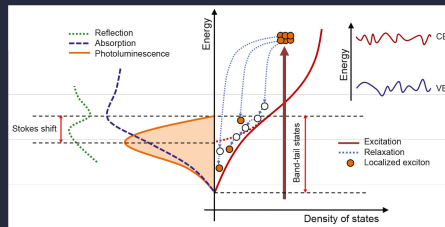




Mohammad Khaled Shakfa (Autor)
Localization Effects in Disordered III-V Semiconductor Nanostructures

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1 Introduction

Smartphones are a perfect example of how modern technologies influence our daily lives. Nowadays it is possible to share the information worldwide within a few fractions of a second through internet connection. This amazing facility makes our world as small as a village, and it is not surprising to call the last four decades as the information age associated with the digital revolution. In addition to the development of optical fibers, the key component of this revolution is indisputably the manufacturing of semiconductors.

Due to the increasing demands industrially as well as scientifically on new optoelectronic devices for specific applications, semiconductor materials with desired energy band-gap are needed. Band gap engineering afforded by the development of the growth techniques allows the construction of novel semiconductor materials which have their band gaps at custom-designed energies that meet the requirements for particular applications [1]. In addition to binary compound semiconductors, this opens up numerous possibilities of three-elements (ternary), four-elements (quaternary), or even five-elements (quinary) semiconductor compounds (or rather alloys). In principle, these higher-order compositions can be synthesized by alloying various semiconductors together [2]. Alloying provides the ability to tailor the energy band gap of a semiconductor through the manipulation of its constituent composition. Furthermore, the ability to adjust the lattice constant of a semiconductor alloy by changing the composition of an involved compound enables the development of heterostructures, which is actually the key element of the design high performance optoelectronic devices [2, 3, 4].

Among semiconductors, dilute III-V nitride and/or bismide semiconductor alloys have emerged as a subject of considerable research efforts over the last two decades driven by not only their unique physical properties but also their great potential for photonic devices [5, 6]. In this thesis, it is focused on two III-V-based compound semiconductor nanostructures: Ga(NAsP) and Ga(AsBi). In particular, quaternary Ga(NAsP) semiconductor structures are promising for the fabrication of intermediate band solar cells [7], for infrared laser emission [8, 9], and, with a tremendous potential, for the realization of monolithic optoelectronic integrated circuits on silicon substrate (silicon photonics) [5, 9]. On the other hand, ternary Ga(AsBi) semiconductor structures have been employed for a variety of applications such as photoconductive terahertz antennas [10], light-emitting diodes (LEDs) [11], and both optically pumped [12] and electrically injected [13] laser diodes.

In the studied GaAs-based compounds band-gap engineering is achieved by varying the amount of the incorporated V-element, i.e., nitrogen or bismuth. Despite the advantage of a shrinking in the band-gap energy, the introduction of a small amount of a V-element, acting as isoelectronic impurities, to a III-V host structure results in an increase in the disorder potential due to the differences, e.g., in size and electronegativity between the incorporated and



substituted anions [5, 6]. The presence of disorder effects within a semiconductor can significantly influence its electronic structure, i.e., the density of localized states (DOS) is increased. Disorder-induced localized states drastically affect carrier recombination processes in semiconductors. The changes in carrier dynamics can be revealed by investigating, e.g., electrical and optical properties of disordered semiconductors [14].

This thesis aims to enrich the understanding of disorder effects on the semiconductor properties. It gives a qualitative as well as quantitative description to some unusual experimentally observed behaviors related to the carrier localization effects due to the disorder potential within the semiconductor structure. Such descriptions provide a useful method that can be utilized to characterize the experimental observation from a semiconductor structure. The adverse disorder-induced effects can be reduced by improving the growth conditions of semiconductor materials. Consequently, the performance of the optoelectronic devices would be enhanced if these conditions are specifically optimized.

