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Defect characterization of Europium implanted Gallium Nitride

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“People are like crystals. It is the defects in them that make them interesting.”

Sir F. Charles Frank

“Perfection has one grave defect: it is apt to be dull!”

William Somerset Maugham

Acknowledgments

Finally here it is, my PhD thesis! So much work, ups and downs, a lot of pleasure, some less good moments, and somehow I managed to get to the end of it after all...

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Introduction

Gallium nitride and related semiconducting materials are in the center of one of the most important breakthroughs in electronics and optoelectronics of the last decade. Since the development of the first blue (450 nm), blue/green, violet and ultra-violet GaN-based light emitting devices by Shuji Nakamura in the early years of the 1990's, worldwide attention has turned to these nitride compound semiconductors. With a brightness up to 100 times stronger than SiC based emitting devices, soon the nitrides found applications in several areas ranging from traffic lights, through outdoor displays, to medical applications. In fact, GaN-based violet lasers are the base technology within the new generation of optical data storage and entertainment systems, such as the Blu-ray Disc system. This new format allowed expanding the standard DVD capacity from 4.7 Gb to about 54 Gb (double layer) of information on a disc. Other technologically relevant applications of GaN are found in the domains of high temperature, high power and fast electronics, being high electron mobility transistors (HEMT) an example of such applications.

Besides these direct applications, the physical properties of GaN kept attracting attention of research groups to explore other capabilities of this interesting material. Due to its resistance to radiation damage, its thermal stability and direct band gap, GaN and related materials are very suitable hosts for optical dopants. Among such dopants, rare-earth (RE) ions have long been employed in phosphors to produce bright luminescence in a wide range of colors of the visible spectrum. RE-luminescence has its origin on the intra-4*f* shell electronic transitions resulting in sharp luminescence

v

emission lines with wavelengths virtually independent of the host material. However, despite the fact that the wavelength is host-independent, the intensity of RE-luminescence depends very strongly on the host material. Classical semiconductors such as Si and GaAs are characterized by relatively narrow band gaps (1.1 and 1.4 eV). Such materials normally present good optical behavior at low temperatures, however at higher temperatures the luminescence output is often considerably quenched. Favennec *et al.*[1] empirically observed that the thermal quenching of RE-luminescence decreases with increasing host semiconductor band gap. As such, with its wide direct band gap (3.4 eV) GaN became an interesting host for rare-earth optical dopants.

Despite the fact that GaN proved its efficiency as a host, several problems were encountered while attempting to optimize the properties of the rare-earth-GaN optical system. Both the most common techniques to introduce dopants in semiconductors present advantages and disadvantages. Doping during growth, employing for example molecular beam epitaxy, does not allow to control the dopant distribution and thus local doping is not possible. Furthermore, possibly the most important disadvantage of this doping method is the solubility limit of the dopant in the host material.

On the other hand, ion implantation allows solving both of those problems. By steering the beam, it is possible to control the local dopant distribution and even more than one dopant species can be introduced in the same region, paving way to color-mixing. Another strong advantage of this technique is the fact that the solubility limit can be overcome, as implantation is a non-equilibrium doping method. However the ion implantation technique presents a very important disadvantage: structural damage brought to the crystal lattice during dopant introduction can seriously hinder the optical outcome.

The work summarized in this thesis is performed in the context of the *RENiBEI* Research Training network, from the European Commission's 5th Framework Improving Human Potential program. The *RENiBEI* acronym stands for *Rare Earth doped Nitrides for high Brightness*

Electroluminescent emitters. The main goal of this network was to understand the fundamental optical interactions of RE-ions in GaN-based semiconductors in order to improve light emission efficiency and device performance. RE doping of the nitride host employing ion implantation was an essential tool in order to accomplish RENiBEL's objectives. Furthermore, the driving force for the research work presented here was to relate the structural, optical and electrical properties of Eu-implanted GaN in order to improve the understanding of the energy transfer mechanism between the nitride host and the rare-earth ions, responsible for the characteristic light emission.

Chapter 1

Properties of III-nitrides and RE in GaN

1.1 III-nitrides historical background and their applications

The past decade has seen a strong interest in wide band gap semiconductors, in particular, gallium nitride (GaN) and related compounds. The need for devices operating at higher temperature and/or higher power has been the motor for this quest. Due to their properties, namely wide and direct band gap, group III-nitrides are expected to operate at higher temperatures, have larger breakdown fields, higher electron saturated drift velocity and better thermal conductivity as compared to more common semiconductors such as silicon and gallium arsenide [2, 3]. Another important characteristic of these III-nitride semiconductors is the ability they show to form alloys. In fact, aluminium nitride (AlN) and GaN have a continuous solid solubility and despite the fact that indium nitride (InN) has limited solubility in GaN, obtaining ternary alloys of $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$ is possible. Controlling the concentrations on these alloys allows engineering the material band gap ranging from 0.7 eV (infrared) for pure InN to about 6.2 eV (ultraviolet) for AlN, covering the entire visible spectrum. For this reason GaN-based semiconductors became interesting for employment in

optoelectronic devices operating in this energy region.

Despite this recent interest, GaN and related semiconductors are known for a long time now. In fact, in the beginning of the 20th century there were already studies on AlN powder. In the early 1930s a study [6] has been performed on the nitrogen compounds of gallium, namely GaN, also in powder form. The step from powder form to single-crystalline nitrides was taken in the 1960s when Maruska and Tietjen [7] employed the hydride vapor phase epitaxy (HVPE) technique to grow GaN layers on sapphire, as they had previously done with GaAs. The quality of the obtained layers was suitable for preliminary studies of a variety of important semiconductors physical properties. However, even when not intentionally doped, these films had a high residual n-type background due to defects and impurities introduced during growth. Hydrogen in particular, has an important role on the passivation of acceptor doping, a mechanism that at the time was not understood. This fact made p-type doping of GaN virtually impossible, explaining the interruption of interest in the development of III-nitrides semiconductors.

The interest in the III-nitrides was only recovered almost 30 years later when other growth techniques became available. Efforts were focused on the growth of these nitrides with less defects and impurities. Since bulk material for GaN substrates was not available and is still nowadays difficult and expensive to grow, heteroepitaxial growth of these films on sapphire or SiC substrates with buffer AlN or GaN layers became a widespread alternative. In 1986 H. Amano *et al.* [8] employed atmospheric pressure metalorganic vapor phase epitaxy (MOVPE) to grow high quality GaN thin films on sapphire (0001) substrates with AlN buffer layers. These films still had elevated dislocation densities (many orders of magnitude higher than the values found for GaAs, for example) due to the large lattice mismatch and thermal expansion coefficients of film and substrate. The following years were accompanied by efforts to reduce unintentional contamination and defect density of the films. Optimizing of growth techniques was accomplished through detailed studies of the influence of temperature and gas flow rates on the film quality. With this, the residual n-type doping was brought to

the present level of 10^{17} cm^{-3} [9]. The breakthrough that brought GaN and related materials again to the spotlight came in 1989 when Amano and collaborators announced [10] they obtained p-type doped material after irradiating a MOVPE grown Mg doped GaN wafer with an electron beam of 10 keV (well below the subthreshold energy necessary for atom displacement). They demonstrated the efficiency of hole injection from the p-type GaN:Mg into the undoped n-type film by fabricating a GaN UV-LED with a p-n junction.

In 1991, Nakamura *et al.* obtained low resistivity p-type GaN:Mg by post-growth thermal annealing in N_2 at temperatures $\geq 700^\circ\text{C}$. They concluded that the reason why p-type dopant activation was so difficult to achieve was the elevated levels of hydrogen introduced in the film during its growth. In fact H is present in most of the precursors employed for GaN growth, such as $(\text{CH}_3)_3\text{Ga}$ and NH_3 in metalorganic chemical vapor deposition (MOCVD) growth. The presence of H leads to the passivation of the acceptor dopant. Nakamura and his collaborators have observed that this reaction can be driven in the reverse direction by either annealing the samples or injecting minority carriers (electrons) using low energy electron beam irradiation [11, 12].

Since the first GaN p-n junction, intensive efforts have been put on the improvement of growth processes to obtain better quality material. Also, GaN-based devices became more complex and efficient, covering a wide range of applications from transistors, through ultrahigh power switches, to laser diodes. AlGaIn/GaN-based electronics have demonstrated [13, 2] superior characteristics. Obtaining GaN-based light emitting devices operating in the blue and ultraviolet region of the spectrum was one of the driving forces of III-nitride research. Again, at the end of 1995 Nakamura and collaborators were on the front line of development of this technology with their InGaIn multi-quantum-well (MQW) active region laser diode [14]. In July 2002, Sumitomo Electric Industries [15], announced the development of a growth technique that allows reducing the density of dislocations in GaN to about $1 \times 10^6 / \text{cm}^2$. The Dislocation Elimination by Epitaxial growth with inverse-pyramidal Pits (DEEP) technique allows reducing dis-

locations by forming inverse-pyramidal pits on the surface of the grown material. This low dislocation material can be used to fabricate blue-violet lasers with superior lifetime performances. Operating in the violet-blue region of the spectrum (380-450 nm), this laser came to replace the red-infrared (650-780 nm) GaAs-based existing lasers. Since the density of information recorded on optical media increases with the inverse squared of the laser wavelength, the violet-blue laser diodes allow increasing the storage capacity on a disc, from the actual 4.7 Gbytes of a red laser device to about 27 Gbytes (54 Gb double layered). In fact, GaN-based lasers were very recently in the center of a battle to establish the format of the next generation of optical data storage [16]. Both Blu-Ray (from Sony) and HD-DVD (from Toshiba and NEC) drives are equipped with blue-violet GaN lasers diodes operating at 405 nm.

Also in the field of wireless communications GaN has proven to be a reliable alternative to Si. Giant of electronics, Fujitsu [17] has developed GaN high electron mobility transistors (HEMT) with high output powers, higher breakdown voltages and cut-off frequencies.

These examples evidence well the technological relevance of GaN and its related compounds and why these materials are and will continue to be the subject of an active research field.

1.2 Growth of crystalline III-nitrides

In the previous section, several nitrides growth techniques were mentioned along with the improvements each of it introduced to the crystalline quality of the grown layers. A common problem to all of those techniques is the choice of an adequate substrate. Throughout the years, due to the non-existence of good quality, affordable and easy to obtain GaN substrates, heteroepitaxial growth of GaN films was performed on several more available substrates. Among some of the most common substrates used to grow nitride films upon are Si, GaAs, SiC, ZnO and sapphire. From this list, SiC offers the best conditions for heteroepitaxial growth since its lattice presents a mismatch of only 3.5% to the one of GaN and its thermal ex-

pansion coefficients are the closest to the ones of GaN. However sapphire substrates became the most popular due to their wide availability, hexagonal symmetry, ease of handling, simple pre-growth cleaning requirements and high temperature (required during film growth) stability. Nevertheless the lattice and thermal mismatches between sapphire and GaN (about 16% of lattice mismatch) are responsible for the considerable amount of strain on the material after post-growth cooling [3].

1.2.1 Nitride growth techniques

Presently mainly two techniques are employed to grow high quality III-nitride films. In metalorganic chemical vapor deposition (MOCVD), also known as MOVPE, metalorganic gases such as tri-methyl X - $(CH_3)_3X$ - or tri-ethyl X - $(C_2H_5)_3X$ - with X being Ga, Al or In, transport these metals onto the substrate. Simultaneously N is introduced through a flow of ammonia (NH_3). Both reactant gases, diluted with H_2 , are introduced in a reactor chamber through a nozzle directing the flow onto a high temperature (~ 1000 °C) heated substrate. The reaction of both gases at the substrate yields a deposited film of Ga, In, or AlN. The disadvantage of this method resides at the elevated substrate temperature necessary to decompose NH_3 . In fact, due to the thermal mismatch with the substrate, postgrowth cooling introduces significant amounts of strain and structural defects into the nitride film. Also, at these high temperatures residual contaminants can be introduced in the film and III-metal desorption, diffusion and segregation can occur. An alternative growth technique that allows reducing the substrate temperature is molecular beam epitaxy (MBE). With this technique, N supplied by microwave plasma excitation reacts with Ga vapor from an effusion cell when both are directed toward a heated substrate. The process is usually performed in an ultra-high vacuum environment to reduce contamination. The main disadvantages of MBE while III-nitride growth technique are related to the growth rate. This rate is limited by the available flux of low kinetic energy reactive nitrogen ions. While attempting to increase this rate Ga droplets are observed to form on the surface. Also, when microwave power is increased, more energetic ions are created. These

more energetic ions are in general detrimental to crystal quality since they can introduce point defects.

