Abstract This chapter gives an introduction to the basics of light-matter interaction in semiconductors, aiming to provide the readers with the background necessary to follow the other chapters of this book. In this chapter topics are addressed, such as the band structure, the density of states, quasi particles and elementary excitations, the optical constants (dielectric function), the role of the free carriers, the influence of temperature and stress on the optical response of semiconductors, the optical transitions, both absorption and emission; also, a description of the main defects in semiconductors. Their role in the optical properties is included, and the physics of low dimensional semiconductor structures in relation to the optical properties is also a matter of discussion.

1.1 Introduction

Since the 60s of last century optoelectronics started to have a relevant presence in diverse applications, especially telecommunications, photoelectric detectors, data displays, optical storage, and light sources, among other. This development was propitiated by the accomplishment of technological breakthroughs in the field of semiconductor materials. In particular, the advances in the semiconductor growth technologies were crucial for the development of the new optoelectronic devices. The development of semiconductor structures, and devices, demands a strong effort of comprehension of the semiconductor properties at different scales. In this sense, there is an increasing request of experimental techniques enabling the understanding of the main properties of semiconductor materials, both as grown, and after processing, e.g. annealing [1], ion implantation [2, 3], wet and dry etching [4–6], impurity diffusion [7], and other processes related to reduced size structures, e.g., QW intermixing [8]. The understanding of the basic optical phenomena in semiconductors is crucial not only for the design of optoelectronic devices, but also for achieving advances in the development of semiconductor structures allowing for new device concepts, e.g. semiconductor photonic crystals.
An optoelectronic device is an electronic device operating with light; therefore, it is subjected to the mechanisms of interaction between solids and light. Optoelectronic semiconductors have properties that can differ from those used in electronics, which is mainly dominated by Si, while its presence in optoelectronics is restricted to photoelectric devices. The semiconductors most widely used in optoelectronics are the III–V compounds and their alloys, and recently the wide bandgap semiconductors, mainly the III-nitrides; which many of them are direct band gap materials. Furthermore, their miscibility offers great possibilities for band gap engineering by alloying different compounds. In spite of the reduced route of some semiconductors in optoelectronics applications, the optical characterization methods are very powerful for the study of any type of semiconductors [9].

The rapid advances in semiconductor manufacturing and the associated technologies have increased the need of optical techniques for the semiconductor analysis, and in situ monitoring/control applications. Optical characterization techniques are unique for studying semiconductor properties: (i) they are non-invasive, (ii) they permit remote sensing; therefore, they are useful for in situ analysis; e.g. growth and other technological steps; (iii) they permit a high spatial resolution allowing to acquire maps of different properties of semiconductors in its diverse forms, from bulk materials to devices; (iv) the use of short laser pulses and fast detectors allows ultrafast phenomena to be investigated; (v) the availability of high sensitive multichannel detectors permits very fast spectral data acquisition suitable for in situ monitoring, but also the acquisition of very rich spectrum maps in reasonably time; (vi) they supply information on crystal quality, but also on lattice disturbances, or symmetry breakdown; (vii) they provide information on a large range of physical properties, e.g. stress, temperature, bandgap, thermal and electrical transport, alloy composition [10–15]; also information about defects and impurities is accessible to optical experiments [16–20]; finally, many optical techniques can be implemented at the production scale.

In this chapter, a resumed overview of the optical properties of semiconductors is presented as a sort of introduction to the rest of the volume. In the following chapters we will present how to analyze the optical properties of semiconductors by selected experimental techniques.

1.2 Optical Phenomena in Semiconductors

When a light beam impacts on a semiconductor surface a part of the incident light power is reflected; while the refracted part propagates across the material being progressively attenuated. The attenuation is the consequence of a series of processes of interaction between the photons of the light beam and the semiconductor atoms. The main light semiconductor interaction phenomena occurring inside the semiconductor are light absorption, and light scattering. Both, light absorption and light scattering, supply rich information about relevant physical parameters of semiconductors; e.g., the energy gaps, energy states of defects, elementary excitations as
excitons, phonons and plasmons, and other aspects relevant to the semiconductor properties; e.g. stress, light polarization. If the semiconductor is transparent to the light one can study the transmission spectrum; instead, if the semiconductor is opaque to the light the reflection spectrum is the one to record. The primary phenomena, reflection and light absorption, are the strongest ones, because of the lower order of interaction between the solid and the electromagnetic wave. The primary phenomena are macroscopically described by the optical constants of the solid; therefore, a macroscopic approach can be done in the frame of classic electrodynamics [21–23].

The propagating light is absorbed during its route across the semiconductor, it exchanges energy with the electrons and other particles, constituting an excitation source for secondary phenomena as luminescence, photocurrent among other. The object of this textbook is the way these phenomena can be studied.

A schematic picture of the main optical processes occurring in a semiconductor is shown in Fig. 1.1. All of the beams indicated in the Figure carry information about the semiconductor properties, which needs to be extracted by an adequate use of the experimental means, and data treatment.

The incident light beam impacts onto the semiconductor surface, resulting in a reflected and a refracted beam respectively, according to the laws deduced in classical electromagnetism for the interaction of an electromagnetic wave with a dielectric. The refracted beam undergoes absorption processes, in which it transfers energy to the lattice, generating e–h pairs, which when recombine reemit light with another wavelength characteristic of the material under study; this phenomenon is known as photoluminescence (PL) [24]. A full description of the mechanisms of light absorption and emission require of a quantum mechanical approach. Note also that the free charges generated by the light beam can be collected by electrodes giving the photoelectric phenomena, which are at the origin of very important optoelectronic devices as photodetectors, and photovoltaic devices; but also, they

Fig. 1.1 Scheme of the different processes of interaction between light and a solid. 1 Incident light, 2 reflected light (front surface), 3 refracted light, 4 scattered light, 5 transmitted light, 6 reflected light (back surface), 7 emitted light
are at the origin of experimental techniques largely applied to the characterization of semiconductors and devices, e.g. the photocurrent techniques, described in Chap. 6 of this volume.

In addition to the absorption processes, the light inside the semiconductor can be scattered. Different scattering mechanisms can take place, which give rise to different experimental techniques. Among them, Brillouin scattering is the scattering by acoustic waves [25]; while the Raman spectroscopy corresponds to the scattering by optical phonons and other elementary excitations [26–30], Chap. 4. Rayleigh scattering is the elastic scattering phenomenon, which can be used to detect the presence of microscopic defects; e.g., dislocations, precipitates and other with size of the order of the light wavelength [31, 32].

The understanding of all these phenomena requires of the study of the fundamentals of the photon-semiconductor interaction. It permits to develop an appreciation of the intrinsic and extrinsic properties of semiconductors. Such analysis is essential to understand the basic principles of optoelectronic devices (light emitting diodes, lasers, photodetectors, and photovoltaics among other); also, they provide information about materials properties necessary for the development of optoelectronics devices.

The optical properties of semiconductors concern the phenomena occurring as a consequence of the presence of light in the semiconductor. On one side, one can consider the incidence of photons onto the semiconductor, and its response to such external light source. On the other side, one can consider the light generated by the semiconductor itself under an external excitation source. Both phenomena are extremely sensitive to the solid structure, and more specifically to the band gap structure. The fundamental bandgap is the threshold energy for different optical phenomena to be observed; in fact, the semiconductor is transparent to light with energy below the bandgap, while it becomes opaque to light with energy above the bandgap. Furthermore, it cannot emit light with energy above the bandgap.

There are different optical responses of semiconductors, which constitute the basis of the experimental tools used for the optical characterization; some of them are described along this volume. These techniques permit to measure different physical magnitudes, giving information about very relevant properties of the semiconductors related to the band structure, the presence of impurities and defects, the loss of periodicity, among other relevant physical magnitudes, e.g. stress and temperature, which can be characterized by optical spectroscopy techniques. These magnitudes are very relevant for the performance and reliability of devices [33–36].

An optoelectronic device can be either a detector or a source of light. However, what converts a semiconductor on a device is the possibility to generate and control the signals arising from the semiconductor, normally by means of an electric field. In this context we are interested on the response of the semiconductor to an external electromagnetic wave, but also on the mechanisms of light generation by the semiconductor.

The physical phenomena involved in these optical processes reveal both extrinsic and intrinsic properties. The semiconductors used in the industry are not
ideal periodic structures, but contain defects that disturb such a periodicity, changing in a significant way their optical and electronic properties; therefore, a huge interest is devoted to the study of the electro-optical signature of defects and impurities. On the other hand, extrinsic factors, as temperature and strain, have a strong influence on the intrinsic properties of semiconductors. Both of them are key factors accelerating the failure of optoelectronic devices [33–36]; therefore, is of prime interest the implementation of experimental techniques revealing changes in the optical properties by temperature and/or strain to be used as qualification tools for devices. Furthermore, the properties of the semiconductors can be tuned by strain, which is particularly relevant when using low dimensional structures, which admit elastic deformation allowing the tunability of the properties of the active parts of the devices.

The optical properties of semiconductors are related to their microscopic structure. Its understanding requires of the knowledge of several basic concepts, e.g.: band structure, fundamental bandgap, defect and impurity levels, quasiparticles, also known as collective excitations, e.g. phonons and plasmons, radiative and non radiative recombination, quantum confinement …

The list of optical characterization techniques is very extensive; nevertheless, we will focus here on some of the most relevant of those techniques, e.g. spectroscopic reflectance techniques (Chap. 2), absorption, luminescence (Chaps. 3 and 5), photoelectric (Chap. 6), and among the light scattering techniques we will focus on Raman spectroscopy by phonons (Chap. 4). There are, by no means an exhaustive list of experimental techniques; however, the ones listed here are among the most widely used ones, being basic tools in many characterization laboratories.

