**UNIVERSIDAD POLITÉCNICA DE
MADRID**

**ESCUELA TÉCNICA SUPERIOR DE INGENIEROS
DE TELECOMUNICACIÓN**

***“EPITAXIAL GROWTH AND CHARACTERIZATION
OF INGAN LAYERS FOR PHOTOVOLTAICS
APPLICATIONS”***

DOCTORAL THESIS

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2017

“Los grandes palacios se
construyen ladrillo a ladrillo”

Víctor J. Gómez

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Abstract

In this work, we have grown the constituent functional blocks of a photovoltaic device based on III-Nitrides compound semiconductors, focusing on the non-intentionally doped (NID) InGa_N layer and on the Mg-doped Ga_N layer. We have introduced two growth methods (MME and DERI) with the purpose of improving the quality of those constituent blocks of a photovoltaic device. All samples have been grown in a molecular beam epitaxy (MBE) reactor.

The Metal Modulated Epitaxy (MME) makes use of the modulation of the shutters of the metallic and dopant sources (In, Ga, Al, Mg, Si) alternating open and close conditions. When the shutters are opened, the growth is performed under metal-rich conditions, while when the shutters are closed it is performed under N-rich conditions. The main goal of the MME method is enhancing the proper incorporation of Mg (p-type dopant) atoms into the crystalline structure (Mg atoms on Ga substitutional site Mg_{Ga}), while keeping a good morphology of the surface. Under N-rich conditions, the Mg atoms are preferentially incorporated in Mg_{Ga} sites, but the surface is degraded. The surface is flattened back when growing under metal-rich conditions. The final result is an enhancement of the hole concentration with a good surface morphology. The overall growth conditions are N-rich.

Non-intentionally doped and magnesium doped Ga_N layers have been grown on Ga_N(0001) pseudo-substrates by Metal Modulated Epitaxy (MME). In order to characterize the hole concentration obtained, the Mg-doped Ga_N layers were also grown on highly resistive (Ga_N:Fe) pseudo-substrates MME. The Hall effect results have been compared with Ga_N layers grown in the intermediate regime (the usual growth method by MBE for high quality layers). The layers grown by MME showed 5 times higher hole concentration than those grown in the intermediate regime. The most important parameters to control the InGa_N grown on Ga_N(0001) pseudo-substrates by MME have been studied. The ratio In/Ga has been identified as the most critical parameter that controls the indium incorporation into the alloy. Diode p-i-n structures (p-Ga_N / i-InGa_N / n-Ga_N) have been grown on Ga_N(0001) pseudo-substrates, processed and characterized, and crucial mechanisms have been identified in order to improve their performance.

The other growth method used in this thesis is Droplet Elimination by Radical-beam Irradiation (DERI). Unlike the MME case, DERI growth of InGaN only modulates opening/closing of the In shutter. DERI consists of two process, the Metal Rich Growth Process (MRGP) and the Droplet Elimination Process (DEP). During the MRGP the In shutter is opened and the layer is grown accumulating In droplets on the surface. When In shutter is closed (DEP) the In droplets are reincorporated epitaxially into the InGaN layer. The overall growth is stoichiometric.

In addition, we have studied the effect of four different buffer layers on the structural and optical properties of InGaN layers grown on Si(111) substrates and their correlation with electrical characteristics. The vertical electrical conduction on the InGaN / buffer / Si, with In composition near 46%, which theoretically produces a band alignment, is analysed. InGaN layers were grown for the first time, up to the best of our knowledge, on Si using droplet elimination by radical-beam irradiation (DERI). The results obtained lead to the possibility of fabricating double junctions InGaN/Si solar cells without the need of tunnel junctions between the two sub-cells, therefore simplifying the design of the final device.

Resumen

En este trabajo hemos crecido los bloques funcionales que constituyen un dispositivo fotovoltaico basado en la familia de semiconductores compuestos conocida como los nitruros, centrándonos en las películas de InGaN no dopadas intencionadamente (NID) y las películas de GaN dopadas con Mg. Hemos introducido dos métodos de crecimiento (MME y DERI) con el objetivo de mejorar la calidad de los bloques constituyentes mencionados para la fabricación de un dispositivo fotovoltaico. Todas las muestras se crecieron en un reactor epitaxial de haces moleculares.

El “*Metal Modulated Epitaxy*” (MME) hace uso de la modulación del estado de los obturadores de metales y dopantes (In, Ga, Al, Mg, Si) alternando entre abierto y cerrado. Cuando los obturadores están abiertos, el crecimiento se realiza en condiciones ricas en metal, mientras que cuando están cerrados se realiza en condiciones ricas en nitrógeno. El principal objetivo del MME es aumentar la incorporación apropiada de los átomos de Mg en la estructura, es decir, en posición de sustitucional de Ga (Mg_{Ga}), mientras que se mantiene una buena morfología de la superficie. En condiciones ricas en nitrógeno los átomos de Mg se incorporan preferentemente en posición de Mg_{Ga} , pero la superficie se degrada. Cuando las condiciones del crecimiento son ricas en metal (obturadores abiertos) la superficie se planariza. El resultado es un aumento de la concentración de huecos en la capa de GaN con una morfología superficial buena. Globalmente, las condiciones de crecimiento son ricas en nitrógeno.

Se crecieron capas de GaN, no dopadas intencionadamente, sobre pseudo-substratos de GaN(0001) por MME. Se han crecido además, películas de GaN dopadas con Mg mediante MME sobre pseudo-substratos altamente resistivos de GaN dopado con Fe. Los resultados de las medidas de efecto Hall han sido comparados con los de capas de GaN crecidas en régimen intermedio (en este régimen se crecen las capas de mayor calidad). Las capas crecidas por MME han mostrado una concentración de huecos 5 veces mayor que aquellas crecidas en régimen intermedio. También se estudiaron los parámetros más importantes que controlan el crecimiento del InGaN mediante MME sobre pseudo-substratos de GaN(0001). Asimismo, se identifica la razón In/Ga como el parámetro crítico

que regula la incorporación de indio en la aleación. Para verificar el comportamiento de las capas de InGa_N, se crecieron, procesaron y caracterizaron estructuras p-GaN / i-InGa_N / n-GaN sobre pseudo-substratos de GaN(0001), por MME, y se identificaron mecanismos cruciales para mejorar su funcionamiento.

El “*Droplet Elimination by Radical-beam Irradiation*” (DERI) es el otro método de crecimiento basado también en la modulación del estado de los obturadores que se ha utilizado en esta tesis. A diferencia del MME, durante el crecimiento de InGa_N por DERI solo se modula el obturador de indio. El DERI está dividido en dos procesos, el “*Metal Rich Growth Process*” (MRGP) y el “*Droplet Elimination Process*” (DEP). Durante el MRGP el obturador de In está abierto y el crecimiento de la capa se produce en condiciones de acumulación de gotas en la superficie. Cuando el obturador de In está cerrado (DEP) las gotas de In se reincorporan en la capa de InGa_N. Globalmente, las condiciones de crecimiento son estequiométricas.

Hemos estudiado el efecto de cuatro capas de amortiguamiento diferentes sobre las propiedades estructurales y ópticas de capas de InGa_N crecidas sobre Si(111) y su relación con las características eléctricas. Se midió la conducción vertical eléctrica de las hetero-estructuras InGa_N / “*buffer*” / Si, para una composición de In cercana al 46%, que produce un alineamiento de bandas. Se crecieron por primera vez, hasta donde llega nuestro conocimiento, capas de InGa_N (~40% de In) sobre sustratos de Silicio utilizando eliminación de gotas por irradiación con haz de radicales-libres (DERI). Los resultados obtenidos apuntan a la posibilidad de fabricar células de doble unión InGa_N/Si evitando la necesidad de una unión túnel entre ambas sub-células, simplificando el diseño del dispositivo final.

List of publications

As first author:

1. High In Composition InGaN for InN Quantum Dot Intermediate Band Solar Cells, **V. J. Gómez**, P. E. D. Soto-Rodriguez, P. Kumar, E. Calleja, and R. Nötzel, *Jpn. J. of Appl. Phys.* **52**, 08JH09 (2013).
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1. Introduction, objectives and work plan

1.1. Introduction

1.1.1. The energy problem

Solar energy is one of the most promising alternatives to reduce the current global warming of the planet induced by greenhouse gases (GHG) arising from the use of fossil fuels. The potential of solar energy is much higher than that of the fossil fuels, or of any other renewable energy since the solar energy impinging on earth in one hour is much higher than the worldwide energy expenditure in one year. There are two main technologies developed to harness the solar energy:

- i. Solar thermal energy → it harnesses the solar energy by heating a fluid inside a circuit to produce steam, which is then used to power a generator that produces electricity. This is an indirect transformation of sunlight into electricity.
- ii. Photovoltaic energy (PV) → it converts solar energy directly into electricity using a semiconducting material. The semiconductor absorbs photons from the sunlight generating electron-hole pairs. Electrons and holes are then separated inside the material by an internal electric field producing an output voltage that can power a circuit. This is a direct conversion of light into electricity.

These two ways of extracting energy from the sun are highly reliable, safe and easy to install, needing relatively low operation and maintenance cost. In addition, once installed, none of them involves any combustion or GHG generation, thus making them environmentally friendly. Therefore, the development of high efficiency and reduced cost solar cells is very desirable.

The research in the field of PVs focuses mainly on the performance increment while reducing the manufacturing costs.

Nowadays, more than 90% of the total solar panels produced worldwide are made out of mono-crystalline silicon (Si), whose price reached 0.6€ per watt with

a 18% efficiency. As an alternative, panels based on low cost materials such as amorphous silicon, polycrystalline silicon and cadmium telluride, have a slightly smaller price (around 0.46€ per watt). However, their shared market is low because their efficiency hardly ever reached 16%. The large density of defects in the above-mentioned materials produces a dramatic reduction on the carriers (electrons and holes) diffusion length and lifetime [Bha94]. Higher efficiencies, close to 30%, are only achievable in thin film III-V multi-junction (MJ) solar cells, such as GaInP/GaInAs/Ge or GaInP/GaInAs/GaInAs. These solar cells are fabricated on germanium (Ge) or gallium arsenide (GaAs) substrates, which are more expensive than Si, and all the junctions are designed to have a better matching to the solar spectrum than with the above-mentioned technologies, leading to a higher efficiency.

Nowadays, single-junction Si solar cells, with a reduced cost and long lifetime (30 years), monopolize the PV market despite their theoretical efficiency limit (Shockley-Queisser) of 33% at the standard AM1.5G under 1 sun of illumination (solar spectrum impinging the earth at a solar zenith angle of 48.19°). Using advanced MJ solar cells based on III-V thin films, higher efficiencies both under 1 sun and under concentration conditions (using lenses to mimic more than 1x sun illumination) can be achieved. Some designs showed efficiencies over 40% under concentration conditions using multilayers of arsenides, phosphides and antimonides on Ge substrates (44.7% for 4 junctions under a 297 suns illumination) [Fra13]. The main drawback of these types of MJ solar cells is their higher price as compared with the silicon technology, making them unsuitable for a massive energy harvesting.

Integration of the mature and relatively cheap Si technology with the efficient III-V solar cells may allow the production of high efficiency and reduced-cost solar cells. Those structures would have a theoretical efficiency limit of 39% (for 1x sun) and of 42.3% under concentration conditions (500x suns) [Kur90]. It is worth pointing out that those theoretical efficiency values could be achieved using a 2 junction solar cell composed by an upper cell with a bandgap energy of 1.74 eV and a bottom cell with a bandgap energy of 1.13 eV [Kur90]. Those bandgap energy values could be obtained using a single semiconductor alloy system, for instance, indium gallium nitride ($\text{In}_x\text{Ga}_{1-x}\text{N}$) from the III-Nitrides system. This

ternary compound semiconductor has been widely used for light emitting diodes (LEDs) and laser diodes (LDs) during the last 20 years.

1.1.2. Group III-Nitrides

Group III-Nitrides (AlN, GaN and InN) have been considered a promising system for semiconductor device applications since 1970, especially for the fabrication of optoelectronic devices working in the ultraviolet to green range. The III-Nitrides (AlN, GaN and InN) are optimal candidate materials for optoelectronic applications at such photon energies, because they provide a continuous alloy system (InGaN, InAlN and AlGaIn) whose direct bandgap energies for the hexagonal wurtzite structure range from 0.65 eV for InN; 3.4 eV for GaN; and 6.2 eV for AlN [Wu09]. Likewise, the strong ionic nature of their chemical bonding gives them a high thermal and chemical stability, making them suitable for applications in aggressive environments and more specifically, under strong concentration conditions for PVs (high temperature operation). Other advantageous properties include: high mechanical stability, high absorption coefficient near the band edge (one order of magnitude larger than that of GaAs), high carrier mobility, large piezoelectric constants and the possibility of passivation by forming thin layers of Ga_2O_3 or Al_2O_3 with bandgaps of approximately 4.2 eV and 9 eV. It is noteworthy, as examples of devices, that the 2014 Physics Nobel Prize was awarded to the development of light emitting diodes (LED) with blue (1994) and ultraviolet (1997) emissions, as well as UV detectors and devices operating at high temperature [Nak95]. Blue LDs based on GaN are commercially available nowadays for Blu-ray disc players and white light for car power headlights.

To reach this state-of-the-art, strong efforts were dedicated to the epitaxial growth of prime quality material. The main problem of the III-Nitrides is the lack of a suitable material to be used as a substrate for homoepitaxial growth at a reduced cost. The main problems of using a foreign substrate (heteroepitaxial growth) are the difference in thermal expansion coefficient and the difference in lattice constant. Consequently, the epilayer grows with a large number of extended defects (stacking faults [Lil08], [Glo08] dislocations [Kap95], [Lee01], [Chi96], stacking mismatch boundaries [Sve96], [Smi95] and grain boundaries [Xu01]).

Different substrates have been tested, such as sapphire (Al_2O_3), silicon carbide (SiC) and silicon (cut by the (111) planes).

In the 1970s, Molecular Beam Epitaxy (MBE) and Metal Organic Vapour Phase Epitaxy (MOVPE) growth techniques were developed and many efforts were focused to make them capable of growing GaN. However, it was not until 1986 that high crystal quality GaN with good optical properties was produced by MOVPE [Ama86]. The breakthrough was the introduction of a thin (30 nm) layer of polycrystalline AlN grown at low temperature (500°C) between the GaN layer (grown at 1000°C) and the sapphire substrate. This AlN interlayer (buffer layer) helps to accommodate the difference in thermal expansion coefficient and lattice constant. During the heating process (from 500 to 1000°C), the AlN develops a texture of small crystallites of preferential orientation (c-axis) on top of which GaN grows. The GaN layer starts with a high dislocation density that decreases rapidly after growing a few microns. A high quality surface was obtained, a crucial factor to grow thin multilayer structures in the following steps of the LED development. Shuji Nakamura at Nichia, a chemical company in Japan, developed a similar method in which the AlN buffer was replaced by a low temperature GaN thin layer [Ama86], [Nak91]. A second major breakthrough was the achievement of p-type conductivity in GaN layers, which enabled the fabrication of GaN p-n junctions [Nak91b], [Nak92]. MOVPE was used by Nichia to develop the first blue and ultraviolet LEDs (1994 and 1997 respectively).

In the case of GaN layers grown by MBE on Si(111), from the early 1994's [Ste94] studies focused on the use of AlN as buffer layers. The best GaN layers grown on Si(111) were achieved by using an AlN buffer [San98], [Hag02], [Hag01], leading to the fabrication of optoelectronic devices [Guh96], [San00]. The first GaN-based ultraviolet (UV) photodetector grown on Si(111) by MBE was demonstrated in 2000 [Pau00]. Applications of III-Nitrides in PVs will be mentioned in the next section.

Heteroepitaxy of GaN on foreign substrates usually generates, as mentioned above, a high density of dislocations, grain boundaries, inversion domains, as well as macroscopic defects (cracks) due to the difference in thermal expansion coefficient (-33% and -17% vs sapphire and Si(111) respectively) and lattice

constant (-25% and 56% vs sapphire and Si(111) respectively). In spite of the high concentration of defects, devices with high efficiency have been produced and are commercially available as LDs on “Blu-ray Disc” players, LEDs for indoor and outdoor white light illumination, traffic lights, car lights, displays and televisions, high power transistors and UV photodetectors. For advanced devices the defect density is reduced by buffer engineering, or using high quality nitride bulk substrates, both prohibitive choices for mass production.

1.1.3. Indium Gallium Nitride

Based solely on the III-Nitrides system (Al, Ga, In)N, the bandgap can be tuned from mid infrared (0.65 eV of InN) to UV (6.2 eV of AlN). Among ternary compounds of this system, a great deal of attention has been devoted to InGaN alloys due to their application to green, blue and UV LEDs and LDs. Despite all the resources invested to study and develop InGaN alloys, some of their fundamental properties remain somehow unclear. For instance, the presence and nature of an electron surface accumulation layer, the accuracy when determining the actual bandgap, carrier effective masses, lattice parameters, and elastic constants, some of them derived from a non-linear combination (bowing parameter) of the corresponding values from the binaries, GaN and InN.

Nevertheless, $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys having a bandgap tuneable between 0.65 eV to 3.45 eV are excellent materials for optoelectronic applications. This bandgap energy span covers the entire AM1.5G solar spectrum. InGaN films show an exceptionally intense photoluminescence, even though they are grown on lattice-mismatched substrates. In addition, the optical and electronic properties of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys exhibit a much higher resistance to high-energy (2 MeV) photon irradiation than the currently used PV materials such as GaAs and GaInP, therefore offering a great potential for space applications. Furthermore, $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys have high temperature resistance making them suitable for solar cells under concentration.

As mentioned before, the highest theoretical efficiency of a double junction solar cell is attained when the bandgaps of the two sub-cells are 1.13 eV and 1.74 eV, both achievable by using InGaN. Several approaches have been addressed,

such as InGaN homojunctions and heterojunctions [Cai13]; multi quantum wells (MQWs) [Dah10]; and InGaN/GaN core-shell wires [Mes15]. So far, the record efficiency reported for InGaN solar cells is established for a p-GaN / i-InGaN-GaN (MQWs) / n-GaN solar cell at 5.95% [Lio11] and 5.99% [Lio13], both grown on a buffered Si(111) substrate. The most recent works done on InGaN solar cells are focused on the design and simulation of the devices. A p-InGaN / i-InGaN / n-InGaN solar cells, for an In content of 62%, have been simulated by Jeon and co-workers showing an efficiency of 33.42% [Jeo16]. The main problem associated to the reports on simulations is that the structural parameters employed are usually better than the state of the art. An efficiency of 6.43% was reported by Kushwaha *et al.* for a simulated p-GaN / i-InGaN / n-GaN heterojunction solar cell [Kus14]. Huni *et al.* reported on the simulation of a p-GaN / i-InGaN (25%) / n-GaN // p-Si / n-Si solar cell showing a photon conversion efficiency near 30% using a 4-terminal approach [Hun17], taking into account realistic and feasible structural parameters. Despite the attractive properties of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys, already described, their growth remains challenging due to technological issues that should be overcome:

- i. At typical GaN growth temperatures (by MBE, 750°C) the equilibrium vapour pressure of InN is more than ten orders of magnitude higher than that of GaN, resulting in a very low In sticking coefficient. The temperature should be significantly reduced to ensure the incorporation of In into the layer. However, low temperatures normally lead to In droplets formation on the surface (InN dissociation temperature is much lower than the In evaporation one) that also hinder In incorporation into the film. In addition, at lower temperatures, the InGaN crystal quality is much lower, due to the reduced surface mobility of the metal adatoms that generates rough surfaces, as well as extended and point defects.
- ii. The large lattice mismatch between InN and GaN (11%) results in highly strained layers and/or layers with a high density of dislocations.
- iii. InGaN tends to separate into InN and GaN at temperatures typically over 500°C and In contents above 20%. This phenomenon, called phase separation, increases as a function of temperature and In content. The majority of III-V ternary and quaternary alloys are predicted to be

thermodynamically unstable and prone to phase separation and metal clustering [Kar98], [Dop98]. The growth by Molecular Beam Epitaxy (MBE, the growth technique employed throughout this work) is performed out of the thermodynamic equilibrium conditions.

- iv. The tendency of InGa_N, non-intentionally doped, is to be highly n-type doped due to point defects. In addition, there is an electron accumulation layer at the surface that hinders p-type doping by pure compensation [Vea06].

1.2. Objectives

The main goal of this thesis is to optimize the growth by MBE of n^{id} InGa_N layers, as well as their characterization aiming at their use for PV applications. The optimization of the growth involves the use of two new methods proposed in the literature: metal modulated epitaxy (MME) and droplet elimination by radical beam irradiation (DERI). It also implies the understanding of the processes related to the growth and the impact of individual parameters on the surface morphology, as well as on the structural, optical and electrical properties.

Specific goals of this thesis are:

- i. To check if the MME growth method may help in the development of an InGa_N-based photovoltaic device:
 - a. The growth and characterization of non intentionally doped (NID) and Mg-doped Ga_N on Ga_N(0001) templates by MME.
 - b. The growth and characterization of NID InGa_N layers on Ga_N(0001) templates by MME.
 - c. The growth and characterization of a p-Ga_N / i-InGa_N / n-Ga_N photovoltaic device using MME.
- ii. To study the effect of four different buffer layers on the InGa_N properties for InGa_N on Si(111) photovoltaic devices:
 - a. The growth and characterization of NID InGa_N layers on buffered-Si(111) by DERI.
 - b. The study of the effect of four different buffer layers on the InGa_N / buffer / p-Si vertical conduction.

1.2.1. To check if the MME growth method may help in the development of an InGaN-based photovoltaic device

The wide range of band gap energies available from InGaN alloys combined with other properties, such as their absorption values, make InGaN very attractive for photovoltaic applications. The structure selected to accomplish this goal was a p-GaN / i-InGaN / n-GaN. The large quantity of reports on growth and simulation of this structures [Kus14], [Jeo16], [Hun17], together with the fact that the records on InGaN-based solar cells have been obtained using those structures [Lio11], [Lio13], make us to decide to use a p-GaN / i-InGaN / n-GaN over other options. This was selected over the InGaN:Mg / InGaN:Si one because the latter introduces new technological problems that still need to be solved (as the Mg doping of the InGaN layer), and that could screen the results on the growth method. The In content of the InGaN layer of the final device will be set to 10% to avoid problems related to the growth of high In content InGaN alloys. This goal was divided into three sub-goals:

1.2.1.1 The growth and characterization of non intentionally doped (NID) and Mg-doped GaN on GaN(0001) templates by MME.

Full control of layers doping processes is a crucial step in the fabrication of any optoelectronic device. The doping study will follow the optimization of NID GaN layers, in which the residual doping will be determined. Magnesium will be used as the acceptor species for p-type doping. Special emphasis will be put on the use of the MME technique to grow Mg-doped GaN layers.

Characterization (mostly structural, optical, and electrical) of the doped GaN layers and a comparison with the results obtained on NID ones will result on a full understanding of the issues related to the doping process.

1.2.1.2 Growth and characterization of NID InGaN layers on GaN(0001) templates by MME.

Full control and reproducibility, when growing InGaN alloys, can be only achieved by means of a deep understanding of the growth process. For this purpose, this work addresses first the growth of NID InGaN layers. It is fundamental to obtain

high crystalline quality layers in order to understand their basic properties/limitations and to allow designing the best strategy to achieve high efficient devices.

The crystal quality of the InGaN layers is assessed from a detailed study of the morphological, structural, optical and electrical properties, carried out by X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Photoluminescence spectroscopy (PL), Atomic Force Microscopy (AFM) and Hall Effect. The results are compared with the state of the art.

1.2.1.3 Growth and characterization of a p-GaN / i-InGaN / n-GaN photovoltaic device using MBE

Prior to the design of a PV device, a detailed study and analysis of the heterostructures involved on its fabrication is necessary. The final device will be monolithically (i.e. all layers) grown by MBE. The fabrication of the devices will include several technological steps, such as UV-lithography, etching and metal deposition of the electrical contacts.

Additionally to the standard characterization of the layers, a specific electrical characterization of the resulting p-i-n junction, and the measurement of the photo-generated current in a solar simulator (conditions of AM1.5G under 1 sun illumination) will be performed.

1.2.2. The study of the effect of four different buffer layers on the InGaN properties for InGaN on Si(111) photovoltaic devices

The inability of a single-junction solar cell to harness the full solar spectrum, gave rise to the idea of stacking solar cells with different energy gap. Theoretically, the maximum obtainable efficiency of a double-junction solar cell is 39%, for a bandgap combination of 1.74 and 1.13 eV. Both values are achievable with InGaN and Si. An additional benefit of InGaN/Si heterojunctions is the alignment of the n-type InGaN conduction band with the valence band of p-type silicon for In composition around 46%, which provides a low resistance ohmic contact [Hsu08]. This fact would avoid the need of TJs between sub-cells strongly

simplifying the solar cell design and fabrication. The bandgap of an $\text{In}_{0.46}\text{Ga}_{0.54}\text{N}$ is 1.8 eV and 1.11 eV for Si, both values are close to the optimum ones. In order to accomplish this goal, it was divided into two sub-goals:

1.2.3.1 The growth and characterization of NID InGaN layers on buffered-Si(111) by DERI

The growth of high quality high In content InGaN alloys on Si remains challenging due to the large lattice mismatch between InN and GaN, low miscibility gap and the relatively low growth temperatures needed. Additionally, growing InGaN alloys directly on Si must deal with the silicon surface nitridation and a poor wetting on the resulting Si_xN_y layer [Gom16]. The silicon nitridation can be avoided by using buffer layers that may, in addition, upgrade the film quality. DERI method can be of great help to grow high quality, thick and homogeneous NID InGaN layers with In content ranging from 30 to 42%. The InGaN layers were NID grown, but the high residual n-type concentration was enough to ensure the band alignment.

The crystal quality of the InGaN layers is assessed in the same way as in the case of InGaN grown by MME.

1.2.3.2 The study of the effect of four different buffer layers on the InGaN / buffer / p-Si vertical conduction.

The vertical electrical conduction is going to be assessed by current versus voltage (I vs V) characteristics. The goal is to find a buffer layer that maximizes the crystal quality of the InGaN epilayer, while keeping the ohmic behaviour of the n-InGaN / buffer / p-Si heterointerface.

1.3. Work plan

A work plan has been established into different tasks aiming to accomplish the specified goals:

1.3.1. Task 1: Systematic study of NID and Mg-doped GaN

The control of the doping level (p and n-type) is paramount for the fabrication of devices. In the case of III-Nitrides the n-type doping poses no significant difficulties but for AlN and high Al% AlGa_N layers, being commonly achieved by using Si as dopant. However, p-type doping is still a serious challenge due mainly to the high ionization energy of the acceptors commonly used, that in AlGa_N layers increases with the mole fraction. In addition, compensation by donor contamination (O, Si) and point defects, aside from the natural tendency of InGa_N layers to have a significant residual n-type character, poses further difficulties. The presence of a high electron density at the layer surface for In mole fractions beyond 50% [Vea06] adds even more difficulties to achieve effective hole transport.

In this work Mg was used as p-type dopant. According to the literature, MME gives the best results in terms of hole concentration ($4.26 \times 10^{19} \text{ cm}^{-3}$ for Ga_N and $2.4 \times 10^{19} \text{ cm}^{-3}$ for In_{0.15}Ga_{0.85}N), mobility and crystal quality [Nam08], [Try09], [Mos13]. Therefore, MME was the growth method selected to study the p-type doping in Ga_N:Mg layers grown on semi-insulating (Fe-doped Ga_N) Ga_N/Sapphire templates with emphasis on doping efficiency and on the effects of Mg atomic incorporation on compensation effects, polarity inversion and the final hole concentration/mobility. The results were compared with Ga_N:Mg layers grown by conventional MBE on the same template type and with the state of the art [Nam08], [Mos13] and [Gun15].

1.3.2. Task 2: NID InGa_N growth

MBE is the technique to grow all III-Nitride layers studied in this thesis. Given the high complexity of the MBE system, the first part of this task will focus on the understanding and mastering all the needed knowledge to operate it.

The substrate selection is critical to grow InGaN layers. In this thesis both, Si(111) and commercial MOVPE GaN/Sapphire templates were used. Each of them has its own advantages and disadvantages. For Si(111) different buffer layers are needed to accommodate the lattice and thermal mismatch, as well as the different crystalline structure (Wurtzite and diamond). The effects of different buffer layers grown on Si(111), on the resulting InGaN layers properties were studied, namely: AlN, InAlN both grown by MBE, as well as sputtered InAlN and SiN produced by direct nitridation of the bare Si(111) surface.

Series of InGaN layers were grown to study the influence of growth temperature and III/V ratio on the layer properties. The III/V ratio refers to the relation between the active nitrogen (N^*) flux and the metal fluxes:

$$III/V = \frac{\phi_{In} + \phi_{Ga}}{\phi_N}$$

A heating tantalum filament covered with a pyrolytic boron nitride (PBN) diffusor (for homogeneity) heats up the substrate. The growth temperature is measured and controlled by a thermocouple located in close contact with the PBN diffusor and connected to a temperature controller. In addition, an optical pyrometer is used to measure the actual temperature on the substrate surface, once its emissivity has been set from a temperature calibration reference. For Si(111) this reference is taken from the transition temperature from the 7x7 to 1x1 surface reconstructions (860°C [Suz93]) to adjust the emissivity, so that the pyrometer provides the actual substrate temperature. For GaN/Sapphire templates, surface reconstruction changes are not easy to determine, so that the calibration is performed by measuring the time needed to desorb a given amount of Ga (monolayers) deposited on the surface [Gal07]. This process is generally checked by looking at the RHEED intensity changes. RHEED is also used to characterize *in-situ* the surface morphology while growing.

1.3.3. Task 3: NID InGaN characterization

The characterization of the grown layers provided essential information on material properties and the influence of growth parameters on them, allowing a quick feedback to set the optimal growth conditions. Characterization was aimed at morphological, structural, optical and electrical properties.