After this introduction, the thesis is organized as follows. **Chapter 2:** This chapter gives an overview of the most important aspects with respect to disorder effects in semiconductors. Furthermore, a brief review of the radiative recombination mechanisms in semiconductors resulting is presented. The last part of this chapter deals with the band anti-crossing (BAC) model. This model was developed to explain the peculiar behavior of the composition dependence of the energy band-gap of dilute III-V nitride and/or bismide semiconductors. **Chapter 3:** This chapter gives a description of the experimental setups employed to investigate the semiconductor nanostructures. Besides, a brief overview of the growth conditions of these structures is given. **Chapter 4:** A qualitative explanation of the most prominent photoluminescence characteristics of disordered semiconductors are presented in this chapter. The impact of both, the excitation intensity and the lattice temperature is also discussed. The last part of this chapter contains a detailed study on carrier dynamics and localization effects in Ga(AsBi)/GaAs single quantum well's. **Chapter 5:** Within its first part, this chapter introduces, some theoretical approaches used for the interpretation of the non-monotonous disorder-induced PL features. While, in the second part of this chapter, the compositional dependence of the theoretically extracted energy scales for disorder is discussed for the investigated nanostructures. **Chapter 6:** A peculiar feature of the PL thermal quenching is experimentally observed in Ga(AsBi)/GaAs heterostructures under relatively low excitation intensities. This chapter provides a well-approved theoretical analysis used to explore this odd behavior. The presented approach is based on the suggestion that the density of localized states consists of, at least, two different components. **Chapter 7:** A summary of the thesis is given in this chapter.



2 Background

2.1 Introduction

In order to provide a reasonable interpretation of an unusual behavior of semiconductors, it is important to develop a detailed understanding of the underlying physical properties. Since this thesis tries to give an explanation of some experimental observations of disordered semiconductors, an overview of the most important aspects regarding disordered semiconductors is presented in this chapter.

The chapter is organized as follows. Section 2.2¹ deals with the origin of disorder in semiconductors translated in crystalline defects including impurity, inhomogeneities, dislocations, grain boundaries, clusters, and so on. The last part of this section shows some examples of the disorder effects in Ga(NAsP) and Ga(AsBi) semiconductor nanostructures. The second part of this chapter, Section 2.3², gives a brief review on the origin and types of the luminescence emission. Besides, recombination mechanisms within semiconductors are presented. Here, radiative recombination processes resulting in the photoluminescence signal are discussed in detail. The last part of the chapter, Section 2.4, introduces the band anti-crossing (BAC) theory, which was developed to interpret the unusual behavior of the composition dependence of the energy band gap dilute III-V nitrides and/or bismides. A comparison between the experimental results and the predictions of the BAC theory is also shown for the anti-crossing of the conduction band and the valence band, respectively.

2.2 Disorder in Semiconductors

From a structural point of view solids, including semiconductors can be classified into three types; ideal crystalline, real crystal, and purely amorphous. An ideal crystalline semiconductor has a periodic structure that is based on the chemical properties of its constituent atoms, i.e., all atoms in the crystal lattice are in equilibrium due to their orderly arrangement. In contrast, the atoms are more or less statistically distributed in space in a purely amorphous semiconductor. Here, no long- or even short-range order can be observed. However, a real semiconductor is not perfect—as an ideal one, but still has a degree of order.

The presence of defects, i.e., a degree of disorder, in a semiconductor influences most of its properties such as mechanical strength, electrical conductivity, and optical response, and hence, influences the performance of the semiconductor in applications. The disorder potential

¹Section 2.2 is based on Refs. [4, 15]

²Section 2.3 is based on Refs. [16, 17, 18]



in a real semiconductor crystal arises from the chemical disorder and displacive disorder. The **chemical disorder** is attributed to the disarrangement of the atomic species within the crystal structure, while the **displacive disorder** can be presented in a semiconductor due to, e.g., the existence of voids or vacancies in its crystal structure [19]. Furthermore, a degree of disorder is also expected for multilayer semiconductor structures, such as quantum wells, resulting from imperfect interfaces between the constituent layers.