1.2.2 Buffer layer

Since in both growth methods sapphire is the most commonly used substrate, a buffer layer is usually required to minimize the effects of lattice and thermal mismatch. Usually AlN or GaN buffer layers are employed. The vast majority of the films employed in this study were grown by MOCVD at the semiconductor group from the university of Montpellier (GES-Montpellier), a partner institution of the RENiBEL network. Their III-nitride growth method is composed by several steps performed at atmospheric pressure. The process begins with a nitridation of the substrate at about 1100 °C under a NH_3 flow to remove impurities from the surface. During this step, a thin layer (20-50 Å) of AlN is formed as N from the ammonia reacts with Al from the sapphire. The temperature is then brought down to about 550 °C to deposit a thin (~ 250 Å) GaN buffer layer. It has been observed that the buffer layer thickness has a strong influence on the quality of the grown film. This low growth temperature causes this buffer layer to be amorphous. By annealing the wafer at a temperature of $\sim 1070^\circ C$ during a few minutes, the buffer layer will crystallize, resulting on a highly defective crystalline template layer that allows reducing the lattice mismatch for epitaxy.

The second phase of the process starts by reducing the temperature to about 980 °C. At this point the reactant gases are allowed to react at the buffer layer surface. A large number of nucleation sites begins to form and will evolve to the shape of isolated monocrystalline islands on top of the buffer layer. These islands will grow laterally and will start to coalesce and the nitride film is grown. This process is schematically represented in figure 1.1. It is possible that during growth, these islands will have slightly different crystalline orientations and, as a consequence, at the coalescence boundaries between islands, a considerable amount of extended defects might form. This has a direct impact on the crystalline quality since after coalescence, the growth will continue upwards and the

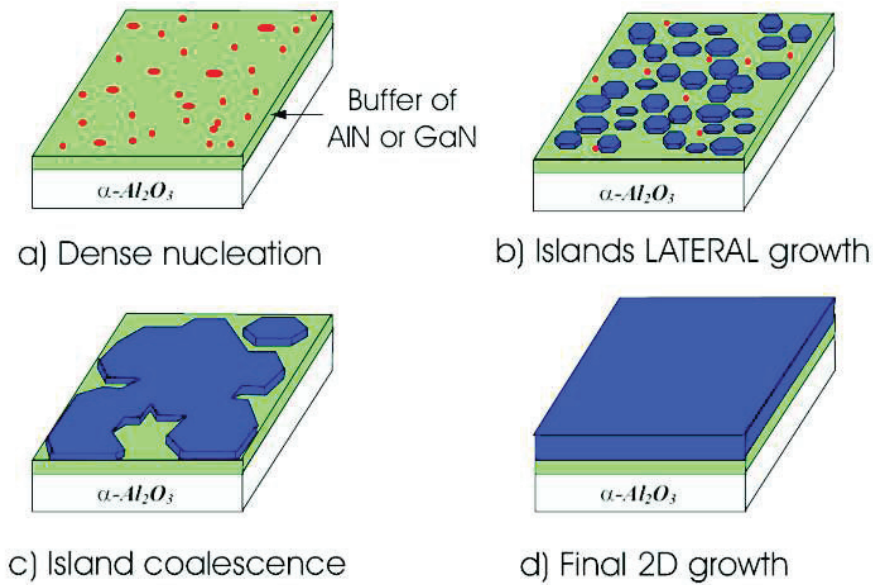


FIG. 1.1: MOCVD growth steps of III-nitrides [18]

stacking faults formed at boundaries will proceed up to the film surface. The grown film is said to exhibit mosaicity. This situation is depicted in figure 1.2. As will be discussed in chapter 2 these structural defects will influence the electrical and optical properties of the nitride film.



FIG. 1.2: Mosaic growth of the III-nitride film

1.3 Brief overview of III-nitride properties

As mentioned in section 1.1, nitrides structural, electrical and optical properties attracted the attention of semiconductor industry to these materials. In this section, a brief overview of III-nitrides' most relevant properties for the present work will be given, with particular emphasis on the properties of GaN. For a more comprehensive description of the properties of III-nitrides, the reader is referred to references [19, 20, 21, 22].

1.3.1 Structural properties

The III-nitrides can crystallize in two structures, namely wurtzite and zincblende. However, the zincblende structure is thermodynamically metastable and thereby less common. In this study, wurtzite GaN films have been employed. For such structure, each of the group-III atoms (Ga, In or Al) is located at the center of a tetrahedron on whose vertices N atoms are found. In the same way, each N atom is surrounded by four group-III atoms. The Bravais lattice of wurtzite can be seen as two inter-penetrating hexagonal close packed sublattices, one with the group-III atoms and the other with N atoms. This structure is illustrated on figure 1.3. This structure is characterized by lattice parameters a and c , as well as by a u -value given by $u=b/c$ where b is a bond length in the direction perpendicular to the hexagons. This direction is commonly referred to as the crystal c -axis. The ideal wurtzite structure is characterized by ratios $c/a = 1.633$ and $u = 0.375$. The parameters of wurtzite GaN are quite close to those ideal values, with $c = 5.1850(5)$ Å, $a = 3.1892(9)$ Å and $u = 0.377(1)$ [19]. The space group symmetry of wurtzite III-nitrides is C_{6v}^4 ($P6_3mc$) with a C_{6v} (6mm) point group symmetry.

1.3.2 Thermal properties

GaN is a robust material with demonstrated superior thermal stability. It has an elevated melting point of 2500 °C, thermal conductivity of 1.3 $Wcm^{-1} °C^{-1}$ and a Debye temperature of 600K. Maruska and Tietjen [7] have studied the lattice parameters of wurtzite GaN as a function of

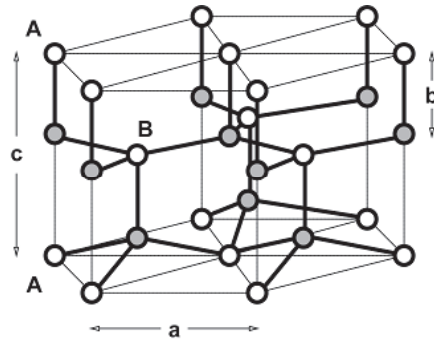


FIG. 1.3: Wurtzite structure of group III nitrides

temperature for the range of 300-900 K. They found a mean coefficient of thermal expansion for the a direction of $\Delta a/a = 5.59 \times 10^{-6} / K$ for the entire temperature range, and a superlinear temperature dependence for the c direction with mean coefficients $\Delta c/c = 3.17 \times 10^{-6} / K$ and $7.75 \times 10^{-6} / K$ for the regions between 300-700 K and 700-900 K, respectively. These values differ considerably from the values of the sapphire substrate: $\Delta a/a = 7.5 \times 10^{-6} / K$ and $\Delta c/c = 8.5 \times 10^{-6} / K$. This difference is responsible for the appearance of strain between substrate and GaN film after post-growth cooling. Strain release leads to cracks and other structural defects that influence the electrical and optical properties of the film.

1.3.3 Optical properties and band structure

One of the reasons why III-nitrides are so interesting for optoelectronic applications resides in the fact that these semiconductors have a direct wide energy band gap. Optical emission from interband electron-hole recombination in the III-nitrides and their ternary alloys covers an important part of the electromagnetic spectrum, ranging from the infra-red, through the entire visible spectrum, to the ultra-violet region (Fig.1.4).

The band gap characteristics of a semiconducting material are responsible for a wide range of its properties. Figure 1.5 illustrates the main features of the band structure of wurtzite GaN, as calculated by Suzuki *et*

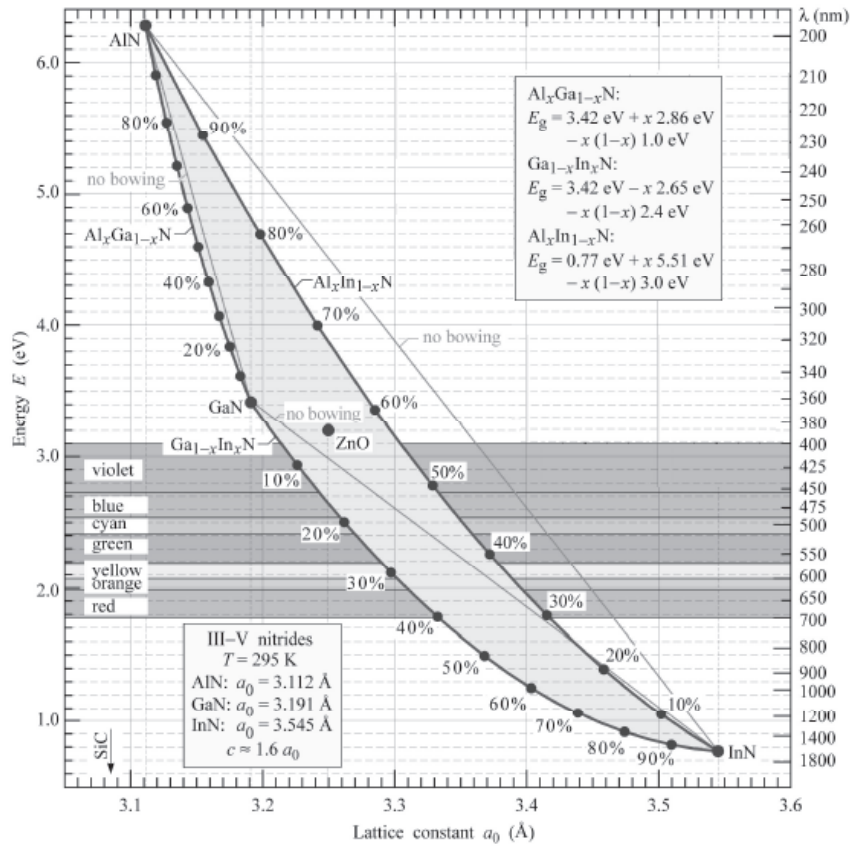


FIG. 1.4: Band gap energy versus lattice constant of III-nitride semiconductors at room temperature [23].

al. in reference [25]. As can be seen, the top of the valence band is split into three states. This splitting is a direct consequence of the fact that the Ga 3*d* core-level energies are resonant with the N_{2s} -like lower valence band states. Due to this resonance, the 3*d* Ga electrons hybridise strongly with both the upper- and lower-valence band *s* and *p* levels. With a band gap energy of 3.39 eV, GaN inter-band luminescence is located at the UV region of the spectrum, as shown on figure 1.4.

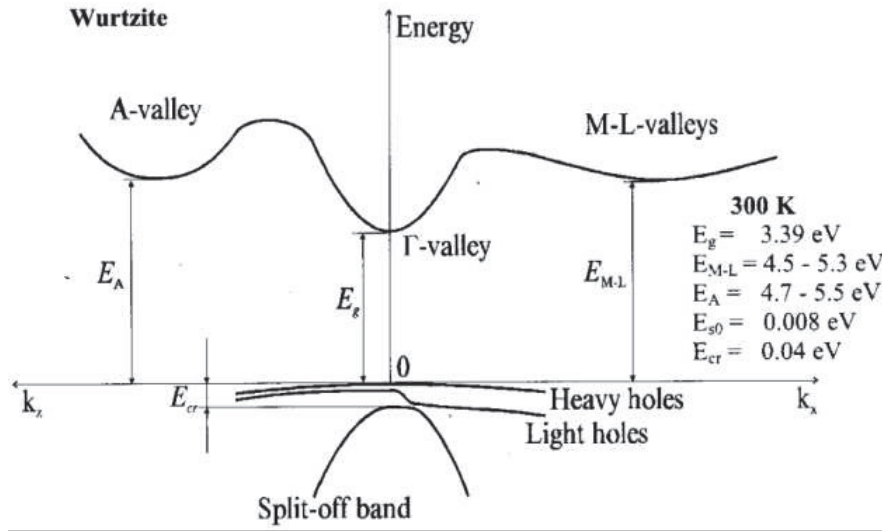


FIG. 1.5: Band structure of wurtzite GaN [24].