As important as the lattice periodicity for practical applications is the breakdown of such periodicity, e.g. by defects, and impurities, but also the translational symmetry interruption by low dimensionality, which plays a paramount role in modern optoelectronic devices; in this context, one will also introduce the optical properties of structures with reduced dimension.

1.3 Band Structure and Fundamental Bandgap

An ordered solid is a structure in which the atoms occupy regular positions forming a lattice; when some of those atoms are ionized free electrons are available; however, these electrons are not purely free, but feel a periodic potential. The Bloch theorem establishes that the one electron wavefunction in a potential with the lattice periodicity is the product of a plane wave and a function with the same periodicity as the lattice [21]. The solution of the Schrodinger equation in such a potential results in continuous energy bands instead of the quantized discrete energy states observed in individual atoms [21, 22]. The band structure diagrams of GaAs [37] and Si [38] in the k space are shown in Fig. 1.2.
At zero temperature the valence band (VB) corresponds to the occupied electron states, while the conduction band (CB) corresponds to the empty electron states; both bands are separated by an energy gap, labelled as the forbidden bandgap, where the presence of electrons is forbidden. The energy interval between the minimum of the CB and the maximum of the VB is the fundamental bandgap, and is the minimum energy necessary to promote an electron from the filled electron states (VB) to the empty electron states (CB). One observes in Fig. 1.2 that in the case of GaAs the extrema of both bands occur at the Γ point of the Brillouin zone; one says that the bandgap is direct; which is not the case for Si, where the two extrema occur at different points of the Brillouin zone; in this case the bandgap is indirect. The direct or indirect nature of the bandgap has relevant consequences for the optical properties of the semiconductors. GaAs is a genuine optoelectronic semiconductor, while Si is the electronic material by excellence, but a poor optoelectronic semiconductor, even if this assertion must be put into context, depending on the type of optoelectronic device. These material specifications can be understood in terms of the band structure. The light emission energy is related to the bandgap; however, the intensity of the emission and the time response is governed by the band structure itself. Good light emitters are direct bandgap semiconductors, while indirect bandgap semiconductors are not.

The fundamental bandgap is an essential magnitude; it determines the threshold for intrinsic light absorption, but also the maximum energy at which a given bulk semiconductor can emit light. One of the great assets of semiconductors for their application in modern optoelectronic devices is the possibility of engineering the bandgap by alloying semiconductors. One can almost construct any band gap from the IR to the deep UV with the only constraint of the control of the lattice parameter and the layer thickness. The bandgap versus the lattice parameters for the most important semiconductors are represented in Fig. 1.3.
1.4 Quasi Particles in Solids

1.4.1 Electrons and Holes

In intrinsic semiconductors, electrons can only occupy either the valence band or the conduction band. At zero temperature, they are in the valence band, and they can start to populate the conduction band if energy higher than the bandgap is supplied. When an electron from the VB is promoted to the CB, it leaves an equivalent positive charge in the valence band, which is known as a hole.

Electrons and holes are free to move in the conduction and the valence bands respectively; however, as mentioned above, they have to move in a periodic potential, therefore, in the effective mass approximation they are considered as quasi particles, with either negative (electrons) or positive (holes) charge, but with a mass different from the free electron mass, because of the presence of the periodic potential; these are the effective masses, $m_e^*$ and $m_h^*$, which are determined by the band structure. In fact, the masses of the electrons and holes are renormalized by the periodic potential to values smaller than the free electron mass [39].

Density of states

The jumps of electrons between the two allowed bands are crucial to the interaction between light and the semiconductor. The rates governing such jumps depend on the number of available states. The density of states, $D(E)$, is the number of energy states available per unit energy, i.e. the number of states in the interval $(E, E + dE)$, is $D(E)dE$. 

Fig. 1.3 Band gap versus lattice parameter for the main semiconductors (http://gorgia.no-ip.com/phd/html/thesis/phd_html/node4.html)
\[ D_c(E) = \frac{\text{number of states}}{V \times dE} \]  

(1.1)

Assuming parabolic bands:

\[ E(k) = \frac{\hbar^2 k^2}{2m^*}, \]  

(1.2)

The density of states per unit volume of the conduction band is:

\[ D_c(E) = \frac{1}{4\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} (E - E_c)^{1/2} \]  

(1.3)

While the density of states of the valence band is:

\[ D_v(E) = \frac{1}{4\pi^2} \left( \frac{2m_h^*}{\hbar^2} \right)^{3/2} (E_v - E)^{1/2} \]  

(1.4)

It is useful to define the joint density of states; the optical transition rate between VB and CB is proportional to a joint density of states defined as:

\[ D_j(E_{cv}) = \frac{1}{4\pi^3} \int dS_k \frac{dS_k}{|\nabla_k E_{cv}|} \]  

(1.5)

where \( E_{cv} = E_c - E_v \), and \( S_k \) is the energy surface over which \( E_{cv}(k) = \text{const} \). The doubly band degeneracy due to the spin is considered by a prefactor 2. This integral will appear later on, when considering the interband optical transitions.

In an intrinsic semiconductor the occupation of the two bands depends on the temperature.

The electron density in the conduction band is:

\[ n = \int_0^\infty D_c(E)f(E)dE \]  

(1.6)

where \( f(E) \) is the Fermi-Dirac probability function. For electrons in the conduction band, \( E > E_c \) (\( E > E_v \)), for non degenerate semiconductors in thermal equilibrium, \( E_c - \zeta_c \gg KT \), \( (\zeta_v - E_v \gg KT) \) so the Fermi function reduces to the Boltzmann
distribution and the density of electrons in the CB and holes in the VB can be expressed as:

\[
n = N_c \exp \left( -\frac{E_c - \zeta_c}{kT} \right)
\]

\[
p = N_v \exp \left( -\frac{E_v - \zeta_v}{kT} \right)
\]

where \( N_c = 2 \left( \frac{m_e^* kT}{2 \pi \hbar^2} \right)^{3/2} \) and \( N_v = 2 \left( \frac{m_h^* kT}{2 \pi \hbar^2} \right)^{3/2} \) are the effective density of states for the bottom (within about \( kT \) of the bottom) of the CB and the top (within about \( kT \) of the top) of the VB respectively. \( \zeta_c \) and \( \zeta_v \) are the Fermi levels for electrons and holes respectively.

In an intrinsic semiconductor:

\[
np = N_c N_v \exp \left( -\frac{E_c - E_v}{kT} \right) = N_c N_v \exp \left( -\frac{E_g}{kT} \right) = n_i^2
\]

### 1.4.2 Excitons

A free exciton is a quasi-particle formed by an e-h pair bound each other by their Coulomb attraction [21–23]. The exciton is formed when an electron is excited from the VB to the CB, and the electron remains attached to the hole by the Coulomb force forming a hydrogen like quasi-particle; it can move through the crystal transporting energy but not charge. The exciton behaves like a hydrogen atom; therefore, the exciton has a number of discrete energy levels given by:

\[
E_{n,\text{exc}} = \frac{\mu e^4}{2\hbar^2 c^2 n^2} = \frac{R_x}{n^2}
\]

where \( \varepsilon \) is the dielectric constant, \( n \) an integer, \( R_x \) the Rydberg energy, and \( \mu \) the reduced mass of the e-h pair:

\[
\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}
\]

The binding energy between electron and hole lowers the e-h transition energy with respect to the bandgap.

\[
E(n) = E_g - E_{n,\text{exc}} = E_g - \frac{R_x}{n^2}
\]
In semiconductors, the large dielectric constant, results in a partial screening of the Coulomb interaction between the electron and hole pair; as a consequence, the exciton is weakly bound, and the distance between the electron and the hole is \textit{large}; the exciton radius (Bohr radius) is larger than the Brillouin zone, which means that the exciton feels the periodic potential, behaving as a quasi-particle in a periodic potential. This kind of exciton is known as a Wannier-Mott exciton. Typical free exciton binding energies are given in Fig. 1.4 [40]. Note that large exciton binding energies are important for optoelectronic devices, since stable excitons at room temperature give strong light emission.

\textbf{1.4.3 Phonons}

The atoms forming the semiconductor lattice vibrate around its equilibrium position with characteristic vibration frequencies related to the atom masses and the force constants. The problem can be classically treated by solving the motion of a linear chain with two atoms per unit cell. The solution of this problem gives two vibration branches in the reciprocal space. When the two atoms of the unit cell vibrate parallel each other the vibration is acoustical, when they vibrate in opposition the vibration is optical. A three dimensional crystal presents three acoustic branches, one longitudinal and two transverse, and 3(N − 1) optical branches, where N is the number of atoms per unit cell. The phonon dispersion relations for Si [41] and GaAs [42] are shown in Fig. 1.5. The three optical modes in the zone center, \(q = 0\), are degenerated in Si; while LO-TO splitting occurs in GaAs, and in general in polar semiconductors; the splitting is the consequence of the lack of inversion symmetry; in polar semiconductors the longitudinal vibrations induce an electric field, which constitutes and additional restoring force.
The collective vibrations when treated in the frame of the second quantization result in quasi-particles called phonons, with characteristic quantized energy, $\hbar\omega$. Light undergoes inelastic scattering by phonons, either acoustic, Brillouin scattering, or optic, Raman scattering (Chap. 3).