Beside the abovementioned rough classification of defects in real semiconductors, they are broadly categorized into four groups according to their dimension (D); point defects (0D), line defects (1D), planer defects (2D), and volume defects (3D).

2.2.1 Point Defects

According to their origin, point defects can be divided in two main categories; intrinsic and extrinsic.

Intrinsic Point Defects

From a thermodynamic point of view, intrinsic point defects naturally occur in semiconductor materials without any external action at thermal equilibrium. In particular, for temperatures above zero-Kelvin, the atoms in a semiconductor do thermal vibrations. When the vibrations are intense enough a single atom is able to jump to a different location leaving a **vacancy** behind, Fig. 2.1(b). This atom can jump to an interstitial position within the crystal lattice; **Frenkel defect**, or to the surface of the crystal; **Schottky defect**. Such defects can increase the disorder positional of a semiconductor crystal if the lattice temperature is increased.

The presence of vacancies in a crystal can enhance the rate of chemical diffusion. The latter takes place when an atom of the same or a different type is able to move through the crystal of a semiconductor over time. Chemical diffusion can also happen in a semiconductor that contains at least two kinds of atoms. In this case, it is possible for two atoms to exchange positions in the lattice, forming a new type of intrinsic point defect which is known as **anti-site defect**.

Extrinsic Point Defects

These kinds of defects are present when at least one foreign atom is embedded within a semiconductor crystal. Such process is common in semiconductor physics and known in this case as **doping**. The doping is widely employed to modify the electrical as well as optical properties of a semiconductor. Depending on the location of the embedded atom within the lattice one defines two kinds of extrinsic point defects:

1. **Substitutional impurity**; when the embedded atom is placed on a lattice site, replacing the native atom, Fig. 2.1(d).
2. **Interstitial impurity**; here, the embedded atom is located at an interstitial lattice site, (e) and (g) in Fig. 2.1.