1.3.4 Electrical properties

As discussed in section 1.1, as-grown heteroepitaxial wurtzite GaN has an elevated intrinsic electron concentration, being the material unintentionally n-type doped. In 1995, Bogusławski *et al.* [26] have attributed this fact to the high density of structural defects introduced during growth, such as nitrogen vacancies, as confirmed by *ab initio* molecular dynamics calculations. In their study, these authors concluded that such native defects introduce energy available states in the band gap.

In more recent studies (2004), Van de Walle and Neugebauer [27] have employed more advanced computational methods to investigate the unintentional n-type conductivity of GaN. From their work the authors concluded that such property of as-grown GaN cannot be attributed to nitrogen vacancies, but is more probably due to the unintentional incorporation of O and Si impurities during material growth. In the same manner as structural defects do, those impurities lead to the formation of energy states in the band gap. Those levels interact with the free charge carriers and can

	GaN	AlN	InN
Lattice parameter a [Å]	3.189	3.112	3.548
Lattice parameter c [Å]	5.185	4.982	5.760
Therm. exp. $\Delta a/a$ [/K]	5.59×10^{-6}	4.2×10^{-6}	4×10^{-6}
Therm. exp. $\Delta c/c$ [/K]	3.17×10^{-6}	5.3×10^{-6}	3×10^{-6}
Therm. conduc. [W/cm K]	1.3	2	0.8
Atomic density [at/cm^3]	8.76×10^{22}	9.58×10^{22}	6.35×10^{22}
Density [g/cm^3]	6.15	3.23	6.81
T_{Debye} [K]	600	1150	660
Melting temp. [$^{\circ}C$]	2500	3000	1100
Brkdown field [V/cm]	5×10^6	$1.2 - 1.8 \times 10^6$	—
e mob. [$cm^2V^{-1}s^{-1}$]	≤ 1000	300	3200
h mob. [$cm^2V^{-1}s^{-1}$]	≤ 200	14	—
Dielec. const. (static)	9	8.5	15
Dielec. const. (hi. freq.)	5.35	4.68 – 4.84	8.4
Refract. index n	2.29	2.1 – 2.2	2.56 – 3.12
Energy gap [eV]	3.39	6.2	0.7 – 1.9 ^{[4][5]}

TABLE 1.1: Basic properties of Ga, Al and InN at 300 K [3, 19].

thereby have a strong influence on the electronic properties of GaN, such as carrier mobilities and diffusion coefficients.

A resume of the basic structural, electrical, thermal and optical properties of GaN, AlN and InN is given in table 1.1.

1.4 Rare-earth elements

The elements of the periodic table constituting the lanthanide series, ranging from cerium (Ce - atomic number 58) to ytterbium (Yb - atomic number 70), are often known as the rare earth (RE) elements (Fig. 1.6). The term

58	59	60	61	62	63	64	65	66	67	68	69	70
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb

FIG. 1.6: The rare-earth elements

rare earth was proposed due to the fact that when the first RE were discovered they were thought to exist in the earth crust only in small amounts and because they had to be extracted from materials known as “earths”, such as lime and alumina. Today it is known that each of them is more common than platinum, gold or silver. RE are never found as free metals in the earth’s crust but rather in compounds of various RE and non-metals. They are all chemically very similar, a fact that makes their complete isolation and classification very difficult.

1.4.1 Properties of rare-earths

The rare earth elements are metals presenting high lustre and electrical conductivity. Their bulk color is often silver, silvery-white or grey. RE rapidly react with oxygen in air, forming oxides. They all have elevated melting points ($\geq 800\text{ }^{\circ}\text{C}$) and tend to form ionic compounds. Most RE-ions are trivalent, with samarium, europium, thulium and ytterbium also having valence +2 and cerium, praseodymium and terbium +4. Their electronic configuration is $[\text{Xe}]4f^n5d^06s^2$ with n varying from 1 (Ce) to 14 (Yb).

1.4.2 RE in GaN for luminescence emission

It is their electronic charge distribution that makes RE very interesting for optoelectronic applications. As illustrated in figure 1.7, the partially filled $4f$ electronic-energy levels are located quite close to the nucleus and are shielded from external fields by $5s^2$ and $5p^6$ outer-shell electrons. For this last reason, the intra $4f^n$ shell electronic transitions result in very sharp optical emission [29] at wavelengths ranging from the ultraviolet to the infra-red. It should be emphasized that the nature of this RE-luminescence is different from that originating from the intrinsic inter-band electron-hole recombination in the host semiconductor, which depends on the material band gap. The wavelength of the RE emitted light is determined solely by the energy of the transition between the $4f$ states and is thereby relatively independent of the host material. However, in the free (isolated) RE^{3+} state, those transitions would be forbidden due to parity conservation

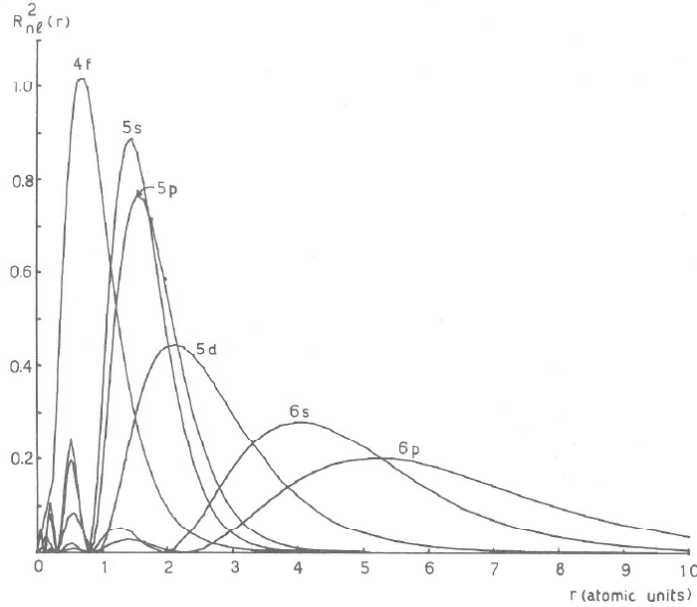


FIG. 1.7: Approximate charge distributions of electrons in $4f$, $5s$, $5p$, $5d$, $6s$ and $6p$ orbitals, evidencing the shielding of the $4f$ electrons by the outer-shell electrons [28].

[29]. When the RE^{3+} is integrated in the matrix of a III-V semiconductor, the crystalline electric field around the RE-ion will produce the splitting of the energy levels - known as Stark splitting. Depending on the total angular momentum quantum numbers of the initial and final $4f$ levels, the wavelength of the radiation, and properties of the host material such as its refractive index and absorption coefficient, certain transitions are predominant, leading to the observed emission.

Figure 1.8 shows the allowed transitions of europium, erbium and thulium in GaN. Steckl *et al.* [31] have reported photoemission from RE-doped GaN covering the entire visible spectrum: red (from Eu at 621 nm and Pr at 650 nm), green (Er at 537/558 nm) and blue (Tm at 477 nm). Apart from the pure RGB colors, these authors obtained mixed colors by co-doping GaN films with combinations of RE ions.

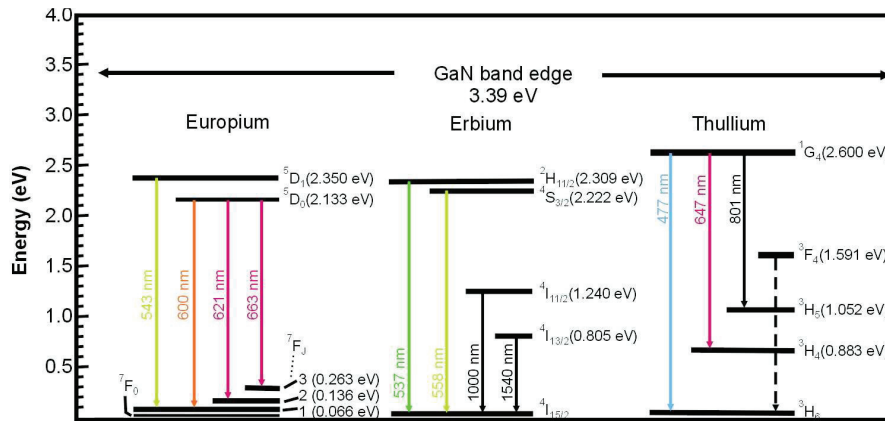


FIG. 1.8: Simplified energy diagram of the 4f levels of Eu, Er and Tm in GaN[30]

Despite the fact that the host material has little influence on the wavelength of the emitted luminescence, it does have a strong effect on the photoemission intensity (radiative transition probability) of that luminescence. The intense light emission obtained from RE-doped GaN can be partially attributed to the ability of GaN to incorporate considerable concentrations of optically active RE species. In conventional semiconductor hosts such as Si or GaAs, elevated RE concentrations result in emission quenching due to degradation of the host material and RE precipitation [32]. Another advantage of using GaN (and wide direct band gap semiconductors, in general) as a host for RE-luminescence is that luminescence intensity does not quench with increasing of temperature until values well above room temperature [31]. This is in good agreement with the empirical studies of Favennec *et al.* [1], as previously mentioned. Due to these properties, luminescence obtained from RE-doped III-nitrides is in competition with inter-band luminescence obtained from $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$ alloys, as described in section 1.1.

Luminescence from RE-doped III-nitrides requires the introduction of these dopants in the host semiconductor. This can be accomplished by three processes, namely diffusion doping, *in situ* doping during growth or by ion implantation. The first method has limited use since RE's have low

diffusivity and III-nitrides have relatively low decomposition temperatures [29]. *In situ* doping is currently the most frequently used method to obtain light emitting devices based on RE-doped III-nitrides [33, 34]. However, this method of introducing RE dopants has quite some important restrictions. The limited solubility of RE's in the host material as well as RE cluster formation, restrain the incorporation of RE in sufficiently high concentrations to reach intense emissions. The introduction of contaminants along with RE might also be a limiting factor. Patterning for lateral color integration, for example, is difficult to achieve by in-situ doping due to lack of control on the dopant lateral disposition.

The samples investigated in this study were prepared by means of ion implantation. This method allows overcoming the limitations of *in situ* doping. By employing this non-equilibrium process the dopant solubility constraints are much more relaxed. Ion implantation allows to introduce elevated dopant concentrations before precipitation starts to play a role. Also, due to the possibility of introducing mass separation, contaminants are eliminated and isotopically pure dopant beams can be used. Furthermore, the implantation technique offers the advantage of exact control of the dopant concentration and depth distribution, as well as the possibility of lateral patterning. However, the strongest disadvantage of this doping technique is the fact that it leads to the introduction of radiation damage in the crystalline lattice. Such structural defects generate non-radiative carrier recombination centers that hinder the material luminescence. Post-implantation thermal treatment steps are frequently employed in order to reduce the radiation-induced damage.

In this chapter, an overview of the fundamental properties of III-nitride materials, with special emphasis on GaN, was given. Such properties allow explaining the increasing interest in choosing these materials as hosts for RE-ion doping, with potential interesting applications in the electroluminescent device industry.

As discussed in the introductory chapter, the main objective of the *RENiBel* network was to understand the fundamentals of the interaction between RE-dopants and III-nitride hosts. To accomplish that goal it is

necessary to deepen this discussion into the electronic band structure of the material.

Chapter 2

Energy band structure of semiconductors

2.1 Band structure in solids

A great variety of semiconductors properties are fundamentally explained by means of their electronic structure. This structure depends on how atoms composing the material are arranged in space and the type of bonds established among them.

Let us consider two free atoms initially separated by an infinite distance. As they progressively approach each other, increasing-strength interactions between electrons and nuclei on both atoms start to manifest. The wave functions of electrons on both atoms begin to overlap having this a direct influence on the electronic states, namely a split in energy, as can be seen in figure 2.1 a). Increasing the number of atoms in the material results on the denser distribution of the electronic states as seen in figure 2.1 b) for a system containing N atoms. Further increasing N to the limit found in real macroscopic systems will result in more compact distributions of electronic states that can then be regarded as continuous distributions, also referred to as bands. These bands have their origin in the orbitals of the more external electrons since the ones closest to the nuclei have very localized wavefunctions that will not overlap.