On the other hand, phonons are the intermediate actors for preserving the momentum selection rule in indirect electronic transitions. Also, they are the main thermal carriers in semiconductors.
1.4.4 Plasmons

When the conduction band is populated with free electrons, the Coulomb attraction between the free electrons and the positive ions constitutes a restoring force for the free electron motion, which can collectively oscillate with a characteristic frequency, $\omega_p$, the plasma frequency. These plasma oscillations can be quantized in energy quantas, $\hbar\omega_p$, constituting elementary excitations, the plasmons. Its oscillation frequency depends on the free electron concentration, $n$ [43], as:

$$\omega_p = \frac{4\pi n^2}{m^*e_o}$$

Plasmons are longitudinal oscillations. The macroscopic electric fields associated respectively with the plasmons and the LO phonons in polar semiconductors can interact in between giving additional longitudinal wave frequencies, (see Chap. 3).

1.5 Extrinsic Factors Affecting the Bandgap: Temperature and Stress

Stress and temperature are extrinsic agents, which play a crucial role in the operation, and reliability of devices. The band gap is sensitive to both of them; therefore, they can be monitored by means of the dependence of the band gap with either temperature or stress; which permits the use of optical measurements as sensitive tools for measuring both magnitudes.

1.5.1 Temperature

The band gap decreases with the increasing temperature because of the lattice expansion and the electron-phonon interaction, which soft the lattice bonds, resulting in a decrease of the bonding energy. The temperature dependence of the bandgap energy is usually described by the semi-empirical Varshni law [44]:

$$E_g(T) = E_o - \frac{\alpha T^2}{T + \beta}$$

where $\alpha$ and $\beta$ are fitting parameters, and $E_g(T)$, and $E_o$ are the band gaps at $T$ and at 0 K respectively. The $\beta$ parameter is supposed to be the Debye temperature; however it does not match with in many cases, even giving negative values; which is usually attributed to the weak theoretical bases of the Varshni law.
Alternative laws have been reported by Viña et al. [45] and O’Donnell et al. [46]. The variation of the bandgap with temperature in bulk semiconductors was the object of theoretical analysis in [47, 48]; the bandgap shrinkage with temperature is due to the thermal lattice expansion, and the electron-phonon coupling. In the case of reduced dimension structures the temperature dependence of the bandgap, $dE_g/dT$ is lowered by reducing the size of the structures, being even negative for the smaller quantum dot (QD) structures. This behaviour was reported in [49]; where, the temperature coefficient, $dE_g/dT$, was studied as a function of the size of PbS quantum dots (QDs) showing a dramatic size dependence. In addition to the bulk contributions of the lattice thermal expansion, and the electron-phonon coupling, Olkhovets et al. [49] considered the mechanical strain, and the thermal expansion of the envelope wave-function. The temperature coefficient as a function of the QDs size, both experimental and theoretically calculated using the above mentioned four contributions is shown in Fig. 1.6.

### 1.5.2 Stress

The band edges are shifted by stress. Under hydrostatic stress the band gap is open for compression and is closed for tension. Under shear or biaxial stress the
The degeneracy of the valence band at the \( \Gamma \) point of the Brillouin zone is lifted, and the valence band is split out in the heavy hole (hh) and the light hole (lh) valence bands \((50, -52)\). The splitting of the bands is a function of the strain value. Figure 1.7 shows the band scheme under stress, both the hydrostatic and biaxial stress components are included.

The splitting in between the two transitions (lh-CB and hh-CB) under biaxial stress is proportional to the strain according to the following expression \([51]\):

\[
E_{lh} - E_{hh} = 2b\left(\frac{C_{11} + C_{12}}{C_{11}}\right)\varepsilon
\]

where \( b \) is the shear deformation potential, and \( C_{11}, C_{12} \) are the stiffness coefficients. The strain is very precisely determined from the lh-ll splitting; often the strain is not high enough to separate the two transitions, which results in the broadening of the corresponding optical spectrum, e.g. luminescence or optical absorption.

### 1.6 Low Dimension Structures

#### 1.6.1 Quantum Confinement

The interest on structures of reduced dimension is continuously increasing. The properties of the semiconductors are the consequence of its repetitive structure; however, when one dimension is reduced to a size for which the repetitive pattern is limited, the phenomenon of quantum confinement appears \([53]\). The electrons are
not more feeling the periodic potential along the direction with the reduced dimension.

The quantum confinement phenomenon results from electrons and holes being squeezed into a dimension that approaches a critical quantum dimension, called the exciton Bohr radius. The strongest confinement occurs when the confinement dimension is smaller than the Bohr radius. The result is an increase of the band gap with decreasing dimension; furthermore, the loss of the translational symmetry results in quantized states for the electrons and holes in the CB and the VB respectively, instead of the continuous bands of the ideal periodic solid. The confinement enhances the radiative recombination rate, even in indirect band gap materials [53]. On the other hand, one can also mention the confinement of phonons, which leads to changes in the phonon spectrum [54].

The simplest quantum confined structures are the quantum wells, which are the active parts of most of the commercial optoelectronic devices. A QW is a system formed by a thin (a few atomic layers) semiconductor layer sandwiched in between two semiconductor layers of higher bandgap energy, it corresponds to 1D confinement, Fig. 1.8.

The central layer of small bandgap energy is the QW, while the two surrounding layers of larger bandgap energy constitute the potential barriers. Its study began in the 70s of the last century [55]. Many textbooks and articles about one dimensional confinement structures are available [56–58]. Multiple quantum well (MQW) structures can be also constructed, they consists of a series of stacked QWs, separated by barrier layers with thickness avoiding electronic coupling between the wells. In the case of narrow spacers electronic coupling between the QWs can occur, and the electronic charge distribution can be delocalized along the direction normal to the QW plane, in this case the MQW structure is termed as a superlattice (SL), Fig. 1.9.
These structures can be grown by molecular beam epitaxy (MBE) or metal-organic chemical vapour deposition (MOCVD) techniques, which permit to control the growth at the atomic layer scale.

If one considers an electron in the CB with an effective mass $m^*_e$ in a potential well with infinite barriers, confinement appears in the direction perpendicular to the barriers. The quantized energy levels can be calculated by solving the Schrödinger equation for a particle in a potential well, using the effective mass envelope function approximation [59–61]. The electron energy states are discrete and depend on the QW thickness according to the following relationship (approximation to an infinity well)

$$E_n(k_x, k_y) = \frac{\hbar^2}{2m^*} \left[ \left( \frac{n\pi}{L_z} \right)^2 + k_x^2 + k_y^2 \right]$$

$$E_n = \frac{\hbar^2}{2m^*} \left( \frac{n\pi}{L_z} \right)^2$$

The energy states in a QW are represented in Fig. 1.10. One should also note that the energy is inversely proportional to the effective mass, which means that the degeneracy of the VB is lifted, the heavy and light hole bands have different energy levels. One has also to take account of the biaxial stress splitting further the lh and hh bands; note that the QWs are frequently strained because of the lattice mismatch with

Fig. 1.10 Energy level scheme of a compressed QW
the barrier layers. There is a critical QW thickness below which the stress is elastically accommodated; beyond this critical thickness dislocations are formed [62].

Quantum confinement can be also achieved in two or three dimensions, i.e. quantum wires (QWRs), and quantum dots (QDs) respectively. Note that the quantum confinement gives an additional degree of freedom for band gap engineering.

1.6.2 The Density of States in Quantum Confined Structures

Contrarily to the continuous parabolic density of states reported for bulk semiconductors, a series of resonances appear in the density of states, corresponding to the discrete levels existing for the different dimensions of confinement, Fig. 1.10. Instead of the square-root dependence with the electron energy of bulk semiconductor (1.3, 1.4), the density of states for a QW presents a discrete distribution:

$$D_{QW}(E) = \frac{m^*}{\pi \hbar^2} n$$

(1.16)

where $n$ is the quantum number of the energy level.

In quantum wires (2D confinement) the density of states is quantified but it depends on $(E - E_c)^{-1/2}$, while for quantum dots (3D confinement) it corresponds to $\delta$ functions (Fig. 1.11).

The localization of the states is very important for lowering the current injection levels in optoelectronic devices, e.g. the threshold current in laser diodes.

The dimension of these structures is smaller than the diameter of the Bohr exciton, which results in an increase of the exciton binding energy, which becomes stable at room temperature. In fact, the confinement of the electrons and holes keep

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Fig. 1.11 Density of states for bulk (a), QWs (1D confinement) (b), QWRs (2D confinement) (c), and QDs (3D confinement) (d) [63]
them closer than in 3D periodic crystals. This makes that the absorption spectrum of low dimensional structures shows exciton related transitions at higher temperatures than bulk materials [55, 64].

1.7 Extrinsic Semiconductors. Energy Levels Inside the Forbidden Bandgap

Very important properties of semiconductors are altered by crystal imperfections. In this way, the controlled addition of impurity atoms permits to tailor the properties of the semiconductors for different applications. Defects in crystalline solids are normally classified according to their dimension as follows:

1. Point defects (zero dimensional defects)
2. Extended defects (dislocations, stacking faults, interfaces, surfaces, precipitates, grain boundaries …).

1.7.1 Point Defects

A point defect refers to an atom missing, or placed in an irregular site in the crystal lattice. Point defects include self interstitial atoms, interstitial impurity atoms, substitutional impurity atoms, vacancies, and antisites in compound semiconductors. One can also include the complexes formed by these defects, as Frenkel pairs, Fig. 1.12.

