenon is known as Burstein—Moss effect [33, 34].

$$E_g = E_{g0} + \Delta E_g^{BM} \quad (2.64)$$

The variation of the band gap due to the Burstein—Moss effect is given by:

$$\Delta E_g^{BM} = \frac{\hbar^2}{2m_{eh}^*} (3\pi^2 n)^{2/3} \quad (2.65)$$

where n is the concentration of free electrons and m_{eh}^* is the reduced effective mass of electrons and holes:

$$\frac{1}{m_{eh}^*} = \frac{1}{m_h^*} + \frac{1}{m_e^*} \quad (2.66)$$

m_h^* being the holes effective mass and m_e^* the electrons effective mass.

On the other hand in addition to this, the decrease of band gap could occur due to the formation of a delocalized states band (Mott) at the bottom of conduction band [29, 35].

Furthermore, the randomised distribution of the impurities into the crystal lattice, has as a consequence the presence of a band tail (Urbach); the different interactions which influenced the mean occupation time of electronic states upon the Fermi level conduct also to the extension of the fundamental absorption edge.

Excepting the Burstein-Moss shift, which is quite easy to estimate for a parabolic conduction band, the influence of the others effects is difficult to be estimated, and the calculus could become very complex.

- **Extrinsic Absorption.**

The extrinsic absorption occurs in doped semiconductors (extrinsic semiconductors) when the absorption of photons with energies lower than the band gap conducts to the displacement of an electron from the valence band to a local impurity level, or from a local impurity level to the conduction band.

- **Free Carriers Absorption.**

When the energy of incident photons is not sufficiently high to determine Band-Band transitions or Band-Local Level transitions, we talk about free carriers absorption. The optical phenomena corresponding to this wavelength domain could be understood onto Drude theory basis, for free electrons into metals [36].

Low frequency electromagnetic radiations incidents onto semiconductor surface interact with the free electrons. A part of the radiation could be reflected, other part absorbed and the rest is transmitted. In Drude theory it is demonstrated that the radiations having frequencies lower than the frequency corresponding to the electron plasma ($\lambda > \lambda_p$) are strongly reflected and the transmission is reduced to zero. The frequency of plasma oscillations is given by [36]:

$$\omega_p = 2\pi f_p = \frac{2\pi c}{\lambda_p} = \sqrt{\frac{ne^2}{\epsilon_0 \epsilon_\infty m_e^*}} \quad (2.67)$$

ϵ_0 , ϵ_∞ are the dielectrics constants for vacuum and for the material at high frequencies respectively, e —the electron charge, n —electrons concentration.

This frequency defines the limit at which the electrons become unable to stop the electric field of the incident electromagnetic radiations and the materials become transparent for the radiations having frequencies higher than ω_p .

The “transparency domain” in Drude theory corresponds to the condition $\omega\tau \gg 1$, where τ is the relaxation time, the condition $\omega_p\tau \gg \omega\tau \gg 1$ corresponds to the “reflection domain” and $1 > \omega\tau > 0$ corresponds to absorption domain (transparency zero).

Hence one can remark that the edges of semiconductors optical window, λ_g and λ_p , are depending on the concentration of free carriers.

The increase of optical window width in the sense of λ_p moving to larger values is done by the decreasing of free carrier concentration. For a fixed small carrier concentration, the condition of transparency $\omega_p\tau \gg 1$, (as ω_p is fixed due to n fixed) suppose an increase of the mobility ($\mu = e\tau/m_e^*$).

- **Absorption of light in a semiconductor material with a metallic interface.**

In an intrinsic semiconductor, photons with energies lower than the gap energy can't be absorbed (Fig. 2.14a). However recent studies showed that if the semiconductor interfaced with a metal, the excitation of surface plasmons in the metal generates short-lived highly energetic carriers that can be injected into the conduction band of a semiconductor [37].