Structural characterization:

Reflection high energy electron diffraction (RHEED)

X-Ray diffraction (XRD)

Transmission electron microscopy (TEM)

Morphological characterization:

Scanning electron microscopy (SEM)

Atomic force microscopy (AFM)

Optical characterization:

Photoluminescence (PL)

Cathodoluminescence (CL)

Absorption spectroscopy

Electrical characterization:

I-V measurements

Hall Effect measurements

Chemical characterization:

Electron Energy Loss Spectroscopy (EELS)

I-V measurements will be of great importance on the characterization of the vertical electrical conductivity of the n-InGaN / buffer / p-Si heterointerface.

1.3.4. Task 4: growth and characterization of p-GaN / i-InGaN / n-GaN photovoltaic device using MBE

The design of efficient InGaN solar cells requires a deep understanding of the previously commented tasks that provide feedback on limitations and fundamental practical aspects to fabricate a real device. Photovoltaic devices based on p-GaN / i-In_{0.10}Ga_{0.90}N / n-GaN can be fabricated on n-type GaN(0001)/Sapphire templates by MBE once the previously commented tasks

are achieved. The final device was processed at the ISOM facilities and characterized in the solar simulator of the Electronics and Semiconductors Group (ElySe) of the Autonoma University of Madrid.

The most relevant parameters of a solar cell are the following:

- *Open circuit voltage* (V_{oc}), being the maximum output voltage achievable under open-circuit conditions (infinite load resistance).
- *Short circuit current* (I_{sc}), being the maximum output current delivered under short-circuit conditions (zero load resistance).
- *Fill factor* (FF), being the ratio of the maximum obtainable power to the product of the open circuit voltage and short circuit current.

1.4. Structure of the thesis

The 2nd chapter of this thesis is dedicated to the description of the most relevant properties of the III-Nitrides. Despite being discussed for the III-nitrides family of materials, it is focused on the GaN and InGaN.

In the 3rd chapter the fundamental experimental techniques employed on this work are described. Those techniques have been used to evaluate the structural, optical, electrical and chemical properties of the samples.

The 4th chapter is devoted to the results obtained on NID and Mg-doped GaN layers grown by MME and its comparison with NID and Mg-doped GaN layers grown in the intermediate regime.

The 5th chapter shows the results related to the growth of NID InGaN layers and the growth of a p-i-n device. In this chapter, the characterization of the InGaN layers and p-i-n devices is also discussed.

The 6th chapter is devoted to the growth of InGaN layers by DERI on Si(111). This chapter also shows the growth of four different buffers on Si and their influence on the InGaN properties and on the vertical electrical conduction.

The conclusions of this thesis and the future work are discussed on the 7th chapter.

2. III-Nitrides properties

The most important structural, optical and electrical properties, together with the band structure and the polarization fields of the binary and ternary nitrides are addressed in this chapter. The properties and elemental parameters of the binary materials were usually measured from bulk crystals grown on foreign substrates such as sapphire, GaAs and Si, or from self-assembled nanocolumns (NCs) or QWs. All of them are subjected to the effects of a high TDD, strain or partial relaxation. Nowadays, the development of III-Nitrides bulk crystal growth techniques, such as Na-flux, hydride vapour phase epitaxy (HVPE) and ammonothermal growth, allows the production of high quality GaN and AlN bulk crystals. They allow the precise determination of the properties and elemental parameters.

2.1. Structural properties of III-Nitrides

The electronic configuration of Ga and N atoms is:

Through a sp^3 hybridization s and p orbitals form four sp hybrid orbitals with a tetrahedron structure at 109.5° . In the case of Ga , three of them are filled with one electron and the fourth one is empty. For N , one is completed with two electrons and the other three are filled only with one. Then Ga and N atoms form three covalent bonds and one coordinate (or dipolar) covalent bond, formed between the two electrons of one N bond and the empty sp orbital of the Ga atom, as shown in figure 2.1. Remember that every covalent bond has an ionic character due to the difference in electronegativity between the constituent atoms. Only bonds between the same element are 100% covalent (N-N for example).

Figure 2.1 Schematic representation of the tetrahedron formed by 3 Ga atoms and 1 N atom. The arrow represents a coordinate covalent bond.

2.1.1. Crystalline structure

The high binding energy of the III-Nitrides, being maximum for AlN and progressively decreasing for GaN and InN, provides chemical, thermal and mechanical stability. Due to this high binding energy, the melting temperature is of 3214 °C, 2518 °C and 1873 °C, for AlN, GaN and InN, respectively [Edg94]. This difference is also present in the decomposition temperature in vacuum, of 1040 °C, 850 °C and 630 °C for AlN, GaN and InN, respectively. These values were obtained by measuring the partial pressure of nitrogen in vacuum while heating up a bulk layer of each binary compound. The extracted value is the one at which the partial pressure increases exponentially [Amb96]. Consequently, the InN should be grown at lower temperatures than the GaN, or under a much higher nitrogen pressure.

III-Nitrides are direct bandgap semiconductors with three possible crystalline structures: wurtzite (WZ), zinc blende (ZB) and rock salt. Under ambient conditions, the thermodynamically stable structure for bulk AlN, GaN and InN is the wurtzite one. The rock salt structure is stable only under high pressures. The high pressure applied to the crystal reduces the lattice dimensions and causes the inter-ionic Coulomb interaction favouring the ionic over the covalent nature of the bond. The structural phase transition to rock salt structure was experimentally observed at 22.9 GPa for AlN, 52.2 GPa for GaN and 12.1 GPa for InN [Mor08]. III-Nitrides in rock salt structure cannot be grown by any epitaxial technique.

The WZ structure has a hexagonal unit cell characterized by four lattice constants: three in-plane lattice constants (a_i) and one out-of-plane (c). Only three of them are independent, two in plane and the one out of plane. The wurtzite structure consists of two interpenetrating hexagonal close packed (hcp) sub-lattices, each with one type of atom, offset along the c-axis by $5/8$ of the cell height ($5c/8$) and containing six atoms of each type.

The ZB or cubic structure is stable when growing on cubic substrates such as Si, SiC, MgO and GaAs, where the substrate pushes the nitride to crystallize in a ZB structure. However, the WZ structure can be present in the form of extended defects (inclusions). In the ZB structure, the position of the atoms within the unit cell is identical to the diamond crystal structure, consisting of two interpenetrating face centred cubic sub-lattices, offset by one quarter of the distance along a body diagonal.

In both structures, WZ and ZB, each atom may be viewed as positioned in the centre of a tetrahedron with the four nearest neighbours located at the four tetrahedron corners. The main difference between both structures lies in the stacking sequence of the atomic planes. In WZ structure the stacking sequence of the (0001) planes of Ga and N is ...AaBbAaBbAa... along the $\langle 0001 \rangle$ direction, while in ZB structure the stacking sequence for the (111) close-packed planes is ...AaBbCcAaBbCc... (Figure 2.2). Therefore, when a change in the stacking sequence occurs (stacking fault), inclusions of cubic-like material may appear in a WZ structure and vice versa.

Figure 2.2 Atomic arrangements of: a) a wurtzite structure and b) a zinc blende structure.

Figure 2.3 shows the spatial arrangement of the interatomic bonds of the two neighbouring stacks (dashed line squares in figure 2.2). In WZ structure the second neighbours of the two central atoms have symmetric positions (fig. 2.3a), while in the ZB structure they have inverted positions (fig. 2.3b).

Figure 2.3 Spatial arrangements of the interatomic bonds in: a) WZ and b) ZB lattices.

In order to define the directions and the crystallographic planes in a WZ structure, Miller index nomenclature with four crystallographic axes is commonly used. This notation provides an intuitive and clear representation of the crystallographic planes in hexagonal structures and allows the unit vectors to be perpendicular to the respective planes. With this notation crystal planes and directions are expressed with Miller indices $[i,j,k,l]$ referred to the four unit vectors a_1 , a_2 , a_3 and c , represented in figure 2.4. The Miller indexes are not independent to each other; they hold the relation: $i + j + k = 0$.

Then, if $[UVW]$ are the indices referring to a triple axis reference system and $[uvw]$ referred to a four-axis reference system the relation between both is given by:

$$U = u - t \quad (2.1.1.1)$$

$$u = \frac{2U - V}{3} \quad (2.1.1.2)$$

$$V = v - t \quad (2.1.1.3)$$

$$v = \frac{2V - U}{3} \quad (2.1.1.4)$$

$$t = -(u + v) = -\frac{U + V}{3} \quad (2.1.1.5)$$

$$W = w \quad (2.1.1.6)$$

$$w = W \quad (2.1.1.7)$$

In the Miller notation the $[100]$ direction is given by $[2\bar{1}\bar{1}0]$. The planes corresponding to the hexagonal prism faces are:

$(100), (010), (\bar{1}10), (\bar{1}00), (0\bar{1}0)$ and $(1\bar{1}0)$ for a three axis reference, corresponding to:

$(10\bar{1}0), (01\bar{1}0), (\bar{1}100), (\bar{1}010), (0\bar{1}10)$ and $(1\bar{1}00)$ in a four axis reference.

It is easy to see that they are equivalent planes. The most important crystal planes in the WZ structure are the c-plane $\{0001\}$, which is the most common plane to grow on, the non-polar m- $\{1-100\}$ and a- $\{11-20\}$ planes and the semi-polar r-plane $\{1-102\}$.

Figure 2.4 Unit vectors represented on a hexagonal prism.

2.1.2. Polarity

The most commonly used crystal plane to grow WZ GaN is the c-plane, $\langle 0001 \rangle$. The atoms are stacked in atomic bilayers with cations on one side and anions on the other side. The WZ structure is not centrosymmetric (no inversion symmetry point) which results in polar faces and therefore two inequivalent growth directions, as shown in figure 2.5. Thus, two polarities can be distinguished: Ga-polar (fig. 2.5a) and N-polar (fig. 2.5b), also referred to as Ga-face and N-face.

Figure 2.5 Atomic arrangement in WZ GaN for: a) Ga-polar and b) N-polar.

Ga-polar corresponds to the $[0001]$ direction, in which Ga atoms are located on top of the basal bilayer, while the N-polar stands for the $[000\bar{1}]$ direction. The polarity is a bulk property that strongly depends on the growth method, the substrate used, the way it is prepared and the growth conditions. Ga-polar nitride layers result when grown by MOVPE on Si-face 6H-SiC and on bare sapphire. High quality Ga-polar GaN layers result when grown by MBE on AlN buffered sapphire and on silicon substrates, while on bare wafers they present N-polarity [Hel98], [Sum98]. Brubaker and co-workers demonstrated that the growth conditions also affects the polarity of the layer [Bru15]. The polarity is established at the very beginning of the growth, during the deposition of the first bilayer, and

it usually remains unchanged during the rest of the growth. However, polarity could be locally inverted at structural defects, such as, inversion domains, stacking faults, substrate surface steps or at different substrate surface termination sites. Only in such cases, two different polarities could coexist in the same epilayer.

The two types of polarities, Ga- and N-polar, affect the growth kinetics and the layer properties in a different way, owing to the difference in the number of dangling bonds ($3/4$ for Ga-polar and $1\frac{1}{4}$ for N-polar). A larger number of dangling bonds (N-polar) reduces the ad-atom surface diffusion length during the growth, leading to rougher layers with lower chemical stability than the Ga-polar ones. In addition, the formation energy of point defects and dislocations is lower for the N-polar case. Thus, making the incorporation of impurities far easier for the N-polar case, as well as the formation of point defects and dislocations [Lil99], [Pta00], [Pta01].

It is worth to mention that the layer termination and the layer polarity are different concepts. The layer termination is a property of the surface, related to the atomic reconstruction. It does not depend on the layer polarity. For instance, a Ga-polar layer could be N terminated under extreme N-rich conditions [Zyw98].

2.1.3. Mechanical properties and strain

The stress and strain present inside a continuous elastic material (such as a block of rubber, a piece of iron or a GaN layer) are connected by a linear relationship that is mathematically similar to the Hooke's spring law.

However, the strain state in a solid medium around an arbitrary point cannot be described by a single vector. The same portion of material, no matter how small, can be compressed, stretched, and sheared at the same time, along different directions. Likewise, the stresses in that material portion can be at once pushing, pulling, and shearing.

In order to reflect this complexity, two second order tensors are required, the stress tensor (σ_{ij}) and the strain tensor (ε_{kl}). Their relation is given by:

$$\sigma = c\varepsilon \quad (2.1.3.1)$$

Where c is the stiffness or elasticity tensor, a fourth order tensor. It could be expressed also in the following form:

$$\varepsilon = s\sigma \quad (2.1.3.2)$$

Where s is the compliance tensor, the inverse of the elasticity tensor. The elasticity tensor is represented by a matrix of $3 \times 3 \times 3 \times 3 = 81$ real numbers. Then the Hooke's law holds that:

$$\sigma_{ij} = \sum_{k=1}^3 \sum_{l=1}^3 c_{ijkl} \varepsilon_{kl}; \quad i, j = 1, 2, 3 \quad (2.1.3.3)$$

At a specific point of the material the strain tensor (ε) represents the displacement of the particles in the neighbourhood of the point, while the stress (σ) tensor specifies the compression, stretching or shearing forces that the particle is suffering at that specific point. The elasticity tensor (c) is a property of the material and depends on temperature, pressure, microstructure and composition.

Due to the inherent symmetries of the three tensors, only 21 elastic coefficients are independent. For our case study, the wurtzite structure, there are 5 independent elastic constants. Hence, the relation between stress (σ_{ij}) and strain (ε_{kl}) for a hexagonal crystal is given by the following equation:

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{zx} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{C_{11} - C_{12}}{2} \end{pmatrix} \times \begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ 2\varepsilon_{yz} \\ 2\varepsilon_{zx} \\ 2\varepsilon_{xy} \end{pmatrix} \quad (2.1.3.4)$$

Only C_{11} , C_{12} , C_{13} , C_{33} and C_{44} coefficients are independent.

The difference in *in-plane* lattice constants between the epilayer (a) and the substrate (a_0) is the main source of strain in the epilayer that accommodates its lattice constant to that of the substrate. As a result, the unit cell of the grown layer is deformed (bond length and angle) and strain energy is building up as the epilayer thickness increases. Another source of strain refers to the difference in thermal expansion coefficients. Once the growth is finished, upon the cooling down process the substrate and the epilayer do not cool at the same rate and the substrate forces the grown layer to follow its *in-plane* lattice change. This strain may be partially relaxed by the generation of dislocations, resulting in a “residual” strain of thermal origin. This is also the reason for having wafer or layer bowing, which is measurable *in situ* (during growth) by reflectometry.

There are two types of deformation: (i) when $a > a_0$ and the grown layer results under *in-plane* biaxial compressive strain (fig. 2.6a), or (ii) when $a < a_0$ and the grown layer results under *in-plane* biaxial tensile strain (fig. 2.6b). It is worth to mention that an *in-plane* compression (tension) inevitably induces a uniaxial *out-of-plane* tension (compression) along the c-axis (the volume of the unit cell remains constant). The energy accumulated by strain is generally released through the formation of dislocations, which are very common in nitrides (to be discussed in section 2.2.2.1).

Figure 2.6 Schematic representation of lattice parameter accommodation between substrate and epilayer resulting in: a) compressive biaxial strain and b) tensile biaxial strain.

In the case of biaxial strain, which preserves the hexagonal symmetry of the unit cell, the strain tensor is reduced to three independent components:

$$\varepsilon_{xx} = \frac{a - a_0}{a_0} \quad (2.1.3.5)$$

$$\varepsilon_{yy} = \frac{b - b_0}{b_0} \quad (2.1.3.6)$$

$$\varepsilon_{zz} = \frac{c - c_0}{c_0} \quad (2.1.3.7)$$

Elastic constant (GPa)	AlN	GaN	InN
C₁₁	396	359.4	223
C₁₂	137	129.2	115
C₁₃	108	92.0	92
C₃₃	373	389.9	224
C₄₄	106	98.0	48
Reference	[Vur01]	[Nakam12]	[Vur01]

Table 2.1 Components of the elasticity tensor for AlN, GaN and InN [Vur01].

Where a and b are the *in-plane* lattice constants and c is the *out-of-plane* lattice constant of the strained epilayer, and a_0 , b_0 and c_0 are the corresponding ones to the substrate. For wurtzite structures, both *in-plane* lattice constants are equal and thus $\varepsilon_{xx} = \varepsilon_{yy}$. The strain along the c -direction is not independent from the *in-plane* one and is given by:

$$\varepsilon_{zz} = -2 \frac{C_{13}}{C_{33}} \varepsilon_{xx} = -2 \frac{C_{13}}{C_{33}} \frac{a - a_0}{a_0} \quad (2.1.3.8)$$

The elasticity tensor coefficients are shown in table 2.1 for AlN, GaN and InN.

2.2. Structural defects

Crystalline solids are viewed as atomic periodic structures. In ideal crystals the atoms, ions or molecules (hereafter only atoms) form the periodic crystal lattice with fixed unit cell parameters. However, real crystals contain imperfections, known as crystallographic defects, which locally disturb the regular arrangement of the atoms, breaking the perfect translational symmetry in the crystal, which in most cases generate electron (hole) states within the bandgap, thus strongly affecting the crystal properties. These defects can be classified according to their dimensional extension as: point, line, planar/surface and bulk/volume defects.

2.2.1. Point defects

Point defects are considered as zero dimensional ones with an extension of one atom and limited to a given lattice site. Point defects occur during growth, doping, heating, cooling, plasma exposition and plastic deformation. As native or intrinsic defects, point defects are most common in semiconductors, having a strong effect on their electrical and optical properties like carrier lifetime, mobility, radiative or nonradiative recombination and compensation effects when doping. The most relevant point defects are: interstitials (atoms incorporated at non-substitutional lattice sites), vacancies (lack of an atom at a lattice site) and anti-sites (exchanged anion-cation at a lattice site). As mentioned before, point defects can act as recombination centres, which trap photo-generated carriers before they reach a solar cell terminal, thus, reducing the carrier lifetime and its overall efficiency. A similar situation occurs for injected carriers in a LED or LD reducing the internal quantum efficiency (IQE) of the device. Further information on the physics of point defects, can be found in references [Zha91], [Wal96], [Wal04] and [Sta00].

2.2.2. Line defects

2.2.2.1 Dislocations

Linear or one-dimensional defects are those whose size in one dimension is much higher than in the other two dimensions. Dislocations, for instance, are linear defects. They represent the border of an unfinished plane in the crystal.

Every dislocation is uniquely defined by its line of dislocation and its Burgers vector. The line of dislocation is the border delimiting a region of disorder within the crystal and it can also be understood as the line of the longest dimension. The quantitative definition of a dislocation is given by the Burgers vector. Its atomistic definition is derived from the Burgers loop in the ideal and the deformed crystal lattices. The loop in the distorted crystal is a closed clockwise circulation around the dislocation line as a chain of basis vectors of the lattice, loop OPQMN (figs. 2.7a and b). The second Burgers loop is plotted on the ideal crystal, i.e. without a dislocation, loop OPQMN (figs. 2.7a and b). The difference between the starting and ending point of both loops defines the Burgers vector (**b**) that describes the magnitude and direction of the lattice distortion, on figures 2.7c and d: $\vec{b} = \overrightarrow{QM}$

Figure 2.7 Determination of the Burgers vector for: a), c) an edge dislocation and b), d) a screw dislocation. Image was adapted from [Kit76].

Every dislocation is uniquely defined by only one Burgers vector and it is invariable in every point of the dislocation. It implies that the dislocation cannot start or terminate inside the crystal because then $\mathbf{b}$ would vary from 0 to any specific value. It could only start or terminate at the crystal surface; the interface with another crystal; or on another defect or dislocation.

Depending on the angle (φ) between the dislocation line and the Burgers vector, dislocations can be classified in the following way:

- When $\varphi = 90^\circ \rightarrow$ edge dislocation. Figure 2.7a shows a pure edge dislocation, visualized as being caused by the abrupt termination of an atomic plane inside the crystal. In this case, the surrounding planes are bent around the dislocation line, being the crystal structure perfectly ordered on either side.
- When $\varphi = 0^\circ \rightarrow$ screw dislocation. Figure 2.7b shows a pure screw dislocation. In order to visualize a screw dislocation, let us consider a cut of the crystal along a plane and a slip of one half across the other by a lattice vector, when the halves fit back together without leaving a defect. If the cut only goes part of the way through the crystal and then slip, the boundary of the cut is a screw dislocation. It comprises a structure in which a helical path is traced around the dislocation line by the atomic planes in the crystal lattice.
- When $0^\circ < \varphi < 90^\circ \rightarrow$ the defect is called a mixed dislocation and can be decomposed into pure edge and screw dislocations components.

Dislocations can move under external applied stress giving rise to the following type of movements:

- Glide or conservative motion: when the dislocation moves in the plane which contains both, its line and Burgers vector. A dislocation able to move in this way is named *glissile* and those moving differently are called *sessile*.
- Dislocation motion by climb occurs when it moves out of the glide plane and thus normal to the Burgers vector.

Threading dislocations (TDs) are those with a dislocation line perpendicular to the sample surface [Mor09]. In III-Nitrides TDs occur usually along the [0001] direction, such as the *c*-plane GaN. GaN layers grown on sapphire have TDs densities (TDDs) in the range of 10^8 - 10^{10} cm⁻² for standard growth and 10^6 - 10^7

cm^{-2} for epitaxial lateral overgrowth method (ELOG) [Muk03], [Det01], while for bulk GaN (grown by HVPE, ammonothermal method, Na-flux) TDD can be reduced down to 10^4 cm^{-2} .

As line defects, TDs may have screw, edge and mixed nature. Screw dislocations have the dislocation line parallel to the c-axis and the Burgers vector. In general, mixed TDs are decomposed into pure screw and edge TDs, and therefore will not be specifically considered in this work. Both edge and screw TDs nucleate in the early stages of the growth and they thread to the crystallites surface, therefore most likely arising from islands merging during growth. When the elastic energy is accumulated in an epilayer, it might be partially released by dislocation formation. The inhomogeneous strain field induced by the dislocation may lead to surface roughening by changes induced in the growth regime. Dislocations can attract point defects (gettering process) like $V_{Ga} - (O_N)_2$ and $V_{Ga} - O_N$ (deep acceptors) and become electrically active [Els98]. Screw dislocations are electrically active and may act as non-radiative recombination centres [Els97]. Mixed dislocations, with a screw component, act also as non-radiative recombination centres [Ros97]. The ideal TDs are charged lines that mostly affect mobility.

TDs may also act as conducting pathways in Schottky barriers and LEDs leading to increased leakage currents that may eventually result in device short circuit [Hsu01]. In general, a high dislocation density of any type has a detrimental influence on the device performance, reducing the efficiency in charge transport, IQE, and electrical noise, being still a major technological challenge.

To study misfit dislocations (MDs) some concepts should be first introduced. The relative difference between the *in-plane* lattice parameter of the relaxed substrate (a_s^{rel}) and the one of the relaxed epilayer (a_e^{rel}) is called lattice mismatch (see fig. 2.8a):

$$\frac{\Delta a^{rel}}{a_s^{rel}} = \frac{a_e^{rel} - a_s^{rel}}{a_s^{rel}} \quad (2.2.2.1)$$

Lattice mismatch gives rise to elastic strain and changes elastically the lattice parameter of the grown layer until relaxation (plastic) occurs. The difference between the strained lattice parameter of the epitaxial layer and the relaxed lattice parameter of the substrate is called lattice misfit (fig. 2.8b).

$$\frac{\Delta a^{str}}{a_s^{rel}} = \frac{a_e^{str} - a_s^{rel}}{a_s^{rel}} \quad (2.2.2.2)$$

Figure 2.8 a) Relaxed lattice parameters of epilayer and substrate b) heteroepitaxial system with misfit dislocation formation and c) MDs network in a heteroepitaxial system.

Strain can be relaxed by the formation of: surface undulations, 3D islands and MDs (fig. 2.18c). The first two mechanisms take place at the initial stage of the growth, while the latter is dominant for thicker layers. In principle, MDs are not supposed to thread up the epilayer and are very efficient in releasing strain. However, TDs can be interconnected to the MDs network [Keh01].

2.2.3. Planar defects

Planar or two-dimensional defects are interfaces between homogeneous regions of the material that include: surfaces, interfaces, grain boundaries, twin boundaries and stacking faults.

A real crystal has a finite size and thus surfaces. The surface is the interface between the crystal and the surrounding media (usually air). The surface has a certain energy formation and a certain strain component (like in the case of a spherical liquid droplet).

2.2.3.1 Grain boundaries

The heteroepitaxy of III-Nitrides on highly mismatched substrates (such as InGaN on Si) leads to the formation of isolated micro crystallites at the early stages of the growth that tend to coalesce as the growth evolves and grains form by energy minimization. Differences in grain orientation can arise from an inhomogeneous substrate or crystallite nucleation leading to either an inclination of the *c*-axis between different grains, named *tilt* (fig. 2.9a), or a rotation of the basal plane between different grains around the *c*-axis, named *twist* (fig. 2.9b).

Figure 2.9 Schematic representations of the micro crystallites of an epilayer when: a) tilt and b) twist is presented.

In the case of tilted grains, a network of screw dislocations forms at the boundaries between them, while for the twisted grains a network of edge dislocations appear at grain boundaries. This can only be applied to low angle grain boundaries.

2.2.3.2 Staking faults

Stacking faults appear in III-Nitrides as alterations of the stacking sequence of Ga and N atomic planes along the (0001) direction. The stacking sequence for a WZ structure is AaBbAaBbAa and its modification may lead to AaBbCcBbCcBbCc or AaBbCcAaBbCc sequences, resulting in ZB inclusions. From another viewpoint, stacking faults may be regarded as “Quantum Dots” of cubic material within a hexagonal matrix, thus having strong emission properties. There are three different types of stacking faults:

Type 1 (I_1) contains one violation of the stacking rule of the Wz structure: AaBbAaBbCcBbCcBb...

Type 2 (I_2) contains two violations of the stacking rule of the Wz structure: AaBbAaBbCcAaCcAa...

Extrinsic (E) BSFs have an additional Cc layer inserted on the midst of the Wz stacking sequence: AaBbCcAaBbAaBbAa...

Type 3 BSFs are not going to be considered in this work because it is intrinsic on the ZB stacking sequence and not on the Wz one. For a deeper insight, the reader is referred to [Sta98] and [Lah14].

The coalescence of islands with different stacking order leads to the formation of complex planar defects: stacking mismatch boundaries (SMBs) and inversion domain boundaries (IDBs). These are typically flat and parallel to the [0001] direction, starting at the substrate surface and running through the entire thickness of the epilayer. In SMBs the stacking sequence is altered across the boundary, whereas at IDBs the occupation of the Ga and N sub-lattices is reversed, so that the polarity changes across the boundary.

2.3. Band structure

III-Nitrides are direct bandgap semiconductors with the conduction band (CB) minimum and the valence band (VB) maximum located at the centre of the Brillouin zone (Γ point, where $\vec{k} = 0$). In addition, a high excitonic binding energy and wide spectral range covered by ternary alloys are major advantages that make them optimal candidates for optoelectronic applications.

While in most ZB semiconductors the VB is degenerate, the case of III-Nitrides is different. In III-Nitrides the hexagonal symmetry of the unit cell together with the ionic character of the *Ga-N* chemical bond generates an asymmetry in the local electric field and a VB splitting (known as *crystal field* splitting) into two sub-bands: one non-degenerate Γ_1 state and two degenerated Γ_6 states. Additionally, the *spin-orbit* interaction (Δ_{SO}) breaks the symmetry of the Γ_6 states splitting them into two non-degenerate sub-bands. Figure 2.10 illustrates the case of WZ GaN. Thus, the VB is split into three sub-bands: the *heavy hole* (HH), the *light hole* (LH) and the *crystal-field split-off hole* (CH). The energies of the valence sub-bands HH (Γ_9), LH (Γ_7) and CH (Γ_7) are given by Chuang and Chang [Chu97]:

$$E_V^{HH} = E_V^0 + \Delta_{CF} + \frac{1}{3} \Delta_{SO} \quad (2.3.0.1)$$

$$E_V^{LH,CH} = E_V^0 + \frac{\Delta_{CF} - \frac{1}{3} \Delta_{SO}}{2} \pm \frac{1}{2} \sqrt{\left(\frac{\Delta_{CF} + \frac{1}{3} \Delta_{SO}}{2}\right)^2 + \frac{2}{9} \Delta_{SO}^2} \quad (2.3.0.2)$$

Where E_V^0 is a reference VB energy, which can be set to zero, Δ_{CF} is the *crystal field* splitting and Δ_{SO} stands for the *spin-orbit* splitting. Even though both splittings cannot be directly measured, they can be indirectly estimated from photoluminescence and photoreflectance measurements of the free excitons A, B and C (excitons involving the three valence bands) as the energy difference between the valence band levels:

$$E_V^{HH} - E_V^{LH,CH} = \frac{\Delta_{CF} + \Delta_{SO}}{2} \mp \frac{1}{2} \sqrt{(\Delta_{CF} + \Delta_{SO})^2 - \frac{8}{3} \Delta_{SO} \Delta_{CF}} \quad (2.3.0.3)$$

The CB energy for GaN can be written as:

$$E_C = E_V^{HH} + E_g = E_V^0 + \Delta_{CF} + \frac{1}{3} \Delta_{SO} + E_g \quad (2.3.0.4)$$

Concerning the effective masses, the symmetry of the unit cell in III-Nitrides with ZB structure allows a parabolic approximation of the VB and CB following the expressions:

$$E(k) = E_0 \pm \frac{\hbar^2}{2 \frac{d^2 E}{dk^2}} k^2 = E_0 \pm \frac{\hbar^2}{2m^*} k^2 \quad (2.3.0.5)$$

Where m^* stands for the *effective mass* of electrons and holes, which in this particular case are isotropic for the three spatial directions. However, III-Nitrides with hexagonal structure present different energy band profiles for the *in-plane* directions (x-y) that yield different values for the effective mass $m_{||}$ parallel to the growth plane and $m_{\perp}$ for the z direction. The effective mass approximation, which is now more strictly constrained to the $\vec{k} = 0$ proximity, gives:

$$E(k) = E_0 \pm \frac{\hbar^2}{2} \left(\frac{k_z^2}{m_{\perp}^*} + \frac{k_x^2 + k_y^2}{m_{||}^*} \right) \quad (2.3.0.6)$$

Thus, two effective masses for electrons and two for holes in each VB (up to six) can be defined in WZ nitrides. Table 2.3 summarizes the values of various crystal parameters.