As mentioned above, electron states are forbidden inside the bandgap, the electrons can only occupy the VB at zero temperature; and they can start to populate the CB if energy higher than the bandgap energy is supplied. According to this picture high concentrations of free carriers at room temperature could only be achieved in narrow band gap semiconductors. However, when the lattice is disturbed by defects, electronic levels become allowed inside the forbidden bandgap. These levels are crucial to control the Fermi level position, and therefore to determine the carrier population of the bands, since they constitute reservoirs for free electrons and/or holes.

Concerning the role of defects in the optical response of semiconductors, one should remember that a semiconductor is characterized by the possibility of having free electrons in the CB and free holes in the VB, even at low temperature. This is achieved by the introduction of impurities, which have the property to transfer free charges to the allowed energy bands in a controlled way, by acting on the density of impurities and its ionization energy with respect to the corresponding band edge, either bottom of the CB or top of the VB.

The point defects can be intrinsic or extrinsic. The intrinsic (also native) defects are those that do not involve foreign chemical species, e.g., vacancies, interstitials, antisites in compound semiconductors, which are cations in the place of anions, or
viceversa; also Frenkel pairs, which are formed by a vacancy and an interstitial. These defects can have electro-optic activity; therefore, they contribute to determine the Fermi level position, also they are scattering centers contributing to the mobility of the free carriers, and to the optical properties of the semiconductors; its presence and density depends on the semiconductor growth conditions, and post growth treatments [65, 66].

Substitutional defects are foreign atoms replacing a host atom. They are intentionally introduced in order to give to the semiconductors their unique properties. It is the controlled incorporation of impurities which permits to exploiting the semiconductor materials for electronic and optoelectronic devices.

Impurities introduce energy levels inside the forbidden bandgap. The defects are classified as donors and acceptors. Donors have extra electrons; when the energy levels associated with donors are close to the CB edge they can be easily ionized populating the CB with conduction electrons. Acceptors have electron deficiency; therefore, when they are close to the VB edge can capture valence electrons, leaving extra holes in the VB.

Donors and acceptors to be effective need to be close to the band edges. According to their position with respect to the band edges one classifies defects regarding its energy level inside the forbidden bandgap as shallow and deep. The shallow levels are poorly localized, therefore, the wavefunction extends over several unit cells [67]. The deep levels have localized wave functions [68].

Both impurities and intrinsic defects can also be unintentionally introduced, which has unwanted consequences for the semiconductor properties, and thereafter for the device operation. This means that a strict control of the residual impurities and defects is necessary. Optical characterization techniques constitute relevant tools for such a purpose, because they supply very sensitive related signals;
therefore, optical techniques are currently used for characterizing the presence of defects and impurities in semiconductors.

### 1.7.2 Extended Defects

The extended defects are defects in which several atoms are involved. Among the extended defects one can list dislocations, stacking faults, precipitates, and grain boundaries [69]. The investigation of their electrooptic properties and the interaction with the point defects is crucial for the device operation. Generally, they are harmful for device performance and reliability; e.g., they play a paramount role in the device degradation during operation [70, 71].

**Statistics of free carriers in doped semiconductors**

The populations of neutral and ionized donors depend on the position of the energy level of the donor, $E_D$, with respect to the Fermi energy, according to the Fermi-Dirac statistics, neglecting $p$:

$$
N_D^0 = N_D \frac{1}{1 + e^{\frac{E_D - F}{kT}}}
$$

$$
N_D^+ = N_D \left(1 - \frac{1}{1 + e^{\frac{E_D - F}{kT}}} \right)
$$

$$
N_D = N_D^0 + N_D^+
$$

Equivalent expressions hold for holes.

Assuming that all shallow donors and acceptors are ionized, the neutrality condition is:

$$
n + N_A^- = p + N_D^+
$$

which together with (1.8) gives:

$$
n = \frac{N_D^+ - N_A^-}{2} + \left[\left(\frac{N_D^+ - N_A^-}{2}\right)^2 + n_i^2\right]^{1/2}
$$

$$
p = \frac{N_A^- - N_D^+}{2} + \left[\left(\frac{N_A^- - N_D^+}{2}\right)^2 + n_i^2\right]^{1/2}
$$

for $n$-type semiconductor $N_D^+ - N_A^- \gg n_i$ and $n = N_D^+ - N_A^-$

The electron concentration in the Boltzmann approximation ($E_D - F \gg K_T$) is given by:
The presence of energy levels in the forbidden band allows transitions between defect related levels and the bands, being responsible for both extrinsic (sub-bandgap) light absorption and emission.

1.8 Doped Semiconductors: Effects on the Band Gap

When defects are present, their electronic occupancy depends on its energy levels with respect to the Fermi level. The energy levels in the bandgap can supply carriers to the bands, being the occupancy of the bands governed by the balance between the ionized donors and acceptors.

The electric compensation relation is:

\[ n + N_A^- = p + N_D^+ \] (1.21)

for an n-type semiconductor, \( N_D > N_A \), one can approximate \( N_A = N_A^- \), and solving the electric compensation equation, for the low temperature range (\( n < N_A \)) one obtains for the free electron concentration:

\[ n \approx \frac{N_c N_D - N_A}{g N_A} \exp \left( - \frac{E_C - E_D}{kT} \right) \] (1.22)

\( g \) is the degeneracy of the donor level. The CB occupancy depends on the concentration of donors and the donor energy, \( E_D \), with respect to the CB. One can obtain a similar equation for holes.

\[ p \approx \frac{N_v N_A - N_D}{g N_D} \exp \left( - \frac{E_A - E_V}{kT} \right) \] (1.23)

At high doping concentrations, many semiconductors characteristics change, due to either the high impurity concentration, or the associated high electron concentration. This is the case of the bandgap energy. In the presence of a significant concentration of impurities the effective bandgap (the energy necessary for transitions between the two bands) is shifted due to three main effects [72–78]:

i. The band filling, which is known as Burstein Moss effect [72–75]
ii. Band tailing due to electron—impurity interaction [75–77]
iii. Bandgap shrinkage due to e-e interaction, which is relevant above a certain critical electron concentration [78, 79].
These effects are summarized in Figs. 1.13 and 1.14.

The Burstein Moss effect was initially described in relation to the absorption threshold shift in InSb with different levels of doping [73]. In fact, the transitions between the VB and the CB occur between states deep in the bands, depending on the density of free carriers, which shall fill the lower energy states of the CB, and the upper energy states of the VB, respectively. So that, the measured optical bandgap energy, $E_{\text{gap}}$, is related to the Fermi level position:
\[ E_{\text{gop}} = E_g + E_F \left( 1 + \frac{m_e^*}{m_h^*} \right) \]  
(1.24)

Remember that for a degenerate electron gas the Fermi level with respect to the bottom of the conduction band is expressed as:

\[ E_F = \frac{\hbar^2}{2m_e^*} \left( 3\pi^2 n \right)^{2/3} \]  
(1.25)

From which the \( n^{2/3} \) dependence of the optical bandgap shift is deduced.

Lee et al. [80] reported the following empiric relation for the optical bandgap, \( E_{\text{gap}} \), of Si-doped GaAs

\[ E_{\text{gop}} = 1.426 + 2.4 \times 10^{-14} n^{2/3} \text{(eV)} \]  
(1.26)

Note that the Burstein Moss shift is inversely proportional to the effective mass; therefore, the shift is more important in semiconductors with light effective masses, in particular, is significantly higher in n-type semiconductors than in p-type semiconductors.

Band tailing appears as a consequence of the random distribution of impurities, which results in potential fluctuations [76]. The consequence is the apparition of band tail states, both above or below the unperturbed band edge, with the consequence of the change in the density of states in the vicinity of the band edges [77], Fig. 1.13.

Finally, bandgap shrinkage occurs for increasing doping concentrations as a consequence of many body interactions, in particular electron-electron, and electron-ionized donor interactions. The band gap shrinkage follows \( n^{1/3} \) dependence. Similar arguments are valid for the valence band in heavily doped p-type semiconductors.

In the case of GaAs the phenomenological bandgap shrinkage for n-type and p-type was given by Yao and Compaan [78]:

\[ \Delta E_g (\text{meV}) = -6.6 \times 10^{-5} n^{1/3} \]
\[ \Delta E_g (\text{meV}) = -2.4 \times 10^{-5} p^{1/3} \]  
(1.27)

The Burstein Moss effect is the dominant effect in n-type GaAs, therefore the optical bandgap is shifted to high energies for increasing electron concentration; however, in p-type GaAs the bandgap shrinkage is the dominant effect and the bandgap is shifted to the low energy for increasing hole concentration. The different behaviour between both types of semiconductor is due to the much lower effective mass of electrons with respect to the holes.
1.9 Interaction of the Semiconductor with Electromagnetic Waves

The optical processes in semiconductors deal with the interaction of light with the ions, electrons, impurities and defects constituting the semiconductor lattice. Many of the optical properties of semiconductors can be studied using classical electromagnetism; while other problems require a quantum mechanics approach.

The particular property of semiconductors with respect to metals and insulators is the presence of both free and bound charges. Both of them interact with the electromagnetic waves and contribute to the physical phenomena reported here.