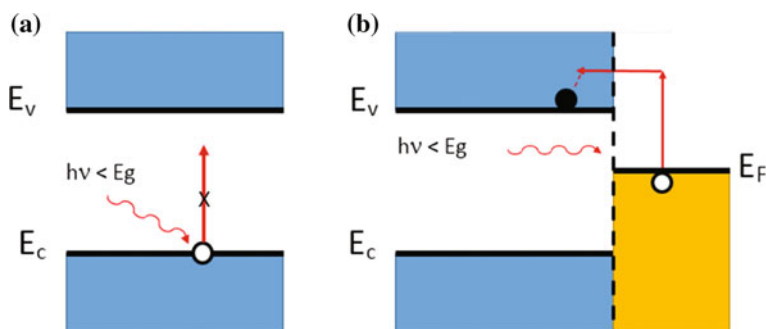


Fig. 2.14 Energy—band diagrams comparing the light absorption mechanism in a bulk semiconductor and a semiconductor interfaced with a metal. Adapted from Chalabi and Brongersma [37], © 2013 Macmillan Publishers Limited

Hence when the metal's Fermi level E_F is above the valence band of the semiconductor, some sub-bandgap photons can photogenerate hot electrons that are sufficiently energetic to be injected into the semiconductor's conduction band hence even photons with energies lower than the band gap energy can be harvested (Fig. 2.14b).

- **Absorption of light in organic semiconductors.**

In organic semiconductors the nature of bonding is fundamentally different from inorganic semiconductors. Organic molecular crystals are Van der Waals-bonded implying a considerably weaker intermolecular bonding compared to the covalent bonds of inorganic semiconductors. Consequently the delocalization of electronic wave functions among neighbouring molecules is much weaker. The situation in polymers is somewhat different, since the morphology of polymer chain can lead to improved mechanical properties. However the electron interaction between adjacent chains is usually also quite weak in this class of materials [38].

Owing to weak electronic delocalization, the optical absorption spectra of organic molecular solids are very similar to the spectra in the gas phase or in solution. Nevertheless, solid state spectra can differ in detail with respect to selection rules, oscillator strength and energetic position; moreover, due to the crystal structure or packing polymer chains a pronounced anisotropy can be found. Additionally disordered organic solids usually show a considerable broadening. In Fig. 2.15 are schematically shown the optical spectra of molecules in different surroundings [38].

As a consequence of this weak electronic delocalization, organic semiconductors have two important peculiarities, as compared to the inorganic counterparts: one is the existence of well-defined spin states (singlet and triplet) like in isolated molecules, which has an important consequence for the photophysics of these materials; the second one originates from the fact that optical excitations ("excitons") are usually localized on one molecule and therefore have a considerable binding

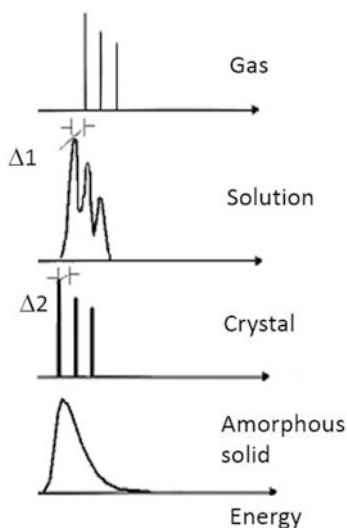


Fig. 2.15 Schematic representation of optical spectra of organic molecules in different surroundings. $\Delta 1$ and $\Delta 2$ denote the respective solvent shift in solution and solid state, respectively

energy, typically 0.5–1 eV. Thus, in a photovoltaic cell this binding energy has to be overcome before a pair of independent positive and negative charge carriers is generated [38].

2.7 Superlattices. Photonic Crystals and Metamaterials

In a conventional material, the response to electric and magnetic fields, and hence to light, is determined by the atoms and molecules arranged in a periodic crystal structure (Fig. 2.16).

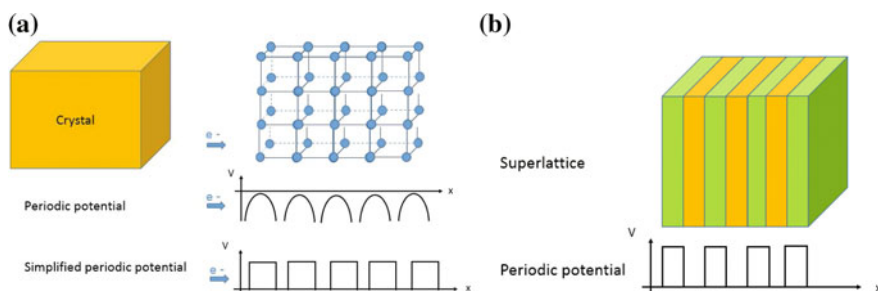


Fig. 2.16 Periodic potential in a crystal (a). Periodic potential in a superlattice (b)