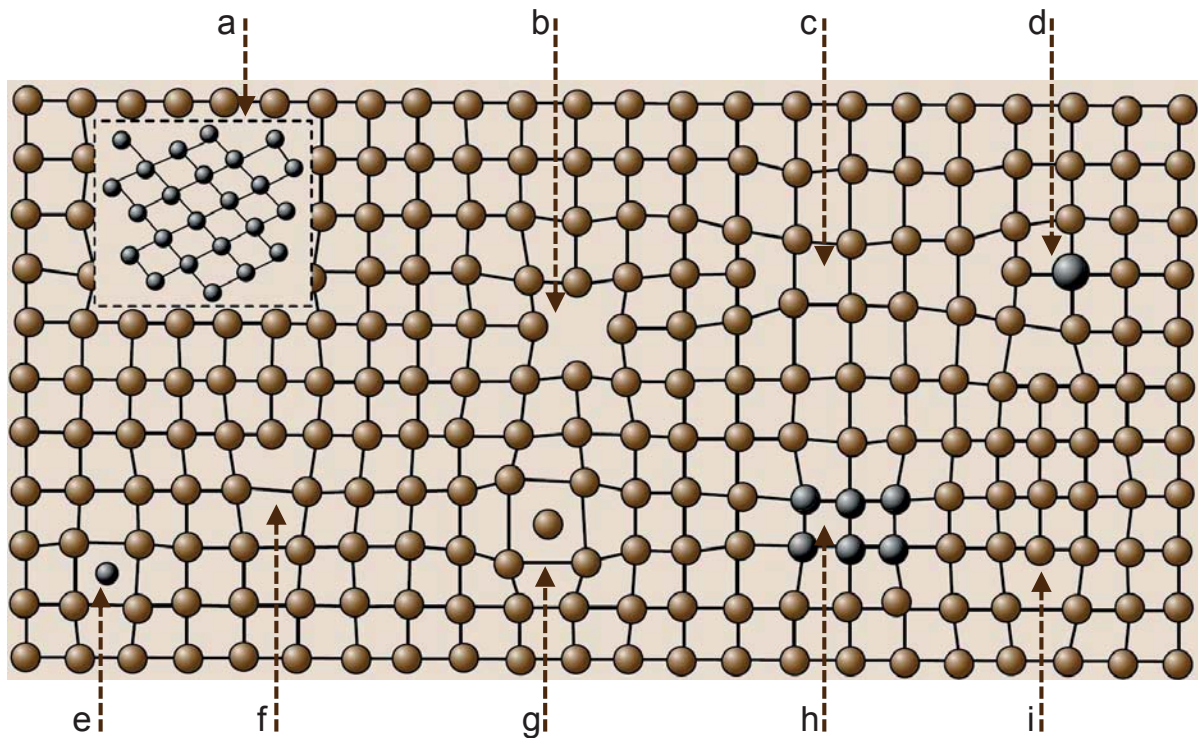


Figure 2.1: Schematic illustration of a crystal lattice with some kinds of defects: (a) incongruous inclusion (cluster), (b) vacancy, (c) vacancy-type dislocation loop, (d) substitutional impurity atom (e) interstitial impurity atom, (f) edge dislocation, (g) self-interstitial atom (h) precipitate of impurity atoms (cluster), and (i) interstitial-type dislocation loop (taken from [15]).

2.2.2 Line Defects

Line defects are purely geometrical faults and called exclusively dislocations. Dislocation lines may be straight or follow irregular curves or closed loops. However, dislocations are classified into two main types. One type is named **edge dislocation** and it happens when an extra plane of atoms is inserted into the lattice, resulting in a localized strain to be introduced into the lattice, Fig. 2.1(f). In contrast, when one side of a crystal is undergone shear stress and displaced by at least one lattice plane, while the opposite side is held fixed. This type of line defects is known as **screw dislocation**. However, several complicated **mixed dislocations** can be formed when edge and screw dislocations are both present in a semiconductor structure.

2.2.3 Planar Defects

Planar defects denote to geometrical irregularities in a crystalline lattice which occur across a planar surface of the crystal. These irregularities are caused either by an internal error in the crystal structure or by imperfect interfaces between two different semiconductor structures. The **internal planar defects** can be divided into



- **Stacking faults** take place when a single plane of atoms within the crystalline lattice is misoriented or out of order.
- **Twin boundaries** are formed when a stacking fault reorients the rest of the crystal, resulting in a mirror plane within the crystal.
- **Grain boundaries** can be found in a crystalline lattice when two or more single crystals of different orientation are get together.
- **Interphase boundaries** arise when one crystalline material shares an interface with another crystalline material.

For the last case of interphase boundaries, and depending on the properties of each material, the interface between the constituent lattices can be

- **Coherent interphase boundaries** are formed when the two lattices have similar geometries. In this case, no defects will be found but a small amount of strain may be introduced due to the material change.
- **Semi-coherent interphase boundaries** occur when the two lattices have similar geometries but a larger lattice mismatch. Here, edge dislocations tend to form due to increased strain within the structure.
- **Incoherent interphase boundaries** are found in materials with a high degree of disorder, i.e., they occur at interfaces of a structure consisted of materials with significantly different geometries.

In contrast to the internal planar defects, **external planar defects** refer to surface defects that are caused by an interaction of the crystal with a gas or liquid environment. Consequently, the crystal periodicity can be interrupted and bonds can also be broken. Such defects occur at the crystal's surface and affect the outermost atomic layers, or surface region.

2.2.4 Volume Defects

This kind of defects is also known as bulk defects and happens when a significant number of point defects are spatially gathered in a so-called **cluster**. Clusters of defects appear generally when a semiconductor crystal is super-saturated with respect to some kind of point defect due to the excessive increase in the concentrations of this defect. In this case, the crystal can achieve an equilibrium condition by condensing the excess defects into clusters with different phase regions.