It is interesting to note the interest of the response of nanosized structures to the light. A case of interest is the interaction with semiconductor nanowires (NWs). See for example the electric field distribution inside a tapered SiNW under a laser beam, resonances and the distribution of the electric field inside the NW depend on the NW diameter, the laser wavelength, and the surrounding media [81–83], Fig. 1.15.

These small objects behave as optical antennas [84].

1.9.1 Macroscopic Approach. Optical Constants

In a solid the bound charges are displaced with respect to the ion cores under the action of the electric field associated with the electromagnetic wave, inducing a polarization proportional to the electric field:

\[ P = \varepsilon_0 \chi(\omega)E \]  

(1.28)

where \( \chi \) is the electric susceptibility, which is related to the dielectric function, \( \varepsilon(\omega) \), according to the relation

Fig. 1.15 Electric field inside a tapered Si NW, for different positions (different diameters) of the laser beam on the NW (532 nm) [83]
D = \varepsilon_0 E + P = \varepsilon_0 (1 + \chi) E = \varepsilon(\omega) E, \quad \varepsilon(\omega) = \varepsilon_0 (1 + \chi(\omega)) \quad (1.29)

The free charges also contribute to the dielectric function through the Ohm’s law

\[ J = \sigma(\omega) E \quad (1.30) \]

where \( \sigma(\omega) \) is the electric conductivity.

Substituting both D and J in the Maxwell equations including both bound and free charges one obtains the dielectric function; which is a complex number.

\[ \varepsilon(\omega) = \varepsilon_{\text{int}}(\omega) + i \frac{\sigma(\omega)}{\varepsilon_0 \omega} \quad (1.31) \]

If one considers the transverse and longitudinal components of the electric field inside the semiconductor one obtains the dispersion relation for transverse waves:

\[ q^2 = \frac{\omega^2}{c^2} \varepsilon(\omega) \quad (1.32) \]

Longitudinal waves only exist if \( \varepsilon(\omega) = 0 \); note that the existence of longitudinal waves is only possible in the complex dielectric medium.

The dielectric function is a complex number; therefore the wavevector of the electromagnetic wave in the solid is also complex, and the electric field inside the semiconductor can be written as a damped plane wave:

\[ \mathbf{E} = E_0 e^{\frac{-q_i}{c} \mathbf{z} \mathbf{t}} e^{i(\mathbf{q}_r z - \omega t)} \quad (1.33) \]

where \( q_r \) and \( q_i \) are respectively the real and the imaginary parts of the wavevector.

The imaginary part of the wavevector is responsible for the wave damping inside the semiconductor. Now the question is: what damping mechanisms can occur inside the semiconductor?:

i. Photons interact with the lattice
ii. Photons interact with defects
iii. Photons interact with valence electrons
iv. Photons interact with free electrons.

The macroscopic properties of the dielectric medium can be described by a complex refractive index, which permits relating the dielectric function and the conductivity:

\[ \tilde{n} = n + i \kappa = \sqrt{\varepsilon(\omega)} \quad (1.34) \]

So, the electric field inside the solid can be written as

\[ \mathbf{E} = E_0 e^{-\kappa q_i z} e^{i(nq_r z - \omega t)} \quad (1.35) \]

where, \( q_0 \) is the wavevector of the electromagnetic wave in the vacuum.
The complex part of the refractive index accounts for the wave damping when
the electromagnetic wave propagates inside the semiconductor; the imaginary part
of the refractive index is the extinction coefficient, while the real part, \( n \), is the
refractive index. Taking account of the intensity loss inside the semiconductor one
can define the absorption coefficient. A fraction of the incident light is reflected,
while the remaining intensity penetrates in the semiconductor, as it travels across,
the wave exchanges energy with the solid according to the exchange mechanisms
listed above; at a distance \( z \) from the surface the intensity of the wave is expo-
nentially reduced, with respect to the ongoing wave intensity, the intensity loss is
associated with a characteristic parameter labelled the absorption coefficient, \( \alpha \):

\[
I(z) = I'_0 \exp(-\alpha z) \quad (I'_0 = I_0 - I_R)
\]

where \( I_R \) is the reflected light intensity at the surface. \( \alpha \) and \( I_R \) are functions of the
wavelength. The intensity of the electric field decreases when travelling across the
semiconductor, reaching \( 1/e \) of its value at the surface at a depth equal to \( 1/\alpha \)
(Beer-Lambert law).

Using (1.35) and (1.36) the absorption coefficient can be expressed as a function
of the optical constants of the semiconductor:

\[
\alpha = \frac{\omega k}{cn} \quad (1.37)
\]

In a conducting medium the absorption coefficient is related to the conductivity
according to:

\[
\alpha = \frac{\sigma}{n e \varepsilon_0} \quad (1.38)
\]

1.10 The Oscillator Model for the Optical Constants

1.10.1 Dielectric Function

Lattice contribution

When considering the lattice absorption one can use a classic damped harmonic
oscillator model for deducing the electrical susceptibility, which is related to the
oscillator frequency, \( \omega_0 \), the oscillator strength, \( f_0 \), and the damping parameter, \( \Gamma \):

\[
\chi = \frac{f_0 N e^2}{\varepsilon_0 m V \omega_0^2} \frac{1}{\omega^2 - i \Gamma \omega} \quad (1.39)
\]
the real and imaginary parts are:

\[ \varepsilon' = \frac{f_0 N e^2}{\varepsilon_0 mV} \left( \frac{\omega_0^2 - \omega^2}{\omega_0^2 - \omega^2 + \Gamma^2 \omega^2} \right) \]

\[ \varepsilon'' = \frac{f_0 N e^2}{\varepsilon_0 mV} \left( \frac{\Gamma \omega}{\omega_0^2 - \omega^2 + \Gamma^2 \omega^2} \right) \]  

(1.40)

The dielectric function adopts the form:

\[ \varepsilon(\omega) = \varepsilon_0 + \frac{f_0 N e^2}{mV} \frac{1}{\omega_0^2 - \omega^2 - i\Gamma \omega} \]  

(1.41)

**Free electron contribution**

In the Drude formalism the electronic contribution to \( \varepsilon(\omega) \) corresponds to the dielectric function of an electron gas of density \( n \):

\[ \varepsilon(\omega) = \varepsilon_\infty \left( 1 - \frac{\omega_p^2}{\omega(\omega - i\gamma)} \right) \]  

(1.42)

where \( \omega_p \) is the plasma frequency, and \( \gamma = 1/\tau \), is a phenomenological damping parameter. Other approaches for the electron contribution to the dielectric function (Hydrodynamic, Mermin) will be revised in Chap. 3.

### 1.10.2 Kramers Kronig Relations

The relations between the real and imaginary parts of the dielectric function, in the electric field linear dependent range, are given by the Kramers Kronig relations:

\[ \varepsilon_r(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_i(\omega')}{\omega'^2 - \omega^2} d\omega' \]

\[ \varepsilon_i(\omega) = -\frac{2}{\pi} P \int_0^\infty \frac{\varepsilon_r(\omega')}{\omega'^2 - \omega^2} d\omega' \]  

(1.43)

where, \( P \) indicates the principal value of the Cauchy integral.

Similar relations can be deduced for the electric susceptibility, and the refractive index. In general, the K-K relations permit to calculate the real part of the optical functions from the imaginary part and vice versa.
1.11 Optical Reflection

The reflectivity, \( r \), defined as the ratio of the electric field of the reflected wave to that of the incident wave, in normal incidence obeys the relation:

\[
r = \frac{\tilde{n} - 1}{\tilde{n} + 1}
\]

while the reflectivity intensity, named as the reflectance, \( R \), is given by:

\[
R = |r|^2 = \left( \frac{\tilde{n} - 1}{\tilde{n} + 1} + \kappa^2 \right) \left( \frac{\tilde{n} + 1}{\tilde{n} - 1} + \kappa^2 \right)
\]

For finite incidence angles the optical constants can be experimentally determined by ellipsometry using the Fresnel formulas for the reflected light. For an angle of incidence \( \theta_i \), the reflectances of the parallel polarized/TM (p-polarized) and perpendicular polarized/TE (s-polarized) waves are related to the complex refractive index, \( \tilde{n} \), according to the following formulas:

\[
R_p = \left( \frac{\tilde{n} \cos \theta_i - \left( (\tilde{n}^2 - \sin^2 \theta_i) \right)^{1/2}}{\tilde{n} \cos \theta_i + \left( (\tilde{n}^2 - \sin^2 \theta_i) \right)^{1/2}} \right)^2
\]

\[
R_s = \left( \frac{\cos \theta_i - \left( (\tilde{n}^2 - \sin^2 \theta_i) \right)^{1/2}}{\cos \theta_i + \left( (\tilde{n}^2 - \sin^2 \theta_i) \right)^{1/2}} \right)^2
\]

As mentioned above, the real and complex parts of the dielectric function are related by the Kramers-Kronig relations, which permit to deduce one of them if one knows the other one.

It is interesting to note that semiconductors have large refractive index; therefore, the light generated inside the semiconductor can suffer total internal reflection; therefore, it cannot be extracted, and remains inside the medium. The critical angle of incidence for photons generated inside the semiconductor is rather small, e.g. 17° for GaAs. This will be relevant to the external quantum efficiency of light emitting devices, for which strategies for light extraction are necessary to improving the efficiency.