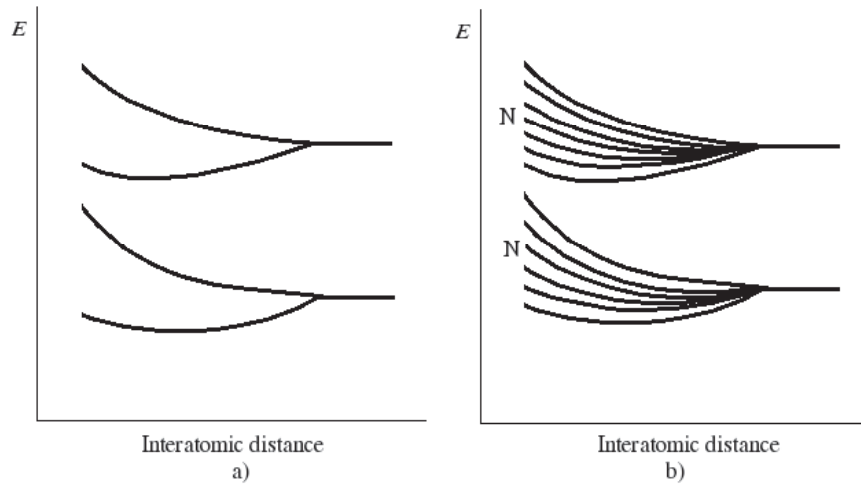


FIG. 2.1: Split of energy of electronic states [35]

2.1.1 Electrons in semiconductors

To understand how the band structure appears in semiconductors we start from a simple system - an electron moving in space without the influence of any potential. In such case, by solving the Schrödinger equation for the system, it is possible to describe the set of energy states E accessible to the electron, as a function of its momentum $p(k) = \hbar k$, schematically illustrated in figure 2.2. Here, $\hbar$ is the reduced Planck constant and k is the module of the electron wave-vector $k = |\vec{k}| = \frac{2\pi}{\lambda}$, being λ the wavelength associated to the electron. A more formal treatment of the quantum mechanical formalism describing the movement of a free electron in space can be found in elementary physics text books, such as reference [36].

However, when an atomic nucleus of charge $+Ze$ is placed somewhere in space, it will induce a well of potential energy capable of localizing the electron. In fact, if the well is infinitely deep and wide, there will exist wave functions limited to the nuclear vicinity, called bound states, as illustrated in figure 2.3. These bound states will be of energy inferior to the one of a free electron with zero kinetic energy.

These two situations - free and bound electrons - are opposite extreme

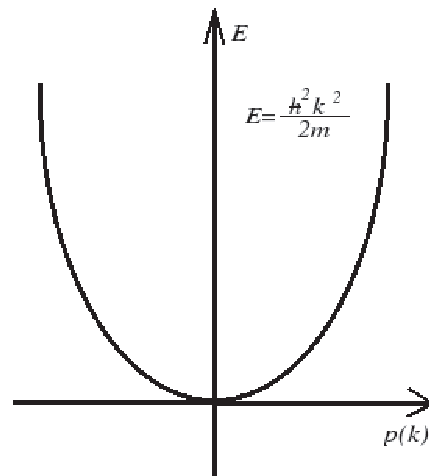


FIG. 2.2: Set of points representing the states of a free particle of mass m .

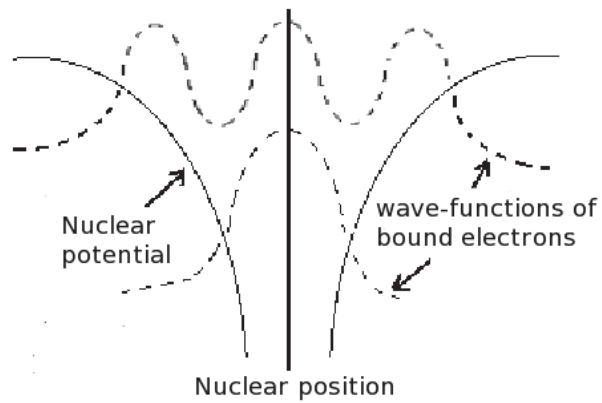


FIG. 2.3: Wave-functions of electrons in a nuclear potential well.

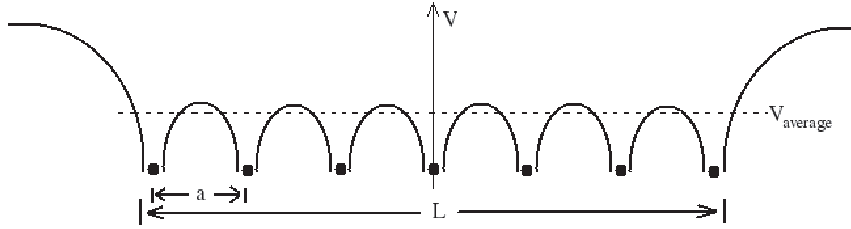


FIG. 2.4: Periodic potential of a lattice of atomic nuclei.

cases of what happens to electrons in semiconductors, however, the intermediate cases are the relevant ones to our purpose.

Let's consider now, for the sake of simplicity, that the electron is confined inside a 1-dimensional semiconductor of size L . Its wave-function can only have certain wavelengths $\lambda = 2L, \frac{2L}{2}, \frac{2L}{3}, \dots, \frac{2L}{n}$, or since $k = \frac{2\pi}{\lambda}$, it can only have certain wave-vectors $k = \frac{2\pi}{2L} = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \dots, \frac{n\pi}{L}$. Furthermore, an electron in a semiconductor will no longer only have kinetic energy, but it will move under the influence of a periodic potential built by the lattice of atoms composing the material. In our one-dimensional semiconductor model, this periodical potential will appear when the atomic nuclei are arranged periodically along the linear segment L with periodicity a , as depicted on figure 2.4.

Considering that the periodic potential is weak and that fluctuations are sufficiently small, the electron will encounter an average potential $V_{average}$ (figure 2.4). This average weak potential can be considered as a small perturbation to the electron's wave-function. The influence of this potential on the electron is small and we speak of the *nearly-free electron approximation* [37, 39]. In fact, neither the shape of the wave-function nor the electron energy will be drastically affected by the presence of such potential.

The assumption that the periodic potential has little effect on outer electrons is validated by two facts: - on one hand, the nuclear force has a short range for interaction and Pauli exclusion principle forbids outer electrons to enter the totally filled inner orbitals; on the other hand, electrons

from the inner shells contribute to significantly reduce the amplitude of the nuclear charge experienced at the site of outer electrons.

The effect of such periodic potential on the electron wave-function was described by Felix Bloch (see for example, reference [39]), as being the modulation of the wave-function by a function having the potential periodicity. The closer to the nuclei electrons are, the stronger the influence of the periodic potential, and the more localized those electrons will be. At the limit, these electrons become bound to an individual ion and will not participate in electric conduction.

In the case of outer electrons, with generic k wave-vectors as previously indicated, for which the periodic potential is weak, the electron energy E is still essentially a parabolic function of k : $E = \frac{\hbar k^2}{2m}$. For electrons with such k -values the crystal will be transparent, and they are “free” to move through the material. However, there will be some special values of k for which the perturbation cannot be considered small, independently of the potential intensity. This happens when the condition $n\lambda=2a$, or $k=\frac{2\pi}{\lambda} = n\frac{\pi}{a}$ is satisfied. Note the analogy with Bragg’s law for diffraction of electromagnetic radiation on a lattice with periodicity a (appendix B). At such k -values electrons are diffracted. The amplitude of the incident wave will strongly decay, losing its intensity to the diffracted wave. However, since the diffracted wave also satisfies the Bragg condition (same k -value), a stationary wave is obtained. These special values of $k = \pm n\frac{\pi}{a}$ where dispersion occurs receive the name of *Brillouin zone boundary* and the regions therein comprised are called *the Brillouin zones*. Depending on the value of n , they are called first Brillouin zone ($n = 1$), second Brillouin zone ($n = 2$), etc.

It can be demonstrated ([37]) that at each Brillouin zone boundary, the electron wave-function Ψ_k will have two values, Ψ_k^+ and Ψ_k^- , to which two *eigenvalues* of energy will be associated: $E_k^+ = E_k + V_k$ and $E_k^- = E_k - V_k$, respectively. In the E/k diagram this appears as a discontinuity at the Brillouin zone boundaries as seen in figure 2.5 b). Due to the crystal periodicity, from the point of view of translation operations, k and $k \pm n\frac{2\pi}{a}$ are equivalent. As such, the electron states can be represented in the

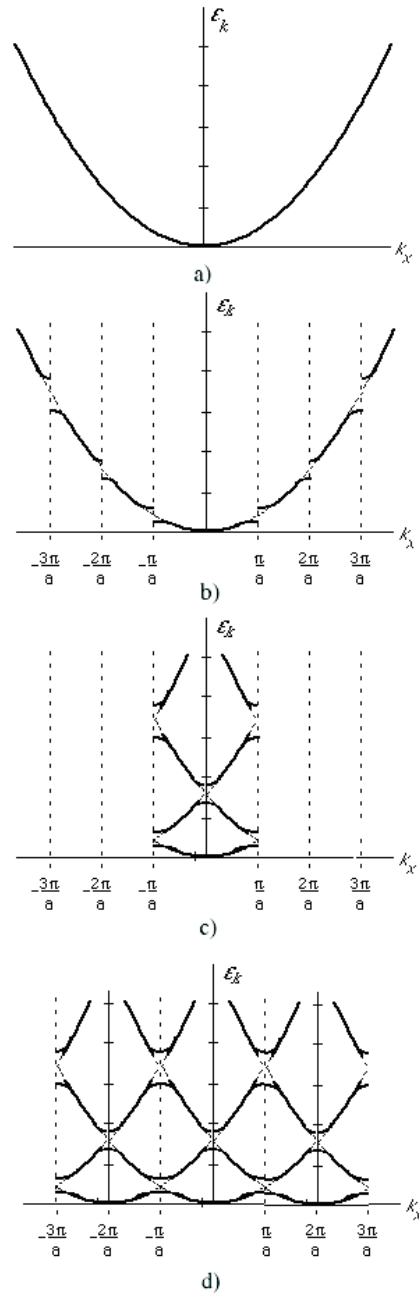


FIG. 2.5: Extended zone schemes. a) represents the E/k diagram for a free electron, b) the equivalent diagram for an electron in a crystal with atoms displayed with a periodicity a , c) the reduced zone scheme and d) the repeated zone scheme. [38]

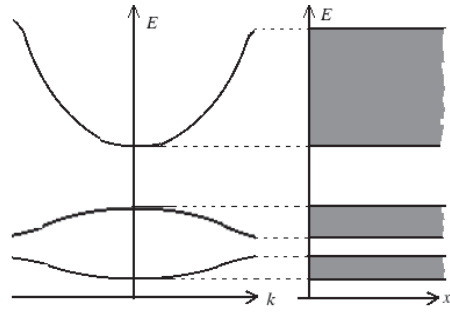


FIG. 2.6: Energy gaps (white areas) between three energy bands (grey areas).

reduced E/k diagram of figure 2.5 c). The energy discontinuity at the borders of the Brillouin zone, as represented in figures 2.5 b), c) and d) is responsible for the appearance of zones of forbidden electronic energy states. Such a region is commonly known as energy gap. Figure 2.6 illustrates the appearance of energy gaps between continuum bands of electron accessible energy states. A schematic representation of the band structure of GaN has already been shown in figure 1.5.

The population of the electron states starts from the levels of lowest energies, following the exclusion principle of Pauli and the Fermi-Dirac distribution function. The inner electrons, also known as core electrons, are found in completely filled bands with an even amount of electrons. This follows up until the valence electrons. The number of valence electrons per unit cell determines whether the last energy bands are partly or totally filled. This directly determines the substance electrical properties. In fact, this allows distinguishing between conducting or insulating (or semi-conducting) materials. A simple metal is, by definition, a substance with odd number of electrons per primitive cell, yielding at least a partly filled energy band. In an insulator, or semiconductor, the last completely filled energy band is separated from the next empty band by an energy gap.