Clusters of vacancies forming small regions within the semiconductor material, where there are no atoms, are called **voids** or bubbles. In contrast, clusters of foreign atoms forming small regions of different phase are called **precipitates**, Fig. 2.1(h). The presence of precipitates in a semiconductor crystal is attributed to the retrograde solubility of native point defects. Another mechanism of the foreign particle formation is called **inclusion** incorporation, Fig. 2.1(a). Inclusions result from the capture melt-solution droplets from the diffusion boundary layer adjacent to the growing interface. This is enriched by the rejected excess component.

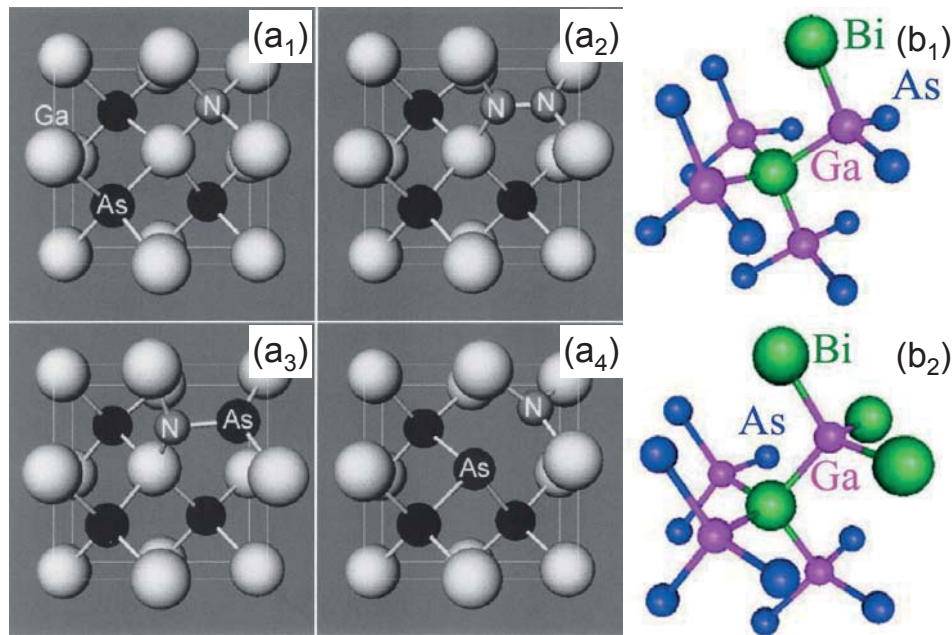


Figure 2.2: Atomic positions in Ga(NAs) for (a₁) substitutional N, (a₂) N–N, (a₃) N–As split interstitials, and (a₄) (As_{Ga}–N_{As})_{nn} complex. Dark and light circles indicate As and Ga atoms, respectively, where N atoms are labeled (after Zhang and Wei [20]). Atoms distribution within the Ga(AsBi) lattice for (b₁) next-nearest-neighbor Bi pairs and (b₂) Bi clusters (after Ciatto *et al.* [23]).

2.2.5 Disordered III-V Semiconductors

In this sub-section, it is focused on the defects in dilute III-V nitride and/or bismide semiconductor alloys. Several types of N-induced defects in dilute III-V nitride semiconductor alloys have been reported in the literature. Zhang and Wei have presented some types of N-related point defects in epitaxial Ga(NAs) alloys [20], which are shown in Fig. 2.2 as follows:

- **The substitutional N** is formed when an N atom is placed on a lattice site of an As atom, Fig. 2.2(a₁)
- **The N-N split interstitial** appears when N₂ molecule replaces an As atom, Fig. 2.2(a₂).
- **The N-As split interstitial** is assumed as a variation to N-N, Fig. 2.2(a₃). Here, the N-As bond length is longer than the N-N bond length.
- **The (As_{Ga}–N_{As})_{nn} pair** is obtained when the N_{As} attracts the As_{Ga}, where *nn* stands for nearest neighbor, Fig. 2.2(a₄). The N_{As} is associated with compressive strain due to the small size of N atom, while As_{Ga} is associated with tensile strain due to two extra electrons in the non-bonding orbital.
- **The (V_{Ga}–N_{As})_{nn} pair** with very low binding energy occurs when some Ga atoms are missed in the lattice structure (V_{Ga}: Ga vacancy).