Figure 2.10 a) Schematic representation of the effect of the crystal field and spin-orbit interaction on the valence band maximum. b) Band diagram of GaN. The three valence sub-bands are represented as heavy holes (HH), light holes (LH) and crystal holes (CH) [Chu96].

2.3.1. Bandgap energy offset

When fabricating a device, layers of different materials are grown upon each other (stack). The knowledge of the band offsets is important to determine the potential confinement properties in MQWs and heterojunctions.

An energy offset (E_{off}) is used to align the bandgaps of different materials. In this thesis GaN is chosen as the reference value for III-Nitrides ($E_{off} = 0$ eV). Then, the energies of the CB and VB edges can be written as:

$$E_V = E_{off} \quad (2.3.1.1)$$

$$E_C = E_V + E_g = E_{off} + E_g \quad (2.3.1.2)$$

The VB-offset of AlN/GaN (E_{off}^{AlN}) heterojunction is taken as 1.12 eV, which corresponds to 40% of the total bandgap difference between the binaries

[Wes06]. This determination was obtained from a measurement of the linewidth of the excitonic transition in an $\text{Al}_{0.18}\text{Ga}_{0.82}\text{N}$ alloy. This value is larger than the previously reported 0.7 eV in [Mar96] that was estimated by x-ray photoemission spectroscopy. However, the latter is closer to the real value as it is free from effects introduced by interface defects and other type of inhomogeneities.

The most widely cited value for the VB offset of InN/GaN heterojunctions is that reported by Martin et al. [Mar96] ($E_{\text{off}}^{\text{InN}} = 1.05 \text{ eV}$) over twenty years ago. More recent studies give values between 0.58 [Kin08] and 0.62 eV [Mos10]. The band alignments between the three binaries are shown in figure 2.11.

For ternary alloys, the VB offset energy is often calculated from [Pal04]:

$$E_{\text{off}}^{\text{InGaN}} = \frac{E_{\text{off}}^{\text{InN}}(E_g^{\text{InGaN}} - E_g^{\text{GaN}}) - E_{\text{off}}^{\text{GaN}}(E_g^{\text{InGaN}} - E_g^{\text{InN}})}{E_g^{\text{InN}} - E_g^{\text{GaN}}} \quad (2.3.1.3)$$

Figure 2.11 Band alignment between the III-Nitride binaries.

2.3.2. Bandgap dependence with temperature and strain

Any variation induced on the bond length will lead to changes of the band structure and thus on the bandgap of the semiconductor. This sub-section will focus on the influence of the temperature and strain on the bandgap value.

When the temperature increases, the crystal lattice expands and the atomic oscillations around their equilibrium lattice site increase. A larger atomic separation leads to lower bandgap energy. This dependence is given by the empirical expression developed by Varshni [Var67]:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \theta_D} \quad (2.3.2.1)$$

Where $E_g(0)$ is the bandgap energy at 0 K, α is an empiric constant and θ_D is the Debye's temperature. Values of these parameters are given in table 2.3.

This expression fits relatively well for unstrained layers. However, for strained layers Varshni's equation is not appropriate and a more accurate description should be introduced. The expression proposed by Fan [Fan51] agrees better with the experimental data for strained layers:

$$E_g(T) = E_g(0) - \frac{a_B}{e^{\left(\frac{\theta_E}{T}\right)} - 1} \quad (2.3.2.2)$$

Where a_B is a constant related to the average photon-phonon interaction and the θ_E is the Einstein's temperature.

The PL emission energies related to free excitons follow quite accurately the bandgap temperature dependence given by Fan's and Varshni's equations. A similar behaviour is found for transitions associated with impurity states, either donors or acceptors (free-to-bound), for temperatures above the carrier freeze-out into the impurity states (neutral donors or acceptors).

The influence of the strain on the bandgap can be quantified from a second order perturbation model, based on a ***k.p*** method [Chu97]. In the strained layer, the *VB* states are modified as:

$$E_V^{HH} = E_V^0 + \Delta_{CF} + \frac{1}{3} \Delta_{SO} + \theta_\epsilon + \lambda_\epsilon \quad (2.3.2.3)$$

$$E_V^{LH,CH} = E_V^0 + \frac{\Delta_{CF} - \frac{1}{3} \Delta_{SO}}{2} + \frac{1}{2} \theta_\epsilon + \lambda_\epsilon \pm \frac{1}{2} \sqrt{\left(\frac{\Delta_{CF} + \frac{1}{3} \Delta_{SO} + \theta_\epsilon}{2} \right)^2 + \frac{2}{9} \Delta_{SO}^2} \quad (2.3.2.4)$$

Where θ_ϵ and λ_ϵ stand for:

$$\theta_\epsilon = D_3 \epsilon_{zz} + D_4 (\epsilon_{xx} + \epsilon_{yy}) \quad (2.3.2.5)$$

$$\lambda_\epsilon = D_1 \epsilon_{zz} + D_2 (\epsilon_{xx} + \epsilon_{yy}) \quad (2.3.2.6)$$

And D_1, D_2 are hydrostatic deformation potential constants affecting the transitions between the CB and VBs, and D_3, D_4 are uniaxial deformation potentials that characterize the splitting of the VB in the presence of strain perpendicular to the [0001] direction (D_4) and along the [0001] direction (D_3).

Now, the *CB* states are given by:

$$E_C(strain) = E_V^{HH}(strain) + E_g + a_{\parallel} \epsilon_{zz} + a_{\perp} (\epsilon_{xx} + \epsilon_{yy}) \quad (2.3.2.7)$$

Where $a_{\parallel}$ and $a_{\perp}$ are the deformation potentials of the epilayer for the out-of-plane and in-plane directions. The change in energy bandgap is, then:

$$\Delta E_g(strain) = 2\epsilon_{xx} \left\{ [a_{\perp} - D_2 - D_4] - \frac{C_{13}}{C_{33}} [a_{\parallel} - D_1 - D_3] \right\} \quad (2.3.2.7)$$

Despite huge efforts to simulate and measure the mentioned material basic parameters, there is a strong dispersion and even contradictory results in the literature, mostly due to poor quality material and differences in strain arising from specific heteroepitaxial growth techniques. Table 2.2 summarizes the values of these parameters.

	AlN	GaN	InN		AlN	GaN	InN	
$\Delta_{CF}[eV]$	-164	19	41	Electrons	$m_{\parallel}^*/m_0$	0.28	0.2	0.12
$\Delta_{SO}[eV]$	19	14	1		$m_{\perp}^*/m_0$	0.32	0.2	0.12
$a_{\parallel}[eV]$	-9.0	-6.5	-3.5		HH	$m_{\parallel}^*/m_0$	2.04*	1.27*
$a_{\perp}[eV]$	-9.0	-11.8	-3.5	$m_{\perp}^*/m_0$		2.08*	1.02*	1.25*
$D_1[eV]$	-3.0	-3.0	-3.0	LH		$m_{\parallel}^*/m_0$	2.04*	1.27*
$D_2[eV]$	3.6	3.6	3.6		$m_{\perp}^*/m_0$	0.20*	0.11*	0.09*
$D_3[eV]$	9.6	8.82	8.82		CH	$m_{\parallel}^*/m_0$	0.24*	2.04*
$D_4[eV]$	-4.8	-4.41	-4.41	$m_{\perp}^*/m_0$		2.04*	0.14*	0.12*
$\alpha[eV/K]$	1.8×10^{-3}	7.7×10^{-4}	2.45×10^{-4}	$\theta_D[K]$		1462	600	624

Table 2.2 Values of the crystal field and spin-orbit splitting, deformation potentials, effective masses and coefficients of the Varshni's law. Values are taken from references [Vur01], [Vur03] and [Pugh99].

2.4. Optical properties of III-Nitrides

The most important features related to the optical properties of III-Nitrides will be addressed in this section. The possible radiative recombination transitions in a direct bandgap semiconductor are presented in figure 2.12.

Figure 2.12 Possible radiative recombination transitions in a direct bandgap semiconductor: band to band (BB), bound to free (E_D), free to bound (E_A), donor acceptor pair (E_{DA}), free exciton (E_{FX}) and donor or acceptor bound exciton (E_{DX} or E_{AX}).

2.4.1. Excitonic emissions

Excitons are quasi-particles that form in semiconductors when electrons and holes are bound into pair states via Coulomb interaction. When exciting an electron from the VB to the CB, it leaves a “missing” electron at the valence band (hole). The properties of holes are similar to those of missing electrons: they are fermions with spin and charge opposite to VB electrons. Then a Coulomb interaction (attraction) may happen between CB electrons and VB holes.

Mathematically, the study of a single electron-hole pair in parabolic bands is identical to that of the hydrogen atom, with the hole acting as a proton. In semiconductor physics, the Schrödinger equation describing the electron-hole pair is called the Wannier equation, and the bound-pair state is the Wannier exciton. The total energy of the exciton is:

$$\hbar\omega = E_g - E_{FX}/n^2 \quad (2.4.1.1)$$

The total energy is reduced, as compared with uncorrelated carriers, by the exciton binding energy (E_{FX}). The exciton can be found in a series of excited states described by the quantum number n . The exciton binding energy is given by:

$$E_{FX} = \frac{1}{2} \frac{\mu \cdot e^4}{(4\pi\hbar\epsilon\epsilon_0)^2} \quad (2.4.1.2)$$

Where μ is the reduced mass of the exciton, i.e. $1/\mu = 1/m_e^* + 1/m_h^*$ (2.4.1.3).

As it was discussed in the previous section, in III-Nitrides the VB splits into 3 sub-bands giving rise to 3 possible excitons:

- (i) An exciton formed by an electron and a heavy hole (HH), called A -exciton (FXA),
- (ii) The one corresponding to light holes (LH), referred to as B -exciton (FXB)
- (iii) That related to crystal holes (CH), labelled as C -exciton (CFX).

In addition to free excitons, bound excitons (BX) as a FX captured by an impurity, either charged or neutral, can also be observed. The BX can be formed by direct trapping of a FX , or by the sequential trapping of a hole (electron) and an electron (hole).

The emission energy corresponding to a BX is lower than that of a FX by the impurity thermal depth. The reduction of the FX energy, upon being trapped by the impurity (localization energy) is not easy to calculate, and it is generally approximated by the empirical Hayne's rule as $E_{LX} = 0.2E_D$ for donors and $E_{LX} = 0.1E_A$ for acceptors. Then, the BX energy is given by:

$$\hbar\omega = E_{DX} = E_{FXA} - 0.2E_D \quad (2.4.1.4)$$

Or

$$\hbar\omega = E_{AX} = E_{FXA} - 0.1E_A \quad (2.4.1.5)$$

At cryogenic temperatures, the PL spectrum is dominated by neutral donor bound excitons (D^0X). At temperatures higher than the D^0X dissociation value, the spectrum is dominated by FX s (for high quality layers). The BX emission can also be identified by its intensity and energy dependence on excitation power. Once excitons are trapped by all existing donor states the D^0X emission intensity saturates and a further increase in excitation power enhances the emission from FX s at higher energy. In all exciton cases, their emission energies at a given temperature do not change with excitation power (to the limit of heating the sample).

2.4.2. Donor-Acceptor pairs

Impurities (intentionally introduced or not) may generate single or multiple states within the bandgap, acting as donors or acceptors with single or multiple charge states. Recombination between free carriers and localized ones at impurities, labelled as free-to-bound, or bound-to-free transitions, generate photons with and energy given by:

$$\hbar\omega = E_g - E_i + \frac{1}{2}kT \quad (2.4.2.1)$$

Where kT is the thermal energy of the carrier and E_i is the impurity state energy (E_A or E_D).

When the density of donors and acceptors is comparable, radiative recombination transitions between trapped electrons and holes (donor-acceptor pair, DAP) may become dominant. If r is the distance between the donor and acceptor impurities, the photon energy is given by:

$$\hbar\omega = E_g - E_D - E_A + \frac{e^2}{4\pi\epsilon\epsilon_0 r} \quad (2.4.2.2)$$

Where the last term accounts for the Coulomb energy stored in the donor-acceptor interaction.

The DAP transitions depend strongly on temperature because at high enough temperatures the carriers will no longer be trapped (ionization of the impurities) and the DAP will not be dominant anymore. They also show a distinct fingerprint in time-resolved PL experiments, because the donor-acceptor pair distance may be short or long, giving rise to multiple time constants (tails).

The interaction of phonons with excitons leads to phonon-assisted transitions. These transitions are quite common in semiconductors with strong ionic character, such as III-Nitrides. This exciton-phonon interaction shows up as PL peak replicas (phonon replicas) at energy steps of fixed energy (phonon energy). The emission intensity ratio between the replicas and the excitonic emission that they replicate depends on the strength of the phonon coupling but, in general, decreases with the number of phonons involved. High quality GaN layers show PL spectra with clear emission lines corresponding to free excitons (A and B), donor-bound excitons (D^0X) and their corresponding phonon replicas. The exciton-phonon (LO) interaction energies in AlN, GaN and InN are 113 meV, 91.8 meV and 73 meV, respectively [Dav98], [Har02] and [Kas02].

2.4.3. Mg- related emissions in doped III-Nitrides

P-type doping of III-Nitrides is still a real bottleneck to develop devices. Mg is the most efficient and commonly used acceptor for III-Nitrides, but the Mg acceptor thermal depth and thus the ionization factor pose a real limitation to the maximum hole density attainable. This depends strongly on the specific III-Nitride considered, being E_A of about 170 meV in GaN with an ionization factor of a few percent at RT. These values increase significantly in AlGaIn alloys as the mole fraction increases, making the problem even worse. Besides, the need of a very high atomic Mg density significantly decreases mobility and produces strong

compensation. Eventually, it can also lead to polarity inversion, complex formation and surface roughening.

Figure 2.13 a) Possible radiative recombination transitions in Mg-doped GaN and their corresponding energies and b) PL spectrum of two Mg-doped GaN films with different Mg concentration, adapted from [Mon10]. Transitions are labelled on the spectrum. Values were taken at 2K. References [Mon08], [Mon09], [Mon10], and [Vur03].

Figure 2.13 shows a diagram of the most common PL transitions observed in a Mg-doped GaN layer. The two PL emission lines at 3.4714 eV and 3.4723 eV are associated to donor bound excitons related to a neutral O donor on the N substitutional site and to Si donor on Ga substitutional site respectively [Mon08].

A rather “shallow” acceptor-related emission at 3.466 eV, called ABE_1 (acceptor 1 bound exciton) [Ste03], [Ler99] is dominant at low to moderate Mg concentrations, being related to Mg-H complexes. Once the complex is broken by thermal annealing ($T^a > 500^\circ\text{C}$) this emission almost vanishes (Mg activation process). The emission at 3.27 eV (called UV luminescence, UVL) is commonly attributed to a shallow-donor-shallow-acceptor transition (is the Donor Acceptor Pair transition, DAP), since its intensity decreases dramatically upon thermal Mg activation by Mg-H complex dissociation [Mon09]. The UVL band is also known as the shallow DAP transition.

Another strong PL emission line at 3.454 eV, called ABE_2 (acceptor 2 bound exciton) is dominant at high Mg concentrations. Experiments on stability upon annealing temperature performed by Monemar et. al. [Mon09] show that the ABE_2 emission is dominant in annealed samples ($T > 500^\circ\text{C}$). This is the expected behaviour of substitutional Mg (Mg_{Ga}) as a deep acceptor.

Finally, the “blue luminescence band” (BL) emission is typically found in undoped, and heavily Mg-doped GaN layers [Res05]. The reported values of the energy position of the BL band vary from 2.70 to 3.00 eV. For undoped samples, its origin is related to transitions from the conduction band or shallow donors to acceptors. In the case of the Mg-doped GaN layers, it is related to the recombination of an electron in the CB (bottom, minimum) (CBM) with the neutral Mg deep acceptor Mg_{Ga}^0 [Mon10]. Experimental results were also confirmed by theoretical calculations [Lyo12].

2.4.4. Yellow Luminescence Band (YL)

Heteroepitaxial n-type GaN layers, either NID or doped, generally show a rather broad (FWHM of about 350–450 meV) and intense RT-PL emission at 2.20-2.25 eV (fig. 2.14) known as the Yellow Luminescence band (YL). The precise YL peak position and shape are usually sample dependent. For optoelectronic devices the YL is detrimental since its large radiative efficiency competes with the band edge emission. Donor impurities, such as C, O, H or Si [Kuc02], presumably in combination with native point defects were suggested as the YL origin. Lattice defects alone, as well as other implanted species (such as B, N and Si) did not

give rise to YL. Carbon-related complexes appeared to act as efficient nonradiative recombination centres [Kuc02], then not related to the YL.

Figure 2.14 PL spectra taken at RT for a GaN samples grown by PA-MBE. YL band is clearly shown peaking at 2.25 eV.

Experiments on Positron Annihilation Spectroscopy to determine the V_{Ga} density, together with Mg-doping (that should reduce the latter) proved almost beyond any doubt that the complex of a shallow donor with V_{Ga} is responsible for the appearance of the YL [Neu96]. It was also shown that the YL is ubiquitous in disordered or defective material regions, particularly close to substrate-layer interfaces and low quality GaN templates.

2.4.5. Luminescence from basal stacking faults

Basal Stacking Faults (BSFs) are optically active with emission lines located around 3.3 and 3.4 eV. According to Lahnemann and co-workers [Lah14] there can be defined three types of BSFs: I_1 (type 1), I_2 (type 2) and E (extrinsic). BSFs are optically active defects, which induce a bound state within the gap of the host crystal where excitons can be localized. Typical PL emission lines associated to

the BSFs are I1 3.40 to 3.43 eV [Cor14], I2 3.32 to 3.36 eV [Tis11] and E ~3.29 eV [Lah14]. It must be noted that these emission energies can be shifted by several factors, including spontaneous polarization fields, electronic coupling of bundled BSFs, coupling between adjacent point defects, strain induced shifts... [Lah14].

2.4.6. UX₁ and UX₂ emission

Photoluminescence spectrum of as-grown GaN nanowires typically exhibits two bands at 3.4526 and 3.4585 eV, labelled as UX₁ and UX₂ respectively. Their origin can be found on the recombination of excitons bound to an unknown point defect, which is thought to be related to the nanowire surface [Cal00], [Cor15]. The UX₁ and UX₂ bands overlap spectrally with the two-electron satellites of the donor-bound excitons of the core of the nanowire [Cor09], making the analysis of their fine structure complicated.

2.5. Mg-doping of III-Nitrides

The epitaxial growth of GaN layers with a high hole concentration has been a challenging issue for many years, and still is for InGaN and AlGaN layers, what possess strong difficulties to develop optoelectronic devices. The major challenges related to p-type doping with Mg are:

- i. Deep acceptor activation energies, ~ 170 meV for Mg in GaN [Mou93], leading to a few % ionization factor (true hole density) at RT.
- ii. Mg solubility limit in the low 10^{20} cm⁻³ range [Nam00].
- iii. Compensation by native defects such as N-vacancies, which have low formation energy in Ga-rich GaN [Sta98].
- iv. Pyramidal extended defects due to inversion domains also act as compensating defects in p-type GaN [Fig02].

Several approaches have been undertaken to overcome the mentioned problems, like: i) Mg δ -doping [Nak03]; ii) co-doping [Kat01]; iii) super-lattice doping [Pta01] and iv) doping using an alternative acceptor such as Be [Bur08].

However, none of the above-mentioned approaches gave satisfactory and consistent results. Prof. A. Doolittle proposed the MME growth method as successful alternative to overcome the challenges posed by Mg doping, particularly for InGaN alloys. Hole concentrations up to 10^{19} cm^{-3} were reported for GaN and $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$ grown on templates by MME [Nam08], [Try09] and [Mos13].

To understand why MME provides this enhancement in Mg-doping efficiency, the Mg incorporation behaviour under different growth conditions has to be first revised.

1) Under N-rich growth conditions, Mg atoms can easily incorporate onto Ga-substitutional sites. Additionally, the formation energy of N-vacancies V_N (a shallow donor) is higher under N-rich than Ga-rich conditions [Wal96]. Then compensation by V_N is lower under N-rich conditions.

2) Under slightly Ga-rich conditions (without droplets accumulation on the surface), Mg atoms tend to incorporate into interstitial sites or segregate to the surface due to a low availability of Ga-substitutional sites, then, less substitutional Mg is incorporated into the layer [Bur03]. Attempts to solve this problem with higher Mg fluxes cause local polarity inversion and Mg-complexes resulting actually in lower Mg-doping efficiency. Moreover, under slightly Ga-rich conditions the formation energy of V_N is reduced leading to a higher compensation.

3) Under extreme Ga-rich conditions generating Ga droplets on the surface, Mg tends to dissolve into the droplets and cannot either incorporate into lattice sites or re-evaporate [Bat04]. Polarity inversion can be avoided by covering the whole surface with metallic Ga, but this would not help Mg-doping. On the other hand, the V_N formation energy further decreases under these conditions and compensation is severe [Wal96].

On the other hand, the layer smoothness under Ga-rich conditions is much better (in general) than that obtained under N-rich conditions. Thus, a high Mg-doping efficiency would yield rough surfaces. However, a periodic change from Ga-rich to N-rich conditions with Mg flux only sent during the N-rich semiperiod would

provide a high Mg-doping efficiency while preserving a good surface morphology. This is the core of the MME growth method that allows achieving high mole fraction InGaN layers with high hole densities [Nam08], [Try09] and [Mos13]. They reported hole densities as high as $4.26 \times 10^{19} \text{ cm}^{-3}$ for GaN and $2.4 \times 10^{19} \text{ cm}^{-3}$ for $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$.

Achieving high hole densities in wide bandgap semiconductors to form p-n junctions with low series resistance is paramount. Even more in the case of solar cells, to allow extracting a maximum V_{OC} by compensating the low minority carrier lifetimes with a higher density of minority carriers. Moreover, a low resistance p-type material relaxes the constraints on grid spacing for the top contact in a solar cell, thus reducing the losses related to the shadow produced by the contact scheme.

In this thesis, MME will be the growth method used for Mg-doping of the GaN layers.

2.6. Polarization in III-Nitrides

Extremely high internal electric fields, over 10^6 V/cm , have been measured in III-Nitrides grown along the c -direction, which are more than one order of magnitude higher than those observed in arsenides. The origin of this electric field is the polarization present in these materials, which may have two components, spontaneous and piezoelectric:

$$\overrightarrow{P_{Tot}} = \overrightarrow{P_{sp}} + \overrightarrow{P_{pz}} \quad (2.6.0.1)$$

2.6.1. Spontaneous polarization

The origin of the spontaneous polarization P_{sp} lies on the strong ionic character of the III-N bond together with the non-centrosymmetry of the unit cell. The wurtzite structure has the highest symmetry compatible with the spontaneous polarization, where the tetrahedron is slightly elongated along the c -direction thus generating a small dipole. The sum of all dipoles is not compensated at the

material edges and generates a macroscopic spontaneous polarization. Two parameters have a strong influence on its value:

- The **Ideality factor**, $c_0/a_0 \rightarrow$ the optimum value for an hcp is 1.633. Ideality factor decreases when going from GaN to InN and further to AlN.
- The anion-cation bond length, u_0 , or **internal parameter** increases when going from GaN to InN and further to AlN.

@300 K	AlN	GaN	InN
$c_0 [\Rightarrow]$	4.981	5.1850	5.7037
$a_0 [\Rightarrow]$	3.111	3.1884	3.5377
c_0/a_0	1.6011	1.6262	1.6123
$u_0 [\Rightarrow]$	0.380	0.376	0.377
Binding Energy E_B [eV]	2.88	2.20	1.98
Bandgap E_g [eV]	6.2	3.45	0.65
$P_{sp} [C/cm^2]$	-0.090	-0.034	-0.042

Table 2.3 Structural values for III-Nitride binaries from [Cho96], [Walu04], [Mora09], [Ber97], [Edg94], [Vur01], [Mor09], [Mat02] and [Bern01].

Both contributions lead to an increase in P_{sp} (GaN < InN < AlN) as it is shown in table 2.3. A positive value has been assigned to the [0001] direction (Ga-polar) and a negative sign to the $[000\bar{1}]$ (N-polar). The P_{sp} value for AlN is the highest because its tetrahedral structure is the farthest from ideality. The ideality for a wurtzite structure is defined by $c = (8/3)^{1/2}a$ and the anion-cation bond length along the c -direction $0.375c$.

2.6.2. Piezoelectric polarization

As mentioned before, the spontaneous polarization results from a deviation of the tetrahedral structure elongation along the c -axis. Thus, any extra tetrahedron deformation along the c -axis will increase the polarization field. If this extra deformation comes from external forces, or strain within the lattice, the extra component is called piezoelectric polarization (P_{pz}):

$$\vec{P}_{pz} = \sum_{i=1}^3 \sum_{j=1}^6 e_{ij} \varepsilon_j \cdot \vec{u}_i \quad (2.6.2.1)$$

Where e_{ij} are the piezoelectric tensor components; ε_j is the strain along the j direction and $\vec{u}_i$ are the component of the unit vector along the i direction. Thanks to the symmetry of the WZ structure the piezoelectric tensor can be reduced to three independent components, e_{15} , e_{31} and e_{33} . In matrix notation:

$$\vec{P}_{pz} = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{15} & 0 & 0 \\ e_{31} & e_{31} & e_{33} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \varepsilon_{xx} \\ \varepsilon_{yy} \\ \varepsilon_{zz} \\ \varepsilon_{yz} \\ \varepsilon_{zx} \\ \varepsilon_{xy} \end{pmatrix} \quad (2.6.2.1)$$

Considering the most usual case, when the layers are biaxially strained perpendicular to the c -direction:

$$\varepsilon_{xx} = \varepsilon_{yy} = \frac{a - a_0}{a_0} \quad (2.6.2.2)$$

$$\varepsilon_{yz} = \varepsilon_{zx} = \varepsilon_{xy} = 0 \quad (2.6.2.3)$$

$$\varepsilon_{zz} = -2 \frac{C_{13}}{C_{33}} \frac{a - a_0}{a_0} \quad (2.6.2.4)$$

From the above-mentioned equations, the $\vec{P}_{pz}$ vector is aligned towards the $[0001]$ direction and its value is given by:

$$P_{pz}[0001] = 2 \frac{a - a_0}{a_0} \left(e_{31} - e_{33} \frac{C_{13}}{C_{33}} \right) \quad (2.6.2.5)$$

Then the $\mathbf{P}_{pz}$ is [0001] oriented if the crystal is biaxially compressed and $[000\bar{1}]$ oriented if the crystal is tensile stressed. Table 2.4 summarizes the values of the piezoelectric tensor components for the binaries AlN, GaN and InN.

The total polarization, P_{tot} , is the sum of both contributions: the spontaneous and the piezoelectric. Together they give rise to an internal electric field of magnitude:

$$\vec{E} = -\frac{\vec{P}_{tot}}{\epsilon\epsilon_0} = -\frac{\vec{P}_{sp} + \vec{P}_{pz}}{\epsilon\epsilon_0} = -\frac{P_{sp}^Z + P_{pz}^Z}{\epsilon\epsilon_0} \cdot \vec{u}_Z \quad (2.6.2.6)$$

For thick samples, this electric field is partially screened by the carriers existing in the layer, traps and surface states, so that the voltage drop across the layer is equal or lower than the bandgap, because when the Fermi level reaches one of the bands, the carrier density becomes huge [Fio99].

Piezoelectric component (C/m^2)	AlN	GaN	InN
e_{31}	-0.58	-0.35	-0.49
e_{33}	1.55	1.27	0.73
e_{15}	-0.48	-0.30	-0.40
Reference	[Rom06]	[Vur01] and [Byk97]	[Rom06]

Table 2.4 Values of the piezoelectric components for AlN, GaN and InN.

The results published by Dr. Jani in his thesis dissertation on InGaN/GaN p-i-n solar cells [Jan08] showed that P_{sp} enhances the carrier transport through the intrinsic region of a solar cell, hence, improving its collection efficiency. Even

though the band gap of InGaN decreases with increasing indium composition and the potential barrier to overcome at the i-InGaN to GaN junction increases, P_{sp} tends to counter this effect by increasing the electric field at the junction. Thus, P_{sp} has a positive effect on the performance of InGaN/GaN p-i-n solar cells [Jan08].

2.7. Specific properties of InGaN

2.7.1. Phase separation

When growing a ternary alloy out of binaries with a large difference in bond length and binding energy (and consequently in lattice constant), the alloy tends to minimize the total energy by splitting into its binary phases. In the case of InGaN, the InN in-plane lattice constant is 11% higher than that of GaN. Ho et al. studied the thermodynamic stability of InGaN alloys using the valence-force-field (VFF) approximation [Ho96]. Considering thermodynamic equilibrium conditions, the Gibbs free energy of mixing in an alloy is given by:

$$\Delta G = \Omega x(1 - x) + kT[x \ln x + (1 - x) \ln(1 - x)] \quad (2.7.1.1)$$

Where x is the In content, k is the Boltzmann's constant and Ω is the interaction parameter. The interaction parameter depends on the elastic constants of the alloy that also depend on the composition. Thus, the interaction parameter depends on the In content and it is assumed to follow Vegard's law. The first term in equation (2.7.1.1) accounts for the mixing enthalpy and the second one for the mixing entropy. This equation applies for fully relaxed alloys (fig. 2.15a).

The solubility limit (at a given temperature) of InN in GaN is determined by the condition $\partial G / \partial x = 0$. The point in which the alloy is thermodynamically unstable is given by the condition $\partial^2 G / \partial x^2 = 0$. When representing In content versus temperature (phase diagrams), the first condition determines the *binodal curve* and the second one the *spinodal curve* (fig. 2.15). Above the binodal curve is the stable region. Between both curves is the metastable region and below the spinodal curve is the unstable region.