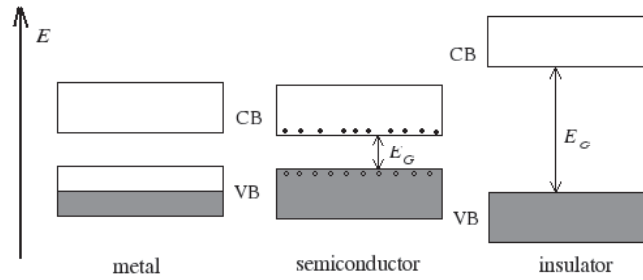
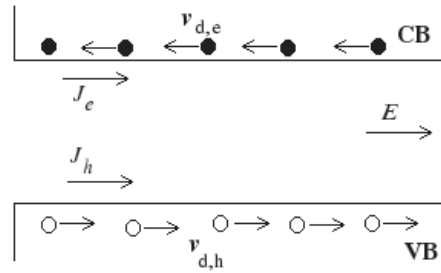


FIG. 2.7: Band scheme for metals, semiconductors and insulators.

2.2 Electronic conduction in semiconductors

At this point, it is important to mention two special energy bands often mentioned in semiconductors terminology. The *valence band* (VB) is the band of states occupied by the valence electrons of a material. A band of states that will never be completely filled with electrons - where there will always be free states available - is known as the *conduction band* (CB). A semiconductor is a particular case of an insulating material, with a small energy gap between the completely filled VB and the next completely empty (at $T=0$ K) band of states (CB), as illustrated on figure 2.7.

Due to the fact that at $T=0$ K the VB is completely filled and the CB empty there will be no electrical current and the semiconductor behaves as an insulator. For temperatures $T>0$ K, some electrons from the top of the valence band can be thermally excited to the bottom of the conduction band following the Fermi-Dirac distribution function. The electrons excited to the CB leave empty states in the VB so that both bands will be partly filled and both will thereby contribute to electrical conduction. The empty states at an almost filled VB, also known as *holes*, are often seen as counter particles with positive charge, for the electrons excited to the CB. In fact, holes behave as a positively charged particle when under the influence of an electric field. With this in mind, it is valid to state that, in a semiconductor, the current is carried by electrons at the bottom of the CB and by positively charged holes at the top of the VB. Due to the nature of their

FIG. 2.8: Charge carriers under the influence of an electric field E .

charge, electrons and holes are accelerated in opposite directions, under the influence of an electric field. Both types of charge carriers will contribute to the total current. In fact, the total current density will be the sum of two contributions with the same sign: $J_e = n(-e)v_{d,e}$ and $J_h = pev_{d,h}$, where e is the electron charge, n and p are the density ($/cm^3$) of electrons in the CB and holes in the VB, respectively and v_d is the carrier drift velocity. Since $v_{d,e}$ has an opposite sign to the applied electric field, J_e will be in the same direction of E , so that it has the same sign as J_h as shown in figure 2.8.

2.3 Optical emission

The optical properties of a semiconductor are dominated by the inter-band transitions. An electron in the VB can be excited across the band-gap into a state in the CB. This excitation can have different causes, such as thermal excitation, absorption of a sufficiently energetic photon, etc. As a consequence of the electron promotion to the CB, a hole is left in the VB, and after a certain period of time the system will minimize its energy by recombining the electron-hole pair. This happens when the electron emits its excess of energy and returns to the initial state in the VB, annihilating the hole. For both situations (upwards - excitation - or downwards - relaxation) transitions between two quantum states occur with conservation of

energy and crystalline momentum:

$$\begin{cases} E_V(k') - E_C(k) = h\nu \\ k' - k = k_\gamma. \end{cases} \quad (2.1)$$

In this example, an excited electron filling a state (E_C, k) in the CB, released its excess energy as a photon of energy $h\nu$ and momentum k_γ and recombined with a hole in a state (E_V, k') in the VB. However, typical energies of de-excitation are of the order of a few eV , implying wavelengths of emitted electromagnetic radiation of the order of $1\ \mu m$, so that k_γ is of the order of $10^{-3}\ \text{\AA}^{-1}$. Comparing this with the typical crystalline momenta, such as the border of Brillouin zone at $\frac{2\pi}{a} \sim 1\ \text{\AA}^{-1}$ with $a \sim 1\ \text{\AA}$, we conclude that k_γ is negligible. As such, $k' - k \simeq 0$, or $k' \simeq k$, meaning that electronic transitions occur for the same value of k . As a consequence, since the most probable transitions are the ones occurring between the top of the VB to the bottom of the CB, in a material where these two points occur at different k -values, no transitions between those two values will be allowed. A material for which the maximum of the VB and the minimum of the CB occur at the same k -value is said to have a direct band-gap. GaN, InN and AlN are examples of direct band-gap semiconductors. Si, BN and GaP are indirect band-gap semiconductors. For indirect band-gap semiconductors, inter-band transitions are still possible, though less probable. These transitions must however, be aided by a phonon. Phonons are lattice vibrations and as opposed to photons, they have high crystalline momenta and negligible energy. So in these transitions, the photon will supply the needed energy (vertical transition component) and the phonon will contribute to the necessary momentum change (horizontal transition component). Indirect band-gap transitions are less probable and depend on the temperature since T controls the phonon population in a material.

2.4 Intrinsic and extrinsic semiconductors

A semiconductor is said to be *intrinsic* when electrical conduction occurs only due to thermal excitation through the energy gap. This can be changed by incorporation of impurities and/or defects present in the material.

2.4.1 Intrinsic semiconductor

The number of occupied states in the CB is given by (ref. [39])

$$n = \int_{E_C}^{\infty} g_e(E) \langle n(E) \rangle dE, \quad (2.2)$$

with $g_e(E)$ the density of states in the conduction band and $\langle n(E) \rangle$ the average state occupation number given by the Fermi-Dirac distribution function:

$$\langle n(E) \rangle = \frac{1}{e^{\frac{E - \varepsilon_F}{k_B T}} + 1}, \quad (2.3)$$

where ε_F is the *Fermi energy*, the energy of the highest occupied quantum state at $T = 0K$ and k_B is the Boltzmann constant. Equivalently, the number of empty states, or holes in the valence band is,

$$p = \int_{-\infty}^{E_V} g_h(E) [1 - \langle n(E) \rangle] dE, \quad (2.4)$$

with $g_h(E)$ the density of holes in the valence band. Taking into account that for typical semiconductors at RT, $E_{Gap} \sim 1 \text{ eV}$ so that $E_{Gap} \gg k_B T$ and $\langle n(E) \rangle \approx e^{-\frac{E - \varepsilon_F}{k_B T}}$ and $1 - \langle n(E) \rangle \approx e^{-\frac{\varepsilon_F - E}{k_B T}}$ (often referred to as *nondegenerated semiconductors condition*), integral evaluations yield:

$$\begin{cases} n = N_C e^{-\frac{E_C - \varepsilon_F}{k_B T}} \\ p = N_V e^{-\frac{\varepsilon_F - E_V}{k_B T}} \end{cases} \quad (2.5)$$

with $N_C = 2 \left[\frac{2\pi m_e k_B T}{h^2} \right]^{3/2}$ and $N_V = 2 \left[\frac{2\pi m_h k_B T}{h^2} \right]^{3/2}$, the effective state density in the CB and CV, respectively.

An intrinsic semiconductor is characterized by $n = p = n_i$, being $n_i = (N_C N_V)^{1/2} e^{-\frac{E_{Gap}}{2k_B T}}$ the intrinsic carrier density. It can be demonstrated [37] that in this case, ε_F will lie very close to the middle of the energy gap, $\varepsilon_F \simeq \frac{E_V + E_C}{2}$.

2.4.2 Extrinsic semiconductor

When conduction is dominated by impurities and/or defects, we speak of an *extrinsic* semiconductor. To simplify, let's consider the example of Si

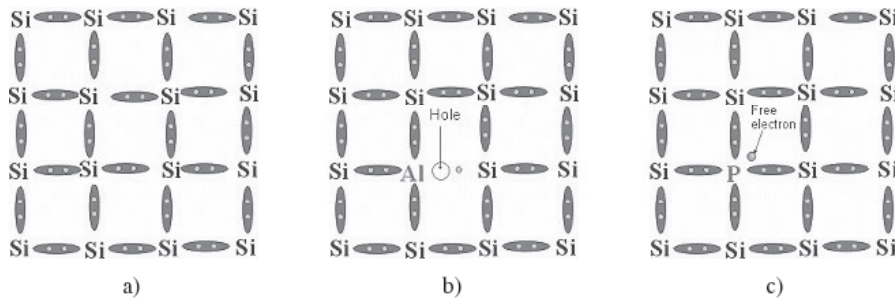


FIG. 2.9: a) Intrinsic Si, b) p-doped Si and c) n-doped Si [40].

in figure 2.9 (for GaN, composed by two atomic species, similar reasoning can be done). In silicon, every Si atom will share its four valence electrons with four neighboring Si atoms forming four covalent bonds (figure 2.9 a)). Replacing one of the matrix Si atoms by Al, for example, will change the number of electrons in the valence band. Since Al has one less valence electron than Si, a hole is created at the valence band (figure 2.9 b)). On the other hand, if a Si atom is replaced by, for example, an atom of P having one more valence electron than the matrix atoms, P will donate its extra electron to the conduction band (figure 2.9 c)). The Si semiconductor where an Al impurity has been introduced is said to be *p-type doped*, since positive charges are introduced in the material due to Al doping. Al is said to be an *acceptor impurity*. Conversely, Si doped with P is said to be *n-type*, as negative charges are introduced in the material. P receives the name of *donor impurity*. Once again, in what GaN concerns, some dopants act as acceptors when replacing Ga or N and some others act as donors. Others even can act both as acceptors and donors in GaN, depending on the element they are replacing in the lattice and/or the position they take (Ga,N-substitutional or interstitial).

In general, electron binding energy is defined as the energy required to remove an electron from its atom. In the case of impurities, the binding energy of the electron to the impurity is usually a factor of a thousand smaller than the ground state binding energy of the free element [39].

For a donor impurity, the binding energy is measured relative to the energy

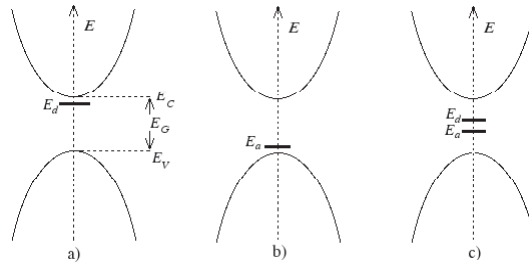


FIG. 2.10: a) donor level, b) acceptor level, c) deep donor and acceptor levels.

of the CB levels to where the electron will go, leaving the donor impurity ionized. As such, donor impurities introduce additional electronic states with energy E_d - figure 2.10a) - in the band gap, which are lower than the energy of the states at the bottom of the CB, E_C . The energy difference is most of the times small compared to the energy gap E_{Gap} .

Concerning acceptor impurities, symmetry arguments allow extending the previous reasoning of electrons and the CB, to holes and the VB. As such, the binding energy of the hole to the acceptor dopant is now measured relative to the VB since the hole will be promoted to a state there. As such, acceptor impurities introduce additional electronic levels at an energy E_a above the top of the VB - figure 2.10b).

At $T = 0K$, the extra electrons in a n-type doped semiconductor are bound to the impurities, as holes are too in a p-type semiconductor. At room temperature almost all impurities will be ionized.

Due to the fact that these levels lie close to the boundaries of the band gap, they are often called *shallow levels*. Shallow levels have a fundamental role in the electrical and optical properties of semiconductors. It is far more probable to have an electron from a shallow donor level being excited into the CB, or a hole from an acceptor level into the VB, than to promote an electron directly from the VB into the CB. It is obvious then that for doped semiconductors, impurities are the major source of free carriers.

Another category of levels can appear in the band gap. In fact, some types of impurities and crystalline defects can be responsible for the presence of deeper levels, closer to the middle of the energy band gap - figure

2.10c). These *deep levels* can also be donors, acceptors, simultaneously donors and acceptors or multiple donor or acceptor. In general, deep levels act as very efficient carrier (electron or hole) traps.