The inhomogeneous N incorporation in Ga(NAsP) results in a degree of disorder, long-range compositional disorder, and can be revealed, e.g., in the cross-sectional transmission electron micrograph (TEM) [21]. Fig. 2.3(a) shows a dark field image of a cross-sectional TEM of

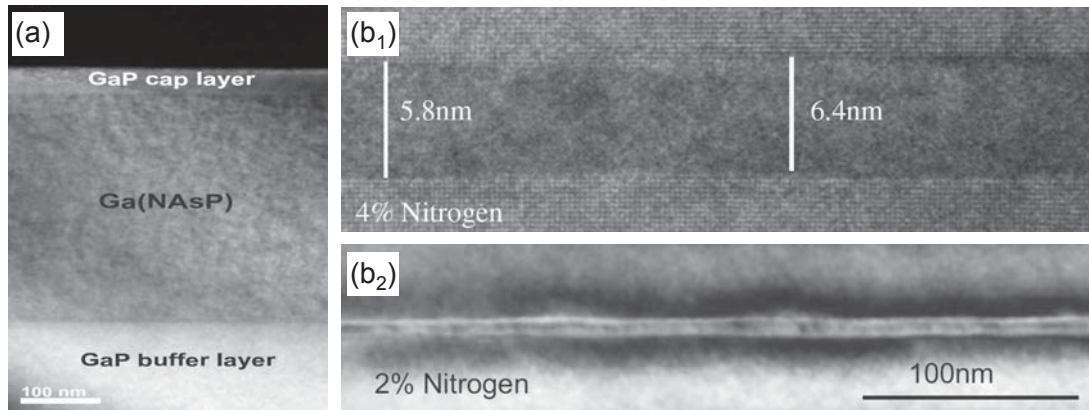


Figure 2.3: (a) dark field image of a cross-sectional TEM of Ga(NAsP) layer grown on GaP, using the strain sensitive (202) reflection (after Jandieri *et al.* [21]). (b₁) high resolution TEM [010] micrographs of a Ga(NAsP)/GaP QW with 4%-N content. (b₂) strain-contrast (202) TEM micrograph of a Ga(NAsP)/GaP QW with 2%-N content. Both b₁ and b₂ are adopted from Ref. [22].

Ga(NAsP) layer grown on GaP, using the strain sensitive (202) reflection. The fluctuations in the intensity indicate the local strain due to lattice constant changes caused by N-related defects. Furthermore, fluctuations in the layer thickness are also responsible for long-range disorder in the case of semiconductor heterostructure such as quantum wells. A high resolution TEM [010] micrograph of a Ga(NAsP)/GaP QW with an N content of 4% is shown in Fig. 2.3(b₁) and it demonstrates a fluctuation in the thickness of the QW as high as about 1 nm [22]. On the other hand, a strain-contrast fluctuation within the QW material can be an additional source of disorder. Such a fluctuation at a scale of 10–50 nm is presented in Fig. 2.3(b₂) for a Ga(NAsP)/GaP QW with an N content of 2% [22].