In the case of strained or partially relaxed InGaN layers grown heteroepitaxially on GaN, Si, Sapphire, etc. Karpov et al. introduced the effect of the deformation on the Gibbs free energy of mixing by including the elastic energy per mole accumulated in the lattice [Kar98]:

$$H_{el} = BN_A \Lambda \left(\frac{\Delta a}{a} \right)^2 \quad (2.7.1.2)$$

$$B = C_{11} + C_{12} - 2 \frac{C_{13}^2}{C_{33}} \quad (2.7.1.3)$$

Where $\Delta a = (a_{InGaN} - a_{subs})$, C_{ij} are the elastic constants of the material and $\Lambda = \frac{\sqrt{3}}{4} a^2 c$ is the molecular volume of the alloy. Now, both phase curves are asymmetric with the maximum located at 79% of In and at 735 °C (fig. 2.15b).

Phase separation effects are expected to be less critical when growing by MBE, since this technique does not proceed under thermodynamic equilibrium. This means that alloys with higher In contents could be achieved. Aseev et al. reported on InGaN layers grown directly on silicon with In content ranging from GaN to InN [Ase15] with minimized phase separation.

While phase separation is a macroscopic effect (easy to determine by XRD), the presence of In composition fluctuations at microscopic scale is a different issue. These localized In-rich regions change locally the bandgap, so that the average bandgap value may be different than the nominal one derived from the average In composition measured (XRD on PL). In regions where the local In content is smaller than that of the surrounding areas, the subsequent potential wells confine carriers quite efficiently (particularly at low temperature), thus representing very efficient radiative recombination channels. This is the main reason why InGaN based blue LEDs are so efficient even though the material had poor quality with a high TDD.

Figure 2.15 Temperature vs In content phase diagrams of wurtzite InGaN alloys for a) relaxed and b) strained layers.

When InGaN based solar cells are considered, both effects, phase separation and local In fluctuations are detrimental. The first one, as a microscopic effect, will pin down the open-circuit voltage (V_{OC}) of the solar cell to the lowest value (highest In content). The second one is a minor issue since solar cells, particularly under concentration conditions, work at a rather high temperature where the local fluctuations do not play a significant role.

2.7.2. Dependence of the structural parameters and bandgap with composition

The properties of the III-Nitride ternary alloys (AlGaN, InAlN and InGaN) are generally estimated by a linear interpolation between the constituent binaries (Vegard's law). The lattice parameter of InGaN is given by:

$$a^{InGaN}(x) = xa^{InN} + (1 - x)a^{GaN} \quad (2.7.2.1)$$

Not all properties can be estimated by a linear interpolation, as the bandgap energy. In those cases, a quadratic approximation is needed, via introducing a second order term. In the case of the bandgap energy it is:

$$E_g^{InGaN}(x) = xE_g^{InN} + (1 - x)E_g^{GaN} - bx(1 - x) \quad (2.7.2.2)$$

Where b is the bowing parameter, which is different for each property and each ternary alloy. The bowing parameter is determined for a given temperature and strain value and in the case of InGaN alloys it ranges from 1.02 to 1.40 eV for low In content (<20%) layers under biaxial strain [Sha96], [Ors14]. However, for strain free InGaN layers b ranges from 1.8 to 2.96 eV [Ors14], [Isl13], [More09] and [Kur04]. It is expectable that

Since the bandgap depends on the temperature and strain, b must be derived considering the specific conditions. InGaN alloys pose further difficulties for an accurate experimental determination of b from optical characterization measurements. The presence of phase separation in the alloys makes quite difficult to determine a meaningful b value, because phase separation may change with alloy composition. Even if the alloys have no phase separation, the local composition fluctuations are usually present. In this case, carriers will be subjected to different potential confinement (local bandgap relative minima) as a function of the temperature and the alloy composition. The best approach would be to determine b at RT (when possible) because confinement at local potentials is no longer present because of carrier thermalization to the alloy CB and VB lowest energies (S-shape behaviour).

In most cases the properties of InGaN alloys are theoretical approximations due to the lack of high quality bulk and homogeneous layers for all compositions due to the immiscibility between GaN and InN. When growth proceeds under thermodynamic equilibrium (MOVPE), InGaN layers with high In content are not easy to obtain because of the high growth temperatures involved that induce InN dissociation and In segregation. MBE is a better choice to grow InGaN layers over the whole composition range, the reasons being two fold: i) much lower growth temperatures and ii) phase separation effects are minimized because of a kinetic regime.

3. Experimental techniques

This chapter explains the characterization techniques employed for the realization of this thesis. They are divided into structural, morphological, optical and electrical characterization techniques.

3.1. Structural characterization

3.1.1. Reflection High Energy Electron Diffraction (RHEED)

RHEED is a unique tool in a MBE system for *in-situ* characterization of surface reconstructions, transitions, growth modes, growth rates and lattice parameters. The basics of RHEED rely on electron diffraction patterns from the growth front by using a grazing incidence (1° to 3°) high-energy electron beam. It consists of a high-energy (typically 10 to 30 keV) electron gun (1), a phosphorus screen (2), a camera (3) and a computer with data analysing software (4) (fig. 3.1). The electron beam under grazing incidence is diffracted at the topmost atomic planes giving information about the processes taking place at the layer surface. The resulting diffraction pattern is observed in the phosphorus screen. The analysis of the diffraction pattern intensity and structure yields information on the above-mentioned growth and material parameters in real time.

Figure 3.1 Schematics of a RHEED system installed in the MBE chamber. 1) Electron gun, 2) phosphorus screen, 3) camera and 4) computer with analysing software.

The RHEED pattern is very sensitive to surface morphology and reconstructions, as well as to crystal orientation. In general, four types of RHEED patterns can be related to the following (figure 3.2):

- Single crystal films with atomically flat surface having wide, micron-size terraces produce a set of sharp diffraction spots lying along the Laue rings (fig. 3.2a).
- Single crystal films with atomically flat surface having a high density of small terraces show sharp diffraction streaks. The streak width is inversely proportional to the terrace size (fig. 3.2b).
- Single crystal films with rough surface produce a transmission-like pattern because electrons penetrate the crystallites, leading to a spotty RHEED pattern (fig. 3.2c). This pattern is usually observed when growing on highly mismatched substrates via Volmer-Weber or Stransky-Krastanov mode. It is usually the case of high In content InGaN on GaN templates or Si substrates.
- Polycrystalline or textured films with random in-plane orientation (also the case of self-assembled nanowires with random in-plane orientation) show a set of concentric circles (fig. 3.2d).

Figure 3.2 RHEED diffraction patterns for: a) single crystal films with atomically flat surface consisting of wide, micron-size terraces (commercial GaN/Sapphire template), b) single crystal film with atomically flat surface consisting of wide density of small terraces (AlN on Si(111)), c) single crystal film with a rough three-dimensional surface (InGaN grown on AlN/Si(111)), d) polycrystalline or textured film (InGaN grown directly on Si(111) under strong N-rich conditions). All RHEED diffraction patterns are from samples grown during this work.

Another important feature of the RHEED tool is the capability of identifying different surface reconstructions that may occur at specific temperatures or under given growth conditions. Si(111), for instance, where the transition from a 1x1 to a 7x7 surface reconstruction happens at 860°C [Suz93], as shown in figure 3.3, can be used as a calibration point of the growth temperature.

Figure 3.3 RHEED pattern of a 7x7 surface reconstruction in a Si(111) substrate at 860 °C.

In this thesis, RHEED is used as a calibration reference point of the substrate temperature and as an *in-situ* tool to analyse the processes taking place on the growth front in real time (fig 3.2). The main substrate temperature calibration is done by measuring the Ga desorption flux by a "line of sight" quadrupole mass analysis [Fer08] (case of GaN templates), or by identifying the surface reconstruction transition (case of Si substrates). For a deeper discussion on RHEED theoretical background and analysis, the reader is referred to [Ich04].

3.1.2. X-Ray Diffraction (XRD)

When X-rays interact with atoms, these will scatter X-ray waves, primarily by the electronic shells, producing secondary spherical waves with the same frequency, blurred slightly due to a variety of effects. This phenomenon is known as elastic scattering (Rayleigh scattering). The scattered waves could also be re-scattered a second time, but this effect is negligible.

In crystalline solids, the waves are scattered by lattice planes separated by the interplanar distance d . The distance between a set of planes in a hexagonal unit cell, with Miller indices (hk) is given by:

$$d_{hkl} = \sqrt{\frac{1}{(h^2 + k^2 + l^2) \frac{4}{3a^2} + \frac{l^2}{c^2}}} \quad (3.1.2.1)$$

And the angle between two planes of Miller indices (hkl) and $(h'k'l')$ is:

$$\phi_{hkl} = \cos^{-1} \left\{ d_{hkl} d_{h'k'l'} \left[hh' + kk' + \frac{1}{2}(hk' + kh') \right] \frac{4}{3a^2} + \frac{ll'}{c^2} \right\} \quad (3.1.2.2)$$

Diffraction occurs when radiation, with wavelength of the order of the atomic spacing, is scattered in a specular way by the crystal atoms (figure 3.4). When scattered waves interfere constructively, they remain in phase since the difference in the optical path between the two waves is equal to an integer multiple of the wavelength. The Laue equations give three conditions for incident waves to be diffracted by a crystal lattice. Being $\mathbf{k}_i$ and $\mathbf{k}_o$ the wave vectors of the incoming and outgoing beam respectively, then, the scattering vector is defined as $\mathbf{k}_o - \mathbf{k}_i = \Delta\mathbf{k}$. With $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ as the lattice primitive vectors, the Laue conditions for the scattering vector are as follows:

$$\mathbf{a} \cdot \Delta\mathbf{k} = 2\pi h \quad (3.1.2.3)$$

$$\mathbf{b} \cdot \Delta\mathbf{k} = 2\pi k \quad (3.1.2.4)$$

$$\mathbf{c} \cdot \Delta\mathbf{k} = 2\pi l \quad (3.1.2.5)$$

If $\mathbf{G} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C}$ is a reciprocal lattice vector, then combining with the Laue conditions the diffraction condition is obtained as $\mathbf{k}_o - \mathbf{k}_i = \mathbf{G}$ and hence $2\mathbf{k}_i \cdot \mathbf{G} = G^2$. This relation can be approximated to the Bragg's law:

$$n\lambda = 2d \sin \theta \quad (3.1.2.6)$$

Where λ is the wavelength of the incident radiation, d is the atomic interplanar distance and θ is the scattering angle (fig. 3.4). For more details about the Laue

conditions, Bragg's law or the mathematical argumentation the reader is referred to [Kit76].

Figure 3.4 Schematic of the incidence of a plane wave on a d -spaced set of atomic planes. In this case $\omega = \theta$ because it is on symmetric geometry (see below). 2θ is the angle between the transmitted beam and the detector.

When using a Cu anti-cathode as X-ray source, two strong lines are generated, Cu- $K\alpha_1$ and Cu- $K\alpha_2$. ISOM institute is equipped with a commercial X'Pert PRO PANalytical XRD system with a Ge(220) hybrid monochromator. The Cu- $K\alpha_1$ X-ray wavelength ($\lambda = 1.540598 \text{ \AA}$) was used throughout this thesis. The X-ray beam impinges on the studied crystal plane at an angle ω ($\omega = \theta$ only for the symmetric geometry, see below). When the Bragg condition is fulfilled, the scattered radiation is detected with a scintillator detector. The typical reference axes in a diffractometer are shown in figure 3.5 with translational axes X, Y and Z and rotational axes ψ (rotation around X-axis), ω (rotation around Y-axis, it is the incident angle) and ϕ (rotation around Z-axis). Additionally the angle between the transmitted beam and the detector is 2θ .

Figure 3.5 a) Reference axis of the diffractometer employed in this work, b) the XRD set-up employed in this work.

Various one-dimensional scans were used in this work, namely: ω -scans, ω - 2θ scans and ϕ -scans. Both ω - and ω - 2θ scans are called “rocking curves”, as both involve “rocking” the sample around the ω axis. In ω -scans the detector remains stationary while the sample is rotated around the ω axis. ω -scans (of a symmetric plane) measure the film quality by scanning the diffraction spot in an arc, detecting broadening (of the diffracted peak) induced by mosaic tilt (fig. 2.12a), screw and mixed dislocations [Hei00], and wafer bowing [Mor09]. Different contributions to the broadening could be separated by making use of reciprocal space maps [Mor09]. In ω - 2θ or 2θ - ω scans, both the sample and the detector are rotated by ω and 2θ degrees respectively. This type of scans probe the diffraction spot along a direction that generally has less broadening. By making use of the Bragg’s law, these scans (of a symmetric plane, $\omega=\theta$) allow the determination of the interplanar spacing (d), and hence the lattice parameter (c). Once the lattice parameter is known and using Vegard’s law (section 2.7.2) the In composition can be calculated. This only applies in the case of fully relaxed samples. If the layers are strained, the calculation of the lattice parameter becomes more complicated, as will be discussed in sub-section 3.1.2.2.

In ϕ -scans the sample is rotated around the ϕ -axis (rotation of the sample around the surface normal vector) while the detector and the source remain stationary. ϕ -scans of an asymmetric plane detects broadening (of the diffraction peak) by mosaic twist (fig. 2.12b), edge and mixed dislocations [Hei00] and [Mor09]. Figure 3.6 shows the 1D scans in the reciprocal space for symmetric (b) and asymmetric (c) planes.

In this work, two diffraction geometries were employed: the symmetric and the asymmetric. The symmetric geometry holds that $2\omega = 2\theta$, whereas in the asymmetric $2\omega \neq 2\theta$ and $2\theta = 2(\omega - \chi)$, where χ is the offset. The offset (χ) is the difference between the incident angle (ω) and $\frac{1}{2}(2\theta)$. The planes are often named as the diffraction geometry in which they are involved. Thus, a symmetric plane holds that $2\omega = 2\theta$, as the GaN(0002), in which $\omega = 17.2833^\circ = \frac{1}{2}(2\theta)$. The GaN(10 $\bar{1}$ 5) is an example of asymmetric plane. In this case $\omega = 31.9211^\circ$, $2\theta = 105.0056^\circ$ and $\chi = -31.9211^\circ$. The asymmetric planes scanned in this work were the (In)GaN(10 $\bar{1}$ 5) for ϕ -scans or reciprocal space mapping (section 1.1.2.2.) and the (In)GaN(10 $\bar{1}$ 2) for pole maps (section 1.1.2.1). Two-dimensional scans used in this work were the pole maps, also called pole figures, and the ω - 2θ vs ω relative reciprocal space maps.

3.1.2.1 Pole figure measurements (PFM)

Since crystal orientation and the degree of mosaicity are critical parameters in thin film devices performance, it is crucial to control precisely the orientation of the crystal. Electron backscattered diffraction technique (EBSD), combined with SEM, has been a popular approach to determine the crystal orientation and epitaxial relationship with the substrate, both being also possible to be determined by TEM. Being cheaper, faster and a non-destructive technique are the main advantages of PFM over TEM.

The PFM is a measurement technique where the detector (2θ) is fixed and the sample is rotated around two angles, ϕ - Ψ , ω - ψ or ω - ϕ . In this work, only ϕ - Ψ (fig 3.7a) and ω - ϕ (fig 3.7b) were employed to determine the epitaxial relationship. The measured intensity is plotted in a pole map as a function of the rotation of both angles.

Figure 3.6 a) ω , 2θ , $\omega-2\theta$ and ϕ directions in the reciprocal space. Shaded areas represent regions of the reciprocal space where the sample would block either the incoming or the outgoing beam. Black dots represent reflections in the reciprocal space. Reciprocal space map (RSM) around the b) GaN (0002) and the c) GaN (10 $\bar{1}$ 5) Bragg reflections.

Figure 3.7 a) ϕ - Ψ pole map around the Si(220) Bragg reflection of an InGaN film grown on Si and, b) ω - ϕ pole map around the GaN(10 $\bar{1}$ 2) Bragg reflection of an InGaN film grown on GaN/sapphire.

The six-fold symmetry shown for InGaN, GaN and sapphire (figure 3.7) is a fingerprint of the WZ structure. For Si, as it is a cubic material, a typical three-fold symmetry is observed. The alignment of the peaks related to both materials means that those set of planes are parallel, Si(220)||InGaN(10 $\bar{1}$ 2) (fig 3.7a) and Sapphire(11 $\bar{2}$ 6)||GaN(10 $\bar{1}$ 2)||InGaN(10 $\bar{1}$ 2) (fig 3.7b).

For a complete epitaxial relationship determination (figure 3.8), it is needed to combine the results of a symmetric reciprocal space map (RSM) and a pole figure. With RSMs the *out-of-plane* epitaxial relationship can be determined while the *in-plane* one is determined with PFMs.

Figure 3.8 a) RSM around the Si(111) and b) PFM around the Si(220).

3.1.2.2 Reciprocal space mapping for composition and strain determination

The ω - 2θ vs ω maps are commonly known as reciprocal space maps (RSM). A 2-axis RSM can be obtained when ω - 2θ scans are repeated for a sequence of offset (χ) values (figs. 3.6b and c). The difference from one offset value to the next ($\delta\chi$) is the omega step size. The difference between the maximum and minimum value of χ is the ω range.

When plotted in reciprocal lattice units (rlu), the 2-axis maps obtained can represent the reciprocal lattice spots that they are measuring. The relation between the angles and the rlu are given by:

$$Q_x = \frac{1}{\lambda} (\cos \omega - \cos(2\theta - \omega)) \quad (3.1.2.1)$$

$$Q_z = \frac{1}{\lambda} (\sin \omega + \sin(2\theta - \omega)) \quad (3.1.2.2)$$

Figure 3.9 Diagram of the relationship between the angles of the diffractometer in real space and the diffraction vector in the reciprocal space [Kid].

RSMs are employed to determine strain and composition in ternary alloys. If the system has been set up such that all the rotations are placed on an absolute scale, then this is equivalent to calibrating the position coordinates for the 000 lattice points to (0,0). In this case, the d -spacing can be obtained from one reflection alone by decomposing it on an in-plane and an out-of-plane reflection. For the case of the $(10\bar{1}5)$ plane, it could be decomposed into the (0005) and the $(10\bar{1}0)$ planes. The equations for the interplanar spacings are:

$$d_{10\bar{1}0} = \frac{1}{Q_{10\bar{1}0}} = \frac{\lambda}{\cos \omega - \cos(2\theta - \omega)} \quad (3.1.2.3)$$

And

$$d_{0005} = \frac{1}{Q_{0005}} = \frac{\lambda}{\sin \omega + \sin(2\theta - \omega)} \quad (3.1.2.4)$$

Where ω and 2θ refer to the $(10\bar{1}5)$ reflection. The strain in a layer can be calculated from:

$$\varepsilon_{xx} = \frac{a - a_0}{a_0} \quad (3.1.2.5)$$

$$\varepsilon_{zz} = \frac{c - c_0}{c_0} \quad (3.1.2.6)$$

Where a and c account for the measured lattice parameter and a_0 and c_0 for the relaxed ones. The values for a and c can be calculated from peak position in the RSM (Q_x and Q_z) together with the Bragg's law and the interplanar spacing for a hexagonal structure:

$$a = \frac{\sqrt{3}\lambda}{3Q_x} \quad (3.1.2.7)$$

$$c = \frac{5\lambda}{2Q_z} \quad (3.1.2.8)$$

The relationship between the *in-plane* and out-of-plane strain is given by:

$$\varepsilon_{zz} = -2 \frac{C_{13}}{C_{33}} \varepsilon_{xx} = -2 \frac{C_{13}}{C_{33}} \frac{a - a_0}{a_0} \quad (3.1.2.9)$$

Then:

$$\frac{c - c_0}{c_0} = -2 \frac{C_{13}}{C_{33}} \frac{a - a_0}{a_0} \quad (3.1.2.10)$$

The values of a_0 , a , C_{13} and C_{33} as functions of the composition (Vegard's law):

$$a(x) = x \cdot a^{InN} + (1 - x) \cdot a^{GaN} \quad (3.1.2.11)$$

$$c(x) = x \cdot c^{InN} + (1 - x) \cdot c^{GaN} \quad (3.1.2.12)$$

$$C_{13}(x) = x \cdot C_{13}^{InN} + (1 - x) \cdot C_{13}^{GaN} \quad (3.1.2.13)$$

$$C_{33}(x) = x \cdot C_{33}^{InN} + (1 - x) \cdot C_{33}^{GaN} \quad (3.1.2.14)$$

Introducing them in the equation (3.1.2.10):

$$\frac{c - x \cdot c^{InN} + (1 - x) \cdot c^{GaN}}{x \cdot c^{InN} + (1 - x) \cdot c^{GaN}} = - \frac{x \cdot C_{13}^{InN} + (1 - x) \cdot C_{13}^{GaN}}{x \cdot C_{33}^{InN} + (1 - x) \cdot C_{33}^{GaN}} \cdot \frac{a - x \cdot a^{InN} + (1 - x) \cdot a^{GaN}}{x \cdot a^{InN} + (1 - x) \cdot a^{GaN}} \quad (3.1.2.15)$$

This is a third order equation that once numerically solved gives the composition and allows calculating the lattice parameters and strain. For InGaN grown on GaN/sapphire the RSMs were measured around the $(10\bar{1}5)$ GaN Bragg reflection, whereas for InGaN grown on Si(111) they were taken around the Si (224) Bragg reflection. In both cases the InGaN peak analysed was the $(10\bar{1}5)$. For a deeper understanding of the XRD measurement technique the reader is referred to [Kid], [Mor09], [Mor09b] and [Nag11].

3.1.3. Transmission Electron Microscopy (TEM)

In TEM an electron beam with energy ranging from 80 to 300 keV is transmitted through an ultra-thin specimen, interacting with the atoms as it passes through it. The electron wavelength is on the order of pm , which allows studying the sample at atomic scale. Figure 3.10 shows a schematic description of the TEM rays diagram. The basic principle of TEM imaging is the study of the local distribution of scattered electrons, in contrast to SEM where only the intensity of the electron beam is considered. In TEM there are two operation modes: diffraction (projection of the diffraction pattern on the screen) and image mode (projection of the image on the screen).

The diffraction pattern originates from the constructive interference of diffracted electrons according to the Laue conditions. The maxima in the diffraction pattern correspond to reciprocal lattice vectors of the analysed specimen. A detailed analysis of the diffraction pattern, in terms of geometry and magnitude of the reciprocal lattice vectors, provides information about the crystal structure of the sample. In the imaging mode, the contrast is measured by two basic techniques called bright- and dark-field imaging.

In the bright-field mode the contrast, when considered classically, is formed directly by occlusion and absorption of electrons in the sample. Only the non-scattered transmitted beam is allowed to pass through the objective aperture to form the image. Thicker regions of the sample, or regions with a higher atomic

number will appear dark, whilst regions with no sample in the beam path will appear bright – hence the term bright-field.

Figure 3.10 Rays diagram of the electron beam paths during TEM operation. Incident (black solid line), transmitted (blue solid line) and Bragg scattered (orange dotted line) electron beams are indicated. Diffraction/imaging modes correspond to measuring in back focal/object planes. Objective is an electromagnetic lens. Adapted from [Wil09].

In the dark-field mode, only the diffracted beams (elastically scattered electrons) are allowed to pass through the aperture and form the image. Considering single-crystals, single-reflection dark-field images of a specimen tilted just off the Bragg condition allow "lighting up" only those lattice defects, like dislocations or precipitates, that bend a single set of lattice planes in their neighbourhood. Analysis of intensities in such images may then be used to estimate the amount of that bending. In polycrystalline specimens, on the other hand, dark-field images serve to light up only that subset of micro-crystals whose reflection complies with the Bragg conditions.

Scanning transmission electron microscopy (STEM) scans a collimated electron beam (< 1 nm in diameter) over the sample, in contrast to TEM where the whole sample is illuminated at once. In STEM, the detector has an annular shape, and the mode is called annular dark field (ADF) or annular bright field (ABF). The main advantages of this configuration include a more efficient signal collection and the possibility of using the primary beam with a second detector, for instance an electron spectrometer leading to electron energy-loss spectroscopy (EELS), which allows simultaneous measurements.

In electron energy loss spectroscopy (EELS) the material is exposed to a beam of electrons with a known, narrow range of kinetic energies. Some of the electrons will undergo inelastic scattering, which means that they lose energy and have their paths slightly and randomly deflected. The amount of energy loss can be measured by means of an electron spectrometer, and interpreted calculating the atomic source of the energy loss. Inelastic interactions include phonon excitations, inter- and intra-band transitions, plasmon excitations, inner shell ionizations and Cherenkov radiation. The inner-shell ionizations are particularly useful for detecting the elemental components of a material. For example, different elements in a sample result in different electron energies in the scattered beam. This can be used to generate an image that provides information on elemental chemical composition, based on the atomic transitions excited by electron-electron interaction.

The STEM-EELS analysis presented in this thesis was performed by Dr. J. Grandal and Dr. M. Varela at the National Centre of Electron Microscopy, Complutense University of Madrid. STEM images were obtained using a JEOL JEM ARM200cF system operating at 200kV and recorded using an annular dark field (ADF) detector. Electron energy-loss spectroscopy (EELS) was performed with the microscope operating at 200 kV.

In order to gain a deeper insight into the TEM the reader is referred to [Wil09].

3.2. Morphological characterization

3.2.1. Atomic Force Microscopy (AFM)

The atomic force microscopy (AFM) is a very high-resolution type of scanning probe microscopy (SPM). The information is gathered by the interaction of the probe (a sharp tip) with the sample surface. The tip is a 3-6 μm -tall Si or Si_3N_4 pyramid with 15 to 40 nm end radius. It is placed at the very end of a cantilever that has a spring constant ranging from 0.01 to 50 N/m. The lateral resolution of AFM is relatively low (~ 30 nm) compared to the vertical resolution that can be as high as 0.1 nm.

Figure 3.11 shows a schematic description of a typical AFM set-up. The tip is scanned over the surface while a feedback system keeps the tip at a constant height (measuring force), or at a constant force (measuring height). As the tip scans, the cantilever bends in reaction to the interaction of the tip with the sample surface. A mirror (typically a few tens of nm Au) attached to the cantilever, reflects a laser beam to a photodetector (usually a split diode photodetector). The photodetector measures the difference in light intensities between the upper and lower elements. The resulting signal is returned to the piezoelectric actuators (scanner) that keep the tip at a constant force or distance from the sample surface.

The AFM can be operated in three different modes: contact mode, non-contact mode and tapping mode. In this work, only the tapping mode is employed and therefore it is only one explained in detail in this section. For a description of the contact and non-contact modes, the reader is referred to [Hau12].

The tapping mode was developed to overcome the problems related to the tip interaction with an adsorbed layer (for example water) on the sample surface, but the resolution is lower than in contact mode. In tapping mode the tip oscillates with an amplitude ranging from 10 to 100 nm requiring rigid cantilevers with a resonance frequency in the range of 200 to 400 kHz. During the measurement, the oscillation amplitude is reduced by the energy loss caused by the tip-surface interaction. This amplitude reduction is used to image the surface.

Figure 3.11 Typical AFM set up: 1) cantilever, 2) sharp tip, 3) piezoelectric element to drive the cantilever oscillation, 4) sample, 5) sample stage, 6) scanner to displace sample and stage in x, y and z directions, 7) laser, 8) photodiode, 9) electronics controller and 10) computer and final image.

3.2.2. Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM) is a type of electron microscope in which the image of a sample is produced by scanning (typically a raster-scan pattern) it with a focused electron beam. The combination of beam position with the detected signal from secondary and backscattered electrons produces an image.

Figure 3.12 depicts a typical SEM set up. A filament located in the “gun” generates the electron beam by either thermionic emission, Schottky field emission or cold field emission. At the ISOM laboratory, the SEM used was a cold Field Emission FEI Inspect F50. Thus, only FE-SEM will be discussed.

Figure 3.12 Schematic of a scanning electron microscope. [Pur].

The electrons are generated by field emission and then accelerated by a huge electric field ($>10^7 \text{ V.cm}^{-2}$) applied to the filament. Such high electric fields decrease the vacuum potential barrier width allowing the electrons to tunnel the barrier and being ejected from the filament. Field-effect cathodes need to work in Ultra High Vacuum (UHV) conditions (lower than 10^{-6} Pa). The tip is usually made of tungsten with a radius of about $0.1 \text{ }\mu\text{m}$. The FE-SEM at ISOM achieves a resolution of 1.2 nm at 30 kV .

When the primary electron beam interacts with the sample, the electrons lose energy via repeated random scattering and absorption within a volume (interaction volume) of the specimen. This interaction results in different signals: secondary electrons, cathodoluminescence, backscattered electrons, characteristic X-Rays, Auger electrons and electron beam induced current (figure 3.13). Only secondary electrons and cathodoluminescence signals are going to be discussed since they were the only ones used in this work.

Figure 3.13 Electron interaction volume with relevant signals. [AMM].

Secondary electrons (SE): are low energy electrons ejected from the k-shell of the specimen surface atoms by inelastic scattering interactions with the beam electrons. Due to their low energy, these electrons originate within a few nanometres from the sample surface and are detected by a scintillator-photomultiplier system. The secondary electrons are collected by attracting them towards an electrically biased grid at about +400 V and then further accelerated towards a phosphor or scintillator positively biased to about +2.000 V. The accelerated secondary electrons are now sufficiently energetic to cause the scintillator to emit flashes of light, which are conducted to a photomultiplier outside the SEM column via a light pipe and a window in the wall of the specimen chamber. The amplified electrical output signal by the photomultiplier is displayed as a two-dimensional intensity distribution. The brightness of the signal depends on the number of secondary electrons reaching the detector.

Cathodoluminescence: it is the photon emission (luminescence) when an excited electron returns to its ground state. It will be analysed in depth in the optical

characterization section. For further information about SEM the reader is referred to [Gol04].

3.3. Optical characterization

The optical characterization of the grown layers is crucial to determine their adequacy to optoelectronic applications. There exists many ways to characterize the optical properties of materials. In this thesis, only photoluminescence (PL) and cathodoluminescence spectroscopy (CL) were used.