Carrier density in an extrinsic semiconductor

Impurities must be taken into account while determining quantities such as carrier concentrations and the position of the Fermi energy in the band gap.

For an n-type semiconductor, let's assume the presence of a shallow impurity with energy E_D below the CB and density N_D such that $N_D \ll N_C$, the effective density of states in the CB. When the Fermi level is far enough from the conduction band ($E_C - \varepsilon_F \gg k_B T$), the density of CB electrons is still given by n in equation 2.5. The amount of ionized donor impurities is given by

$$N_D^+ = N_D[1 - P_e(E_D)] = \frac{N_D}{1 + \frac{1}{2}e^{\frac{\varepsilon_F - E_D}{k_B T}}}, \quad (2.6)$$

where $P_e(E_D)$ is the donor level occupation probability. The total amount of free electrons will then be given by the sum of contributions from the intrinsic process (thermal excitation from VB to CB) and impurity ionization. Since the semiconductor is neutrally charged, the total amount of negative created charges must equal the total positive charge. This results in $n = N_D^+ + p$. Replacing here the results for n and p from 2.5 and N_D^+ , we obtain

$$N_C e^{-\frac{E_C - \varepsilon_F}{k_B T}} = \frac{N_D}{1 + \frac{1}{2}e^{\frac{\varepsilon_F - E_D}{k_B T}}} + N_V e^{-\frac{\varepsilon_F - E_V}{k_B T}}. \quad (2.7)$$

Considering now that the dopant concentration is such that $N_D \gg n_i$ and that the Fermi energy is well below the donor level energy ($E_D - \varepsilon_F \gg k_B T$), we obtain $N_D^+ = N_D$. This result indicates that under the required conditions, all donor impurities will be ionized. Remembering also that $np = n_i^2$, $n = \frac{1}{2}[N_D + \sqrt{N_D^2 + 4n_i^2}]$. In this regime ($N_D \gg n_i$) we obtain $n = N_D$, and the concentration of electrons in the CB will be much higher than the concentration of holes in the VB. In this case, the semiconductor is said to be *extrinsic* - its properties are dominated by the impurities,

as opposite to what happens in a intrinsic semiconductor. Electrons are said to be the majority carriers whereas holes are referred to as minority carriers.

Carrier concentrations are, as we have seen, dependent on the temperature. The regime described above stays valid through a wide range of temperatures, however increasing T high enough will result in a strong increase of the intrinsic electron-hole pairs generation up to a point where $n_i > N_D$. Beyond this point, even doped semiconductors will behave as intrinsic. On the other hand, decreasing T to low enough values, the probability of finding donor levels in their neutral state (occupied with an electron) increases, with the consequence that n will decrease. Electrons at the CB will de-excite back to the donor levels, where they will be “frozen”. This is often known as the “donor freeze-out” regime.

This discussion can easily be extended to p-type semiconductors using simple charge symmetry arguments.

2.5 Doping

As seen in the previous section, properties of semiconductors can be altered through the introduction of impurities into the semiconductor lattice. Doping can be achieved by introducing the dopants during semiconductor growth, thermal diffusion into the semiconductor or with ion implantation. According with the desired property change, either electrical, optical or magnetic, different dopants can be employed.

2.5.1 Electrical doping

Semiconductor doping has most of its application on the modification of materials electrical properties. Obtaining n- and p-type materials is crucial for the design of micro-electronic components. As described in 2.4.2, dopants will introduce extra electron states in the semiconductor band gap. Here, shallow donors play an important role, since they control the carrier density in the material. The energy position in the band gap will depend on the dopant chemistry and where it is incorporated into the host crystalline

lattice. Again, GaN and related semiconductors introduce extra complexity as compared to mono-atomic semiconductors as Si and Ge. In fact, one has to consider the effect of dopants when replacing Ga or N in the lattice.

Obtaining n-type GaN has never constituted a problem, since typical as-grown GaN has already an elevated free electron concentration. This has its origin on defects created during growth. However the way these defects are introduced doesn't allow to control the carrier density.

Si is the most used dopant to obtain n-type GaN [41] in a controlled way, creating a shallow level at about 30 meV [42] below the CB, when it replaces Ga. Oxygen will also create a donor state at 30 meV but only about 10% of the O ions will become electrically active. S and Te induce donor levels at 48 ± 10 and 50 ± 20 meV below the CB, respectively [41]. p-type GaN is more difficult to obtain. This happens mainly due to the high free electron concentration in the undoped GaN and due to the inexistence of suitable shallow acceptors. Mg is the most commonly used dopant to obtain p-type GaN but still its far from being an ideal acceptor since it induces an acceptor level at about 170 meV [41] (compared to the 30 meV of Si as donor). With these values, ionization efficiencies of only a few percent are obtained at room temperature. This implies that, in order to obtain p-doping, elevated concentrations of Mg are required. It has been observed that [41] co-doping of Mg with P enhances the substitution of Ga by Mg. Another possible p-type dopant in GaN is Ca, creating an acceptor level at about 165 meV below CB. Finally, Be is also predicted to have an acceptor behavior, inducing a shallower (~ 60 meV [43]) level than Mg. However, Be tends to react with N and form Be_3N_2 leading to a low solubility of Be in GaN.

As previously mentioned, deep levels in the band gap play an important role on the electrical properties of the material since they can trap carriers in a very efficient manner. Transition metals were reported [44] to create deep levels in GaN. However Cu, Cr, V, Mn, Fe and Ni are known contaminants in MOCVD and HVPE grown GaN. As contaminants, these elements will introduce deep levels in a non-controlled way, which in general is unwanted.

Other authors [45] have reported that Ti, Ni and Au, besides intro-

ducing deep levels in the band gap of GaN, will also act as donors. Rare earth ions have also been reported by Filhol *et al.* [46] to introduce several levels in the band gap of GaN. Among these, some deep levels that will be involved in the luminescence mechanisms, as will be discussed later.

2.5.2 Magnetic doping

Another application of dopants is the modification of the magnetic properties of materials. Electron spin manipulation has opened the possibility for spintronic devices, such as spin-controlled switches and memories [48]. Integration of this new technology in the existing semiconductor applications is of capital importance for such devices. For this purpose, several groups are actively investigating the magnetic properties of such systems, in particular, ferromagnetism in dilute magnetic semiconductors (DMS). Ferromagnetic behavior has been observed for some III-V semiconductors doped with about 1-5 at. % Mn, such as GaMnAs, InMnAs and ZnMnSe. However, the Curie temperature for these materials is still too low ($T_C \sim 110$ K) to take advantage of their magnetic properties at room temperature. Theodoropoulou *et al.* [49] have studied the magnetic properties of *p*-doped GaN implanted with 3-5 at. % of Mn. They observed ferromagnetic behavior in this system with T_C of ~ 250 K. However, they report that the ferromagnetic properties are due to the formation of Mn platelets with the same structure of GaN but different lattice constant. Dhar *et al.* [50] reported room temperature ferromagnetism from several transition metal (TM) doped GaN but also observed that this behavior results from the formation of precipitates rather than from a homogeneous alloy.

Hashimoto *et al.* [51] investigated the magnetic properties of MBE Eu-doped GaN and observed evidence of a ferromagnetic-like phase, through the measurement of hysteresis and saturation at 300 K. However they also observed the gradual saturation of the magnetic moment with increasing magnetic field at low temperatures, this being an indication of the co-existence of a paramagnetic and ferromagnetic-like phases. Another RE which showed more interesting properties is Gd. Dhar *et al.* [52] have also investigated the magnetic properties of GaN:Gd layers. They report an

extraordinarily large magnetic moment ($4000 \mu_B$ per Gd atom) and ferromagnetism at temperatures above room temperature, with a Curie temperature around 360 K, even for Gd concentrations as low as 10^{16}cm^{-3} . A DMS with such an elevated T_C is obviously a very attractive candidate as a source of spin-polarized carriers to be employed in future semiconductor-based spintronics.

Nevertheless, the mechanisms responsible for the magnetic behavior induced by dopants such in the nitrides is still far from understood.

2.5.3 Optical doping

GaN and related materials became interesting mainly due to their optical properties. With its direct band gap of width 3.4 eV, GaN is an interesting material for optoelectronics, namely for ultra-violet, violet, blue, green and yellow light emitting devices [47]. Pankove and Hutchby have performed an exhaustive study of the luminescence properties of 35 dopants implanted into GaN [53]. These authors have observed that Mg, P, Zn, Cd, Ca, As, Hg and Ag produce a characteristic spectral photoluminescence signature. They also reported a broad peak at about 2.15 eV (yellow region of the visible spectrum).

The above examples, inter-bands transition luminescence and luminescence from impurity-induced carrier recombination are not the only reason why GaN became interesting for optoelectronics. As pointed out in the introductory discussion, the nitrides are also suitable hosts for a category of known luminescent agents, the rare earth elements.

Rare earth elements as optical dopants in GaN

As described in section 1.4.1, the rare earth partly filled $4f$ electron orbitals are so deeply buried within the electronic shell that they are shielded by the outer $5s$, $5p$ and $6s$ electron orbitals. Intra $4f$ shell electronic transitions result in very sharp optical emission whose wavelength is almost independent of the host material. Different RE ions will yield luminescence

emission with different wavelength. For example, Eu emits around 630 nm (red), Tm around 480 nm (blue) and Er around 540 (green) and 1540 nm (infra-red). It has been demonstrated [32] that combining several RE ions as optical dopants, color combination can be used to obtain other colors.

It should be emphasized that RE luminescence is of different nature than the one obtained from inter band transitions and electron-hole pair recombination. In the first case, luminescence results from electronic transitions inside the RE $4f$ electron shell, whereas in the latter case the luminescence wavelength is dependent on the band-gap energy or the energy level in the band-gap that a dopant induces.

As mentioned in section 1.4.2, GaN is a suitable host for RE dopants due to its ability to incorporate a significant concentration of those optical dopants without precipitation and without PL or EL intensity quenching [30]. However, the mechanism of energy transfer from the GaN host material into the RE $4f$ electronic orbitals is still not fully understood.

Measurement of the optical spectrum of RE in III-V semiconductors indicates that these ions will be in the $3+$ oxidation state. Density functional theory (DFT) studies performed within the RENiBEL network [54] have been employed to conclude that the RE ions have a strong affinity to the substitutional position of the group III element in the lattice. In this position, the RE intra-shell $4f$ - $4f$ transitions will be allowed and thereby RE characteristic light emission can be observed. These same studies indicate that, despite the fact that RE substitutional impurities do not introduce any deep donor or acceptor levels in GaN (as they behave as isoelectronic impurities), they may introduce carrier traps. These results are in agreement with the work of Lozykowski [55]. In his work on the kinetics of RE-ions luminescence in III-V semiconductors, he proposes a model for the energy transfer from host to the $4f$ electrons.

Lozykowski points out several arguments, both experimental and theoretical, indicating that trivalent RE ions constitute isoelectronic substitutional impurities leading to the creation of bound states in the band gap of III-V's. Among those arguments is the difference in covalent radius of

the III group element and the RE^{3+} ions. That difference would account for a strain field in the close vicinity of the impurity that would generate a perturbing potential. This potential can be attractive either for electrons or for holes and it can even bind to an exciton as a single entity.

In his model, Lozykowski proposes three possible mechanisms of energy transfer. In the first mechanism the energy of excitons bound to the isoelectronic center is transferred to the RE $4f$ core electrons.

In a second mechanism, the RE-induced trap is occupied by an electron (hole) and it will attract a free hole (electron) from the valence (conduction) band. The recombination energy of the bound electron (hole) with the free hole (electron) is transferred to the $4f$ shell through a nonradiative Auger mechanism.

The third mechanism consists of the transfer through an inelastic scattering process in which the energy of a free exciton near the trap is given to the localized core excited states. When the initial and final states are not resonant, the energy mismatch is accommodated by, for example phonon emission or absorption.