The aforementioned disorder effects in dilute III-V nitrides are also expected in Bi containing III-V semiconductor structures, since the relatively large size of Bi atom results in a degree of disruption in the lattice of the new materials, i.e., dilute III-V bismides. Using x-ray absorption spectroscopy and an appropriate theoretical simulation method, Ciatto *et al.* investigated the local structure around Bi atoms in Ga(AsBi) layers grown on GaAs as a function of Bi content aiming to detect short-range order [23]. It was found that static disorder in the Bi next-nearest-neighbor interatomic distances dramatically increase when the Bi content is increased. In particular, the Bi atoms are randomly distributed for a Bi content of 1.2%, tend to form next-nearest-neighbor pairs when the Bi content is increased up to 1.9%, and form small Bi clusters for higher Bi content (2.4%). Figs. 2.2(b₁) and 2.2(b₂) show two different local configurations of atom distribution within the lattice structure of Ga(AsBi) in the case of a next-nearest-neighbor Bi pair and for a Bi tetramer (cluster), respectively. In the second case, a central Bi atom is surrounded by three Bi next-nearest-neighbors, where all Bi atoms are next nearest neighbors of each other. However, the existence of Bi clusters within Ga(AsBi) structures is confirmed by Wu *et al.*, even for Bi content as low as 1.5% [24]. This can be seen in high resolution TEM micrographs of the corresponding sample as presented in Fig. 2.4(a₁). Here, clusters remain coherent to the matrix and tend to be formed in spherical shape. A cluster

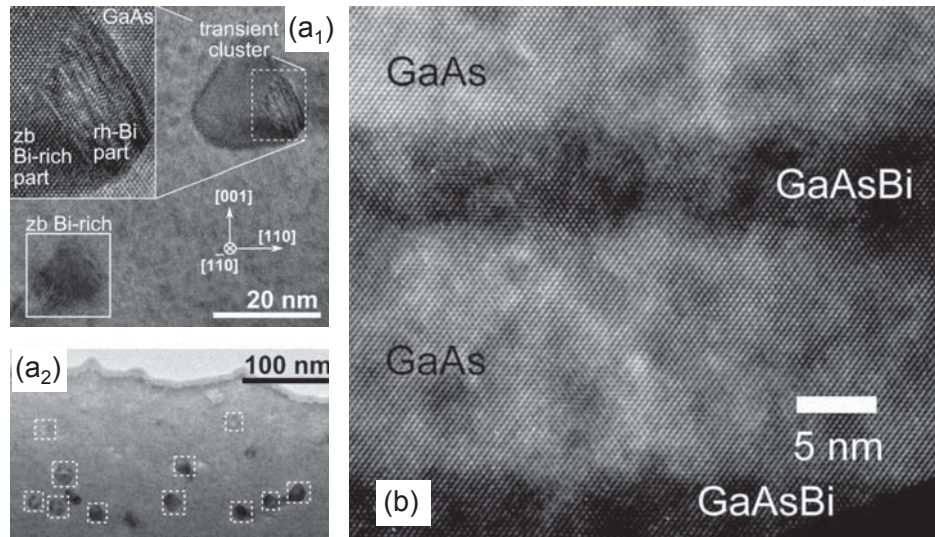


Figure 2.4: (a₁) high resolution and (a₂) bright field TEM image for a Ga(AsBi) layer with Bi content of 1.5% and 4.7%, respectively. (b) cross-sectional TEM image of a Ga(AsBi)/GaAs MQWs-sample with Bi content of 4.8% (zb: zincblende and rh: rhombohedra). (a₁) and (a₂) are adopted from Ref. [24] while (b) from Ref. [25].

diameter ranging between 12 and 22 nm is obtained for a Ga(AsBi) layer with Bi content of 4.7%, shown in Fig. 2.4(a₂) Furthermore, imperfect interfaces are also observed in the case of Ga(AsBi) heterostructures. An example is shown in Fig. 2.4(b) for a Ga(AsBi)/GaAs MQWs-sample with Bi content of 4.8% [25]. Here, fluctuations in layer thickness are demonstrated through TEM measurements.

2.3 Photoluminescence

Luminescence is a light signal produced by spontaneous emission in a material in which electrons in excited states drop down to lower levels. However, depending on the excitation method luminescence can be mainly categorized as follows [26],

- **Photoluminescence (PL)**; the luminescence takes place when a light source, e.g., laser, is used to excite the carriers in the material.
- **Cathodoluminescence (CL)**; in this method an electron beam is used as excitation source. This technique is utilized to obtain extremely high spatial resolution of the luminescence beyond the optical diffraction limit. Here, the luminescence signal is usually detected using a system based on a scanning electron microscope (SEM).
- **Electroluminescence (EL)**; the luminescence is caused by an electric current flowing through the material. This phenomenon is employed in many optoelectronic devices such as the light emitting diode (LED).
- **Chemiluminescence**; the luminescence is caused by a chemical reaction. When chemiluminescence happens in an organism, it is called bioluminescence