1.12 Optical Transitions. Light Absorption and Emission

The main optical loss mechanism is the absorption of light by the semiconductor. Once the light penetrates inside the semiconductor it undergoes a series of absorption phenomena because of the exchange of energy between the refracted light beam and the different constituents of the solid.
1.12.1 Einstein Coefficients

The basic processes of interaction between light and matter are described by the Einstein coefficients. One can describe three interaction processes: (i) absorption, (ii) spontaneous emission, and (iii) stimulated emission.

Einstein described these processes as follows:

If one considers two energy levels of an atom, i and f, with populations $N_i$ and $N_f$ respectively, a light beam with energy $(E_f - E_i)$ (angular frequency $\omega_{if} = (E_f - E_i) / h$) can interact with the atom; by absorbing a photon an atom in the lower energy state, $E_i$, is excited to the upper energy level, $E_f$, absorption phenomenon, the rate of the atom population change is given by:

$$\frac{dN_i}{dt} = -B_{if} N_i e^\omega = -\frac{dN_f}{dt}$$  \hspace{1cm} (1.47)

$B_{if}$ is the absorption Einstein coefficient, and $e^\omega$ is the energy density of the incident photons, which is described by Planck’s law.

The reverse transition can also occur and the excited electron can fall down to the initial state. This process can be achieved in two different ways, namely spontaneous or stimulated.

In the spontaneous emission one photon with energy $h\omega_{if}$ is generated. The rate of spontaneous emission is

$$\frac{dN_i}{dt} = A_{fi} N_f = -\frac{dN_f}{dt}$$  \hspace{1cm} (1.48)

$A_{fi}$ is the Einstein coefficient for spontaneous emission, it has dimensions of time$^{-1}$, and the inverse of the Einstein coefficient is the characteristic time of the spontaneous emission transition, $A_{fi} = 1/\tau_{sp}$.

The transition from f to i can also be achieved with the participation of a photon with energy $h\omega_{if}$. The electron in the f state can be induced by an incident photon to emit a photon when falling down to the i state, the two photons being in phase; this is the stimulated emission mechanism. The stimulated rate of decay of the excited states depends on the third Einstein coefficient, $B_{fi}$:

$$\frac{dN_f}{dt} = -B_{fi} N_f e^\omega = -\frac{dN_i}{dt}$$  \hspace{1cm} (1.49)

One can also define the stimulated emission characteristic time, $\tau_{stim}$, as:

$$\tau_{stim} = \frac{1}{B_{fi}e(\omega)}$$  \hspace{1cm} (1.50)
In equilibrium the net rate of upward transitions equals to the net rate of downward transitions:

\[ B_{if} N_i e^{\omega \tau} = A_{fi} N_f + B_{fi} N_f e^{\omega \tau} \quad (1.51) \]

By thermodynamic considerations Einstein established the relation between the three coefficients:

\[ B_{if} = B_{fi} \]
\[ A_{fi} = \frac{2 \hbar \omega^3 n^3}{\pi c^3} B_{fi} \quad (1.52) \]

where \( n \) is the refractive index.

The three transitions are summarized in Fig. 1.16a. This holds for discrete levels. However, when dealing with semiconductors one has to consider the density of states and the occupancy of the bands, see Fig. 1.16b.

Fig. 1.16 a Two level scheme transitions. b Transition scheme in a semiconductor
1.12.2 Microscopic Description of the Optical Absorption in Semiconductors

The absorption process is described by quantum mechanics in terms of the electron photon interaction using time dependent perturbation theory. In the frame of a semiclassical approach the Hamiltonian describing the interaction between the electromagnetic wave and the electrons, uses a classical electric field for the electromagnetic wave, while the electrons are treated by Bloch functions in a quantum mechanics approach.

The Hamiltonian describing the motion of the electrons in the presence of the electromagnetic field is:

\[
H = \frac{1}{2m} \left[ \mathbf{p} + e \mathbf{A} \right]^2 + V(r)
\]

where \( A \) is the vector potential, and \( V \) is the electric potential.

In the electric dipole approximation the electron-photon interaction Hamiltonian becomes:

\[
H_{e-p} = \frac{e}{mc} \mathbf{A} \cdot \mathbf{p} = -e \mathbf{r} \cdot \mathbf{E} = H_+ e^{-i\omega t} + H_- e^{-i\omega t}
\]

\[
H_+ = \frac{e}{2m} A_0 e^{iqr} \cdot \mathbf{p}
\]

\[
H_- = \frac{e}{2m} A_0 e^{-iqr} \cdot \mathbf{p}
\]

In a semiconductor the fundamental transition refers to the transition of an electron from the VB to the CB. The two terms of the Hamiltonian correspond to the transition from the VB to the CB (absorption), while the reverse transition corresponds to the emission, either spontaneous or stimulated.

The electron in the valence band absorbs a photon \((\hbar \omega)\) from the incoming light beam when the energy of the photons is enough to promote the electron through the forbidden band to the conduction band. The electron in state \(i\) has momentum \(k_i\) and energy \(E_i(k_i)\), while the final state has momentum \(k_f\) and energy \(E_f(k_f)\). The conservation rules establish both momentum and energy conservation:

\[
k_f = k_i + \mathbf{k}
\]

\[
E_f(k_f) = E_i(k_i) + \hbar \omega
\]

These rules allow only transitions between different bands (interband transitions).
Using the Fermi’s golden rule one can estimate the optical transition rates:

\[
W_i(k_i) = \frac{2\pi}{h} \sum_{k_f} \left| \langle \phi_{e,k_i} | H + | \phi_{e,k_f} \rangle \right|^2 \delta_{k_i + q,k_f} \delta(E_c(k_f) - E_v(k_i) - \hbar\omega)
\]

\[
= \frac{2\pi}{h} \left( \frac{eA_0}{2m} \right)^2 |p_{cv}|^2 \delta_{k_i + q,k_f} \delta(E_c(k_i + q) - E_v(k_i) - \hbar\omega) = B q \delta(E_c(k_f) - E_v(k_i) - \hbar\omega)
\]

(1.56)

The \(\delta\) Kronecker accounts for the momentum conservation, while the \(\delta\) function entails the energy conservation. The summation is over all the final states in the conduction band respecting the conservation rules and the spin.

Contrarily to the isolated atoms, one has to integer to all the possible initial states weighted by the probability that the final state is empty to calculate the transition rate per second and unit volume:

\[
R_{abs} = \frac{2}{V} \sum_{k_i} W \uparrow (k_i) f_v(k_i) (1 - f_e(k_f))
\]

(1.57)

The photon momentum is much smaller than the electron momentum, therefore the momentum conservation rule can be simplified to: \(k_f = k_i = k\), which means that the optical transition is vertical in the k-space; Fig. 1.16b.

Assuming that the conduction band is empty, the absorption rate takes the form:

\[
R_{abs}(\omega) = \frac{2\pi}{\hbar} \left( \frac{eA_0}{2m} \right)^2 |p_{cv}|^2 \int_{FBZ} \frac{d^3 k}{(2\pi)^3} \delta(E_c(k) - E_v(k) - \hbar\omega)
\]

(1.58)

The integral appearing in (1.58) is the joint density of states. Assuming parabolic bands:

\[
E_c(k) = E_c + \frac{\hbar^2 K^2}{2m_e^*}
\]

\[
E_v(k) = E_v - \frac{\hbar^2 K^2}{2m_h^*}
\]

(1.59)

The transition rate takes the form:

\[
R_{abs}(\omega) = \frac{2}{\pi\hbar} \left( \frac{eA_0}{2m} \right)^2 |p_{cv}|^2 \left( \frac{2\mu}{\hbar^2} \right)^{3/2} (\hbar\omega - E_g)^{1/2}
\]

(1.60)

where, \(\mu\) is the reduced mass of the e-h pair.
The transition rate can be related to the absorption coefficient

\[
\alpha(\omega) = \left( \frac{e}{m} \right)^2 \left( \frac{1}{2\pi \varepsilon_0 n_\infty c} \right) |p_{cv}|^2 \left( \frac{2\mu}{\hbar^2} \right)^{3/2} (\hbar \omega - E_g)^{1/2}
\]  

For a direct transition between the valence band and the conduction band the absorption coefficient varies as the square root of the difference between the photon energy and the fundamental bandgap. The bandgap measured from optical absorption is the optical bandgap. The absorption root square law is plotted in Fig. 1.17, together with the experimental values at 5K and RT of an InSb crystal [85].

This is valid for an intrinsic semiconductor with the VB filled and the CB empty, otherwise, one has to take care of the respective occupancy of the bands:

\[
R_{abs}(\omega) = \frac{2\pi}{\hbar} \left( \frac{e A_0}{2m} \right)^2 |p_{cv}|^2 2 \ast \int_{FBZ} d^3 k \frac{1}{(2\pi)^3} f_v(k)(1 - f_c(k)) \times \delta(E_c(k) - E_v(k) - \hbar \omega) = B_{vc} f_v(k)(1 - f_c(k))
\]

and the absorption coefficient is:

\[
\alpha(\omega) = \left( \frac{e}{m} \right)^2 \left( \frac{1}{2\pi \varepsilon_0 n_\infty c} \right) |p_{cv}|^2 2 \ast \int_{FBZ} d^3 k \frac{1}{(2\pi)^3} f_v(k) \times (1 - f_c(k)) \delta(E_c(k) - E_v(k) - \hbar \omega)
\]

Fig. 1.17 Absorption coefficient versus photon energy. The inset is the experimental absorption edge of InSb at RT (1) and 5 K (2), showing tailing at RT due to CB filling [85].
1.12.3 Microscopic Description of the Stimulated Emission in Semiconductors

The emission corresponds to the reverse of absorption, the electron falls down from the upper level, \( f \), to the lower level, \( i \); in our case it refers to the transition of the electron in the CB to its equilibrium state in the VB. This transition can be stimulated by the electromagnetic wave; in fact, the electromagnetic wave induces the transition of the electron from the CB, down to the VB, loosing the energy emitted as a photon, which adds to the electromagnetic wave that stimulated the transition.