3.3.1. Photoluminescence (PL)

In PL the VB electrons of a semiconductor are excited to the CB by means of a laser beam with an energy higher than the semiconductor. The excited electrons interact with phonons until they reach the CB edge (thermalization process and recombine radiatively with VB holes, thus emitting a photon with a characteristic energy of the semiconductor [Gfr00].

Figure 3.14 PL set up at ISOM laboratory.

A He-Cd laser of 325 nm wavelength (3.818 eV) and 25 mW output power has been used in this thesis. The sample is placed inside a cryostat allowing

measurements from 9 to 300 K (Sumitomo CH-204SFF with a HC-4A compressor). The light emitted by the sample is collected by two lenses and analysed by a Jobin-Yvon THR 1000 monochromator in combination with a Horiba Jobin-Yvon DPM-HV photomultiplier. A schematic of the PL set-up is shown in figure 3.14.

PL spectra at RT usually show broadened and red-shifted peaks compared to the LT ones, mainly due to thermal expansion, phonon interaction and the broadening of the Fermi-Dirac distributions. From excitonic emissions, defect related, and DAP signals, the bandgap energy and overall sample quality can be determined. For InGaN alloys, the bandgap energy can be related with the composition through the Vegard's law (section 2.7) provided the layers are fully relaxed. For more details on PL spectroscopy, the reader is referred to [Per93].

3.3.2. Cathodoluminescence (CL)

In essence, CL spectroscopy follows the same principles described above for the PL but in this case the excitation is provided by an electron beam instead of a laser beam. The electron beam can be focused on a small area (tenths of nm²) giving a spatial resolution not achievable by standard PL.

Spatially resolved CL allows a precise correlation between emission and the spatial location where the emission comes from. For InGaN alloys, small differences in composition or doping can be traced down as a function of the position, providing useful information about trends with, for instance, morphology.

3.4. Electrical characterization

3.4.1. I-V measurements

A current-voltage characteristic (*I-V* curve) is a relationship between the electric current through a circuit, device or material, and the corresponding voltage, or potential difference across it. To measure an *I-V* curve of a sample it is necessary to deposit metallic contacts on it (see appendix A for details on the contact processing).

Typical I - V curves show either an ohmic, a rectifying behaviour, or something in between as shown in figure 3.15. A linear relation between the current and the voltage (fig. 3.15a) characterizes an ohmic behaviour, known as the Ohm's law:

$$I = V/R \quad (3.4.1.1)$$

Where R is the resistance of the material. It could be written also as:

$$\vec{j} = \sigma \vec{E} \quad (3.4.1.2)$$

Where $\vec{j}$ is the current density at an arbitrary point in the material, $\vec{E}$ is the electric field at that point and σ is the conductivity of the material.

Figure 3.15 Typical I - V curves for: a) ohmic and b) rectifying behaviour.

The rectifying behaviour, typical of diodes (such as solar cells or Schottky junctions) is shown in figure 3.15b. In this case, the relationship between the current and the voltage is given by the Shockley diode equation [Sho49]:

$$I = I_s \left(e^{\frac{eV_D}{nkT}} - 1 \right) \quad (3.4.1.3)$$

Where I_s is the reverse bias saturation current, V_D is the voltage across the junction and n is the ideality factor, which typically varies between 1 and 2. When $n=1$ the main mechanism for recombination of carriers is the surface and bulk recombination; whereas for $n=2$ the main one is the junction recombination.

3.4.2. Hall Effect

Hall Effect measurements allow determining fundamental transport properties such as: carrier concentration (n), carrier mobility (μ), sheet resistance (R_s) and the Hall coefficient (R_H). The basic principle behind the Hall Effect is the Lorentz

force resulting from the combination of electric and magnetic forces on a point charge. A charged particle q travelling at a speed $\vec{v}$ inside an electric and a magnetic field of magnitudes $\vec{E}$ and $\vec{B}$ respectively experiences a force:

$$\vec{F} = q\vec{E} + q\vec{v} \times \vec{B} \quad (3.4.2.1)$$

To measure the Hall Effect in a bar-shaped, n or p-type semiconductor (figure 3.16) a constant current should flow along the x-axis, from left to right, in the presence of a magnetic field along the z axis, from bottom to top. The carriers drift away due to the Lorentz force: electrons to the negative y-axis, while holes to the positive y-axis due to opposite charge and velocity. This effect, results in carrier accumulation at opposite sides of the bar [Hal79] generating a potential drop across, called the Hall voltage:

$$V_H = \frac{IB}{ed} \quad (3.4.2.2)$$

Where I is the current, d is the sample thickness and e is the elementary charge ($e = 1.602 \times 10^{-19} \text{ C}$). The Hall voltage is negative for n-type semiconductors and positive for p-type semiconductors. It is convenient to use the sheet carrier concentration ($n_s = nd$):

$$n_s = \frac{IB}{e|V_H|} \quad (3.4.2.3)$$

Hence, by measuring the Hall voltage the sheet carrier concentration and hence the bulk carrier concentration can be calculated. Determining the sheet resistance one can obtain the Hall mobility:

$$\mu = \frac{|V_H|}{IR_S B} = \frac{1}{en_s R_S} \quad (3.4.2.4)$$

If the thickness of the layer is known, the bulk resistivity ($\rho = R_S d$) (3.4.2.5) and the bulk carrier concentration ($n = n_s/d$) (3.4.2.6) can also be calculated.

Figure 3.16 Schematic of a current flowing through an n-type semiconductor that is inside a magnetic field.

In order to determine both n_S and μ , a combination of a resistivity and a Hall voltage measurements is needed. The Van der Pauw technique (explained below) is widely used in semiconductors to determine the resistivity of uniform samples [Pau58] and [Pau58b]. The objective of the resistivity measurement is to determine the sheet resistance R_S . Van der Pauw demonstrated that there are actually two characteristic resistances R_A and R_B , associated with the corresponding terminals shown in figure 3.17. R_A and R_B are related to the sheet resistance R_S through the Van der Pauw equation:

$$e^{-\frac{\pi R_A}{R_S}} + e^{-\frac{\pi R_B}{R_S}} = 1 \quad (3.4.2.7)$$

That can be solved numerically to derive R_S . The bulk resistivity is then calculated as $\rho = R_S d$ (3.4.2.8).

The Hall measurements goal in the Van der Pauw configuration is to determine the sheet carrier concentration (n_S) by obtaining the Hall voltage (V_H) from a series of voltage measurements at constant current I and magnetic field, B . There are practical aspects that must be taken into account for Hall Effect measurements, such as the size and quality of the ohmic contacts, the sample uniformity and an accurate determination of its thickness.

Figure 3.17 Schematics of the Van der Pauw configuration used in this work

Sample geometry is critical to use the Van der Pauw configuration in the sense that they must be regular. Different configurations are shown in figure 3.18. The average diameter of the contacts (D) should be smaller than the sample thickness (t) and the distance between contacts (L). Relative errors caused by non-point contacts are of the order of D/L . In this thesis, the geometry selected was the square with the contacts inside the perimeter due the preparation simplicity (fig. 3.19d).

Figure 3.18 Different geometries for Van der Pauw measurements: a) cloverleaf, b) square with contacts at the corners, c) square with contacts at the edges and d) square with contacts inside the perimeter. [NIS].

3.4.3. Solar cell characterization

The solar cell characterization is commonly performed using a solar simulator (also known as artificial sun), a device that provides illumination close to the natural sunlight under certain conditions, so that the test can be controlled and done indoors.

In this thesis, a solar simulator using a Xenon arc lamp was used to test solar cells. These lamps deliver high intensities over an unfiltered spectrum that matches reasonably well the sunlight. However, many undesirable sharp atomic transition peaks are present in the Xe spectrum, what pose a in some spectrally sensitive applications. Prof. Alejandro F. Braña de Cal performed the solar cell tests at the Autonoma University of Madrid (UAM).

The solar radiation closely matches a black body radiator at about 5.800 K. As it passes through the atmosphere, sunlight is attenuated by scattering and absorption; the more atmosphere through which it passes, the greater the attenuation. Different solar spectrums are defined as:

The **AM0**: is the sun spectrum outside the atmosphere. It is approximated by the 5.800 K black body spectrum.

The **AM1**: is the sun spectrum after travelling through the atmosphere to sea level with the sun directly overhead.

The **AM1.5**: is the sun spectrum at a solar zenith angle of 48.19°. This spectrum is the most commonly used to characterize a solar cell.

Important figures of merit of a solar cell are (figure 3.19):

Open circuit voltage (V_{oc}) is the maximum achievable output voltage under open-circuit conditions.

Short circuit current (I_{sc}) is the maximum output current under load short-circuit conditions. The maximum output power delivered by the device is $P_m = (I_m \times V_m)$. By choosing properly the load resistor the output power can be as high as $0.8 \times (I_{sc} \times V_{oc})$.

The *output power* (P) delivered that results from the product ($I \times V$). The maximum P value is ($I_{mp} \times V_{mp}$) that can be as high as $0.8 \times (I_{sc} \times V_{oc})$, by choosing the proper load resistor.

Figure 3.19 Typical I - V curve of a solar cell under dark and illumination conditions.

The *fill factor* (FF) is the ratio of the maximum obtainable power to the product of the open circuit voltage and short circuit current: $FF = \frac{I_{mp} \times V_{mp}}{I_{sc} \times V_{oc}}$. This is a key parameter in evaluating a solar cell performance. The fill factor is directly affected by the cell series and shunt resistances and diode losses. Increasing the shunt resistance (R_{sh}) and decreasing the series resistance (R_s) lead to a higher FF , thus resulting in greater efficiency bringing the cell output power closer to its theoretical maximum.

3.5. Molecular Beam Epitaxy (MBE)

All samples considered in this thesis were grown with a RIBER Compact 21S Plasma Assisted-Molecular Beam Epitaxy (PA-MBE) system, capable to handle up to 2 inches diameter samples. A schematic of the system is shown in figure 3.20.

The MBE system has two chambers: the introduction (IC) and the growth chamber (GC). The IC where samples are loaded is equipped with a heating filament for outgassing the samples heating them up to 500 °C prior to be introduced into the GC. The GC, where the growth takes place, is equipped with solid sources (Knudssen cells) for metals and dopants, an inner cryogenic panel that surrounds all them to foster pumping speed (UHV), and a substrate holder can be heated up to 1000 °C. The system also includes an optical pyrometer and a RHEED system (with a 15 keV electron gun from Staib Instruments) for *in-situ* characterization and monitoring. Samples are transferred from the IC to de GC and vice versa using a magnetic transfer arm.

The UHV regime is achieved by an ion pump in the IC ($\sim 1 \times 10^{-9}$ torr) and a mixture of ion and cryogenic pumps in the GC ($\sim 2 \times 10^{-10}$ torr), than can be pushed down to $\sim 1 \times 10^{-11}$ torr with the use of cryopanel. The pressure in both chambers is measured by a hot-filament ionization gauge (Bayard-Alpert). In addition, the GC is equipped with a retractable hot-filament ionization gauge (Bayard-Alpert) for flux measurements.

As mentioned before, Knudsen effusion cells [Boy64] are used for Al, Ga, In metals and doping (Si for n-type and Mg for p-type). Knudsen cells have pyrolytic boron nitride (PBN) crucibles heated with a filament placed around them and thermally shielded with Ta shrouds. The cell temperature is measured by a thermocouple in direct contact with the bottom of the crucible. Mechanical shutters, placed in front of each cell, allow a very fast beam flux interruption, what enables to control material composition and interfaces abruptness down to a monolayer. A special cell is used for Mg doping: a RIBER S40 VCOR 110 valved one designed to be used with corrosive materials such as Mg, with two heating

zones, the reservoir and the tip. It is equipped with a needle valve in the tip, which allows a precise and reproducible control of the Mg flux.

The active nitrogen (N^*) is provided by a radio-frequency plasma source where high purity (99.999999%) molecular nitrogen (N_2) dissociates into very reactive atomic species (N). The source cavity is coupled with a LC circuit that provides a resonant frequency of 13.56 MHz to generate the plasma. An optical detector inside the cavity picks up the 746.8 nm spectral line signal from atomic N species in the plasma estimate the amount of active nitrogen.

The substrate is placed in an indium-free molybdenum holder that is placed on the GC oven and heated by radiation. When using GaN/Sapphire templates, the sapphire backside is covered with a 2 μm thick titanium layer to help heat transfer to the substrate (sapphire is almost transparent due to its 9 eV bandgap).

The impinging molecular fluxes are calibrated in (0001) GaN (for Ga and N), (0001) InN (for In) and (0001) AlN (for Al) in equivalent growth units from SEM measurements in thick layers. The growth temperature should be low enough to avoid nitride decomposition and metal desorption. Growth must be kept under excess of nitrogen in order to incorporate all the group III elements, so that the supplied metal limits the growth rate. The growth rate in nm/min is the ratio between the layer thickness and the growth time. A direct relation between the beam equivalent pressure (BEP) measured by the Bayard Alpert gauge and the growth rate in nm/min can then be established. Similarly, the active nitrogen flux expressed in nm/min is estimated from a compact layer grown under metal excess (the growth finishes with metallic droplets on the surface). In this case, all the active nitrogen is incorporated into the layer and the growth is limited by the amount of nitrogen supplied.

Figure 3.20 Scheme of a RIBER Compact 21 S MBE system used in this work.

MBE growth is characterized by: a) low growth rate down to one monolayer per second; b) low growth temperature; c) smooth grown surfaces with atomic steps and large flat terraces; d) precise control of layer composition and morphology; e) abrupt variation of chemical composition and interfaces; f) high purity due to

the UHV environment; and g) possibility of *in-situ* control of the crystal growth at atomic level (RHEED).

Different atomistic processes may occur on the substrate surface during growth (fig. 3.21): deposition, diffusion on terraces, nucleation on islands, nucleation on second-layer islands, diffusion to a lower terrace, attachment to an island, diffusion along a step edge, detachment from an island or desorption.

Figure 3.21 Different processes taking place on the substrate surface during MBE growth.

The occurrence of a particular process depends on various parameters from which the most important ones are the surface temperature and the misfit between the layer and the substrate. Accordingly, three growth modes are described (fig. 3.22):

- i. Frank-van der Merwe (FV) → Also known as 2D or layer-by-layer growth mode. Ideally, a new monolayer starts growing once the previous one is completed. A particular case of the FV is the step flow growth.
- ii. Volmer-Weber (VW) → Direct nucleation of small islands to minimize energy arising from strong lattice mismatches. Surfaces are quite rough. A particular case of the VW is the columnar growth.

- iii. Stranski-Krastanov (SK) → Considered as an intermediate between FV and VW, it starts as VM until the energy accumulated by mismatch relaxes and islands are grow on top.

Figure 3.22 Different growth modes by MBE.

Nucleation and growth processes, as well as the resulting layer structure and morphology are largely determined by the growth mode. Since Ga is preferentially incorporated, the In excess tends to segregate to the surface where it forms droplets in addition to a 2 – 3 monolayer (ML) wetting layer. The growth conditions are determined, among other factors, by the ratio between the group III fluxes and the nitrogen flux: $III/V = \frac{\phi_{In} + \phi_{Ga}}{\phi_N}$, called III/V ratio. According to this parameter, the growth can be classified in the following types:

- $III/V < 1$ → N-rich conditions. Metal adatoms mobility is poor leading to rough surfaces and even to nanowires (NWs). Growth rate is determined by the sum of metal fluxes.
- $III/V > 1$ → Metal-rich conditions. Metal adatoms mobility is higher leading to flat surfaces with the potential appearance of metal droplets. Growth rate is determined by the nitrogen flux.
- $III/V = 1$ → Stoichiometric conditions that result in flat surfaces. Growth rate can be determined either by the nitrogen flux or by the metal flux.
- $III/N \gg 1$ → Droplets regime. A high density of metal droplets accumulates on the surface.

The alloy composition of InGaN alloys grown under N-rich conditions is determined by the ratio between the indium growth rate and the sum of the individual metal growth rates:

$$\%In = \frac{v_{In}}{v_{In} + v_{Ga}}$$

For Metal-rich conditions:

$$\%In = \frac{v_N - v_{Ga}}{v_N}$$

Because Ga incorporates preferentially over In and only the N flux in excess to the Ga one will help In incorporation into the lattice. Both expressions are only valid for temperatures below the onset of In-N decomposition (In-N decomposition starts over 470 °C [Gal07]), the Ga-N one is much higher. It is worth to mention that the In desorption temperature is significantly higher than the In-N decomposition one (over 600 °C [Gal07]), leading to droplet accumulation. The opposite happens to GaN. The expression for the In-N decomposition rate is given by:

$$\phi_{dec}^{InN} = C x_{In} e^{\left(-\frac{E_a^{dec}}{kT}\right)} \quad (3.5.0.1)$$

Where C is the decomposition pre-exponential factor (it is a constant for each reaction that defines the rate due to frequency of In-N bonds broken), x_{In} is the mole fraction of the InGa_N film, k is the Boltzmann's constant, T the temperature and E_a^{dec} is the activation energy of the decomposition process. The most recent and precise values reported for the E_a^{dec} are 1.92 ± 0.11 eV [Gal07] and 1.84 ± 0.12 eV [Gac12]. The value of the C-prefactor found in [Gac12] is 2.55×10^{25} atoms/cm²s and of 3.4×10^{28} atoms/cm²s in [Gal07]. The In desorption rate is given by:

$$\phi_{des}^{In} = A \phi_{Imp}^{In} e^{\left(-\frac{E_a^{des}}{kT}\right)} \quad (3.5.0.2)$$

Where ϕ_{Imp}^{In} is the impinging In flux and A is the desorption pre-exponential factor (it is a constant for each reaction that defines the rate due to frequency of In-In bonds broken), and E_a^{des} is the activation energy of the In desorption process. Gallinat and co-workers reported a value for the E_a^{des} of 2.49 ± 0.13 eV and of [Gal07].

The optimal conditions to grow GaN by PAMBE are slightly metal rich (intermediate metal-rich growth regime) to enhance metal adatoms diffusion yielding flat surfaces [Hey00]. Gacevic et al. showed that not all the In flux

impinging on the substrate is incorporated into the InGa_N layer when the growth is performed in the intermediate metal-rich growth regime [Gac12]. It has also been observed that under metal-rich conditions, depending of the In composition and growth temperature, phase separation may appear. Thus, slightly N-rich conditions are preferred to reduce phase separation despite the fact that surface flatness is worsened.

In this thesis three different growth mechanisms are considered, the conventional one, the Metal Modulated Epitaxy (MME) and the Droplet Elimination by Radical-beam Irradiation (DERI). The last two have been selected because of the advantages they offer in growing InGa_N alloys.

The MME method was first proposed by Prof. Doolittle [Nam08] to growth efficient Mg-doped (In)Ga_N layers. MME is a periodic growth with abrupt transitions between metal-rich and N-rich growth conditions (fig. 3.23). N-rich conditions are used to enhance Mg incorporation in Ga substitutional sites while preventing the formation of V_N (compensation), at the expense of roughening the layer surface. Next, metal-rich conditions (without Mg flux) smooth out the layer surface.

This periodic growth is achieved by cycling (in the order of seconds) the corresponding shutters opening/closing while keeping the N^* constant. Metal droplets may build up under metal-rich half cycles, which are depleted during the N-rich one. Non-optimal opening/closing timing may lead to incomplete droplets depletion. NID InGa_N layers over the whole composition range, as well as p-type doped with 0 to 22 In% have been successfully grown by MME [Mos13], [Fab15]. Results on p-InGa_N of a hole concentration of $2.4 \times 10^{19} \text{ cm}^{-3}$ for $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$ [Mos13] and a residual n-type concentration of $2 \times 10^{15} \text{ cm}^{-3}$ for Ga_N [Fab15] grown at $2 \mu\text{m} \cdot \text{hr}^{-1}$. To summarize the main advantages of MME:

- i. Higher hole concentrations due to a higher Mg incorporation in substitutional sites reducing compensation by V_N .
- ii. Good surface morphology in terms of roughness.

Figure 3.23 Schematic representation of the MME growth method when the shutters are a) opened and b) closed.

DERI method (fig. 3.24), proposed by Prof. Nanishi et al., [Yam09], [Yam13] consists of two processes: a metal rich growth (MRGP) and a droplet elimination one (DEP). During the MRGP InGaN is grown under metal-rich conditions ($\phi_{In} + \phi_{Ga} > \phi_N$) with the restriction of Ga flux to be smaller than that of N^* ($\phi_{Ga} < \phi_N$) to ensure In incorporation into the layer. Since Ga is preferentially incorporated the In excess tends to segregate to the surface where it forms droplets in addition to a 2 – 3 monolayer (ML) wetting layer. During the DEP process these droplets are transformed into InGaN by shutting down the In flux (In droplets act as reservoirs) while keeping the $\phi_{Ga} < \phi_N$ condition. Once all droplets are transformed (observed by RHEED intensity) the MRGP starts again to avoid N-rich GaN growth and smoothing out possible roughness. Since the Ga/ N^* ratio is kept constant all the way the In content of the InGaN layer is basically the same during both processes. By repeating the MRGP and DEP a thick and homogeneous InGaN layer can be successfully grown [Yam13]. The In content being determined only by:

$$\%In = \frac{v_N - v_{Ga}}{v_N}$$

The main advantages of the DERI method are:

- The combination of the MRGP and the DEP enables the possibility to grow under metal-rich conditions ending with a rather flat surface.
- There is no need for a precise control of fluxes as far as the mentioned relative flux ratios are kept.

Figure 3.24 Schematic of the DERI method. A) Metal Rich Growth Process and b) Droplet Elimination Process.

4. MME growth and characterization of Mg doped GaN layers on GaN(0001) on Sapphire templates

4.1. Introduction

The development of efficient III-Nitride based devices, such as light emitting diodes (LEDs), lasers, and solar cells, requires achieving high levels of n- and p-type doping. N-type doping of III-Nitrides poses no problems and Silicon is the most common n-type dopant employed in this materials system. However, p-type doping is still a big challenge. Mg has been proven the most effective p-type dopant. The large acceptor activation energy of the Mg atoms ($\sim 160 - 170$ meV) [Mou93], together with the low hole mobilities result in limited performance of the Mg-doped nitride based devices. For example, LEDs and lasers have a reduced performance because of reduced hole injection. The lack of degenerate p-doped films increase the complexity of the design of tunnel junctions [Kri13], [Kri13b], thus, limiting III-Nitride solar cells to single junction structures.

In the last decade, MME has been introduced as a new growth method within a PA-MBE reactor, in which only the metal fluxes (Al, Ga, In, Si and Mg) are modulated in a short periodic fashion while exposing continuously to a nitrogen plasma flux. With this method a dramatic increase in the hole concentration ($> 10^{19} \text{ cm}^{-3}$) has been demonstrated [Nam08]. Details on the MME growth method can be found in section 2.5 and in references [Nam08], [Try09] and [Nam13].

The conventional MBE growth of GaN is well documented in the literature [Hey00], [Pob05], [Kob07]. Three distinct growth regimes are identified: Ga-rich, N-rich and an intermediate regime. The best crystal quality GaN layers are usually grown on the intermediate regime, where a constant Ga ad-layer (between 1 and 2 monolayers) is accumulated on the surface [Hey00]. The MME approach, when applied to higher temperatures or in a predominantly droplet rich regime, results in atomically smooth surfaces normally only found when growing in the Ga-droplet regime. Conversely, MME does not allow droplets to accumulate, making it viable for devices that traditionally depend on smooth

droplet free interfaces. In this chapter the influence of the Mg flux on the hole concentration is analysed. In addition, a comparison between MME and conventional growth will be discussed, focusing mainly on the surface morphology, PL emission and carrier (hole) concentration results.

All the GaN films of this chapter were grown on commercial Fe-doped GaN-on-Sapphire templates. Fe-doped GaN layers are highly resistive, allowing Hall Effect measurements of the grown film to be carried without parallel conduction via the substrate and therefore a straightforward interpretation. The templates were degassed according to the procedure described in appendix a.

4.2. Non-intentionally doped GaN grown on insulating templates for residual concentration analysis

In this section, GaN films, grown by conventional MBE growth (in the intermediate regime) and by MME, are compared in terms of surface morphology, PL emission and residual carrier concentration.

For the layer grown by conventional MBE in the intermediate regime (labelled IR0) the Ga flux was 9 nm/min and the N* flux was 6 nm/min. The substrate temperature was set to 690 °C, leading to a Ga desorption rate of 2.8 nm/min but keeping a net metal coverage on the growth front. The effective growth rate was 6 nm/min. The temperature was calibrated using RHEED, according to the Ga desorption curves proposed by Fernández-Garrido et al. [Fer08]. This temperature allows to accumulate 2 Ga monolayers on the surface, resulting in a growth in the intermediate regime.

For the layer grown by MME (named MME0) the Ga and N* fluxes were 5 and 4 nm/min respectively. The substrate temperature was set to 600 °C. According to figure 4.1 a temperature of 600 °C is high enough to produce good surfaces [Nam08] and the growth can oscillate from Ga-droplet conditions to N-rich conditions without entering in the intermediate regime. The shutters modulation scheme was set to 10 seconds opened and 5 seconds closed. Growth conditions were chosen to obtain metal-rich growth, while still consuming all excess metal into the film each modulation cycle.

Figure 4.1 Ga Flux vs Substrate Temperature diagram showing the different growth modes for GaN growth by PA-MBE. The red arrow indicates the regime used in this chapter for MME growth. Diagram adapted from [Hey00].

Figure 4.2a shows the transient RHEED intensity during the MME growth of the GaN film. The shaded regions indicate the time when the metal shutters were opened. The decrease in RHEED intensity upon opening of the metal shutters seen in fig 4.2a is attributed to the accumulation of excess metal on the surface. This behaviour has been reported for GaN [Mos09], AlN [Bur06], [Bur07] and InGaN [Mos13]. The final RHEED pattern of the GaN layers (fig. 4.2b and c) is bright and streaky, fingerprint of a smooth and dry surface, with no Ga droplets or ad-layers at the end of the growth.

Figure 4.2 a) Transient RHEED intensity of the GaN layer grown by MME. Shaded regions indicate when the Ga shutter was open. RHEED patterns at the end of the growth of GaN layers b) grown in the intermediate regime and c) grown by MME.

The top-view SEM micrographs of the non-intentionally doped GaN films are shown in fig. 4.3. Both films are compact and flat, as expected for the conditions used. The root mean square surface roughness, measured by AFM, is 0.7 nm in both cases. No extended defects or droplets are found in none of the samples. In terms of morphology, no clear difference is found between both growth methods. In the intermediate regime case the layer is grown under Ga accumulation on the surface (between 1 and 2 monolayers), which leads to an increase in the surface diffusion length of the Ga and N adatoms. An increase in the surface diffusion length allow the atoms to reach sites energetically more favourable. This gives rise to a reduction on the defects of the film. The best GaN films are typically grown in this regime.

The MME growth mechanism involved is significantly different. MME was proposed to increase the proper incorporation of Mg atoms in Ga substitutional sites, while reducing the degradation of the film. One of the key benefits of the MME technique is the use of Ga-rich conditions to smoothen the surface out and prevent extended defects resulting from faceting. This is followed by N-rich conditions to promote Mg incorporation onto the Ga-substitutional sites, while

reducing the production of compensating N-vacancies [Sta98]. By repeating this process, a surface comparable to the one grown in the intermediate regime was obtained.

Figure 4.3 Top-view SEM micrographs of the non-intentionally doped GaN films grown in the intermediate regime (IR0) and by MME (MME0). The scale bar is 1 μm in both cases.

The optical properties of both films were analysed by low temperature (10 K) photoluminescence spectroscopy (Figure 4.4). Both spectra are dominated by the transition associated to the free exciton A (corresponding to the Heavy-Holes valence sub-band), located at 3.4785 eV [Cor14]. The FWHM of the X_a emission peak is 9 and 15 meV for the IR0 and the MME0 samples respectively. In the case of the IR0 sample, another strong emission line is located at 3.471 eV. This emission is attributed to the neutral donor bound exciton (DBE), associated to the O_N or to the Si_{Ga} , and the emission energies are 3.4714 and 3.4723 eV respectively [Mon08]. Due to the limited resolution of the setup it is not possible to fully determine the origin of the emission. In the MME0 spectrum this transition does not appear, but the peak corresponding to the X_a is broad enough to suggest that either the peak is broadened by defects, or that both peaks are not resolved due to the measurement parameters.

Figure 4.4 Low temperature (10 K) PL spectra of the GaN films a) grown in the intermediate regime and b) grown by MME. Both spectra are normalized to the unity and intensity is represented in logarithmic scale. Emission peaks are labelled for clarity.

A possible origin of the emission lines located around 3.2 and 3.4 eV are basal stacking faults (BSFs). The related emission of the BSFs was discussed on section 2.4.5. Typical PL emission lines associated to the BSFs are I_1 3.40 to 3.43 eV [Cor14], I_2 3.32 to 3.36 eV [Tis11] and $E \sim 3.29$ eV [Lah14].

For the MME0 layer the ultra-violet luminescence (UVL) band is also observed. This band is broad and covers the energies associated with the BL band. Both bands could overlap. The zero phonon line (ZPL) is labelled in the MME0 corresponding spectrum (fig. 4.4). The UVL band is attributed to a DAP transition from a shallow donor to a shallow acceptor [Res05]. The shallow acceptors are usually Si_{Ga} or O_N (with activation energies of 30 and 33 meV respectively [Moo02]), as it was reported by Dingle and Ilegems [Din71]. Both layers show YL emission in the range of 2.20 – 2.25 eV (data not shown here).

The layer grown in the intermediate regime has a lower FWHM of the X_a emission line, lower intensity in the BL band and no presence of the UVL band. Thus, showing a superior optical quality.

Both layers were electrically characterized by room temperature Hall Effect measurements, with Van der Pauw geometry using In ohmic contacts. The layers were characterized as-grown. Results of the Hall Effect measurements can be found in table 4.1.