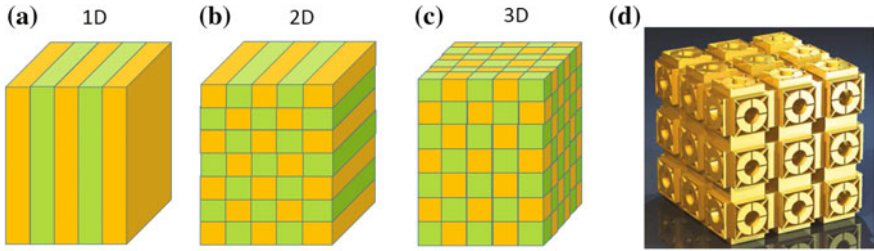


Fig. 2.17 Photonic crystals or metamaterials with a 1D (a), 2D (b) and 3D (c, d) periodic structure constituted from different materials or any artificial units (d) Reprinted with permission from D. Ö. Güney, Th. Koschny, and C. M. Soukoulis, “Intra-connected 3D isotropic bulk negative index photonic metamaterial,” *Opt. Exp.* 18, 12352 (2010) © 2010 Optical Society of America

By engineering many tiny identical structural units (artificial atoms) in a periodic arrangements, a huge combination of new materials can be tailored. These new class of materials with a periodic structure in 1D, 2D or 3D have completely new properties compared to constitutive materials (Fig. 2.17).

From geometrical point of view superlattices, photonic crystal and metamaterials are similar. Generally the term of superlattices is employed in electronics to define a periodic structure of two or more materials layers (see Chap. 2, Sect. 2.4). If the superlattice is made of two semiconductor materials with different band gaps, the electrons are confined in a periodic multi quantum well potential (similar to the periodic potential in a single crystal) that modify the conditions for charges to flow through the structure. In function of the thickness of the constitutive layers, different type of carrier conduction mechanisms can occur.

A photonic crystal is a periodic optical nanostructure that affects the motion of photons in much the same way that ionic lattices affect electrons in solids. Photonic crystal are also called semiconductors of light [39]. In a semiconductor there is a band gap for electrons between the valence and conduction band and the electrons cannot have energies on levels which correspond to the gap. In a photonic crystal, a periodic structure is created by regions of different dielectric constant, which can be approximated by a periodic potential. Although “photonic” refers to light, the principle of the band gap applies equally well to electromagnetic waves of all wavelengths [39].

The band gap in a semiconductor arises from the diffractive interaction of the electron wave function with the periodic atomic lattice resulting in a destructive interference for particular wavelengths. To observe the diffraction of light, a periodic lattice of artificial atoms is necessary with the lattice constant comparable with the light wavelength for which the bandgap is needed. That is why for visible wavelengths the lattice constant and artificial atoms should be in the range of hundred nanometers [40]. Photonic crystals occur naturally in opals or in butterfly wings (Fig. 2.18).

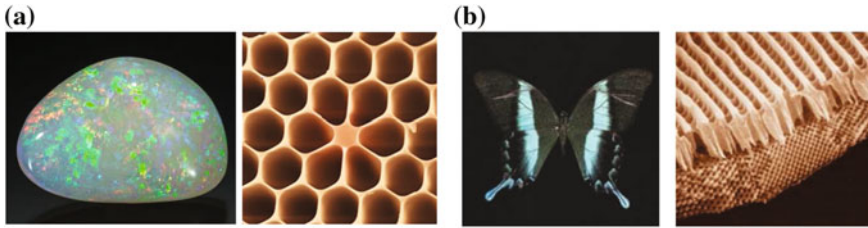


Fig. 2.18 Natural photonic crystals **a** Opals. **b** Photonic crystal structure in the butterfly wings Reprinted with permission from Yablonovitch [39]

The difference between photonic crystals and metamaterials is that in photonic crystals the lattice constant have to be comparable in size with the wavelength ($a \cong \lambda$), because the effect of the band gap arises from diffraction. In the case of metamaterials the subunits (artificial atoms) and lattice constant have to be much smaller than the wavelength ($a \ll \lambda$) because diffraction should not appear [40].

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