The transition probability for stimulated emission is:

\[
W_{\text{stim}}(k_f) = \frac{2\pi}{\hbar} \sum_{k_f} \left| \left\langle \phi_{v,k}\left| H_+ \right| \phi_{c,k_f} \right\rangle \right| \delta(E_c(k_f) - E_v(k_i) - \hbar\omega)
\]

(1.64)

\[
R_{\text{stim}}(\omega) = \frac{2\pi}{\hbar} \left( \frac{e A_0}{2m} \right)^2 |p_{cv}|^2 2 \ast \int_{\text{FBZ}} \frac{d^3 k}{(2\pi)^3} f_c(k)(1 - f_v(k)) \times \delta(E_c(k) - E_v(k) - \hbar\omega) = B_{cv} f_c(k)(1 - f_v(k))
\]

(1.65)

The net stimulated emission rate is:

\[
R_{\text{stim}} - R_{\text{abs}} = B_{cv}(f'_v - f'_c)
\]

(1.66)

Note that under strong light excitation the non equilibrium free carrier concentration is very high, and a single Fermi level does not make sense, but one can consider that it splits out in a quasi Fermi level for electrons, \( F_e \), and another for holes, \( F_h \); the occupancy functions follow the Fermi Dirac statistics are:

\[
f_v = \frac{1}{1 + e^{(E_c - E_{\text{v}})/kT}}
\]

\[
f_c = \frac{1}{1 + e^{(E_c - E_{\text{c}})/kT}}
\]

(1.67)

Under a large flux of photons, intense excitation, the quasi Fermi levels for electrons and holes are inside the conduction and valence bands respectively; then, one can define a reverse absorption coefficient:

\[
\alpha_{\text{stim}}(\omega) = \left( \frac{e}{m} \right)^2 \left( \frac{1}{2\pi \hbar \omega_0 \hbar \omega} \right) |p_{cv}|^2 2 \ast \int_{\text{FBZ}} \frac{d^3 k}{(2\pi)^3} f_c(k) \times (1 - f_v(k)) \delta(E_c(k) - E_v(k) - \hbar\omega)
\]

(1.68)
The absorption rate has to consider the net balance between absorption and stimulated emission. Therefore, it can be obtained by dividing the difference of transition rates by the energy light flux, which is the product of the energy density and the group velocity:

\[ \alpha(\omega) = \alpha_1(\omega) - \alpha_\downarrow(\omega) = \frac{B_{cv}(f_v - f_c)}{c/n} \]  

(1.69)

Note that the net absorption coefficient determines the conditions for which gain and losses are dominant respectively. Light with energy \( E_g < \hbar \omega < F_c - F_h \) undergoes optical gain (\( \alpha(\omega) < 0 \)) Bernard-Durrafourg condition [86]), while light with energy \( \hbar \omega > F_c - F_h \) undergoes optical losses (\( \alpha(\omega) > 0 \)). The population inversion threshold occurs for \( f_c = f_v \).

### 1.12.4 Microscopic Description of the Spontaneous Emission in Semiconductors

In the case of the spontaneous emission, the emission rate can be expressed as:

\[
R_{sp}(\omega) = \left( \frac{e^2}{m} \right)^2 \left( \frac{\pi}{\epsilon_0 n^2 \omega} \right) \frac{1}{V} |p_{cv}|^2 2 * \int_{FBZ} \frac{d^3 k}{(2\pi)^3} f_c(k) \times (1 - f_v(k)) \delta(E_c(k) - E_v(k) - \hbar \omega) = A_{cv} f_c(1 - f_v)
\]

(1.70)

\( A_{cv} \) is the Einstein coefficient for spontaneous emission.

\[ R_{sp} = A_{cv} f_c(1 - f_v) \]  

(1.71)

According to the relation between the Einstein coefficients, one can establish the relation between \( R_{stim} \) and \( R_{sp} \)

\[ R_{stim} \approx R_{sp} \left( 1 - \exp \left( \frac{E - \Delta F}{KT} \right) \right) \]  

(1.72)

On the other hand, one can establish the relation between spontaneous emission and optical absorption by means of the van Roosbroeck-Shockley relation [87]:

\[
R_{sp}(\hbar \omega) = \frac{8\pi n^2}{\hbar^3 c^2} \frac{(\hbar \omega)^2}{\exp(\frac{\hbar \omega - \Delta F}{KT}) - 1} \alpha(\hbar \omega)
\]

(1.73)
where $n$ is the refractive index, $\alpha$ the absorption coefficient, and $\Delta F$ is the splitting between the quasi Fermi levels for electrons and holes respectively. This relation permits to convert the spontaneous emission spectrum into the absorption spectrum.

The spontaneous emission is the product of the absorption spectrum, which is proportional to the joint density of states and the distribution of non-equilibrium electron and holes, Fig. 1.18 [88].

### 1.12.5 Indirect Optical Transitions

The photon momentum in the optical transitions is negligible with respect to the crystal momentum, therefore the optical transitions were vertical in the k-space. However, in indirect bandgap semiconductors, Si, Ge, AlAs, GaP, SiC among other, the minimum of the CB and the maximum of the VB are separated away in the k-space. Therefore, the momentum conservation rule is not satisfied in band to band transitions, but one needs an extra contribution to conserve the momentum, Fig. 1.19. The extra momentum can be supplied by phonons. Other sources of extra momentum occur by the alloy disorder or scattering mediated by impurities, but in pure and lightly doped semiconductors the transitions between the bands are assisted by phonons.

The problem is treated in the frame of the second order perturbation theory, because the absorption process occurs in two steps, involving electron-phonon interaction, and electron-photon interaction respectively. The absorption coefficient in the vicinity of an indirect bandgap follows a quadratic dependence with the photon energy, instead of the square root dependence reported for direct band gap semiconductors (1.61) [89]:

$$\alpha(\omega) \approx (\hbar \omega - E_g - \hbar \omega_{ph})^2$$  \hspace{1cm} (1.74)
For an indirect band gap semiconductor the conservation of momentum requires that the absorption of a photon is assisted by a phonon, either absorbed or emitted [90].

1.12.6 The Influence of Disorder and Doping in the Absorption Coefficient. Urbach Tail

As mentioned above the band edge absorption follows a root square dependence with photon energy; however, an exponential tail is often observed bellow the bandgap energy [91–93]. This is the Urbach tail, which appears as a consequence of the transitions between tail states below the band edges, due to doping inhomogeneities, internal strains, or disorder, all giving rise to microscopic electric fields; also, fluctuations of the band edges due to lattice vibrations can contribute to the tail states. The absorption coefficient tail follows an exponential law [91]:

\[ \alpha(\omega) = \alpha_0 \exp\left(\frac{\hbar \omega - E_0}{E_u}\right) \]  \hspace{1cm} (1.75)

where \( \alpha_0 \) and \( E_0 \) are materials parameters and \( E_u \) is the Urbach energy.

A scheme of the absorption plot including the Urbach tail is shown in Fig. 1.20 [94].
Other absorption processes

The main absorption process is the fundamental absorption when an electron transits from the VB to the CB. However, we have described the existence of energy levels inside the fundamental bandgap associated with impurities and/or intrinsic defects; therefore, one can consider the possible transitions from those levels to the free bands, but also the transitions in between them. This is also applicable to the case of quasi-particles as the excitons.

1.12.7 Defect and Impurity Absorption

The main extrinsic absorption processes are summarized in Fig. 1.20. In addition to the fundamental bandgap absorption one can distinguish donor to CB, VB to acceptor, VB to donor, acceptor to CB, and acceptor to donor transitions [65, 95–98]. Figure 1.21 shows the extrinsic absorption of the EL2 deep level in semi-insulating GaAs. The three curves correspond to the changes induced by light, which quenches the absorption by transferring EL2 into a metastable state [99] (Fig. 1.22).

1.12.8 Excitonic Absorption

The theory of excitons is beyond the scope of this text, it is based on many body formalisms. However, under appropriate experimental conditions one observes an
absorption peak below the band gap energy, which is due the exciton formation. The absorption curve deviates from the $\alpha(\omega) \approx (h\omega - E_g)^{1/2}$ law for band to band absorption. Excitons also contribute to the absorption above the bandgap energy, where a continuous absorption is observed, this continuum is described by the Sommerfeld factor, which depends on the energy difference between the CB continuum and the fundamental hydrogen level of the exciton [100].

The absorption spectrum of GaAs at different temperatures, showing the exciton absorption contribution, and the subsequent quenching of the exciton absorption once it is thermally dissociated at room temperature is shown in Fig. 1.23 [102].

The excitonic absorption in QWs is sensitive to temperature but not so dramatically as in the bulk, because the electron and hole confinement keep them close together increasing the binding energy, so excitonic transitions are observed up to room temperature in GaAs QWs, Fig. 1.24 [102].
1.13 Carrier Recombination. Luminescence

The absorption process generates carriers in excess of thermal equilibrium. They come back to equilibrium by the process of carrier recombination. In this process excess electrons of the conduction band fall down spontaneously to the valence band recombining with excess holes. The energy released in this process can be emitted as a photon. This emission is the luminescence phenomenon, which will be discussed in Chaps. 4 and 5 of this volume. It corresponds to the spontaneous emission described above.
Transitions other than band to band can occur when energy states in the forbidden band gap exist associated with defects and impurities. These states are revealed in the luminescence spectrum by characteristics emissions.