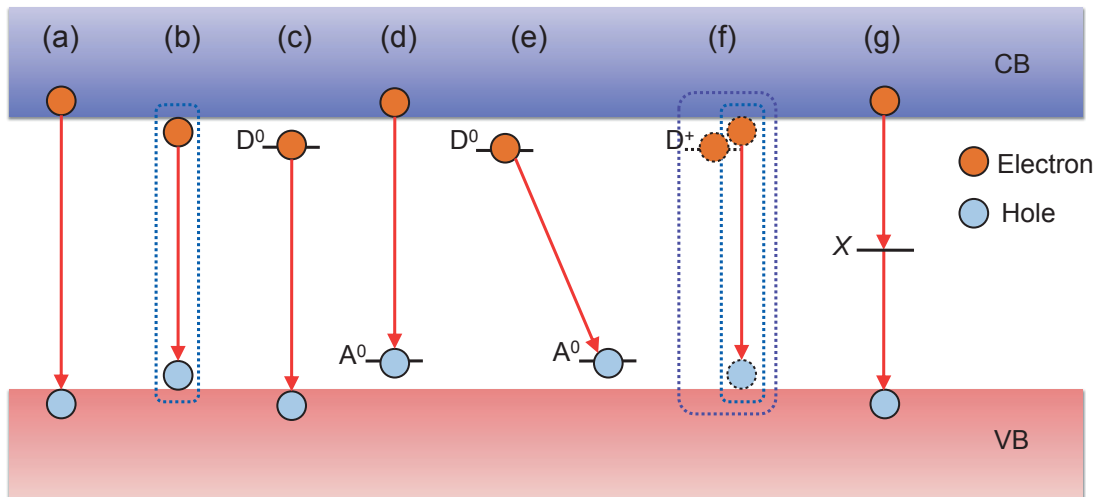


Figure 2.5: Schematic illustration of optical transitions in semiconductors.

Next, it is focused on the photoluminescence (PL), since it is the method which is employed to characterize the semiconductor structures presented in this thesis. Analyzing the PL signal provides much important information about the photo-excited material system, for example, but not limited to, impurity levels. Furthermore, the PL intensity could be the best way to check the optical efficiency as well as the material quality of a semiconductor, since it reflects the interplay between the usually desirable radiative and defect-induced non-radiative recombination.

Optical Transitions in Semiconductors

When a photon is absorbed into a semiconductor material an electron in the valence band (VB) is able to rise to an excited state –higher in energy– leaving a so-called *hole* behind. However, this photo-excited electron can undergo different processes, including thermal relaxation and energetic (optical) transitions. Optical transitions in semiconductors results in either radiative or non-radiative recombination, and can be furthermore categorized into two groups; intrinsic and extrinsic. When an electron and a hole recombine through radiative recombination, a photon is emitted and its energy is dependent on the energetic distance between these electron and hole.

If the photon energy of the excitation source is high enough, excited-electrons can reach the conduction band (CB). An excited-electron can directly drop to VB and radiatively recombine with a hole; this process is named **band-to-band** radiative transition and takes place at relatively high temperatures, Fig. 2.5(a). The band-to-band transition in indirect gap semiconductors such as GaP is called an indirect transition and it needs phonon assistance in order to keep the momentum conservation. In contrast, Direct-gap semiconductors such as GaAs do not necessarily need phonon assistance for radiative transitions.

At low temperatures, an excited electron can be united with a hole through the Coulomb attractive force arose between them. This form of an *electron-hole (e-h) pair* is usually called a **free exciton (FE)**. Here, the intrinsic PL emission occurs via excitonic recombination instead of band-to-band transition–in the pure semiconductors, Fig. 2.5(b).