Furthermore, according to this author, the RE-associated trap does not necessarily imply that the RE ion occupies a perfect substitutional group III element lattice position. In fact, depending on its chemical activity, the RE ion can form a more complex center, involving other impurities or native defects. This opinion was shared by other research groups, including RENiBEL. In another DFT study, Filhol *et al.* [46] have investigated the structure and electrical activity of RE (Eu, Er and Tm) and RE-defect complexes in GaN. They concluded that the configuration where the RE ion substitutes the Ga atom (RE_{Ga}) does not generate any deep band gap states. This result appears to be consistent with the fact that only a small amount of all the RE ions are optically active, despite Extended X-ray Absorption Fine Structure (EXAFS) measurements ([56]) showing that RE_{Ga} with C_{3v} point symmetry is the most common geometry where RE in GaN are found.

Concerning RE-defect complexes, the same RENiBEL studies ([46]) point RE_{Ga} associated to a nitrogen vacancy ($\text{RE}_{\text{Ga}}\text{-N}_V$) as the most favorable

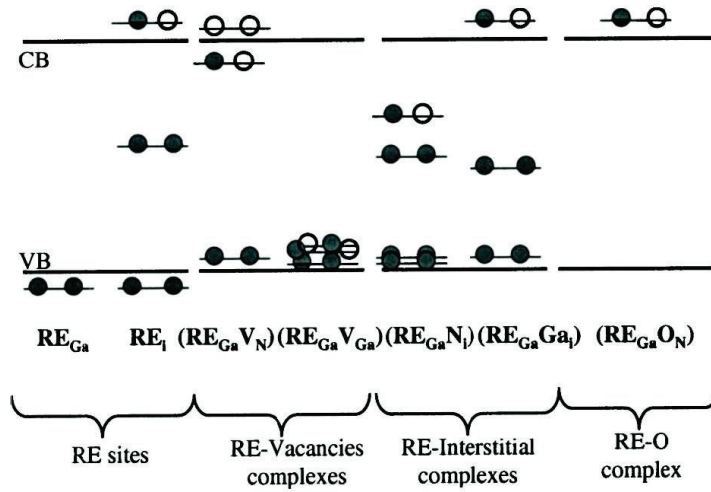


FIG. 2.11: Schematic of energy levels at Γ of RE-defect complexes in GaN [46].

to form and the most stable pair (up to 1000 °C). This defect complex is expected to create a half-filled level at about 0.2 eV below the E_C for the three RE elements they investigated. Other RE-defect configurations were experimented. Figure 2.11 graphically summarizes their results.

Whatever the host-RE energy transfer mechanism might be, it must provide the 4*f*-core electrons with enough excitation energy to allow the intra-4*f* transitions responsible for the characteristic optical emission. The most energetic luminescence observed from an intra-4*f* transition is the spectral line observed at around 381.6 nm from the $^5D_3 \rightarrow ^7F_6$ transition from Tb^{3+} in GaN. To this value corresponds an energy of 3.249 eV. As such, the lower limit for a trap in the band gap, involved in the population of the $Tb^{3+} \ ^5D_3$ level, is $E_C - 0.2$ eV. Considering that the same energy transfer mechanism involving similar defects for all RE-ions is valid, this sort of argument immediately excludes any RE-defect complex, creating deeper levels, to be involved in centers responsible for high energy optical transitions.

As discussed above, dopants can be employed to engineer a wide range of materials properties. However, those properties are not only conditioned by the presence of a foreign species in the host lattice, but by any element responsible for the break of crystalline periodicity. More generally, crystalline defects, independently of their origin, have an important role on the material behavior. The preceding discussion on RE-ions as optical dopants in GaN has evidenced the important role of intrinsic semiconductor defects such as vacancies and interstitials. Due to their relevance, a brief overview on defects in semiconductors will be presented in the following chapter.

Chapter 3

Defects in semiconductors

3.1 Structural defects classification

The perfect crystal is an ideal structure where the constituent host atoms, molecules or ions are periodically arranged in space, forming a pattern extending itself in the three-dimensional space. However, in a real crystal, the structure is always disturbed by some irregularities. Crystalline imperfections, or defects, will always be present at normal pressure and temperatures. Defects are usually classified according to their dimensional extension ([57]):

- Zero-dimensional or point defects:
 - Vacancies;
 - Interstitials;
 - Impurity or dopant atom:
 - Substitutional,
 - Interstitial.
- One-dimensional or line defects:
 - Strings of point defects;

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- Edge dislocations;
 - Screw dislocations;
- Two-dimensional or surface defects:
 - Stacking faults;
 - Grain boundary;
 - Twin boundary;
 - Interface boundary at precipitates.
- Three-dimensional or volume defects:
 - Voids;
 - Bubbles;
 - Precipitates.

The way these defects are introduced in the semiconductors can have several origins. Some are introduced during growth, as for example described in section 1.2, while others are introduced during other subsequent processing steps, such as doping by means of ion implantation as will be discussed later on chapter 5.

3.2 Point defects

Thermodynamics plays a determining role on the number of defects in crystals. One can speak of a balance between the crystal energy, that tends to be minimized, and its entropy, that tends to be maximized. The crystal energy is minimal for a perfect crystalline lattice, whereas entropy increases with the formation of defects.

At temperatures above 0 K , a crystal cannot exist in a state of perfection. Lattice atoms are in continuous vibration about their equilibrium position. The vibration amplitude increases with increasing temperature and can be represented as a statistical distribution of thermal energy over the lattice atoms. As such, there will always be a non-zero probability that

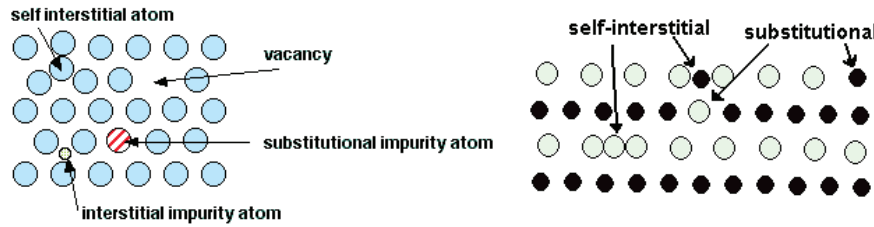


FIG. 3.1: Point defects in mono-atomic and diatomic crystalline lattices [58].

sufficient energy is locally concentrated on a group of atoms and that one of them acquires sufficient energy to spontaneously abandon its equilibrium position. A lattice imperfection is formed.

Point defects constitute the simplest form of defects. Figure 3.1 illustrates several types of point defects existing in monoatomic and diatomic crystals. An atom missing from its lattice site, is referred to as a vacancy, whereas an atom occupying a position other than a regular lattice site constitutes an interstitial defect. When an impurity or dopant is introduced in the lattice, according to the position it will occupy, it can be named substitutional (when replacing a host atom on its lattice site) or interstitial (when it doesn't occupy a regular lattice site).

The various types of intrinsic defects in a crystal are thermally activated, each one having its own formation energy [37]. As such, it is to be expected that a certain kind of point defect with the lowest formation energy will be more abundant in the lattice. However there is an important restriction: *charge neutrality* - the crystal must remain neutrally charged. Thereby, this restriction assures that the concentration of the most abundant defect type is lowered while the concentration of the most abundant type of the opposite charge is increased. In a diatomic ionic crystal, such as GaN, charge neutrality can be achieved by either balancing the number of positive and negative ion vacancies - *Schottky defects*, or maintaining the number of vacancies and interstitials of the same ion at equal levels - *Frenkel defects*.

The formation energy of an interstitial defect is higher than that of a

vacancy. For this reason, in a pure (undoped) crystal, the concentration of interstitials will, in general, be several orders of magnitude lower than the vacancy concentration. Also, due to the fact that an interstitial occupies a non-regular site, the lattice surrounding the defect will become strained.

The several types of point defects can interact with each other. The type of interaction depends on the distance between the defects. As such, short range interactions account for the formation of vacancy-interstitials pairs (also known as *Frenkel pairs*) and divacancies, for example. Frenkel pairs are of particular relevance for this work since their production is favored during ion implantation. As will be discussed in chapter 5, the radiation damage caused by ion implantation consists (among other sorts of defects) of an equal number of vacancies and interstitials, being frequently interstitials associated to neighboring vacancies. The lattice strain near these pairs is such that if the separation between them is short, they will spontaneously recombine in order to reduce the strain. However, when this is not the case, a defect inducing lattice expansion - such as an interstitial, tends to pair (without recombination) with a neighboring defect that induces lattice compression - a vacancy. As an example we have stable Frenkel pairs. The intensity of this elastic type of interaction varies with r^{-3} , r being the distance between the two defects.

Another sort of longer range interaction is related to the charge the involved defects have. Electrostatic interaction can result in the pairing of two defects with charges of the opposite sign. The interaction energy in this case varies with r^{-1} .

In stoichiometric compound crystals of the form A_xB_{1-x} , such as GaN where the Ga and N atoms form two interpenetrating sublattices, the complexity of defects is increased. At a certain temperature, $T > 0\text{ K}$, a certain concentration of vacancies and/or interstitials will be present in each sublattice. Besides, antisite defects (A in the lattice site of B and vice versa) may also be present.

The nature of a point defect determines the mechanism through which it can move through the crystal lattice [59]. As such, a defect in a substitu-

tional lattice site will move by jumping to the next equivalent substitutional site when this becomes empty through the generation of a vacancy. On the other hand, a defect in an interstitial position will move by jumping to a neighboring equivalent position. An interstitial can also exchange positions with an atom on a regular lattice site which will be displaced into another interstitial site.

Vacancy and interstitial dynamics are governed by their diffusivity which reveals an Arrhenius-form dependence on the temperature and activation energy ([57]):

$$D = D_0 e^{-\frac{E_a}{k_B T}}, \quad (3.1)$$

being E_a the activation energy for the diffusion process and D_0 an exponential pre-factor related to the migration entropy.

Being mobile, point defects may vanish by annihilating with point defects of opposite nature or by aggregation with defects of the same kind. Point defects can also diffuse towards the crystal surface or towards extended crystalline defects, which will act as sinks for point defects. Aggregation is at the origin of defect clusters. By forming such structures, defects are allowed to lower their free energy. Due to their nature, clusters have a high impact on the lattice strain, leading to local lattice expansion. In the case of GaN, these structures are thermally quite stable, being observed even at temperatures as high as 1300°C [60].

3.3 Line and surface defects

The amount of energy required for the formation of an extended defect is much higher than that of point defects. For this reason it is unlikely that this kind of defects spontaneously forms at temperatures above 0 K .

Extended defects are frequently formed during the crystal growth phase, for example as described on section 1.2.1; during ion implantation, as a consequence of the clustering of point defects; by the influence of applied forces to the crystal, or by strong temperature gradients.

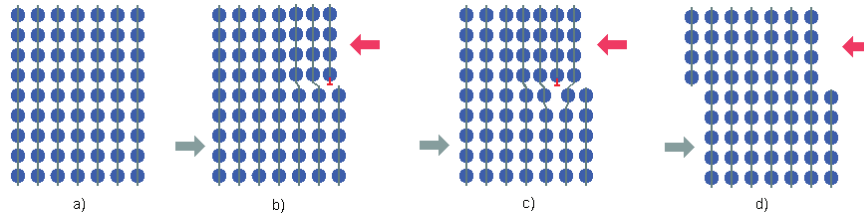


FIG. 3.2: Slip motion in a crystal lattice under stress [57].

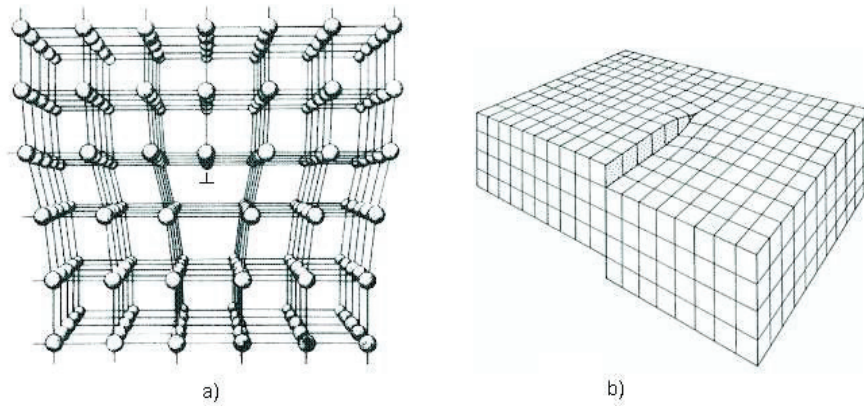


FIG. 3.3: a) edge and b) screw dislocations [57].