Sample	Type	Doping (cm ⁻³)	Mobility cm ² /(V.s)	Resistivity (Ohm.cm)
IR0	n	1.3 x 10 ¹⁷	414	0.12
MME0	n	5.2 x 10 ¹⁷	190	0.19

Table 4.1 Hall Effect measurements of samples IR0 and MME0.

The results of the Hall Effect measurements show that the layer grown on the intermediate regime has 4-times less residual n-type concentration than the one grown by MME. This could be related to less incorporation of impurities (typically Si_{Ga} and O_N). The PL spectrum of both samples show clearly that the sample grown by MME has a higher density of defects, which might be related to a higher density of compensating defects. Thus, leading to a higher residual n-type concentration. This might be due to the difference in growth rate; Gunning et al. demonstrated that at high growth rates (~2 μm/hr) the residual doping concentration fell to 10¹⁵ cm⁻³ [Gun15]. In this case the difference is of 0.12 μm/hr when Ga shutter is opened. Electron mobility in the IR0 sample is two times larger than the mobility in the MME0. The resistivity is two times less in the IR0 than in the MME0. The differences found in these results might be attributed to the difference in growth rate and temperature. To study both effects on the MME growth, two sets of experiments are proposed (future work): one series increasing the growth temperature and a second one increasing the growth rate.

According to the results, both layers showed similar morphology, but the layer grown on the intermediate regime showed better optical quality and superior electrical properties. Based on these results, the intermediate regime seems to be superior for the growth of non-intentionally doped GaN layers.

4.3. Mg-doped GaN grown on insulating templates for hole concentration analysis

In this section, p-type doped GaN films, grown by conventional MBE growth (in the intermediate regime) and by MME, are compared in terms of surface morphology, PL emission and hole concentration.

Besides the challenges for efficient Mg-doping of GaN layers, discussed on sub-section 2.5, it should be added that the Mg incorporation is strongly dependent on the III/N ratio, the self-compensating defects, the polarity of the GaN layer and the existence of inversion domains that limit the upper solubility of Mg.

Bhattacharyya and co-workers [Bha04] obtained hole concentrations on c-plane GaN of $3 \times 10^{18} \text{ cm}^{-3}$ and resistivity of $0.3 \text{ } \Omega\text{-cm}$ with high Ga fluxes (BEP: $1.3 \times 10^{-6} \text{ torr}$), high substrate temperatures ($\sim 770 \text{ } ^\circ\text{C}$) and high Mg fluxes (BEP: $1.5 \times 10^{-8} - 1.5 \times 10^{-7} \text{ torr}$). The authors stated that Mg incorporates more effectively with extreme Ga-rich conditions resulting in a dissolution of Mg in the Ga film, which increases the Mg sticking coefficient.

In 2009, Namkoog and co-workers [Nam09] reported extremely high hole concentrations above 10^{19} cm^{-3} for Mg-doped GaN films using the MME technique. The authors modulated the Ga and Mg shutters with a constant duty cycle, achieving hole concentrations of $1.5 \times 10^{19} \text{ cm}^{-3}$, Hall mobilities of $0.5 \text{ cm}^2/\text{V.s}$ and resistivity of $0.9 \text{ } \Omega\text{-cm}$. E. Trybus reported in her PhD thesis hole concentrations as high as $4.26 \times 10^{19} \text{ cm}^{-3}$, a mobility of $0.28 \text{ cm}^2/\text{V.s}$ and a resistivity of $0.5 \text{ } \Omega\text{-cm}$ using the MME technique on Mg-doped GaN films grown at $600 \text{ } ^\circ\text{C}$ [Try09]. Simon et al. [Sim08] also studied the effect of III/V ratio on the resistivity of Mg-doped GaN layers using substrate temperatures of $600 \text{ } ^\circ\text{C}$ and a Ga flux ranging from $1.30 - 1.71 \times 10^{-7} \text{ torr}$ BEP, which corresponded to a change from N-rich conditions to Ga-rich conditions. They discovered that Ga-rich conditions are necessary for highly conductive p-type layers, but Ga-rich conditions may also lead to higher leakage current, detrimental to vertically conducting devices. It was recommended that vertical devices should employ a modulation of Ga and N_2 fluxes to prevent leakage while maintaining high p-type

conductivity, enforcing the idea that MME will be a beneficial technique for nitride-based devices.

Another key aspect of the MME approach for Mg-doping is the use of sufficiently low substrate temperatures where an abrupt transition is available between Ga-droplet and N-rich conditions without an intermediate phase (see figure 6.1). The low substrate temperature ensures that transitions from Ga-droplet to N-rich regimes are abrupt and the intermediate Ga-rich regime is thermodynamically unstable. Under these conditions, the Ga bilayer is either in the process of building up or in the process of depleting and cannot be sustained without the addition of droplets. At the low substrate temperatures, the consumption of the Mg-saturated Ga bilayers and droplets only occurs through growth of the GaN film as Ga desorption is minimized.

For the layers grown on the intermediate regime (named IR1, IR2 and IR3) the Ga flux was 9 nm/min and the N^{*} flux was 6 nm/min. The substrate temperature was set to 690 °C, for a desorption rate of 2.8 nm/min. The effective growth rate was 6 nm/min. The temperature was calibrated as in previous section.

For the layers grown by MME (labelled MME1 to MME7) the Ga and N^{*} were 5 and 4 nm/min respectively. The substrate temperature was set to 600 °C. According to figure 4.1 a temperature of 600 °C is high enough to produce good surfaces [Nam08] and the growth can oscillate from Ga-droplet conditions to N-rich conditions without entering in the intermediate regime. The shutters modulation scheme was set to 10 seconds open and 5 seconds close. Growth conditions were chosen to obtain metal-rich growth, while still consuming all excess metal into the film each modulation cycle. The valve of the Mg cell was modulated together with the Ga shutter. However, the valve was opened up to the 90% and closed down to the 15% to avoid possible failures or unbalancing of the controller when the valve went to 100% or 0% repeatedly. The layers were grown at seven different Mg reservoir temperatures, ranging from 150 to 300 °C. The Mg tip temperature was fixed at 450 °C for all the growths. Table 4.2 shows the growth conditions for all the samples studied:

Sample	T _S (°C)	φ _{Ga}	φ _N	T _{Mg Res} (°C)	T _{Mg Tip} (°C)
IR1	690	9	6	225	450
IR2	690	9	6	250	450
IR3	690	9	6	275	450
MME1	600	5	4	150	450
MME2	600	5	4	175	450
MME3	600	5	4	200	450
MME4	600	5	4	225	450
MME5	600	5	4	250	450
MME6	600	5	4	275	450
MME7	600	5	4	300	450

Table 4.2 Growth parameters for the samples grown varying the Mg reservoir temperature. Fluxes are given in nm/min.

Top-view SEM micrographs are shown in figure 4.5. At a first look the layers doped with Mg show a significant change on their surface morphology from flat (fig. 4.3) to rough surfaces (fig. 4.5). Out of the ten Mg-doped GaN layers grown, MME4 shows the flattest surface. Sample IR3 shows the best surface among the samples grown in the intermediate regime. This is a surprising result because it is the sample with the highest Mg reservoir temperature (275 °C) of the IR series, and as the Mg flux is increased the morphology of the sample is expected to degrade and the surface to get rougher. Sample MME4 shows the best surface morphology among the samples grown by MME. This sample was grown at a mid-Mg reservoir temperature (225 °C). There is a clear degradation of the surface morphology as the temperature of the Mg reservoir, i.e. the Mg flux, increases beyond 225 to 300 °C for the MME growth method used. It has been observed that the incorporation of Mg into the structure produces a degradation of it [Bha04], [Nam08], [Try09].

Figure 4.5 Top-view SEM micrographs of the Mg doped GaN films grown in the intermediate regime (left) and by MME (right). The scale bar is 1 μm in all cases.

Figure 4.6 Low temperature (10 K) PL spectra of the Mg-doped GaN films grown in the intermediate regime (left) and grown by MME (right). All the spectra are normalized to the unity and intensity is represented in logarithmic scale. Emission bands are labelled for clarity. Dashed lines mark the transitions.

In the emission spectra of the samples grown in the intermediate regime (fig. 4.6 left) the DBE and the ABE₂ emission lines can be found. The DBE is associated to the residual donors (Si_{Ga} or O_N), the related emission energies are 3.4723 and 3.4714 eV, respectively [Mon08]. The resolution of the setup employed is not enough to distinguish between both lines. The acceptor bound exciton, ABE₂, emission line is presented at 3.454 eV and is dominant at high Mg concentrations [Mon09]. This is the acceptor associated to the Mg substitutional at Ga site (Mg_{Ga}).

In the emission spectra of the samples grown by MME (fig 4.6 right) the emission lines associated to the X_a, ABE₁ and ABE₂ are presented. The X_a emission line is attributed to the free exciton (A-exciton) formed by an electron and a heavy hole (HH), its emission energy is 3.4785 eV [Cor14]. Typically Mg-doped GaN films

show DBE instead of the FXA emission [Mon08], [Mon09], [Res05]. This difference might be produced by the MME growth method, but still needs further investigation. Both ABE transition depends on the [Mg]. The intensity of both transitions varies with the reservoir temperature of the Mg cell. At the lowest temperature (150 °C) only the ABE₁ is presented but as the temperature is increased both peaks vary till only the ABE₂ is present (300 °C). Then the ABE₁ emission line dominates at low to moderate [Mg] and the ABE₂ becomes dominant at high [Mg].

The ABE₁ is related to the Mg-H complexes and is dominant at low to moderate Mg concentration. The formation of such complexes deactivates the Mg atoms, passivating them and avoiding the proper p-type doping. Those complexes are unstable versus temperature, in such a way that an annealing process at high temperature is beneficial to increase the final hole concentration. The ABE₂ is related to the Mg_{Ga} and is dominant at high Mg concentration. In order to obtain efficient p-type doping Mg atoms should be incorporated preferentially on substitutional Ga sites (Mg_{Ga}).

A series of weak emission lines are found in the range 3.34 to 3.43 eV (labelled as DAP in the spectra, fig 4.6). Monemar et al. attributed those emission lines to discrete DAP lines [Mon08], [Mon09]. They studied their dependence with temperature and found that their dependence is very similar to ABE₁ and ABE₂, quenching at 50 K [Mon09]. However, there is not a detailed model for these lines at present.

The dominant emission for almost all spectra is the UVL band. The zero phonon line (ZPL) is located at 3.27 eV, and one or two phonon replicas are found in almost all samples. They are the 1LO and the 2LO, located at 3.18 and 3.09 eV, respectively. It is attributed to the shallow-donor to shallow-acceptor transition. This transition decreases in intensity upon annealing, which is known to lead to dissociation of the Mg-H complexes [Mon09]. Therefore, a high intensity on the UVL band is associated to a high density of Mg-H complexes, and thus, to a high density of passivated Mg atoms.

The BL band usually appears at very high Mg concentrations ($>10^{20} \text{ cm}^{-3}$). It is commonly assigned to a deep donor-shallow acceptor, where the donor is suggested to be a $V_N\text{-Mg}_{Ga}$ complex. Monemar et al. [Mon09] demonstrated that its origin should not be due to any $V_N\text{-Mg}_{Ga}$ donor, but its origin is still unknown. In general, the contribution of the BL band to the spectra is screened by the UVL band, which is dominant. All the samples showed YL band emission (data not shown here).

Figure 4.7 a) Hole concentration as measured by Hall vs Mg reservoir temperature and b) resistivity vs Mg reservoir temperature for the GaN layers grown in the intermediate regime and grown by MME. Dashed lines are a guide to the eye.

Hall Effect measurements were performed to extract hole concentration and resistivity values of the Mg-doped GaN layers. For simplicity Van der Pauw geometry using In ohmic contacts were employed in this study. The highest hole concentration ($4.9 \times 10^{18} \text{ cm}^{-3}$) was achieved for the sample grown by MME at a Mg reservoir temperature of 225°C . For the samples grown in the intermediate

regime the maximum hole concentration achieved was $9.1 \times 10^{17} \text{ cm}^{-3}$, ~5 times lower than the one achieved with the MME growth method. The hole concentration for the films grown in the intermediate regime (fig. 6.7a) decreases as the Mg reservoir temperature (i.e. the Mg flux) increases. The mechanism behind this behaviour is the self-compensation. As the hole concentration increases the Fermi energy moves towards the valence band and reduces the formation energy of the V_N (self-compensating defect) [Wal96]. The sample MME1 (150 °C) show n-type behaviour and is not shown in the figure 4.7. For the MME grown films the hole concentration (fig. 4.7a) initially increases until it reaches a maximum (MME4, 225 °C). Under these optimum conditions for proper incorporation of the Mg atoms into Ga substitutional sites is achieved. Above 225°C the hole concentration decreases. This behaviour is attributed to the creation of self-compensating defects in the film, as in the case of the films grown in the intermediate regime. The main mechanism for self-compensation is the creation of V_N [Wal96]. Another mechanism involved is the passivation of the Mg atoms with the formation of Mg-H complexes. As it was discussed in the PL results, the ABE1 emission line is attributed to the Mg-H complexes. The ABE1 emission line is dominant over the ABE2 (attributed to the Mg_{Ga} acceptor) in most of the samples, except for the samples grown at high Mg reservoir temperatures (high Mg concentration). It has been demonstrated that the ABE1 emission line (i.e. the Mg-H complexes) is unstable versus temperature (>700 °C) [Mon09] and an annealing of the samples could reduce the intensity of the ABE1 emission line, and therefore, the amount of Mg-H complexes, which would increase the hole concentration. Under such conditions, a higher N-rich growth will help in order to increase the formation energy of the V_N [Wal96], thus reducing the amount of self-compensating defects.

The resistivity (fig. 4.7b) of the films grown in the intermediate regime increases as the Mg flux does. The resistivity of a semiconductor is inversely proportional to the mobility and carrier concentration. Therefore, a decrease in the carrier concentration gives rise to an increase in the resistivity of the film. For the films grown by MME, the resistivity decreases as the hole concentration increases and reaches a minimum when the hole concentration is maximized (MME4, 225 °C).

Beyond that point, the resistivity increases again as the semiconductor gets self-compensated and Mg atoms start creating defects in the film.

4.4. Conclusions

According to the results for non-intentionally doped GaN films, both layers showed similar morphology, but the layer grown by conventional MBE in the intermediate regime showed better optical quality and superior electrical properties.

However, for the optimization of the p-type doping, the MME growth method enhances the incorporation of Mg atoms on Ga substitutional sites, while reducing the formation of self-compensating defects (V_N). Additionally, the use of extreme metal rich conditions (leading to droplets accumulation) reduces the appearance of extended defects, such as inversion domains. The layers grown by MME showed ~5 times higher hole concentration than the layers grown by conventional MBE in the intermediate regime. Therefore, for the same Mg reservoir temperature (i.e. Mg flux) the hole concentration is higher for the MME grown films. The maximum hole concentration achieved in this work is $4.9 \times 10^{18} \text{ cm}^{-3}$. This is one order of magnitude less than the values reported in other works [Nam08], [Try09]. This difference could be due to the high residual n-type concentration found in the undoped GaN films (section 4.2) or due to the conditions used for the MME growth. In this case the fluxes employed were 5 and 4 nm/min for Ga and N* fluxes respectively. They are low as compared to those used by G. Namkoong and E. Trybus on their works. Higher fluxes will lead to a higher accumulation of droplets on the growth front, and therefore, to an increase in the dissolution of Mg into the droplets, preventing their re-evaporation [Bha04] and to a reduction of the polarity inversion domains [Fig02]. With the values employed in this chapter, when the Ga shutter is closed, the conditions are too N-rich, leading to rough surfaces and even to the growth of 3D structures as it was shown in figure 4.5.

The UVL band was found to be the dominant emission. As it was discussed, this emission is related to a DAP, where the acceptor is the Mg-H complex, which is known to passivate the Mg atoms. Optimal MME growth conditions typically leads

to the incorporation of the Mg atoms into Ga substitutional sites. The emission associated to the Mg_{Ga} acceptor is the ABE_2 , which appears at high Mg concentrations. Thus, optimal MME growth conditions are expected to lead to strong ABE_2 emission intensities, and even to dominate the PL spectra. In order to confirm the origin of the UVL band in the MME grown films, temperature dependant PL spectroscopy is proposed, as well as low temperature PL measurements of annealed GaN:Mg films grown by MME. Those experiments are proposed as future work.

5. Metal Modulated Epitaxy (MME): growth and characterization of NID InGaN layers on GaN(0001)/Sapphire templates

5.1. Introduction

InGaN alloys are prone to phase separation through spinodal decomposition. Thermal decomposition and indium surface segregation lead to inhomogeneities in the indium content of the alloy. However, even those inhomogeneities have been demonstrated to improve radiative emissions in LEDs structures due to enhanced carrier localization. However, other structures such as solar cells [Try08] and laser diodes [Nak99] require more uniformity to obtain efficient devices.

These detrimental processes are related to the growth conditions, and therefore, they can be minimized or even suppressed. To reduce thermal [Sta03] and spinodal decomposition [Str10], a reduction in growth temperature is necessary, while nitrogen-rich conditions can be used to inhibit indium surface segregation [Neu03]. However, lower substrate temperatures and growth under nitrogen-rich conditions are both associated with a reduction in the crystal quality of the material.

The requirements of InGaN suggest that a different growth approach should be taken into account. Namkoong and co-workers [Nam13] applied successfully the metal modulated epitaxy (MME) growth method for the growth of high quality InGaN alloys.

5.2. Experimental procedure

MME was described with detail in chapter 3 (section 3.5). It consists in a periodic growth with abrupt transitions between metal-rich and N-rich growth conditions. Metal-rich conditions are used to smoothen the surface and to prevent compensating extended defect and N-rich conditions are used to promote the

incorporation of In and Ga without the production of compensating N-vacancies. This periodic growth is achieved by modulating the state of the metal shutters (open/close) while maintaining constant the N^* flux.

The important parameters for the MME growth are: the growth temperature, III/N ratio, In/Ga ratio and the shutters modulation scheme (opening and closing time intervals).

The growth temperature together with the III/N ratio are the most relevant parameters since they have a direct influence on the surface ad-atom diffusion length, and therefore on the morphology of the InGaN film. The higher the temperature the more energy the ad-atoms have, increasing the surface diffusion length and allowing them to be allocated in positions that minimize their energy. In addition, the temperature also controls the In losses through the In-N decomposition rate and the metallic In desorption rate (section 3.5).

Figure 5.1 RHEED patterns of :a) GaN film regrown by MME, b) InGaN film grown by MME at III/N ratio of 1.2 and at a T_s of 400 °C and c) InGaN film grown by MME at III/N ratio of 1.9 and at a T_s of 525 °C. The contrast is enhanced for pattern c, to distinguish the streaks.

The III/N ratio for the conventional growth was defined in the section 3.5. As it was shown by Gacevic et al. [Gac12] not all the In contents can be obtained in the ternary when growing in the intermediate growth regime. The In/Ga ratio controls the In content of the alloy, together with the temperature, as in the conventional growth. Shutters modulation scheme (opening and closing times) have an influence on the morphology. By changing the opening (closing) time, the metal (N)-rich growth time could be longer or shorter, influencing directly the morphology of the film.

On the following sections the influence of the above-mentioned parameters on the morphology, structural and optical quality of the InGaN film are described in detail. The parameters are studied separately, by varying one of them at a time while the others are kept constant. Thus, in not all the individual situations, a perfect MME is achieved and metallic droplets could be accumulated on the surface. Only when all the parameters are well understood and their influence in the growth are known, a perfect MME grown sample can be grown.

The RHEED pattern at the end of the growth of the 20 nm thick GaN film (fig. 5.1a) is bright and streaky, fingerprint of a flat and dry surface (without metal accumulation on the surface). Figure 5.1 also shows the RHEED pattern of two different InGaN films described later in this chapter. The templates were degassed according to the procedure described in appendix a.

5.3. III/N ratio vs growth temperature diagram

In this sub-section, the effects of the III/N ratio and temperature on the morphology of the InGaN films grown by MME are presented. Figure 5.2 shows the III/N vs growth temperature employed. All the samples were grown at fixed values of In/Ga ratio (0.5) and shutters modulation scheme (opening/closing: 5"/10"). The Ga flux was kept at 9 nm/min and the In flux to 4.6 nm/min. The N* flux was varied from 5.2 to 11.3 nm/min. The III/N ratio was varied by changing only the N* flux, except for the lowest values (0.8 and 0.9). For such low III/N ratios Ga and In fluxes were reduced.

5.3.1. Influence of the III/N ratio

To study the influence of the III/N ratio on the morphology and structural properties of the InGaN layers two sets of samples were grown at 400°C and at 475°C (series named R1 and R2 respectively). In both cases, the temperature is low enough to neglect In-N decomposition and In desorption. Table 5.1 summarizes the growth conditions for the samples of these two series. In all cases, the layer thickness was set to 220 nm.

Figure 5.2 III/N ratio vs temperature (°C) growth diagram. All the samples were grown at fixed values of In/Ga ratio (0.5) and shutters modulation scheme (opening/closing: 5/10 both in seconds).

Sample	III/N	ϕ_{Ga}	ϕ_{In}	ϕ_N	Temperature (°C)
R1A	1.5	9	4.6	9	400
R1B	1.2	9	4.6	11.3	400
R1C	0.9	6.8	3.4	11.3	400
R1D	0.8	6	3	11.3	400
R2A	2.6	9	4.6	5.2	475
R2B	2.2	9	4.6	6.2	475
R2C	1.9	9	4.6	7.2	475
R2D	1.5	9	4.6	9	475

Table 5.1 Growth conditions of samples from series R1 and R2. Elemental fluxes are given in nm/min.

As it was discussed in section 3.5, the MME growth process consists of two different processes. In the first one, the surface is exposed to the three elemental fluxes (opening-period) while in the second is exposed only to the active N flux (closing-period). Three different scenarios can be described:

- i. $0 < \text{III}/\text{N} < 1$
- ii. $1 < \text{III}/\text{N} < 2$
- iii. $2 < \text{III}/\text{N} < 3$

For a perfect MME process it is necessary to accumulate droplets during the period when the shutters are opened (opening-period) and to consume them in the subsequent period when the elements-III shutters are closed (closing-period). Without the modulation of the shutters metal droplets would accumulate on the surface for $\text{III}/\text{N} > 1$. Modulation to N-rich conditions (closing-period) allow the excess of metal on the surface to be consumed and to be reabsorbed into the layer.

The surface morphology of samples from series R1 is shown in Figure 5.2 by means of top-view and cross-section SEM images. None of the InGa_N layers shows metallic droplets on the surface. For $\text{III}/\text{N} < 1$ all the metal is consumed during the opening-period of the MME growth, such that during the closing-period there is no metal on the surface to be consumed and consequently, no droplets are built up on the surface. For the cases of higher III/N ratios (1.2 and 1.5) the surface is also clean of droplets. With these values of III/N ratios and growth temperature (400°C), the excess of metal is incorporated to the layer during the closing-period.

All the layers show a rough surface. This is due to a combination of low growth temperature (400 °C) and high N-rich conditions during the closing-period. Both parameters have the effect of reducing the ad-atom surface diffusion length. Samples R1C and R1D, with metal fluxes 10 to 20% lower than the N-flux, exhibit a compact morphology with a rough surface. However, for samples R1A and R1B the difference in fluxes is much larger during the closing-period and this leads to columnar structures instead of compact layers as can be seen in the cross-

section SEM micrographs (fig. 5.3). The RHEED pattern of sample R1B is bright and spotty, fingerprint of a rough and dry surface (shown on figure 5.1b).

Figure 5.3 Plan-view (left) and cross-section (right) SEM images of samples from series R1 grown at 400 °C. The scale bar is 1 μ m for all the micrographs. The dashed line represents the InGaN/GaN interface.

Figure 5.4 Symmetric $\omega/2\theta$ diffraction profiles, around the GaN(0002) Bragg reflection, of samples from series R1.

The In content and the uniformity in In content of the InGaN layers were assessed by means of $\omega/2\theta$ rocking curves around the GaN(0002) Bragg reflection (fig. 5.4). All the InGaN layers show similar In content around 25%. With these values of III/N ratio and shutters modulation scheme all the metal is consumed and incorporated into the layer leading to a constant In composition. Considering these results, it is worth to study higher III/N ratios. The FWHMs values of the ω -rocking around the InGaN(0002) peak are shown in table 5.2. The results are poor for InGaN on GaN heteroepitaxy due to the combination of non-optimal growth parameters.

Sample	FWHM InGaN(0002)
R1A	1.6°
R1B	1.2°
R1C	1.1°
R1D	1.0

Table 5.2 Values of the FWHM of the ω -rocking of the InGaN(0002) Bragg reflection for samples of series R1.

Series R2 was proposed to study higher III/N ratios together with an increase in temperature (from 400 to 475°C), which would allow the metal ad-atoms to enhance their surface diffusion length. The left column of figure 5.5 shows plan-view SEM images of the samples of this series. Those grown with III/N ratios values 1.9, 2.2 and 2.6, showed accumulation of metallic droplets on the surface at the end of the growth, which were removed with HCl. Only the sample grown with III/N=1.5 (R2D) showed a clean surface, leading to the best surface morphology. For III/N > 1.5, the morphology gets worse, going from compact to 3D morphology. The increase in III/N ratio is achieved via reduction of the N* flux, which leads to In and Ga droplets formation on the surface during the opening-period (metal-rich). When changing to N-rich conditions (closing-period) not all the metal can be reincorporated to the layer and remains on the surface in the form of droplets. Its presence on the surface leads to InGaN overgrowth on the droplet, or avoids the compact growth under the droplets. This results in 3D growth and generation of macrodefects on the surface.

In this series of samples, the ratio is increased by decreasing the N* flux, which should lead to a reduction of the In incorporation. During the opening-period, Ga and In droplets are accumulated on the surface, which are then reincorporated during the closing-period (N-rich). However, in this reabsorption Ga atoms are preferentially incorporated versus In ones due to the higher sticking coefficient of Ga at this temperature. For example, in the case of sample R2A (with Ga = 9, In = 4.6 and N = 5.2 nm/min), the equivalent to 0.7 nm of metal is accumulated on

the surface during the opening-period (5 seconds). During the closing-period (10 seconds) the N^* flux could incorporate up to 0.87 nm of metal. According to this simple calculation, all the metal in excess should be consumed. However, this is not the case since the metal coming from the droplets cannot be viewed as a standard molecular flux. The droplet surface is nitridated, which makes its kinetic completely different (fig. 5.6a), avoiding a free movement of the metal atoms. The mechanism that governs the growth under the droplet is a diffusion driven process through the droplet (fig. 5.6b). This leads to the generation of macrodefects on the surface, which reduce the quality of the InGaN film.

Figure 5.7 shows $\omega/2\theta$ diffraction profiles of the samples from the R2 series. The scans were recorded around the GaN(0002) Bragg reflection. As it was expected, the In incorporation is decreased as the III/N ratio is increased. Only sample R2D shows a well-defined, broad and single InGaN(0002) peak, indicating that phase separation is minimized, although there is still an indication of composition fluctuation on the InGaN alloy. The crystal quality of the rest of the samples R2A-R2B-R2C is very low, as expected from the morphology. The (0002) diffraction peak is not present in the scans performed on those samples, presenting a tail to the left of the GaN(0002) peak. The reduction in indium incorporation is attributed to the reduction of nitrogen flux (in order to increase the III/N ratio), as Ga is preferentially incorporated into the film. For sample R2D the FWHM value of the ω -rocking around the InGaN(0002) peak is 0.53° , which is 3 times lower than the same sample grown at 400°C (R1A). The growth temperature is therefore assumed a critical parameter on the MME growth of InGaN.

Figure 5.5 Plan-view (left) and cross-section (right) SEM images of samples from series R2 grown at 475 °C. The scale bar is 1 μm for all the micrographs. The dashed line represents the InGaN/GaN interface.

Figure 5.6 Defects associated with the growth on In droplets. a) Typical regrowth of a droplet and b) typical surface underneath a droplet. The scale bar is $5\ \mu\text{m}$ for both micrographs.

Figure 5.7 Symmetric $\omega/2\theta$ diffraction profiles, around the GaN(0002) Bragg reflection, of samples from series R2.

5.3.2. Influence of the substrate temperature

In this sub-section, the effect of the growth temperature on the properties of the InGaN layers is inspected. For this purpose, three sets of samples were grown at three different III/N ratios: 0.8, 1.5 and 1.9 (labelled T1, T2 and T3 series respectively). The details on the fluxes used are described in Table 5.3.

Sample	III/N	ϕ_{Ga}	ϕ_{In}	ϕ_{N}	Temperature (°C)
T1A	0.8	6	3	11.3	375
T1B	0.8	6	3	11.3	400
T1C	0.8	6	3	11.3	450
T2A	1.5	9	4.6	9	400
T2B	1.5	9	4.6	9	475
T2C	1.5	9	4.6	9	550
T2D	1.5	9	4.6	9	600
T3A	1.9	9	4.6	7.2	475
T3B	1.9	9	4.6	7.2	525

Table 5.3 Growth parameters for the series T1, T2 and T3. Elemental fluxes are given in nm/min.

Figure 5.8 depicts the micrographs of the T1 series and the morphology dependence with the substrate temperature of the InGaN layers ($\text{III}/\text{N} = 0.8$). The three samples are compact layers with rough surfaces. As the temperature is increased, the ad-atom surface diffusion length is enhanced and a decrease in the surface roughness would be expected. This series of samples are all grown with at $\text{III}/\text{N} = 0.8$, which means that growth is carried out under N-rich conditions in both opening- and closing-periods. Growing under N-rich conditions has a negative effect on the ad-atoms surface diffusion length. The effect of the temperature on the ad-atoms mobility is countered by the effect of the excess of active nitrogen. $\text{III}/\text{N} = 0.8$ together with the low growth temperature are the main responsible for the rough surface showed. Sample T1C, grown at the highest substrate temperature, exhibits a columnar structure, which may be attributed to a further decrease in the III/N ratio at the surface.

Figure 5.8 Plan-view (top) and cross-section (bottom) SEM images of samples from series T1, grown with $\text{III}/\text{N} = 0.8$. The scale bar is $1\ \mu\text{m}$ for all the micrographs. The dashed line represents the interface.