### 1.13.1 Non-radiative Recombination

The excess carriers can be also annihilated by recombination processes in which the energy released is not transformed into photons, but it is dissipated differently, namely generating phonons. Also, the energy can be transferred to another particle, either electron or hole, resulting in a hot carrier (Auger recombination) \[103\]; Auger recombination is more likely to occur in heavily doped semiconductors or at very high excitation levels. Alternatively, the recombination energy can be transferred to a neighbor atom in the lattice, which can be removed from its lattice site, leaving behind a point defect; this process is known as recombination enhanced defect reaction (REDR) \[104, 105\]. This mechanism is relevant to the stability of devices under operation. All these mechanisms are known as non-radiative recombination (NRR) processes. The NRR processes establish competitive recombination paths with the radiative recombination processes; therefore, they play a relevant role in the internal quantum efficiency (IQE) of semiconductors. The internal quantum efficiency is defined as the ratio of the number of photons generated in the semiconductor to the number of generated e-h pairs, if one emits one photon for each generated e-h pair the quantum efficiency at that particular excitation wavelength is the unity. Note that the IQE is also used in solar cells as the ratio of the number of carriers collected by the solar cell to the number of photons of a given energy incident on the solar cell. Therefore, NRR processes reduce the IQE limiting the performance and reliability of devices.

### 1.13.2 Luminescence

Photoluminescence (PL) is the opposite to optical absorption; furthermore, it needs from optical absorption to occur; however, optical absorption is not the only way to produce free carriers in excess of thermal equilibrium necessary for the subsequent recombination, and luminescence emission; but other excitation sources can be used; in particular, the excitation can be achieved by means of energetic particles, e.g. electrons in cathodoluminescence (CL) emission (Chap. 5). Also, the excess charge carriers can be injected by an electric bias; this emission is known as electroluminescence, and is at the origin of the operation of the light emitting devices.
The different recombination paths are schematically shown in the real space diagram of Fig. 1.25.

The recombination is characterized by a characteristic time, the recombination time.

If the equilibrium carrier populations are $n_0$ and $p_0$ respectively, under carrier generation using an external excitation source, the carrier populations are increased, becoming $n$ and $p$, this excess carrier population decays to equilibrium by recombination.

\[
\begin{align*}
    n &= n_0 + \Delta n \\
    p &= p_0 + \Delta p \\
    \frac{dn}{dt} &= G - R_{sp} = -A(np - n_0p_0)
\end{align*}
\]

Therefore,

\[
\begin{align*}
    d\Delta n/dt &= -A(n_0 + p_0 + \Delta n)\Delta n \\
    \Delta n &= (\Delta n)_0 \exp(-t/\tau_r)
\end{align*}
\]

the recombination time is

\[
\tau_r = [A(n_0 + p_0 + \Delta n)]^{-1}
\]

For low generation $\Delta n \ll$ and the lifetime becomes

\[
\tau_r = [A(n_0 + p_0)]^{-1}
\]
In n-type semiconductor \( n_0 \gg p_0 \), therefore the minority carrier lifetime is

\[
\tau_r = [An_0]^{-1}
\]

(1.80)

While for high generation level \( \Delta n \gg \), the lifetime is:

\[
\tau_r = [A\Delta n]^{-1}
\]

(1.81)

One can distinguish different lifetimes according to the classification provided by Bube [106]:

- **Free lifetime**: lifetime of free carriers without considering trapping
- **Excited lifetime**: lifetime of an excess carrier considering free and trapping times
- **Minority carrier lifetime**: The free lifetime of the carrier type with lower density in extrinsic semiconductors.
- **Majority carrier lifetime**: the same as before but for the carrier type with the higher density. Is the relevant parameter in electronic devices.
- **e-h pair lifetime**: The free lifetime of an e-h pair, normally is determined by the lifetime of the first captured carrier, usually the minority carriers, specially under low excitation conditions. This is the relevant time for luminescence emission.

The spontaneous emission rate was deduced using the Fermi’s Golden rule; it describes the rate at which electrons in filled states (CB) transit into empty states (VB). It is proportional to the probability of the upper level to be filled times the probability of the lower level to be empty. The sum is made over the initial and final states. Note that instead the absorption process where almost all the states in the bands are available, in the emission process only a narrow interval of energy states, around a few \( KT \) from the band edges, is available. The result is the very narrow luminescence linewidth as compared with the broad absorption transitions.

For parabolic bands, low doping and low excess carrier concentration (weak excitation), one can approach the Fermi occupation functions to Boltzmann distributions, and the spontaneous transition from CB to VB rate takes the form [107]:

\[
R_{sp}(\omega) \approx \alpha(h\omega - E_g)^{1/2} \exp\left(-\frac{h\omega - E_g}{KT}\right)
\]

(1.82)

The peak energy shifts and the full width at half maximum broaden with \( T \) as [107]:

\[
E_{\text{peak}} = E_g + \frac{1}{2} KT
\]

\[
\text{FWHM} = 1.8 KT
\]

(1.83)
In indirect transitions the participation of phonons is required in order to satisfy the momentum conservation rule, as it was discussed for the absorption in indirect bandgap semiconductors. The band edge luminescence obeys the following relation [107]:

\[
R_{sp}(\omega) \approx \frac{(\hbar \omega - \hbar \omega_{ph} - E_g)^2}{1 - \exp(-\frac{\hbar \omega_{ph}}{KT})} \exp\left(-\frac{\hbar \omega + \hbar \omega_{ph} - E_g}{KT}\right) + \frac{(\hbar \omega - \hbar \omega_{ph} - E_g)^2}{\exp(\frac{\hbar \omega_{ph}}{KT}) - 1} \exp\left(-\frac{\hbar \omega - \hbar \omega_{ph} - E_g}{KT}\right)
\]

(1.84)

The first term refers to phonon absorption, and the second to phonon emission. The peak energy and the FWHM also depend on T according to [107]:

\[
E_{peak} = E_g - \hbar \omega_{ph} + 2KT
\]

\[
FWHM = 3.4KT
\]

(1.85)

Note that one has to take account of the dependence of \(E_g\) with T for the assessment of the peak shift with T.

### 1.13.3 Diffusion Length

In electroluminescence and CL, and in a minor extent in PL the high energy side of the intrinsic luminescence can be modified by the semiconductor self-absorption, because of the long path traveled by the photons when they are generated deeply in the semiconductor, e.g. in CL experiments one can reach penetration depths above one micrometer, for which non negligible absorption of the high energy luminescence photons occur, which is not the case for PL because the penetration depth of the excitation light is only a few tens of nm. However, the generated carriers run a certain distance before the recombination, this distance is the carrier diffusion length, \(L_D\), which more precisely is the average distance between the carrier generation point and the recombination point. One can also relate the diffusion length to the recombination time, or the carrier lifetime.

\[
L_D = (Dt)^{1/2}
\]

(1.86)

\(D\) is the diffusivity, and is expressed in m\(^2\)/s. The minority carrier lifetime and the diffusion length depend strongly on the recombination processes and the density of recombination centers, both radiative and non radiative.
This means that the recombination is not necessarily occurring inside the volume of light absorption, but the light generation volume is enlarged with respect to the carrier generation volume.

### 1.13.4 Surface Recombination

The surface of the semiconductors with its dangling bonds is a highly efficient recombination player. The excess carriers can reach the surface, when they are generated within the diffusion length distance, recombining there. Usually, the surface recombination is expressed as a surface current:

\[
J_{\text{surface}} = -eS\Delta n
\]  

(1.87)

\(\Delta n\) is the excess carrier concentration at the surface with respect to the bulk equilibrium value. \(S\) is the surface recombination velocity (SRV), it is expressed in velocity units, \(\text{m} \cdot \text{s}^{-1}\) and depends on the nature of the semiconductor, the doping level, and the surface termination [108, 109].

Several strategies are defined to reduce \(S\); e.g. surface passivation, dielectric coating.

### 1.13.5 Exciton Recombination

Often exciton recombination is dominant in the luminescence emission. Exciton luminescence depends on the exciton binding energy, for low binding energy it is only observed at low temperature. Wide bandgap semiconductors as GaN, and especially ZnO, have a large free exciton binding energy [110, 111], see Fig. 1.4, which should permit excitonic emission even at room temperature. The lineshape of the free exciton luminescence takes the following expression:

\[
R_{sp}(h\omega) \approx \frac{\hbar \Gamma}{2\pi} \exp\left(\frac{h\omega - E_X}{kT}\right) - 1 \left(\frac{h\omega - E_X}{\frac{\hbar \Gamma}{2}}\right)^2
\]

(1.88)

where \(\Gamma\) is the full width at half maximum (FWHM) and \(E_X\) is the exciton binding energy.

For strong exciton phonon coupling it results in the following expression:

\[
R_{sp}(h\omega) \approx \frac{1}{(2\pi)^{1/2} \sigma} \exp\left(-\frac{(h\omega - E_X)^2}{2 \sigma^2}\right) \frac{1}{\exp\left(\frac{h\omega - E_X}{kT}\right) - 1}
\]

(1.89)

where \(\sigma = 0.425 \Gamma\).
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