In general, the deformation of a crystal can be classified as elastic - when it is reversible (when stress is removed, the crystal returns to its initial shape), or plastic - when the deformation is permanent and irreversible. There are two frequent modes of plastic deformations in crystals. The first mode, *slip*, is associated with a particular kind of line defects, namely dislocations. The two simplest kinds of dislocations are known as edge and screw dislocations. Figure 3.2 illustrates how the slip mechanism occurs in a crystal under applied stress (figs. 3.2 b), c) and d)) [57]. The upper part of the crystal slips over the lower part. This process can result in the reminiscence of edge dislocations and/or screw dislocations (figure 3.3) that occur during the slip motion.

The other frequent mode of plastic deformation is named *twinning*. Like

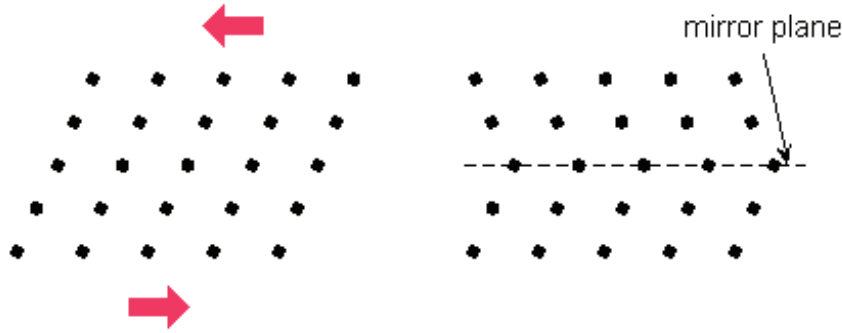


FIG. 3.4: During deformation atoms can be pushed out of place. If this happens to produce a symmetrical arrangement, a deformation twin is formed.

slip, twinning is also mediated by dislocations. At its origin is the fact that the applied stress causes coherent formation of dislocations along successive crystal planes. As each dislocation propagates through the crystal it displaces a lattice plane by a non-Bravais lattice vector. The net effect of the passage of a set of dislocations is a region in which the crystalline ordering is the mirror image (along the plane of the movement) of the original crystal. This process is schematically represented on figure 3.4 [61].

For MOCVD grown GaN, one of the reasons for the elevated dislocation density ($\sim 10^{10} / \text{cm}^2$ as compared to $< 10^2 / \text{cm}^2$ for Si and $< 10^4 / \text{cm}^2$ for GaAs) found in the grown films is related to the several temperature steps during growth (see section 1.2.1). Those steps associated to the thermal mismatch between the sapphire substrate and the GaN film are often responsible for the formation of cracks on the film. Another reason is the coalescence boundaries between grains on the GaN/AlN buffer layer.

3.4 Volume defects

Finally, voids, gas bubbles and precipitates constitute a third category of defects often found in semiconductors. As it will be discussed in more detail in chapter 5, the immense amount of energy locally deposited during ion bombardment leads to severe lattice disorder. During this process, besides

generation of point defects as described in section 3.2, more complex structures can be formed. For example, in their review on ion implantation in GaN, Kucheyev *et. al* [41] give evidence of the formation of N_2 bubbles in GaN films bombarded with 2 MeV Au ions at a fluence of about 10^{16} ions/cm². Precipitate formation is another example. Employing MBE to grow doped RE-doped nitrides can result in the formation of precipitates when dopant concentrations are higher than the material solubility limit [29]. This constitutes one of the principal disadvantages of RE-doping of nitrides employing molecular beam epitaxy.

So far, the most relevant properties of GaN and related semiconductors have been discussed. Also, rare-earth elements have been pointed-out as important dopants in those materials for optoelectronic applications. It is however essential to obtain insight in how such dopants interact with the host material resulting in emission of luminescence.

In chapter 2 the origin of energy bands in semiconductors was briefly presented, as well as the effects of doping to the material band-gap. In this scope, shallow and deep band-gap levels have been discussed. Not only dopants themselves can be regarded as imperfections in the host crystalline lattice, but also are frequently associated with other structural defects responsible for band-gap levels. Such defects have their origin, for example, in size differences between host and dopant ions. Those differences can cause strain fields in the lattice and consequently induce energy levels in the band-gap [55].

In the current chapter, a general summary of the most common sorts of structural defects in crystalline materials was presented. Often, the doping process itself is the main cause of structural defects in doped semiconductors. In particular, as mentioned in the introductory chapter, RE doping of GaN by means of ion implantation introduces significant amount of lattice imperfections. Such implantation-induced structural defects have an impact on the optical output since they can act as non-radiative recombination centers, resulting in a reduction of light emission efficiency. However, the role of defects in the luminescence process is far from understood - as

discussed in section 2.5.3, it is thought that some defects might play an important role in the RE:GaN luminescence excitation mechanism.

Chapter 8

Conclusions

This work consisted of a study of defects introduced in GaN during Eu-doping by ion implantation. For that purpose Eu has been implanted in GaN thin films at several experimental conditions (fluence, implantation direction and substrate temperature).

After implantation, the structural properties of the doped films have been investigated by Rutherford backscattering and channeling spectrometry. Structural characterization was often complemented with other techniques, namely X-ray diffraction, and optical studies performed by photo and cathodoluminescence. To complete the study the doped films were electrically characterized by Deep Level Transient Spectroscopy in order to investigate the effect of structural defects and the RE-dopant on the GaN band-gap.

RBS/C indicates that Eu-implantation introduces disorder in the GaN lattice. This disorder is distributed in depth through the crystal into two regions, one closer to the surface and another coinciding with the implanted ion projected range. The surface damage region is characterized by an elevated degree of structural disorder. The second damage region (EOR), is characterized by a considerable degree of lattice disorder without however reaching the levels of the surface damaged region.

Even though the integrated lattice disorder level (surface+EOR) increases sigmoidally with increasing dopant fluence, the disorder level of

both regions increases at different paces with increasing Eu fluence. While the surface disorder region reaches amorphous levels already at intermediate fluences, the disorder intensity at the EOR region appears to saturate at intermediate-high fluence values. An efficient dynamic annealing mechanism assures that point-defects formed during implantation are immediately recombined (or diffuse away from this region) resulting in the saturation behavior at the EOR region. As the amorphization of the surface region proceeds in the direction of the bulk, the EOR disorder level proceeds until it too reaches the amorphous level and meets the surface, now amorphous, region.

RBS/C further revealed that aligning the Eu-beam with the c-axis of GaN allows to considerably reduce the degree of structural damage. Along that direction the Eu beam is channeled through the crystal and the individual ions experience far less collisions with host atoms and thereby create considerably less structural damage along their path inside the crystal, until they finally come to a stop.

In any case, room temperature implantation in both geometries generates substantial levels of structural defects that hinder the luminescence output of the doped material: no RE-related luminescence is observed after implantation. Annealing at temperatures of the order of 1000°C is required to - only partly - recover the structural damage, and observe RE-related luminescence. After annealing, RE-luminescence is stronger for the channeled implantation geometry as this geometry generates a higher number of optically active centers, as compared to random implantation that introduces a considerably higher level of luminescence quenching structural defects.

Complete lattice damage recovery requires extreme annealing conditions that are not practical, requiring special equipment and conditions in order to avoid material degradation. Indeed at only about 1000°C surface degradation of GaN starts to occur under conventional ambient. Hence, it is necessary to prevent the formation of damage rather than attempt to recover it afterwards. We have observed that implantation damage can be strongly reduced by elevating the substrate temperature during implanta-

tion. Results here presented indicate that the level of structural disorder measured by RBS/C on a film implanted at 180°C is inferior to the level observed in a RT implanted and subsequently annealed film at 950°C. Moreover, considering that at 950°C only partial recovery of lattice damage is achieved and that higher annealing temperatures will lead to surface decomposition, it can be concluded that implanting at substrate temperatures of about 200°C is a more efficient method of introducing higher dopant fluences while keeping structural damage at reduced levels.

Surprisingly, even without post-implantation annealing, weak RE-related luminescence is observed for samples implanted at temperatures as low as 50°C. Interestingly, it has been observed that this “as-implanted” luminescence is considerably stronger for the case of random implantation, for which RBS/C shows a much higher level of structural damage as compared to channeled implantation. A plausible explanation for this fact is that not all structural defects quench the RE-luminescence. Considering that some defects will be involved in the RE excitation mechanism and that more defects of both kinds (quenching and optically active) are introduced by random implantation, higher “as-implanted” luminescence is expected for that geometry. Further, if defects involved in luminescence form temperature stable complexes with the implanted RE-ions and luminescence quenching defects are recombined upon annealing, stronger luminescence is expected from channeled implanted and annealed samples. Indeed defect recombination upon annealing is more efficient for channeled implanted samples. As a result, after annealing more quenching defects are still present for the random implanted samples and therefore luminescence is weaker for this implantation geometry.

Besides GaN, AlInN films have also been implanted with Eu. PL and CL studies have shown that the host composition strongly affects the luminescence output of the RE-implanted films. On one hand, much stronger RE-related luminescence was observed for AlInN, as compared to GaN. On the other hand, the measured luminescence lines are considerably broader and slightly red-shifted as compared to RE:GaN.

The influence of the mass of the implanted ion on the formation of

damage was investigated by comparing the effects of implanting ^{132}Xe , ^{153}Eu , ^{158}Gd and ^{166}Er . Results indicate that little difference is found in the level of structural damage caused by the implantation of the three RE ions, but that, as expected, the level of damage caused by Xe implantation is considerably inferior.

Deep Level Transient Spectroscopy was used to investigate the role of structural defects on the formation of electrical defects in the band-gap of RE-implanted GaN. Characterization of as-grown control GaN films has revealed the presence of two major defects generating two electron trap levels in the band-gap of GaN. Measurements on Eu-implanted films shows that several band-gap levels are introduced during implantation. To tentatively determine whether some of those defects are Eu-related or implantation damage related, two other ion species have been implanted in similar films, namely Gd (another RE-ion) and Xe (an inert ion). By comparing the DLTS signatures of defects measured in all samples it was possible to conclude that the majority of the defects are most probably caused by structural defects introduced during implantation, as they were observed in all samples, including Xe-implanted. Not all defects were present in all samples. One particular defect was only observed in Eu-implanted samples (and not for Xe). Such defect introduces a level in the band-gap at about 230 meV below the conduction band of GaN. This value is close to the RENiBEL calculated value from Density Functional Theory studies for the $\text{RE}_{\text{Ga}} - V_{\text{N}}$ defect in Eu, Er and Tm-doped GaN: 200 meV below the conduction band. Such defect is thought to be involved in the excitation mechanism of the RE $4f$ electrons resulting in the typical sharp luminescence of RE:GaN.

Even though the work here presented provides experimental evidence for the theoretical predictions, further investigation is necessary in order to confirm that such defect is involved in the the RE:GaN luminescence mechanism. In order to clearly conclude whether such band-gap level is indeed RE-related a conceptually simple experiment can be executed, namely the implantation of a RE radioisotope. Such isotope should have a suitable half-life ($\sim$ hours) in order to allow implantation and subsequent DLTS

characterization. By acquiring DLTS spectra at different time intervals during the RE parent-isotope half-life, it should be possible to conclude whether certain defects are indeed RE-related. If the amplitude (concentration) of a certain defect decreases with time and if the decay constant matches that of the isotope half-life then clear evidence is given of the origin of that particular defect.

To gain further insight on the role of structural defects on the RE-luminescence, a more extensive study is required. All samples implanted at several implantation conditions should be characterized by all of the techniques employed in this work: RBS/C, HRXRD, PL, CL and (radioactive) DLTS. By gathering information from all these techniques, and by investigating the same parameters on similar samples implanted with other RE ions, such as Tm and Er, it should be possible to further clarify the mechanism responsible for the energy transfer between host and RE-ions leading to the typical luminescence. Such knowledge would allow to optimize the doping conditions in order to maximize light emission of fabricated devices.

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