Figure 5.9 Symmetric $\omega/2\theta$ diffraction profiles around the GaN(0002) Bragg reflection of samples from series T1.

The In content of the InGaN layers from series T1 remains almost constant as the temperature is increased from 375°C to 450°C (fig. 5.9). A small variation is consistent with small fluctuations of the fluxes or growth temperature during the growth along one hour. InGaN peaks are symmetric and lorentzian-like, accounting for a good uniformity in composition and the suppression of phase separation.

Figure 5.10 Variation of the morphology of the InGaN layer by varying the temperature, for the T2 series. The morphology is studied by plan-view (top) and cross-section (bottom) SEM. Samples were grown at $\text{III}/\text{N} = 1.5$. The scale bar is $1\ \mu\text{m}$ for all the micrographs. The dashed line represents the InGaN/GaN interface.

Series T2 was grown at higher III/N ratio (1.5) and within a broader temperature range (from 400 to 600). Figure 5.10 shows the dependence of the morphology with the substrate temperature, varying from columnar-like (T2A) to compact and flat (T2B) and finally to compact layers but with holes (T2C and T2D). The combination of a low growth temperature with N-rich conditions (during the closing-period) reduce the ad-atom mobility until columnar growth regime is reached. By increasing the substrate temperature (475 °C) and hence the ad-atom mobility, flat and compact layers can be grown. A further increase in temperature (550 and 600 °C), that surpasses the onset for In-N decomposition and In desorption, results in InGaN layers with holes and trenches on the surface. Both defects can be attributed to indium losses, mainly to the In-N decomposition. This deterioration was also reported by Gacevic and co-workers [Gac12]. They found that an increase in temperature over 600 °C leads to the reduction of the In ad-coverage to less than 1 monolayer, thus inducing significant surface degradation.

Figure 5.11 Symmetric $\omega/2\theta$ diffraction profiles around the GaN(0002) Bragg reflection of samples from series T2.

Samples T2A and B show the same In incorporation (25%) but as the temperature increases and surpasses the onset for In-N decomposition the In incorporation starts to decrease (fig. 5.11). The InGaIn(0002) peak shifts to lower In contents until it disappears. At 550 °C, an InGaIn shoulder is present while at 600 °C, the GaN(0002) peak just shows a tail that extends to its left (low indium content). None of them shows any accumulation of droplets on the surface.

The T3 series was grown at a higher III/N ratio (1.9) with a substrate temperature of 475 and 525 °C, in order to minimize the In losses while enhancing the ad-atom mobility. A clear change in morphology can be observed when going from 475 to 525 °C (fig 5.12). Sample T3A shows a chaotic surface full of defects while sample T3B shows a compact and flat surface. The RHEED pattern of sample T3B is streaky, fingerprint of a flat surface (shown on fig. 5.1c).

Figure 5.12 Plan-view (left) and cross-section (right) SEM images of samples from series T3, grown with a III/N ratio of 1.9. The scale bar is 1 μm for all the micrographs. The dashed line represents the interface compares

Sample T3B showed a low density of droplets accumulated on the surface, meaning that the temperature is high enough to start the decomposition of the In-N bonds. The $\omega/2\theta$ diffraction profiles of the InGaN layers from series T3 are shown in fig.5.13, indicating a clear improvement on the crystal quality for sample T3B. The symmetry of the InGaN(0002) peak and its lorentzian-like shape suggest a good uniformity in indium composition and no signs of phase separation. The FWHM of the ω -rocking around the InGaN(0002) reflection is 0.51° , the lowest value achieved. RSM analysis of the sample T3B (fig. 5.14) shows an In content of 10% and a 25% of relaxation according to the simulations performed by means of the Panalytical X'Pert Epitaxy software. The thickness of the InGaN film was 220 nm. Therefore, a III/N ratio slightly below 2 and a temperature slightly over the onset of In-N decomposition lead to films with lower surface roughness, and higher structural quality.

Figure 5.13 Symmetric $\omega/2\theta$ diffraction profiles around the GaN(0002) Bragg reflection of samples from series T3.

In summary, the effects of the III/N ratio and the temperature on the morphology and structural properties of InGaN films have been studied. The effect of the III/N ratio can be evaluated in three different regimes:

- i. $\text{III/N} < 1 \rightarrow$ All the metal is consumed in the opening-period of the shutters and no growth takes place during the closing-period. This is not a true MME growth process.

- ii. $1 < \text{III}/\text{N} < 1.5 \rightarrow$ During the closing-period the growth conditions are too N-rich. This situation leads to rough surfaces and macrodefects associated to the accumulation of droplets (fig. 5.5) and even to columnar growth.
- iii. $1.5 < \text{III}/\text{N} < 2.0 \rightarrow$ In this case when closing the shutters the growth is performed in slightly N-rich conditions. The flattest compact layers with higher compositional uniformity are obtained in this regime.
- iv. $\text{III}/\text{N} > 2.0 \rightarrow$ all the growth is performed in metal rich conditions. When shutters are opened metallic droplets are accumulated on the surface, and when closing the shutters the N flux is too low to consume all the metal on the surface. Thus, inducing surfaces with macrodefects associated to droplets.

Figure 5.14 Reciprocal Space Map (RSM) of sample T3B recorded around the GaN(10-15) Bragg reflection. The dashed line, corresponding to the fully relaxed InGaN alloys and the solid line, corresponding to the InGaN alloys fully strained to GaN are shown for clarity.

The substrate temperature has a large influence on the surface ad-atoms mobility, on the In incorporation and on the accumulation of droplets. At low enough temperatures (below 450 °C) the ad-atoms mobility is too low to produce flat enough InGaN layers. As the temperature increases, the ad-atom mobility is enhanced and the surface gets flatter and the amount of macrodefects is reduced. At temperatures over 525 °C the In-N bonds start to decompose and metallic indium is accumulated on the surface. Depending on the temperature, accumulation of some monolayers or droplets is possible, with the corresponding surface degradation. Over 600°C the desorption of In starts to be noticeable.

Optimum conditions for MME growth of InGaN were identified at III/N = 1.9 and a substrate temperature of 525°C.

5.4. Control of the In content, the In/Ga ratio

In this sub-section the effect of the In/Ga ratio on the properties of the InGaN films is presented. For this purpose, three samples with different In/Ga ratios were grown (series IG). All the samples were grown at the optimized values, found in previous sub-section: III/N ratio of 1.9, growth temperature of 525°C and shutters modulation scheme of 5"/10" opening/closing times. Table 5.4 summarizes the growth conditions for the three samples. Layer thickness was set to 220 nm.

Sample	In/Ga	ϕ_{Ga}	ϕ_{In}	ϕ_{N}	Temperature (°C)
IGA	1.0	6.8	6.8	7.2	525
IGB	0.8	7.6	6.0	7.2	525
IGC	0.5	9	4.6	7.2	525

Table 5.4 Values for the growth parameters for the In/Ga ratio series. Elemental fluxes are given in nm/min.

The surface morphology of the InGaN films is shown in figure 5.15. The three films show a flat surface, free of macrodefects. The root mean square (rms) surface roughness value ranges from 1.01 nm (IGC) to 1.52 nm (IGA); AFM

images are not shown. Those values are comparable to the ones published by Namkoong and co-workers in 2013 using MME [Nam13]. All the layers show droplets accumulation on the surface. As it was discussed on the temperature effect sub-section, 525 °C is a temperature high enough to promote the In-N decomposition, but not sufficiently high to activate the In desorption process. Thus, In droplets accumulation is not completely avoidable.

Figure 5.15 On the left column: plan-view SEM images of the samples from series IG. The scale bar is 1 μm for all the micrographs. On the right column symmetric $\omega/2\theta$ diffraction profiles around the GaN(0002) Bragg reflection of the same samples.

The right column of figure 5.15 shows the symmetric $\omega/2\theta$ diffraction profiles around the GaN(0002) Bragg reflection of all the InGaN films of series IG. As the In/Ga ratio increases the In content of the film is also increased. Peaks are symmetric and lorentzian-like indicating a minimization of the phase separation and a good uniformity in composition. The values of the FWHM of the ω -rocking

around the InGaN(0002) Bragg reflection are in the range of 0.5° and 0.6° . The diffraction profiles only show the peaks related to the GaN(0002) and InGaN(0002) reflections. All the films showed droplets accumulation on the surface, due to the temperature employed (525°C).

It is demonstrated that the indium content of the alloy can be tuned by controlling the In/Ga ratio. In this case, it should be noted that the final In content is not the expected one from the values of the molecular fluxes due to the temperature employed to grow the films, as it was explained before.

5.5. Effect of the shutters closing time

To study the effect of the shutters closing time on the properties of the InGaN films, four layers (series CT) were grown with four different closing times: 10, 15, 20 and 30 seconds, while maintaining the same opening time of 5 seconds in all of them. All the samples were grown at the optimized values, found previously in section 1.3.2 of this chapter (sample T3B): III/N ratio of 1.9, growth temperature of 525°C and In/Ga ratio of 0.5. The values for the Ga, In and N fluxes were fixed to 9.0, 4.6 and 7.2 nm/min, respectively. Layer thickness was set to 220 nm.

Figure 5.16 SEM top-view micrographs (top) and AFM images (bottom) of the InGaN layers of series CT. The scale bar on the SEM micrographs is $1\ \mu\text{m}$. The height bar is 14 nm for all the AFM images.

The InGaN films grown are compact and flat as confirmed by SEM micrographs (fig. 5.16). The values of the rms roughness (according to AFM measurements)

are in the range of 1.0 to 1.2 nm. This result is in the same range as those published by Gacevic et al. [Gac12], where the InGaN films were grown by conventional MBE method in the intermediate regime, and by Namkoong and co-workers [Nam13], in which the InGaN films were grown by MME.

Figure 5.17 Symmetric $\omega/2\theta$ diffraction profiles around the GaN(0002) Bragg reflection are shown for the CT set of InGaN films, grown at a III/N ratio of 1.9, at a substrate temperature of 525 and at a In/Ga ratio of 0.5.

Figure 5.17 shows the symmetric $\omega/2\theta$ diffraction profiles around the GaN(0002) Bragg reflection of all the InGaN films of series CT. The peaks related to the InGaN(0002) Bragg reflection of samples CTA and CTC are highly symmetric, whereas the ones from samples CTB and CTD show a tail extended to lower In contents. This is attributed to the compositional lattice pulling effect [Kon15], [Kaw96], [Kaw98], which occurs to minimize the lattice mismatch between the InGaN film and the GaN buffer by reducing the indium incorporation and favouring the relaxation of the strain in the early stage of the growth. In this case, samples CTB and CTD shows higher degree of relaxation than samples CTA and CTC.

This could be attributed to a more remarkable lattice pulling effect on samples CTB and CTD, but its origin is not clear. The In content and the degree of relaxation of the layer are calculated from the position (Q_x , Q_z) of the InGaN(10-15) peak in the RSM. The In content of the films is in the range of 10 to 14%. Films are highly strained, with relaxation values between 20 (samples CTA and CTC) and 40% (samples CTB and CTD). Figure 5.18 shows the RSM of the sample CTB around the GaN(10-15) Bragg reflection.

Figure 5.18 Reciprocal Space Map (RSM) of sample CTB recorded around the GaN(10-15) Bragg reflection. The dashed line, corresponding to the fully relaxed InGaN alloys, and the solid line, corresponding to the InGaN alloys fully strained to GaN, are shown for clarity.

The FWHM values for the ω -rocking around the InGaN(0002) Bragg reflection are 0.5° , 0.3° , 0.3° and 0.2° for samples CTA, CTB, CTC and CTD, respectively. The increase in the closing time leads to a significant reduction in the FWHM value. This can be explained in terms of a more efficient metal consumption during the closing-period. The best InGaN layers are grown in the so-called intermediate metal rich regime with a metal ad-coverage between 1 and 2 monolayers. Gacevic and co-workers [Gac12] grew InGaN films (with In contents ranging from 10 to 25%) in this regime showing similar results for relaxation, rms

and FWHM. This result suggests that 10 seconds is not enough time to consume the metal on the surface and consequently the ad-coverage is over 2 monolayers. By increasing the closing time, more metal is consumed and the ad-coverage can be between 1 and 2 monolayers, similar to the intermediate me-rich regime, and showing superior structural properties than the layers grown with lower closing times and a similar vale of rms roughness.

Figure 5.19 Low temperature (10K) PL spectra of the layers from series CT. The intensity axis of all the spectra are plotted in the same scale for comparison.

The optical emission properties of the InGaN films were studied by means of photoluminescence spectroscopy at 10 K (fig. 5.19). All four InGaN films showed emission in the range 2.6 -2.7 eV with very little dispersion as expected by the low dispersion on the In composition of the InGaN layers shown by XRD (fig. 5.17). The FWHM of the PL emission peaks are 280, 260, 290, and 270 meV, they have a dispersion of ± 15 meV. They do not follow a trend as in the case of

the ω -rocking FWHM. No YL emission was observed for any sample indicating a low density of point defects and impurities, as discussed in section 2.4.4.

In this section, the effect of the closing time of the shutters (closing-period) on the structural and optical properties of the InGaN layers has been studied. The closing time is identified as a secondary parameter in the optimization of the growth of InGaN films by MME. Its effects are focused on reducing the surface rms and the FWHM value of the InGaN(0002) peak.

5.6. Growth of the p-i-n structure

In this sub-section, p-i-n structures (figure 5.20) are monolithically grown on n^+ GaN-on-Sapphire templates. Two similar structures were grown, with the only difference of the intrinsic InGaN layer thickness: 100 nm for the PIN1 sample and 200 nm for the PIN2 sample.

Figure 5.20 *P-i-n structure growth on GaN-on-Sapphire templates.*

All studied samples were grown on GaN:Si templates and in the same molecular beam epitaxy (MBE) reactor following the degas procedure as described in appendix a. After degassing the substrate temperature was lowered to 600 °C to grow a 20 nm thick GaN layer by MME (details on the GaN MME growth can be found in chapter 6) to flatten the surface.

The intrinsic InGaN layer was grown at III/N=1.9 and a temperature of 525 °C (optimum conditions for InGaN found on section 5.3.2). The fluxes were 9.0, 4.6 and 7.2 nm/min for the Ga, In and N fluxes respectively. The shutter modulation scheme was 5/15 (opening/closing times). Two structures with different InGaN thickness were grown (100 and 200 nm).

After the growth of the InGaN layer, the temperature was raised from 525 to 600 °C at a rate of 20 °C/min. The p-GaN layer was grown by MME at 600°C with Ga and N* fluxes of 5 and 4 nm/min, respectively. The shutters modulation scheme was set to 10 seconds open and 5 seconds close. The Mg cell used for the p-GaN layer was set at 225 and 450 °C, reservoir and tip temperatures respectively. With these growth conditions the hole concentration achieved in GaN was $4.9 \times 10^{18} \text{ cm}^{-3}$. Details on the p-GaN grown by MME can be found in section 6.3. The thickness of the p-GaN and the i-InGaN were selected according to the simulations on p-GaN / i-InGaN / n-GaN heterostructures performed by Kushawaha and co-workers [Kus14].

Figure 5.21 RHEED pattern of the different layers presented in the p-i-n structures studied in this work. a) GaN layer regrowth by MME, b) contrast enhanced InGaN grown by MME, and c) Mg-doped GaN layer grown by MME.

The RHEED pattern of the 20 nm thick GaN film at the end of the growth (fig. 5.21a) is bright and streaky, fingerprint of a flat and dry surface (without metal accumulation on the surface). The RHEED pattern of the InGaN film is streaky and dark (fig. 5.21), meaning that the surface is flat and metal is accumulated on it. The contrast of the pattern in figure 5.21b is enhanced in order to distinguish the streaks. The third pattern (figure 5.21c) corresponds to the Mg-doped GaN layer at the end of the growth. The pattern is spotty with faint streaks between

the spots. A spotty RHEED pattern is a fingerprint of a rough surface, typical of Mg-doped GaN layers. For the technological process, the reader is referred to the appendix b.

5.6.1. Device results

The devices were measured with the solar simulator located in the Autonoma University of Madrid (UAM) and the help of Prof. A. Braña. The solar simulator is equipped with a Xe lamp of 2 kW producing a AM 1.5G solar spectrum. Figure 7.9 shows the J-V curves obtained for both devices: PIN1 (fig. 5.22a) and PIN2 (fig. 5.22b). In order to calculate the current density the shadow effect of the probe and the area of the contact have been taken into account, giving an 85% of total area illuminated.

Figure 5.22 J-V curves for: a) PIN1 (InGaN thickness of 100 nm) and b) PIN2 (InGaN thickness of 200 nm).

The J-Vs shows no photovoltaic characteristics on any of the processed devices. No difference can be observed between the dark and the illuminated curves. The voltage was limited to 0.5 V to avoid degradation of the p-contact.

Figure 5.23 Schematic representation of the double diode model.

In order to analyse the devices, the J-V curves were fitted to the double diode model (fig. 5.23). Only the results for the PIN1 are shown since results are almost identical. The single diode equation assumes a constant value for the ideality factor n . The ideality factor is a function of the voltage across the device. At high voltage, when the recombination in the device is dominated by the surface and the bulk regions, its value is close to unity. However, at lower voltages, recombination in the junction dominates, and the ideality factor approaches to two. Then, the junction recombination is modelled by adding a second diode in parallel with the first one (with $n=1$) and with an ideality factor typically of 2. Practical measurements of the illuminated equation are difficult as small fluctuations in the light intensity overwhelm the effects of the second diode. Since the double diode equation is used to characterise the diode it is more common to look at the double diode equation in the dark. The double diode equation in the dark is as follows:

$$J = J_{01} \left\{ \exp \left[\frac{e(V - JR_S)}{n_1 kT} \right] - 1 \right\} + J_{02} \left\{ \exp \left[\frac{e(V - JR_S)}{n_2 kT} \right] - 1 \right\} + \frac{V - JR_S}{R_{shunt}} \quad (5.6.1.1)$$

Where n_1 and n_2 are the ideality factor and they will be assumed to be 1 and 2. Both “-1” terms inside exponentials are typically ignored because for voltages over 40 to 100 mV both “-1” terms become negligible. Figure 7.11 shows the dark J-V of the PIN1 and the fitting to the double diode model. The values employed are shown on table 5.5.

J_{01} (mA/cm ²)	2×10^{-12}	R_s (Ω .cm ²)	100
J_{02} (mA/cm ²)	1×10^{-6}	R_{shunt} (Ω .cm ²)	479

Table 5.5 Values employed for the fitting of the dark J-V curve of the PIN1 structure to the double diode model.

Figure 5.24 Dark J-V curve of the PIN1 device plotted together with its fitting to the double diode model.

The J_{01} factor accounts for the bulk and surface recombination. Its value depends on the surface and interface recombination velocity. Typical values obtained for GaAs solar cells ($\sim 10^{-16}$ mA/cm²) [Gal06] are 4 orders of magnitude lower than the one obtained in this work 2×10^{-12} mA/cm². It means that the recombination of minority carriers is much higher in our case and it is limiting the performance of the grown device. Any defect or impurity within or at the surface of the semiconductor promote recombination. Since the surface of the device

represents a severe disruption of the crystal lattice, the surfaces of the device are a site of particularly high recombination. The dangling bonds at the surface of semiconductor cause a high local recombination rate. The defects at a semiconductor surface are caused by the interruption to the periodicity of the crystal lattice, which causes dangling bonds at the semiconductor surface. The reduction of the number of dangling bonds, and hence surface recombination, is achieved by growing a layer on top of the semiconductor surface, which ties up some of these dangling bonds. This reduction of dangling bonds is known as surface passivation. The lifetime of the material is contingent upon the concentration of minority carriers. Limiting surface recombination can lessen the rate at which minority carriers are depleted. If the rate of minority carrier depletion can be limited, the lifetime of the material can be extended. Typically, wide-band gap nitrides (AlN or AlGaIn) are grown to eliminate the dangling bonds [Mäc02]. A method similar to surface passivation is to deposit a wide band gap semiconductor at the surface that bends the bands to generate an electric field; this is called a window layer. Window layers are widely used in III-V solar cells [Gal90] due to relative ease of growth and advantages in fabrication.

The J_{02} factor accounts for the recombination at the space charge region. Its value can be calculated as:

$$J_{02} = e \frac{n_i W_{scr}}{\sqrt{\tau_n \tau_p}} \quad (5.6.1.2)$$

Where n_i is the intrinsic concentration, W_{scr} is the width of the space charge region (scr) and τ_n and τ_p are the lifetime of the charge carriers. Typical values obtained for GaAs solar cells ($\sim 10^{-10}$ mA/cm²) [Gal06] are 4 orders of magnitude lower than the one obtained in this work 1×10^{-6} mA/cm². A high value of J_{02} means a low value of the charge carrier lifetime in the scr, making the recombination at the scr noticeable. Thus, limiting the overall device performance.

The value of the shunt resistance (R_{shunt}) is 479 $\Omega \cdot \text{cm}^2$. A low R_{shunt} causes power losses by providing a low resistance alternative path for the current. Shunts can be classified in processing-related shunts and material-related shunts.

Processing-related shunts are produced by the growth method (MBE in this work) or by the device processing. Linear edge and nonlinear edge shunts, cracks and holes and scratches are typical processing-related shunts. The most common material-related shunts are strongly recombinative crystal defects, stacking faults, clusters, inclusions and inversion domains [Brei04], [Nau15].

Another cause of reduced performance is the series resistance of $100 \text{ } \Omega \cdot \text{cm}^2$. The main sources of series resistance of the devices presented are the metal contact to the p-GaN and the p-GaN itself. The metal contact employed was a 50 nm Ni – 200 nm Au annealed at $400 \text{ } ^\circ\text{C}$ for 5 minutes in a N_2 atmosphere. Typical annealing temperatures reported for this contact scheme are in the range of 500 to $750 \text{ } ^\circ\text{C}$ [Qia00] and [Che15]. A temperature of 400°C selected to protect the InGaN layer, since over $500 \text{ } ^\circ\text{C}$ the In-N bonds start to decompose, leading to a degradation of the InGaN layer. One possible solution to improve the p-GaN contact is to anneal it at a higher temperature. Chen and co-workers improved the contact resistivity by annealing in air instead of N_2 ambient [Che15]. An increase in the hole concentration of the p-GaN layer will also lead to a reduction in the series resistance.

Another possible problem comes from the InGaN layer. According to the simulations performed by E. Trybus on her thesis [Try09], as the doping level of the intrinsic region is increased, the volume of the depletion region is reduced. Figure 5.25 shows the simulations published by E. Trybus. Electron-Hole Pairs (EHPs) generated in the depletion volume will be sweep across the junction by the electric field and will be collected. EHPs generated more than one diffusion length away from the depletion region will recombine before they are collected and do not contribute to the photogenerated current. Therefore, a higher doping level on the intrinsic region means a reduced photocurrent.

Figure 5.25 Simulation of the energy bands profile of the p-i-n heterostructure varying the doping level of the intrinsic region. Adapted from [Try09].

Hall Effect measurements performed on a non-intentionally doped InGaN layer, grown under the same conditions on semi-insulating GaN:Fe templates as the control sample, yielded a residual n-type concentration of $8.8 \times 10^{17} \text{ cm}^{-3}$. Then, according to Trybus findings, the depletion volume of our p-i-n structure is reduced significantly. This explains the poor J-V curves observed (fig. 5.24). One way to overcome this problem is to compensate the material by doping with Mg. Another possible solution is the deposition of the InGaN layer at a higher growth rate. Gunning et al. demonstrated GaN films with a residual n-type concentration of $1\text{-}2 \times 10^{15} \text{ cm}^{-3}$ [Gun15]. Those films were grown at $2 \text{ }\mu\text{m/hr}$, which is a growth rate not achievable by a standard MBE reactor. These InGaN layers were grown at $0.4 \text{ }\mu\text{m/hr}$, and the maximum achievable rate of the RIBER Compact 21S reactor is $\sim 0.8 \text{ }\mu\text{m/hr}$. Therefore, growing at $\sim 0.8 \text{ }\mu\text{m/hr}$ can be the next step to try in order to improve the device performance.

Threading dislocations (TD) are known to be minority carriers killers in epitaxial layers [Che01], [Fan81], [Yam85]. Sumiya and co-workers reported on the

dependence of the minority carriers' lifetime and minority carriers' diffusion length with the TD density [Sum02]. Both parameters decreased when the density is increased, thus reducing the overall performance of the device. Calculations on the dislocation density in the reference InGaN film, carried out by Dr. M. Xie using XRD, give a value of 10^{11} cm^{-2} . In order to improve the device performance, the density of dislocations should be reduced. The GaN-on-Sapphire templates employed have a dislocation density of 10^8 cm^{-2} . The use of templates with a lower dislocation density will lead to an improvement in the density of dislocations in the InGaN film, giving rise to an improvement of the photovoltaic response of the final device.

5.7. Conclusions

In this chapter the effects of the III/N ratio, substrate temperature, In/Ga ratio and closing time on the MME growth of InGaN films have been studied. The III/N ratio and the substrate temperature have been identified as critical parameters for the growth, as they control the morphology and structural properties of the resulting InGaN film. The In/Ga ratio was found to be critical in controlling the indium incorporation in the InGaN alloy. The closing time was identified as a parameter with less impact on the properties of the resulting layer. Optimum conditions for the MME growth of InGaN layers were identified in this chapter, leading to minimization of rms roughness and YL emission, while maximizing the uniformity in In composition and PL emission. The optimized film was grown with a III/N = 1.9, growth temperature of 525 °C, In/Ga = 0.5 and at a modulation scheme of 5 seconds open and 15 seconds close.

All the knowledge achieved during these two chapters (on the p-GaN and i-InGaN layers) has been applied to a final p-i-n device. Once processed, J-V curves did not showed any photovoltaic response. Experimental data was fitted to the double diode model. Results showed high values of the J_{01} , and J_{02} , a low shunt resistance and a high series resistance. The main problems of the device were the high recombination rate at the surfaces, interfaces and space charge region. In addition, the low shunt resistance, the high series resistance and the high residual n-type doping of the intrinsic InGaN layer reduced the overall performance of the device. Without solving the addressed issues, it is impossible

to conclude whether the use of MME to grow p-i-n heterostructures for photovoltaic applications will improve the reported efficiency of the InGaN-based solar cells [Lio11], [Lio13].

6. Suitability of different buffer layers for InGaN-on-Si photovoltaic devices

6.1. Introduction

Due to the inability of a single solar cell to absorb light over the entire solar spectrum, a stack of multiple sub-cells (tandem) has been proposed and studied intensively during the last few decades [Ols02]. Most of these efforts have focused on material systems such as Ge, InP, GaAs and GaSb. However, a limited work has been reported on the use of InGaN alloys to produce this type of tandem solar cells. The wide range of band gap energies available from these alloys, their direct band gap character and a high absorption coefficient, make them very attractive candidates for multi-junction photovoltaic (PV) applications. Multi-junction solar cells can reach energy conversion efficiencies higher than 30% for double junction cells [Gre08] and above 40% for a triple one [Kin07]. A maximum theoretical efficiency for double-junction cells is 39% and it can be achieved with two sub-cells with bandgaps of 1.74 and 1.13 eV respectively; values that can be obtained with an InGaN sub-cell and a Si one. Then, the integration of InGaN alloys with the mature Si PV technology would yield high efficiency solar cells at a reasonable cost.

One of the main problems to address in tandem cells technology is the current match and ohmic contact between sub-cells, yet being transparent to light absorption. Krishnamoorthy et al. [Kri13] demonstrated low resistance tunnel junctions (TJ) using GaN/In_{0.25}Ga_{0.75}N/GaN heterostructures and by introducing GdN nanoislands in an n⁺⁺-GaN/p⁺⁺-GaN junction [Kri13b]. However, TJs are quite challenging for high In content InGaN alloys because of the poor p-doping efficiency with Mg.

An additional benefit of InGaN/Si heterojunctions is the alignment of the n-type InGaN conduction band with the valence band of p-type silicon for In composition around 46%, which provides a low resistance ohmic contact [Hsu08]. This fact would avoid the need of TJs between sub-cells strongly simplifying the solar cell design and fabrication.

Yet another benefit of using an $\text{In}_{0.46}\text{Ga}_{0.54}\text{N}/\text{Si}$ combination is that the band gap values of those sub-cells would be 1.8 eV ($\text{In}_{0.46}\text{Ga}_{0.54}\text{N}$) and 1.1 eV (Si), quite close to the predicted values (1.74 and 1.13) to achieve the maximum theoretical maximum efficiency in a double-junction solar cell.

The growth of high quality InGaN alloys remains challenging due to the need of a relatively low growth temperature, the large lattice mismatch between InN and GaN, and hence the tendency to low miscibility and phase separation [Tak00], [Ho96], [Str89]. Additionally, growing InGaN alloys directly on silicon, as compared to GaN/sapphire templates, must deal with the silicon surface nitridation and a poor wetting on the resulting Si_xN_y layer [Gom16]. Silicon nitridation can be avoided by using buffer layers that may, in addition, upgrade the film quality, but should not hinder the vertical conduction in case of PV applications.

To obtain high quality, thick and homogeneous InGaN layers in a wide composition range, the DERI method, already discussed in section 3.5, can be of great help. In the DERI method, there is no need of an accurate control of the In flux. The In content can be tuned by controlling the Ga to N^* beam flux ratio. However, all previous reports on InGaN layers grown by DERI were done on GaN/Sapphire or on InN/GaN/Sapphire templates. No reports have been found (to the best of our knowledge) on Silicon substrates.

This chapter deals with the effects of different buffer layers on the vertical electrical conduction between InGaN layers and a silicon substrate in relation with the structural and optical quality of the InGaN layer. The goal is to determine an optimal buffer layer that maximizes the InGaN crystal quality while keeping an ohmic behaviour of the n-InGaN/ buffer-layer /p-Si heterojunction. The quality of the InGaN layers was assessed by scanning transmission electron microscopy (STEM), electron energy-loss spectroscopy (EELS), scanning electron microscopy (SEM), atomic force microscopy (AFM), x-Ray diffraction (XRD) and cathodoluminescence (CL) at room temperature. The vertical electrical conduction was derived from I-V characteristics.

6.2. Experimental procedure

The substrates were prepared according to the procedure described in appendix

a. The buffer layers studied were the following:

- i. AlN layers grown by MBE at 860°C with nominal thickness of 6, 24, 42 and 84 nm.
- ii. A 6 nm thick $\text{In}_{0.10}\text{Al}_{0.90}\text{N}$ layer grown by MBE at 550°C.
- iii. RF-sputtered $\text{In}_{0.39}\text{Al}_{0.61}\text{N}$ at room temperature with nominal thickness of 5 and 20 nm.
- iv. Intentionally nitridated Si at 860°C to generate a 2-3 nm thick $\beta\text{-Si}_3\text{N}_4$ layer.

The AlN buffers were grown first depositing 4.5 nm of Al on the Si(111) surface at 860 °C and then turning on, so that the spontaneous formation of Si_3N_4 was prevented [Cal99],[Luo07]. The AlN buffers were then grown at the same temperature, with Al and N fluxes of 4.5 and 4.7 nm/min respectively. A streaky 1x1 RHEED pattern was observed at the end of the AlN buffer growth, indicating a smooth and flat surface.

A nominal 6 nm thick $\text{In}_{10}\text{Al}_{90}\text{N}$ buffer layer was grown at 550°C to study the influence of adding In to an AlN buffer layer, which should improve the electrical conductivity. The buffer growth also started with a 4-5 nm of Al pre-deposition at 550 °C. The fluxes were set to $\phi_{\text{Al}} = 4.5$ nm/min, $\phi_{\text{In}} = 3$ nm/min and $\phi_{\text{N}} = 8$ nm/min. A spotty RHEED pattern, typical of 3D-growth, was observed during the whole growth. The In composition was set to 10% due to the inherent difficulty to incorporate In in the alloy at such high temperature (550°C) [Fer08]. Lower temperatures would not be adequate for Al containing alloys.

Polycrystalline $\text{In}_{0.39}\text{Al}_{0.61}\text{N}$ layers 5 and 20 nm thick were deposited by rf-sputtering at RT on Si (111) substrates. Rf-sputtering was employed due to its capability to deposit high In content InAlN alloys with a reasonable crystal quality. The In composition was selected to reduce the lattice mismatch between the InGaN epilayer and the buffer, from 5% (AlN) to only 1%. According to [Nun16] sputtered $\text{In}_{0.36}\text{Al}_{0.64}\text{N}$ showed PL emission of 1.75 eV (at RT). A further increase on the In content ,of the InAlN buffer layer, to reduce the lattice mismatch between the InGaN layer and the InAlN buffer would result in a reduction on the photons that arrive at the hypothetical Si bottom cell ($E_{\text{G}} = 1.11$ eV at RT); thus, reducing the overall efficiency of the device.

Intentional nitridation of the Si substrate (no Al predeposition) at 860 °C during 5 min under $\phi_N = 8$ nm/min generated a 2-3 nm thick β -Si_xN_y layer. According to [Wie13] a continuous, reproducible and somehow crystalline β -Si_xN_y layer is formed when nitridation is performed at high enough temperatures (850°C). The crystal quality of the III-Nitride epilayer grown on it drops dramatically when the Si_xN_y is produced at either intermediate (450°C) or low (150°C) temperature [Wie13]. In these cases the Si_xN_y layers seem to be amorphous. Under proper nitridation conditions (above the 7x7→1x1 transition temperature), the Si surface is converted into crystalline β -Si₃N₄(0001) [Ahn01], [Wu02] that may be lattice matched to Si(111) [Ahn01]. Rawdanowicz et al. suggested that amorphization of the β -Si₃N₄ layer occurs during the TEM specimen preparation, due to the Ar⁺ ion milling [Raw05], the reason why these layers, when inspected by TEM, appear as amorphous.

All the InGa_xN layers described in this study were grown using the DERI method already described at 550 °C. It is important to maintain always an excess of In (even with In droplets) to maximize the In content in the alloy. An unbalance between N and In fluxes may lead to pure GaN growth. The optimal conditions to grow the InGa_xN films in this work were 2 minutes of MRGP and 1 minute of DEP. Between 19 and 30 cycles were used (depending on the fluxes used) to obtain the same InGa_xN thickness (~0.5 μ m) in all samples. The In composition was varied between 30 and 42%. The growth conditions can be found on table 6.1.

Buffer	Thickness (nm)	ϕ_{Ga} (nm/min)	ϕ_{In} (nm/min)	ϕ_N (nm/min)
AlN	6	3.1	5.0	5.0
	24	4.6	6.9	7.8
	42	4.6	6.9	7.8
	84	4.6	6.9	7.8
In _{0.10} Al _{0.90} N (MBE)	6	2.7	5.0	5.0
In _{0.39} Al _{0.61} N (spt)	20	4.6	6.9	7.8
Si _x N _y	3	4.6	6.9	7.8

Table 6.1 Growth conditions of the InGa_xN layers of the most representative samples.

6.3. Results and discussion

6.3.1. Surface structure, composition and morphology

The structural and chemical composition of a 42 nm thick AlN buffer layer was analysed by plan-view TEM and EELS respectively. STEM-EELS measurements were carried out in an aberration-corrected JEOL ARM200cF electron microscope operated at 200 kV and equipped with a cold field emission gun and a Gatan Quatum EEL spectrometer. Samples were prepared by conventional mechanical grinding and Ar ion milling. In addition, the morphology of both InGaN films and the buffer layers were inspected by SEM and AFM. The differences in InGaN surface morphology are significant and very dependent on the buffer layer employed for the range of In contents employed in this work.

Two of the most influential characteristics of the buffers are the coverage and the crystal orientation. Buffer layers covering partially the substrate will let areas exposing bare silicon where the InGaN epilayer may also grow with different quality, blurring somehow the overall effect of the buffer. In figure 6.1a the plan-view high angle annular dark field (ADF) micrograph of the 42 nm-thick AlN buffer shows sub-micron size grains, together with a significant density of nanopores with diameters ranging from 10 to 20 nm (fig. 6.1b shows one nanopore magnified). EELS measurements identified the elements present inside and outside (in the vicinity) the nanopore. Inside the nanopore (fig. 6.1c, bottom curve) the silicon L_1 , L_2 and L_3 edges are the only ones observed indicating that the nanopore threads down to bare silicon. The nitridation of the Si surface at the bottom of the nanopores seems to be avoided by the shadowing effect produced by the close nanopore walls. The EEL spectrum taken at the nanopore vicinity (fig. 6.1c, top curve) shows the lines corresponding to the aluminium L_1 , L_2 , L_3 edges and the nitrogen K edge, convoluted with those from silicon, indicating that AlN is grown on Si. The 284 eV edge that appears on both spectra corresponds to the carbon K edge.

Figure 6.1 a) ADF micrograph of a 42 nm thick AlN buffer layer. b) ADF micrograph of a nanopore. c) EEL spectra inside the nanopore (blue) and on its vicinity (black).

SEM micrographs of the InGaN epilayers surfaces grown on top of the different buffers are shown in figure 6.2. Depending on the buffer layer used, different features are observed. In the case of the AlN and InAlN MBE buffers (inset of the figures 6.2a, b and c) the surface is covered by macroscopic defects (white dashed circles in the inset of figures 6.2a, b and c), and nanopores (black circles in the inset of figures 6.2a, b and c). The density of the nanopores is higher for the case of the 24 nm AlN than for the 42 nm AlN and 6 nm InAlN (MBE), and the diameter of them is lower for the 42 nm AlN buffer. The density of surface defects is higher for the case of the 6 nm InAlN (MBE) than for the 24 nm AlN and 42 nm AlN. Due to the presence of nanopores in the buffer layer, the InGaN islands can nucleate directly on the (In)AlN or on the bare Si at the bottom of the nanopores. The islands continue growing, both vertically and laterally, until they coalesce into a compact and grainy layer. The effect of a lower density of nanopores is a reduction on the parasitic growth of InGaN on bare Si and yielding smoother InGaN epilayers, as in the case of the InGaN layers grown on a 42 nm AlN.

Figure 6.2 Top view SEM images of InGaN layers grown on: a) 24 nm AlN buffer, b) 42 nm AlN buffer, c) 6 nm $\text{In}_{0.10}\text{Al}_{0.90}\text{N}$ MBE, d) Si_3N_4 and e) 20 nm sputtered $\text{In}_{0.39}\text{Al}_{0.61}\text{N}$. Inset shows AFM images of the starting buffer layer. The black circles mark some of the nanopores, and the dashed circles the macroscopic defects. In all cases, the scale bar is 1 μm .

The intentional nitridation of the Si surface under optimum conditions (temperature over 860 °C [Wie13]) produces a thin (2-3 nm) $\beta\text{-Si}_3\text{N}_4$ layer [Ahn01], [Wu02]. The InGaN epilayer grown on top shows a smooth surface, comparable to the one growth on the 42 nm AlN (fig. 6.2d). The polycrystalline sputtered InAlN buffer presents a grainy surface which leads to rough InGaN epilayers (fig. 6.2e).

6.3.2. Compositional uniformity

The compositional uniformity (at macroscopic level) of the InGaN films was assessed by symmetric $\omega/2\theta$ scans around the Si (111) Bragg reflection. Figure 4.3 shows the $\omega/2\theta$ diffraction profiles of all samples, where the Si (111) and InGaN (0002) reflections are shown in all cases. The reflections from the buffer layers could only be measured for AlN with thickness above 24 nm. The 6 nm AlN and InAlN epitaxial buffers are too thin to distinguish any diffraction peak from

the noise level. Neither the Si_xN_y interlayer nor the polycrystalline sputtered InAlN show any diffraction peak.

All InGaN layers, independently of the buffer used show similar InGaN (0002) single diffraction peaks. The absence of double diffraction peaks together with the relatively narrow InGaN reflections confirm the absence of significant (measurable) phase separation. This result is quite interesting because avoiding phase separation in InGaN alloys is challenging, especially when growing alloys close to the low miscibility gap (30 to 70% of In) and with a large mismatch with the substrate (>8%). All InGaN layers are partially relaxed (>80%) as derived from RSM data around the Si(224) Bragg reflection (data not shown here).

Figure 6.3 Symmetric $\omega/2\theta$ diffraction profiles around the Si(111) Bragg reflection are shown for the InGaN layers grown on: a) 6 nm, b) 24 nm, c) 42 nm and d) 84 nm thick AlN, e) 6 nm thick InAlN, f) Si_xN_y and g) 20 nm sputtered InAlN. In all cases the InGaN(0002) Bragg reflection is shown.

All InGaN diffraction peaks deviate from an ideal Lorentzian symmetry showing a tail extended towards lower indium contents, which may be attributed to the compositional *pulling effect* at the early stages of the growth. This effect, which has been observed in both nanowires [Kon15] and thin films [Kaw96], [Kaw98], happens to ease the lattice mismatch between the InGaN layer and the buffer by reducing the In incorporation.

6.3.3. Crystallographic uniformity

ω -rocking scans were recorded around the InGaN (0002) reflection in order to determine the InGaN layers crystallographic uniformity (in terms of the dispersion on the alignment of the c-planes of the InGaN epilayer). Figure 6.4 shows the ω -rocking (0002) full width at half-maximum (FWHM) value versus the In content for all InGaN layers. The samples could be divided into three groups depending on the buffer layer used: i.- (In)AlN MBE buffer layers, ii.- Si_xN_y buffer and iii.- InAlN sputtered buffer layers. InGaN layers grown on (In)AlN epitaxial buffers have the lowest FWHM values, followed by those grown on Si_xN_y layers (~ 2.5 times higher), to end up with those grown on sputtered InAlN which is the worst case (~ 5.5 times higher). This result is not very surprising since low FWHM values are expected from the highest buffer crystal quality that also bring an epitaxial relation to the epilayer. On the other hand, the polycrystalline nature of the sputtered InAlN buffer induces a similar misorientation on the grown InGaN layer that also becomes polycrystalline. The InGaN epilayers grown on Si_xN_y have a FWHM of $\sim 2.5^\circ$. This value is lower than the ones obtained for the layers grown on sputtered InAlN. This is most likely due to the high nitridation temperature (860°C), that is known to form a somehow crystalline or polycrystalline (β -) Si_xN_y layer [Wie13]. As can be seen in figure 6.4, the type of buffer has a deeper impact on the FWHM value than the indium content (within the range studied), or the growth conditions.

Figure 6.4 ω -rocking FWHM values of InGaN (0002) Bragg reflections vs In content for the different buffer layers used.

6.3.4. Epitaxial relationship

The epitaxial relationship between the silicon substrate and the InGaN epilayer was investigated by phi-psi pole figures around the Si (220) Bragg reflection. This configuration was selected due to the similar $\omega/2\theta$ values for the Si(220) ($\omega/2\theta = 23.65^\circ/47.30^\circ$) and for the InGaN(10-12) ($\omega/2\theta \sim 23.3^\circ/46.6^\circ$). The pole maps were recorded in the ranges $\Psi = 30.00 - 50.00^\circ$ and $\phi = 0 - 360^\circ$. The four pole maps of figure 6.5 show the three-fold symmetry of the Si(220) planes. The six-fold symmetry (typical of wurtzite structures) of the InGaN(10-12) is shown for the InGaN layers grown on AlN (fig. 6.5a), epitaxial InAlN (fig. 6.5b) and Si_xN_y (fig. 6.5c). There is no evidence of InGaN related peaks when the sputtered InAlN buffer is used. The peaks corresponding to epitaxial (In)AlN buffers are not observed in any pole map. This is most likely due to its low thickness together with the fact that the position of the (In)AlN (10-12) reflection is coincident with the InGaN (10-12) one. The epitaxial relationships for InGaN layers grown on

epitaxial (In)AlN buffers and on Si_xN_y are determined by the $\omega/2\theta$ scans and pole maps as: $\text{InGaN (0001)}\parallel\text{Si (111)}$ and $\text{InGaN (10-10)}\parallel\text{Si (11-2)}$.

The intentional nitridation of the Si surface, at high enough temperatures, produces a somehow crystalline or polycrystalline $\beta\text{-Si}_x\text{N}_y$ layer. Epitaxial relationship between InGaN and Si(111) when using Si_xN_y interlayer has been widely observed when growing GaN [Wie13], [Gac15], and InGaN [Gom16] on $\text{Si}_x\text{N}_y/\text{Si}$. In this work, at the conditions selected for the nitridation the Si surface is converted into crystalline $\beta\text{-Si}_3\text{N}_4(0001)$ [Ahn01], [Wu02] that may be lattice matched to Si(111) [Ahn01]. This is, most likely, the reason why there is an epitaxial relationship between the InGaN layer and the silicon substrate. Another possible explanation was proposed by Tamura *et al.* [Tam01]. They proposed that the thin Si_xN_y layer covered partially the Si surface, thus leaving some holes with bare Si that allowed an epitaxial relation between the III-Nitride film and the Si substrate. The III-Nitride islands nucleated on those holes would eventually overcome the SiN thickness and start growing laterally (symilar to an ELOG process) thus providing a rather high quality film. However, up to the best of our knowledge, no experimental evidence of the existence of these “pin-holes” has been reported, when nitridating the silicon surface inside the MBE growth chamber. The determination of this mechanism is not the scope of this work.

The pole figure from the InGaN layer grown on sputtered InAlN (fig. 6.5d) reveals the three peaks corresponding to the Si(220) planes, while the six peaks related to InGaN are not detected. As mentioned before, it is assumed that the polycrystalline nature of this buffer promotes the growth of polycrystalline InGaN. Due to the random *in-plane* orientation of the grains (twist) in polycrystalline layers, signals neither from InGaN nor from sputtered InAlN can be seen in the pole map. Despite of being polycrystalline, the InGaN layer is mostly c-plane oriented as determined from $\omega/2\theta$ scans (fig. 6.3g).

Figure 6.5 ϕ - Ψ pole maps around the Si(220) Bragg reflection for InGaN layers grown on: a) AlN, b) epitaxial InAlN (MBE), c) Si_xN_y and d) sputtered InAlN.

6.3.5. Cathodoluminescence

The analysis of the optical properties of InGaN layers was carried out by means of RT-PL and CL (figure 6.6). Both kinds of measurements at RT are very sensitive to the presence of non-radiative recombination centres. Out of the series of grown InGaN layers on (In)AlN buffers, the one grown on the thinnest AlN (6 nm) buffer does not show CL emission (fig. 6.6a), most likely due to a high density of non-radiative recombination centres. The other InGaN layers grown on thicker AlN buffers, do show CL emission with comparable intensity (less than a factor of two) pointing to a rather good optical quality. The lowest optical quality is obtained in InGaN layers grown on epitaxial InAlN buffers (fig. 6.6e).

InGaN layers grown on Si_xN_y (fig. 6.6f) and on sputtered InAlN (fig. 6.6g) show CL emission intensity comparable the layers grown on AlN buffers (above 6 nm

thick) (figs. 6.6b, c and d). The shoulders and double peaks that appear in the PL spectra point to an inhomogeneous In composition that may be attributed to the mentioned compositional pulling effect.

Figure 6.6 CL spectra at RT of InGaN layers grown on: a) 6 nm, b) 24 nm, c) 42 nm, and d) 84 nm thick AlN, e) 6 nm thick epitaxial InAlN, f) Si_xN_y and g) sputtered InAlN.

Dobrovolskas et al., [Dob17] studied by PL InGaN layers grown by DERI finding two PL bands originating at regions with different InGaN compositions: one near the substrate with lower In% and another near the surface with a higher In%. These results are in good agreement with lattice pulling effects and indicate that the lower energy emission in figure 6.6 corresponds to the upper region in the InGaN layer. When only one of the emissions is present, it could be due to a higher density of defects of that InGaN sub-layer. The In% values given in figure

6.6 were estimated from equations (2.7.2.2) and (2.3.2.7) using a bowing parameter of 2.5 eV [Ase15] and taking into account the strain of the InGaN layer (measured by RSM, according to section 3.1.2.2).

6.3.6. Electrical characterization

The samples were electrically characterized by measuring the I-V characteristic between vertical contacts (fig. 6.7). Ti/Al/Ni/Au contacts were deposited on top of the NID n-type InGaN layers (residual electron density of $\sim 10^{18} \text{ cm}^{-3}$) grown on different buffers and annealed at 400 °C during 5 minutes to form an ohmic contacts, while Al/Au was deposited on the backside of the p-type Si substrate. Horizontal pairs of contacts were used on the InGaN layers and p-type substrates to verify their ohmic behaviour and to calculate the contact resistivity ($\sim 10 \text{ } \Omega\text{cm}^2$ in case of contacts on p-Si and $\sim 20 \text{ } \Omega\text{cm}^2$ for contacts on InGaN).

Figure 6.7 Vertical I - V curves of samples grown on: a) 6 and 24 nm, b) 42 and 84 nm thick AlN, c) 6 nm thick InAlN, d) Si_3N_4 and e) 20 nm thick sputtered InAlN.

Figures 6.7a and 6.7b show the I-V characteristics of the InGaN layers grown on the thin (6 and 24 nm) and thick (42 and 84 nm) AlN buffer layers. In the case of the thin AlN, a non-ideal rectifying behaviour is observed, whereas for the thick ones it is ohmic. From the results obtained in previous sections, thin AlN buffer layers present a large density of nanopores, which can induce the growth of InGaN directly on the bare Si substrate together with the growth on the corresponding buffer layer. In any case, one may expect a highly defective interface, which would prevent the ideal electrical conduction. However, for the case of thick (42-84 nm) AlN buffer layers (Figure 6.7b) an ohmic behaviour is observed. This type of buffer layer presented a lower density of nanopores and smaller diameter, leading to a larger size of the grains.

Two current flow mechanisms are proposed: one through the nanopores and another through grain boundaries. The former is the dominant for the thin AlN (6 and 24 nm) (fig. 6.7a), in which the density of nanopores is one order of magnitude higher and its diameter is between 2 and 5 times larger as compare to the thick (42 and 84 nm) AlN buffer layers. In addition, the poorer coverage of the Si surface by the AlN buffer layer, leads to less connection between grains and thus to less grain boundaries. Both facts together make the conduction through nanopores the dominant mechanism for the mentioned structures. For the case of thick AlN buffer layers the dominant current flow mechanism is related to the grain boundaries; the nanopores density and diameter are both decreased by 10 and 2-5 times, respectively, together with the larger size of the grains that allow an increase in the number of grain boundaries. Grain boundaries are known to facilitate charge transfer across insulating layers [Bie07]. This strong transport property would not be achieved if the AlN buffer were both compact (absence of nanopores) and monocrystalline. In that case, the charge transport could only take place by tunnelling, which would not be allowed at the measured currents. To support this explanation, Musolino et. al. [Mus15] reported electroluminescence of GaN nanowires grown on AlN buffered Si. They concluded that the grain boundaries present in the AlN buffer allows the current to flow through them.

The results obtained for the other three buffers cannot be explained in the same way due to the intrinsic differences between buffers. Further investigations should be performed in order to clarify those results.

6.4. Conclusions

In summary, we have identified that the use of an AlN buffer layer (of thickness between 42 and 84 nm) leads to an improvement of the structural and optical properties of the InGaN epilayer, while keeping the ohmic behaviour of the heterointerface. This could help in a possible integration of III-nitrides with Si solar cells by avoiding the use of a tunnel junction, simplifying the design and fabrication of the device. Several transport mechanisms have been suggested to understand the differences in electrical behavior. However, focusing on AlN buffers, transport through nanopores and grain boundaries seem to be most likely the ones playing a role, though there is no direct evidence. In addition, the successful growth of InGaN films by DERI on buffered Si substrates is achieved and reported for the first time.

7. Conclusions and future work

The most relevant results obtained throughout this thesis and the future work, aimed to their improvement are summarized in this chapter.

7.1. Conclusions

In the framework of this thesis the constituent blocks of an InGaN photovoltaic device were realized (compact (In)GaN and GaN:Mg layers) all grown by plasma assisted molecular beam epitaxy (PA-MBE).

1. The advanced DERI growth method has been successfully implemented for the first time to the growth of InGaN films on silicon and buffered-silicon substrates. Best results, in terms of morphology and structural and optical quality, were obtained for the AlN-buffered silicon substrate, using a layer thickness between 42 and 84 nm.
2. With the introduction of an AlN buffer layer (of thickness between 42 and 84 nm), the need of a TJ between the two potential sub-cells can be avoided after further improvement. We observe ohmic characteristic between the n-InGaN/AlN/p-Si heterojunction, which can simplify the design and fabrication of an InGaN-on-Si-based 2J photovoltaic device.
3. A possible mechanism for the vertical charge transport on the n-InGaN/buffer/p-Si heterojunction has been proposed. The results are of major importance for a future InGaN-on-Si double-junction solar cell fabrication.
4. The most critical parameters for the growth of InGaN films by MME, namely III/N ratio and growth temperature, have been identified. The indium incorporation on the InGaN alloy can be controlled by means of the In/Ga ratio. The exposing time to the N^{*} plasma, although important, was identified as a parameter with less impact on the crystal quality of the resulting layer.
5. Optimum conditions for the growth of InGaN layers by MME were identified, leading to minimization of surface roughness and YL emission, maximization of the uniformity in In composition, and improved InGaN PL

emission. The optimized film was employed on the development of a p-i-n hetero-structure made out of p-GaN/i-InGaN/n-GaN.

6. Undoped GaN films were grown both in the intermediate regime and by MME in order to know the residual n-type doping concentration. Films grown in the intermediate regime showed lower residual n-type concentration. This could be attributed to the growth conditions employed for the film grown by MME. Two experiments are proposed to reduce the residual n-type concentration.
7. The MME growth method have been demonstrated to be more suitable for the growth of Mg-doped GaN films, with higher hole concentration. The layers grown by MME showed ~5 times higher hole concentration than the layers grown in the intermediate regime, making them better for applications where a higher hole concentration is needed.
8. Mg doped GaN layers grown both in the intermediate regime and by MME were compared in terms of morphology and PL emission. Both set of layers showed similar morphology and PL emission. The PL emission was related with the Mg flux and the hole concentration.
9. GaN/InGaN/GaN p-i-n heterostructures were monolithically grown by PA-MBE using the MME growth method. The heterostructures showed promising structural (no trace of phase separation) and optical (absorption) properties.
10. P-i-n heterostructures were processed into a device. Although J-V curves did not showed any photovoltaic response, the possible problems leading to a lack of PV response were identified, being fundamentally two main technological issues that need to be solved for a fully functioning device.

7.2. Future work

In the presented thesis, several critical points for the realization of a solar cell based on III-nitrides were studied. Two main approaches were studied: on one hand, the possible integration of III-nitrides with Si solar cell technology via the introduction of buffer layers, and secondly the growth of p-i-n III-nitrides heterostructures for photovoltaic applications.

On the integration of III-nitrides with Si solar cell technology there is still a lot of room for research:

1. In order to fabricate a double junction solar cell, p-InGaN/n-InGaN on a Si solar cell, all the nitride layers should be optimized. The use of the MME growth method, together with the use of AlN buffer layers, could lead to layers with higher quality, and to higher doping levels (especially in terms of p-type doping).
2. One of the problems associated to the realization of III-N solar cells on Si is related to the preferred crystalline orientation used in the silicon industry, i.e., (100) orientation. The majority of the growths of InGaN on silicon are carried out on the (111) orientation. Shon and co-workers [Sho14] demonstrated the growth of InGaN LEDs on amorphous substrates, thanks to the introduction of transferred graphene interlayers. This approach could be employed for the growth of InGaN p-n junctions on Si(100).
3. Only the two terminal approach is usually considered for the double-junction InGaN-Si tandem solar cells. The challenges associated to the growth of InGaN on Si will be reduced with the use of the four terminal approach. The use of thicker GaN/AlN buffer layers, or even of step-graded buffers, will be allowed by the four terminal approach. The only restriction will be imposed to the transparency of the buffer layer, i.e. its bandgap energy should be higher than the Si bandgap energy, to avoid photon losses. In addition, the use of tunnel junctions could be avoided, thus, reducing the device complexity.

Regarding devices grown on GaN-on-Sapphire templates, further optimization will be beneficial to the final device. The main points to be studied are:

1. To identify the best growth conditions for the InGaN:Mg, making use of the MME growth method, for the realization of p-InGaN layers, and to study the Mg doping of InGaN layers grown by MME with different In contents.
2. To correlate the emission peaks of the acceptor bound excitons (ABE1 and ABE2) with the Mg-H complex or with the Mg_{Ga}. For this purpose power and temperature dependent measurements should be done for

GaN films with different Mg concentrations. They should be done before and after annealing.

3. To improve the photorresponse of the p-i-n structures the doping level of the intrinsic InGaN layer needs to be reduced. Growing at a higher growth rate or, even, doping with Mg to compensate will lead to an improvement on the photogenerated carriers.
4. To improve the performance of the final device, a reduction of the series resistance needs to be achieved. It can be reduced by annealing the contacts to the p-GaN at a higher temperature and/or doing it in air ambient. Growing a p-GaN layer with higher hole concentration will also lead to a reduction of the series resistance.

Appendix A: Substrate preparation

All samples were grown in a plasma assisted molecular beam epitaxy (PA-MBE) reactor equipped with a radio frequency nitrogen plasma source and standard Knudsen effusion cells for metals (Al, Ga and In) and a RIBER valved corrosive source (S40 VCOR 110) for the p-type dopant (Mg).

The GaN-on-Sapphire templates employed in this work were manufactured by Kyma technologies. The templates employed were highly resistive Fe-doped GaN, to avoid the interaction of the template with the Hall effect measurements, and Si-doped for the layers that was not measured by Hall effect and for the p-i-n structures. Prior to the growth, the templates were outgassed in two steps: first inside the introduction chamber at 500 °C during 30 minutes and afterwards in the growth chamber at 700 °C for 30 minutes.

The Si(111) substrates were manufactured by university wafers. All the Si substrates were p-type doped. Prior to the transfer into the growth chamber, the Si substrates were outgassed at 500°C during 30 min to remove water vapour and any traces of solvents. Once in the growth chamber, they were heated at 900 °C during 30 minutes to remove the native oxide. The temperature was then slowly decreased (5°C/min) until a clear 7x7 surface reconstruction was observed (at 860 °C) by RHEED [Suz93].

Appendix B: Device processing

In this sub-section, the processing of the p-i-n structures is described in detail. (Figure B.1). A standard acetone-methanol rinse followed by N₂ blow-drying was used to clean the samples before and after processing; this will be referred as standard cleaning process.

A MESA pattern is first defined on the epitaxial p-i-n structure using photolithography. The photoresist is cured at 110 °C for 2 minutes prior to be etched using chlorine/argon plasma in an Inductively Coupled Plasma (ICP) tool (Figure B.1c). ICP is preferred over Reaction Ion Etching (RIE) as it provides a better etching anisotropy, which is required to maintain vertical MESA walls and to avoid short-circuiting. At the end of the etch process, an extended ohmic contact is deposited using an e-beam metal evaporator (fig. B.1d). A Ti/Al/Ni/Au (20, 120, 40 and 50 nm, respectively) metal stack is used for the n-type contact. After the metal evaporation, the sample is soaked in acetone for six hours, followed by the standard cleaning process mentioned at the beginning of this section. Following the resist lift-off, the contacts are annealed in a RTA for 5 minutes at 400 °C in a N₂ atmosphere to improve the contacts properties (fig. B.1e).

A second photolithography step is employed to pattern windows for the p-contact, consisting in a 50 nm Ni – 200 nm Au deposition by e-beam (fig. B.1h). After lift-off, the sample is annealed in an N₂ atmosphere at 400 °C for 5 minutes (fig. B.1i). The schematic of the top view of the final device is shown in figure B.2.

Figure B.1 details the processing of the p-i-n structures, a) deposit of the resist, b) cure and develop of the resist, c) MESA etch, d) contact deposition, e) lift-off and annealing, f) second deposit of resist, g) cure and develop of the resist, h) p-contact deposition, and i) lift-off and final annealing.

Figure B.2 schematic representation of the top view of the final device.

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